

Proceedings of ICEESEN2024, 5-7 September 2024, Cappadocia,



THE 4th INTERNATIONAL CONFERENCE ON ENERGYENVIRONMENT AND STORAGE OF ENERGY

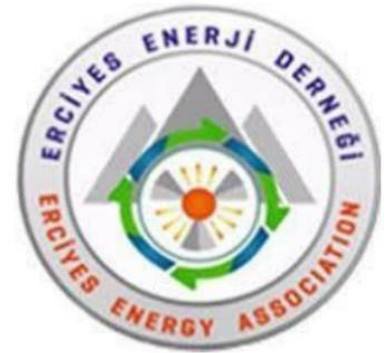
ICEESEN 2024
Conference Proceedings
5-7 September 2024
Cappadocia, Türkiye

Editor in Chief:

Prof. Dr. Selahaddin Orhan Akansu

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**PROCEEDINGS OF THE 4th
INTERNATIONAL
CONFERENCE ON ENERGY, ENVIRONMENT AND
STORAGE OF ENERGY
ICEESEN 2024**



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Prof. Dr. Selahaddin Orhan Akansu**

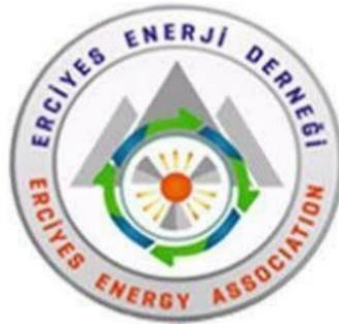
**Co-Editors
Dr. Eyüp Atioğlu
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ORGANISED BY
Erciyes Energy Association
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ICEESEN 2024, Conference Proceedings, 5-7 September, Cappadocia, Türkiye.**

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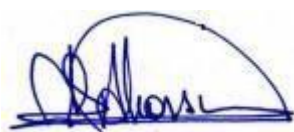


In this conference, 127 presentations from 25 different countries were carried out.

The following are the number of presentations as per country;

Türkiye	60	United States of America	8
Spain	6	Nigeria	2
Algeria	3	Tunissia	1
India	3	Morocco	9
Qatar	1	Italy	1
Pakistan	7	Greece	1
Egypt	2	Northern Cyprus	1
United Kingdom	3	Romania	3
United Arab Emirates	1	China	4
Azerbaijan	3	Eastern Cyprus	1
Korea	2	Kosovo	1
Russia	1	South Africa	2
Canada	1		

Thank you for your interest and participation in our conference.



Prof. Dr. Selahaddin Orhan AKANSU

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PREFACE

This is the fourth International Conference on Energy, Environment and Storage of Energy, ICEESEN 2024. Symposium was held virtually and brought together experts and scientists from different fields.

A total of 127 presentations were done, including keynote speakers, workshop speakers and article presentations at ICEESEN 2024. The symposium was successfully held with an online participation of over 127 participants from 25 different countries.

I hope the studies and improvements that have been done and will be made in the future will contribute to leave a more livable world for future generations. As the scientific community, we have more jobs than expected and it is our duty to move forward with awareness of this.

I would like to thank the symposium honor, organization, management and scientific committee members, reviewers, invited speakers, session chairs, participants and the symposium secretariat who contributed to the successful implementation of the symposium.

Best Regards,

Prof. Dr. Selahaddin Orhan AKANSU

On Behalf of ICEESEN Organizing Committee

INTERNATIONAL CONFERENCE ON ENERGY, ENVIRONMENT AND STORAGE OF ENERGY CONFERENCE SCHEDULE

05-09-2024 Thursday

OPENING CEREMONY AND WELCOME SPEECH - (09.30-09.45)

PLENARY SPEECH (09.45-10.30)

PROF.DR. MARC ROSEN

(SUSTAINABLE ENERGY, SUSTAINABILITY, AND ENVIRONMENTAL IMPACT)

Coffee Break (10.30-10.45)

1. SESSION- HYDROGEN (10:45-12:00)

Session Chair: Dr. A. Aziz Atabani Room-2

2. SESSION- GLOBAL WARMING (10:45-12:00)

Session Chair: Prof. Dr. Izzet Karakurt Room-1

10:45-11:00	Coal Pyrolysis Studies: Application to In-Situ Superheat Steam Hydrogen Production	Alpaslan Atmanli	10:45-11:00	Effect of Sludge Retention Time (Srt) On Bioregeneration of Powdered Activated Carbon Loaded With Paracetamol	Gülmire İlyasoğlu
11:00-11:15	Additive Manufacturing of Vessels for Hydrogen Storage	Abdul Hai Alami	11:00-11:15	Microplastic (Polystyrene) Toxicity OnAquatic Primary Producer Nostoc Muscorum and Effect of Carbon Deprivation On Polystyrene Film Breakdown	Tasneem Fatma
11:15-11:30	Direct Use of Oxygen and Hydrogen Produced By Electrolysis In An Industrial Natural Gas Burner	Bugrahan Alabas	11:15-11:30	Quantifying The Correlation Between Co2 Emissions and Renewable EnergyIndicators	Mine Sertsöz
11:30-11:45	Efficient Photocatalyst of a Binary P-N Heterojunction, Ag3po4/Cu2o for Degradation of Endosulfan and Hydrogen Evaluation	Rajkishore Patel	11:30-11:45	Harnessing Machine Learning for Surrogate Modeling and Circular Carbon Economy: Multi-Objective Optimization In CO2-to-Methanol Conversion	Ermias Girma Aklilu
11:45-12:00	Novel Integrated Hydrogen Liquefaction Process Using Photovoltaic Panels and DiffusionAbsorption Refrigeration	Masoud Taghavi	11:45-12:00	Calculation of Global Warming Potential of Conventional and Organic Chardonnay Grape Production	Kübranur Birtok

LUNCH

PLENARY SPEECH (13:00-13:40) PROF. DR. QINGYAN CHEN (THERMAL SCIENCE , BUILDING ENVIRONMENT AND ENERGY, AIRFLOW AND POLLUTION SIMULATION)					
PLENARY SPEECH (13:45-14:25) PROF. DR. MEHMET KITIŞ (WATER/WASTEWATER TREATMENT AND REUSE, MEMBRANE PROCESSES, WATERSHED MANAGEMENT)					
Coffee Break (14:30-14:45)					
3. SESSION- SOLAR (14:45-16:00) Session Chair: Prof. Dr. Nafiz Kahraman Room-1			4. SESSION- WASTE MANAGEMENT (14:45-16:00) Session Chair: Prof. Dr. Mehmet KITIŞ Room-2		
14:45-15:00	Experimental Study of a Solar Assisted Storage System for Shelf-Life Enhancement of Tomatoes	Muhammad Khalid	14:45-15:00		
15:00-15:15	Thermodynamic Analysis of Solar Tower Based Integrated System for Power Production	Yunus Emre Yuksel	15:00-15:15	Treatment of Dyeing Industry Wastewater: a Comparison Between The Uv/Peroxydateand Uv/Persulfate Processes	Yasmine Laftani
15:15-15:30	Predicting Solar Cell Temperature On Soiled Surfaces Using Machine Learning and Thermal Analysis: Implications for Energy Production	Kudzanayi Chiteka.	15:15-15:30	Toxicity Evaluation of Raw and Treated Chrome Tanning Wastewater By Powdered Marble Adsorption With a Biotest Orge and Lettuce.	Saliha Elabbas
15:30-15:45	a Solar-Powered Combined Plant Based On Supercritical Co2 Brayton Cycle for Power, Heating, and Hydrogen Generation; Energetic and Energetic Performance Investigation	Fatih Yilmaz	15:30-15:45		
15:45-16:00	Parameter Extraction and Optimisation of a SolarCell Using Matlab: a Theoretical Perspective	Bernard Tonderayi Mangara	15:45-16:00	Comparison of Different Spatial Interpolation Techniques for Estimating Areal Precipitation In Türkiye	Filiz Dadaser-Celik
Coffee Break (16:00-16:15)					

5. SESSION- ENERGY (16:15-17:45) Session Chair: Prof. Fooad Karimi Room-1			6. SESSION- FUEL-ENGINE-COMBUSTION (16:15-18:00) Session Chair: Prof. Dr. Iğın Yaşar Room-2		
16:15-16:30	Strain Effects in Type I and Type II Core/Shell QuantumDots for Energy Storage	Derya Malkoç	16:15-16:30	Effect of Various Hydrogen Injection Angles On Engine Performance and Emissions	Semih Yılmaz
16:30-16:45	Design of an Effective Braking System for Electric Vehicles	Adeleye Otepola	16:30-16:45	Investigation of The Effect of Addition of Natural Gas to a Gasoline Engine On Engine Performance and Emissions	Talip Akbiyik
16:45-17:00	Highly Efficient Teng System Decorated With Biomass Material Into The Silicone	Sema Yurdakul	16:45-17:00	Experimental Studies On a Freezer With Partial-Loaded Conditions	Fazli Okan Bovatekin
17:15-17:30	Implementation of a Real-Time Powertrain Test Bench for Fuel Cell Electric Vehicles	Gökay BAYRAK	17:15-17:30	Detailed Characteristics of Polycyclic Aromatic Hydrocarbons and Toxicity In a Diesel Engine Running On Diesel and Biodiesel Blends With Alcohols	Alpaslan Atmanli
17:30-17:45	Activated Carbon Production from Chestnut Shells for Energy Storage and Conversion Applications	İbrahim Keleş	17:30-17:45	formation of Polycyclic Aromatic Hydrocarbons In a Diesel Engine Fueled With Diesel and Biodiesel Containing Low Concentrations of C3/C4/C5 Alcohols	Alpaslan Atmanli
17:45-18:00	A Study on The Determination of Storage Performance In Batteries With Diverse Characteristics of Energy Obtained From Solar/Wind Hybrid Renewable Energy Systems	Sevde Çetinkaya	17:45-18:00	Obstacles and New Technologies Related to Hydrogen Powered Jet Engines	Kenneth Looby
18:30-19:30	DINNER				
19:30-20:30	GOREME TOUR				

06-09-2024 Friday						
PLENARY SPEECH (09.30-10.15) PROF.DR. NADİR YILMAZ (COMBUSTION, CFD, ROCKET PROPULSION AND AUTOMOTIVE ENGINEERING)						
Coffee Break (10:15-10:30)						
7.SESSION-ENERGY-SIMULATION (10:30-12:00) Session Chair: Dr. Gabriel Ibarra-Berastegi Room-1			8.SESSION- FUEL-ENGINE COMBUSTION(10:30-12) Session Chair: Prof. Dr. Nafiz Kahraman Room-2		9. SESSION- GREENHOUSE(10:30-12:00) Session Chair: Prof. Tasneem Fatma Room-3	
10:30-10:45	Analisis of Security Supply With Energy Resources of European Union to Ensure Its Energy Security	Fita Nicolae Daniel	Electrolysis Unit Design to Improve The Combustion Process In a Diesel Engine	Talip Akbiyik	Will renewable energy transition and green credit speak louder towards achieving COP28 targets across BRICS countries: novel evidence from Regression Discontinuity Design	Muhammad Akhtar
10:45-11:00	Energy Source of The Near Future: Gashydrate Research	Günay Çifci	Multi-Stage Combustion Kinetics of Solid Fuels In Chemical Looping Combustion: An Advanced, Clean Combustion Technology	Dr. Fatih Gulec	Techno-Economic Analysis of Wind-Powered Green Hydrogen Production Based On Modular Pem Electrolyzer: a Case Study for Izmir, Türkiye	Engin Deniz Gülay
11:00-11:15	Assessing The Potential of Concentrated Solar Power (CSP) Technology for Addressing Energy Challenges In Syria: a Simulation Study Using Greenius Software	Mudar Taha	Experimental Investigation of The Impact of Aqueous Ammonia, Hydrogen and Diesel Fuel Mixtures on Exhaust Emissions and Engine	Mehmet Sarıtaş	Thermodynamic Analysis of Desiccant Dehumidification Assisted Evaporative Cooling System for Greenhouse Farming in Multan (Pakistan)	Fakhar Abbas
11:15-11:30			Investigation of the Effect of Ammonia on Hydrogen/Kerosene Mixtures	Alperen Alabaş	Overview of Evaporative Cooling Systems for Greenhouse Temperature And Humidity Control	Muhammad Adil
11:30-11:45	Population-Based forecast Model for The Primary Energy Consumption of Algeria	Izzet Karakurt	Simulation and Assessment of Emissions Reduction Potential of An ORC-Based Exhaust Heat Recovery Model Automobile Application	Julius Thaddaeus	Determining The Effect of User Profiles On Energy Peak Loads In Buildings for Different Climatic Regions	Aslihan Şenel Solmaz
11:45-12:00	Cistus Shells Used As a Sustainable Matrix for Bioenergy Production Through Slow Pyrolysis Process: Kinetic and Thermodynamic Study	Hammadi El Farissi	Investigation of Combustion Kinetics of Raw and Torrefied Rose Pulp, and Chicken Manure Mixtures With Local Lignite	Sema Yurdakul		
LUNCH						

PLENARY SPEECH (14:15-15:00)
PROF. DR. BERNA HASÇAKIR
(CARBON CAPTURE AND STORAGE METHODS FOR CLIMATE CHANGE)

Coffee Break (15:00-15:15)

10. SESSION-HEAT TRANSFER (15:15-17:00)			11. SESSION- ENERGY - (15:15-17:00)		12. SESSION- GREEN-HOUSE-BATTERY (15:15-17:00)	
Session Chair: Prof. Dr. Nadir Yılmaz Room-1			Session Chair: Prof. Dr. Ahmet Sedat Şarman Room-2		Session Chair: Prof. Gamze Genç Room-3	
15:15-15:30	Heat Transfer Performance of Al ₂ O ₃ /Cu-H ₂ O Nanofluids	Oulahou Younes	Effect Of Fin Structures, Pcm, And Porous Media On Latent Heat ThermalEnergy Storage Performance	Emrehan Gürsoy	Estimation of Greenhouse Dehumidification Requirements for Tomato and Cucumber Crops	Aneela Sarwar
15:30-15:45	Numerical Investigation of HeatTransfer Improvement of Ring Turbulators Placed In a Pipe	Ayşenur Selvi	Situation of Romanian Energy Resourcesfor Stability and Ensure Energy Security	Fita Nicolae Daniel		
16:00-16:15	Determination of Bubble Behavior and Gas-Solid Distribution Characterization In a Fluidized Bed System	Oguzhan Erbas	Outlier Detection In Energy Consumption of Courier Motorcycles Using Acceleration Patterns From Gps Data	Ilgin Gokasar	Comprehensive Characterization of Activated Carbon Functionalized With Fe ₃ O ₄ and L-Arginine	F. Ezgi Yağmur
16:15-16:30	Numerical Analysis of Geometrical Parameter Influence On KENICS Static Mixer Efficiency	Ahmed Mouissi	ENERGY AND EXERGY ASSESSMENT OF GEOTHERMAL ENERGY-BASED TRIGENERATION PLANT	Yunus Emre YUKSEL	Assessing The Environmental Impacts of International Financial Inflows In Clean Energy R&D and Production In Asian Countries	Abdul Khaliq
16:30-16:45	Impact of Shading On Cooling Loads: a Case Study of a Building	Yasin Kaya	Global Trends of The Significant Wave Height Until 2100 Around Offshore Wind Farms: Implications	Gabriel Ibarra-Berastegi		
16:45-17:00	Multiwalled Carbon Nanotube Modified Li ₂ ZnTi ₃ O ₈ As Anode With Improved Electrochemical Performance for Lithium Ion Batteries	Halil Şahan	Performance Enhancement of Li-Ion Batteries By Electrospraying-Assisted Coating of Boron Nitride Nanotubes On Separators	Jaewoo Kim	Recent Developments On Battery Thermal Management Systems By Cooling With Minichannel	Seyfi Sevinç

Coffee Break (17:00-17:15)

13. SESSION- ENVIRONMENT (17:15-18:30) Session Chair: Prof. D. Filiz Dadaşer-Çelik Room-1			14. SESSION- ENERGY (17:15-18:30) Session Chair: Prof. Dr. Abdul Hai Alami Room-2		15. SESSION- ENERGY (17:15-18:30) Session Chair: Prof.Dr.Bilge Albayrak Çeper Room-3	
17:15-17:30	A Nature-Like Technology for The Restoration of Technogenically Disturbed Limestone Quarry Lands	Ivlieva Margarita	The Effect of Flow Rate On Thermal, Electrical and Overall Performance of Solar Hybrid Pvt Panels	Kadir Zengin	Energy Efficiency and Environmental Assessment of a Business In a Small Rural Town On The U.S./Mexico Border In Texas	Jalal Rastegary
17:30-17:45	Chemical Analysis of The Concentration of Heavy Metals, In Particulate Matter, Pm: 2.5 and Pm: 10 Mg/M3, In The Fly Ash Of: Tc "Kosovo", Complex "Trepça" and Factory "	Donika Sylejmani	The Effect of Cleaning Photovoltaic Panel Surfaces Using a Cleaning Robot On Panel Efficiency: An Experimental Study	Serhat Küçükçörün	Parametric Studies On a Freezer With Pcm	Mehmet Furkan Koparan
17:45-18:00	Employing The Trend Analysis for Modelling The Energy-Related Carbon Dioxide Emissions of Türkiye	Izzet Karakurt	Enhancing Solar Energy forecasting Through Chaos Theory and Echo State Networks: a Case Study of TheKonya Eregli Solar Power Plant	Taraneh Saadati	Valorization of The Aquatic Wasted Pterocladia Capillacea Biomass Into Sustainable Valued Products to Flourish The Blue Economy	Nour El-Gendy
18:00-18:15	forecasting Meteorological Drought Using Artifical Neural Networks	Fadime Kiliç	Enhancing Surplus Energy Prediction for High Penetration Renewable Energy Systems Using Regularized Support Vector Machine	Foad Karimi	Process Analysis of a Flexible Gasification Based Thermochemical Conversion Concepts of Biogenic Residues and Wastes Into Biomethane and Biochar	Kostis Atsonios
18:15-18:30	Dft and Dft-D3 Calculations of Hcooh Adsorption and Decomposition On Perfect and Defective Au(110) Surfaces	Boungou Cedric Clarfeler			Effect of H2 Dilution On Biogas Mixture In a Industrial Burner	Bugrahan Alabas
GALA DINNER						

07-09-2022 Saturday						
16. SESSION- ENVIRONMENT (10:00-11:15) Session Chair: Prof. Halil Şahan Room-1			17. SESSION- ENERGY (10:00-11:15) Session Chair: Dr. Jalal Rastegary Room-2		18. SESSION-OPTIMIZATION (10:00-11:15) Session Chair: Prof. Dr. Nuray Ateş Room-3	
10:00-10:15	Mapping The forest: Quantifying and Visualizing the Distribution Patterns of Tree Species In Shangla District of Kpk, Pakistan	Javed Iqbal	Effects of Ambient Temperature On Compressive Strength of Recycled Thermoplastic Materials Used In Wind Turbine Blades	Cihan Çiftci	Multi-Objective Optimization of Hess Topology and Sizing for Metro Vehicles Using Nsga-Iii	Mehmet Fidan
10:15-10:30	Study The Effect of Smog On The Anatomical and Physiological Behaviour of Some Selected Trees	Rabia Ghaffar	The Importance of Drain Sizing In The Stability of Embankment Dams	Latifa Bendaoudi	Development of a Detailed Multiphysics Model For The Dynamic Performances of Bev On Real Driving Cycles In The City of Naples, Italy	Daniele Piazzullo
10:30-10:45	Comparative Study of Nutrient and Heavy Metal Behavior Along Oued Sebou	Ahlam Saad	Modelling Hydrological Processes In The Kartalkaya Reservoir Basin (Kahramanmaraş, Türkiye) Using Swat	Ahmet Hakan Bekar	Design, Control and Integration of Synchronous DC-DC Step Down Converter with Hybrid Controller Created Using ANN and PID in MATLAB/Simulink Environment to Electrolysis System	Mustafa Ergin ŞAHİN
10:45-11:00	Environmental Performance Assessment of Different Csp Steel Types With Sol-Gel Coating	Manuel Botejara-Antúnez	Hydraulically-Efficient Hydraulic Design for Multioutlet Submains-I: Methodology	Gürol Yildirim	Experimental Investigation of Diesel, Aqueous Ammonia and Cng Blends On Performance and Emissions In a Compression Ignition Engine	Happy Sinkala
11:00-11:15	Modelling Burdur Lake Water Level Dynamics Using Artificial Neural Networks: Multi-Layer Perceptron Approach	Mehmet Soylu	Hydraulically-Efficient Hydraulic Design for Multioutlet Submains-II: Comparative Analysis	Gürol Yildirim	Investigation of Using the Groundwater Treatment Sludge As a Coagulant for Brewery Industry Wastewater Treatment: a Circular Economy Approach	Pelin Soyertaş Yapicioğlu
11:15-11:30	Risk Prioritization of Pesticides In Wastewater According to Concentrations and Contaminant Properties	Hatice Duman	Corporate Carbon Footprint Calculation: İncesu Municipality Example	Ali Kemal Ergül		
Coffee Break (11:15-11:30)						

07-09-2022 Saturday						
19. SESSION- ENVIRONMENT-FUEL-ENGINE (11:30-12:45) Session Chair: Dr. Numan Yanar Room-1			20. SESSION- ENERGY-ECONOMY (11:30-12:45) Session Chair: Dr. Masoud Taghavi Room-2		21. FUEL-ENGINE-COMBUSTION (11:30-12:45) Session Chair: Prof. Nour Sh. El-Gendy Room-3	
11:30-11:45	Investigation of Half-Metallic Dichalcogenide Alloy for Highly Selective Gas Adsorption	Ahmad Ayesh	Responsible Governance, CSRPerformance and Firm Value Creation	Ben Chikha Souhaila	Techno-Economic Investigation On Solar Based Anaerobic Co- Digestion of Industrial Sewage Sludge and Malt Spro15ut Waste for Biohydrogen Production	Dr. Pelin Soyertaş Yapicioğlu
11:45-12:00	Improving Pediatric Dose Measurements with Deep Learning Models for Accurate Internal Dosimetry in Nuclear Medicine	Khaoula Laazouzi	State-Flow Based Energy Management System In Micro-Grid Including Fuel Cell	Hamid Bentarzi	Predicting Higher Heating Values of Pure Biodiesels: a MultipleLinear Regression Approach	Mert Gülüm
12:00-12:15	Experimental Investigation of TheEffect of Gasoline Addition On Performance and Emissions In AnRCCI Diesel Engine	Talip Akbiyik	The Effect of Macroeconomic Variables On Ecological Footprint:Panel Data Review On Oecd Countries	Sümeyye Rafia Yıldız	a Roadmap of a Techno-Economic Analysis and Better Usage of Biomass for Technology InvestorsOn Biomass Power Industry	Ahmet Sedat Şarman
12:15-12:30	Thermal Coupling of PEM FuelCell Stack With Metal Hydride Hydrogen Storage System: a Computational Study	Uday Raj Singh	Robust Framework for Real-TimeTechno-Economic Self-Healing InMicrogrids Amid Cyber-Physical Attacks Utilizing Sensitivity Analysis	Elnaz Yaghoubi	Trends In Naoh Deconstruction of Maize Stalk Fractions In TheProduction of Bioethanol	Tolulope Eunice Kolajo
12:30-12:45	Advancements In Combustion Technology: The Role of Nanoparticle Fuel Additives, Mechanisms and Theories	Dr. Raşit Atelge	Effect of N2 Dilution On DynamicFluctuation of Propane-Hydrogen Flame	Murat Taştan	Investigation of Cultivation Conditions and Harvesting Methods of Microalgae Species to Be UsedAs Biomass	Yalçın Mete Coşkun
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SUSTAINABLE ENERGY, SUSTAINABILITY AND ENVIRONMENTAL IMPACT

Prof. Dr. Marc Rosen

Abstract

Sustainable development is a critical, central and important goal and means for human and societal activity. It can be argued that sustainable development constitutes one of the greatest challenges facing society and humanity. Even if we cannot simply achieve sustainability, we can certainly shift our actions to be more sustainable and thereby allow for movement towards sustainable development.

The global recognition of the importance of sustainability is receiving increasing recognition year by year, and perhaps is most evident in the unanimously approved Sustainable Development Goals of the United Nations for the period 2015-2030. Progress is being made in most countries on the Sustainable Development Goals, although according to most experts at a slower pace than had been hoped for and anticipated. Thus, more effort is needed to shift society further along toward sustainability.

Energy sustainability is of great importance to any activities and plans for overall sustainable development, and the achievement of sustainability. This is particularly important given the following: The pervasiveness of energy use throughout almost all aspects of societies and the lives of people. A great deal of the activities undertaken by people, industry, governments and other organizations involve energy use, often at a very high intensity. This is particularly evident in industrialized countries.

The importance of energy in economic development of societies and the living standards attained by people. There is a strong correlation between access to a reliable and secure supply of energy and wealth creation, which in turn normally translates into improved living standards. This often results in a growing need for more energy supplies.

The significant impacts that energy processes and systems have on the environment and the ecosystems within them. Fossil fuels are particularly concerning regarding the impact of their combustion and utilization in other ways on climate change, as well as other types of environmental impact. But even non-carbon energy resources like renewable energy and nuclear energy have impacts on the environment and living systems. Thus addressing these concerns, through sustainable energy, is one important focus of efforts to achieve sustainability more broadly and holistically.

Beyond the above topics, many factors that need to be considered and appropriately addressed in moving or shifting towards energy sustainability are examined in this keynote address. These include the following:

The appropriate selection of energy resources bearing in mind sustainability criteria. This normally is a central focus of sustainable energy and efforts to support it.

The facilitation of the use of sustainable energy resources, particularly through the use of appropriate energy carriers. This is a more subtle factor, but it is important especially in light of efforts to promote alternative carriers like hydrogen and ammonia, which go beyond our more conventional energy carriers like electricity and thermal energy.

The enhancement of the efficiency of energy-related processes. Although inadequate to achieve sustainability on its own, greater efficiency slows down the rate at which finite resources are being depleted and has other benefits like reduced equipment and infrastructure requirements.

The holistic adoption of environmental stewardship in energy activities. This is often the prime reason for considering the expanded utilization of sustainable energy resources, and is very much at the heart of sustainable energy.

The addressing and management of other key sustainability measures. These other measures include economics, equity, land use, lifestyle, sociopolitical factors, population and many others. All relevant factors need to be considered, understood and addressed to support efforts in line with sustainable energy, and thereby allow them to be successful.

In closing the address, conclusions are provided related both on options for energy sustainability and on means to achieve sustainable development and overall sustainability, and speculations are provided on future directions for sustainable energy.



INDUSTRIAL APPLICATIONS ON WATER EFFICIENCY AND WASTEWATER REUSE

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Cleaner production (CP) is a proactive environmental protection strategy focusing mainly on the reduction of resource consumptions, prevention or minimization of wastes, wastewaters, emissions, etc. CP attempts to use the materials of the manufacturing process in a more efficient way as well as reduce risks to humans and the environment through all phases of the life cycle of the processes. CP has significant environmental, economic and social benefits, such as reduction of operating costs, reduction of ecological damage and improved company image. The CP approach has become increasingly popular since the mid-1990s.

In parallel with the increasing population and industrialization, available water resources on a global scale are also decreasing rapidly. While the industrial water use in less developed countries has a share of 10-30% in total water use, this rate varies between 50 and 80% in industrialized countries. Developing strategies for the sustainable use of water sources in industries is necessary and compulsory. Integrated approaches such as CP and water control measures can provide effective results in reducing water consumption in industries. In addition to water use, wastewater amount and wastewater pollution loads can also be reduced with water efficiency practices. With such practices, not only water consumption and wastewater generation can be reduced in industrial facilities, but also energy consumption, chemical use, environmental discharge and emissions, and production costs can be diminished. Efficiency studies should be carried out not only for water but also for other inputs such as chemicals, energy, and raw materials in the industrial facilities. In this way, higher level of technical, economic and environmental benefits can be achieved in reducing resource use and improving environmental performance in industrial facilities. Water Efficiency Feasibility Study for a specific industrial facility may basically include following sections: characterization of the facility, current water use and pricing, process-based and other water use points, examination of relevant sectoral best available techniques (BAT) reference (BREF) documents and reports of similar facilities related to water use, potential reductions in water use and wastewater production, identification of the current status, determination of the sectoral BATs to improve water efficiency, and cost-benefit analysis.

Various steps for assessing water efficiency in industries are summarized as following: preparation of data collection and onsite survey forms, analyzing related sectoral BREF documents, field studies and data collection, water efficiency and water balance calculations, current status analysis, comparison of the specific water consumption values of the facility with those reported in BREF documents, determination of potential savings/reductions, determination of final BAT list to be implemented, evaluation of the savings/benefits to be achieved by the implementation of the final BAT list, economic/financial assessments, and lastly implementation. Within the scope of current status analysis; water use and wastewater generation points should be determined, specific water consumptions (water consumption (for example L/kg product) per unit product mass/volume/piece etc.), specific wastewater amounts (wastewater generation (L/kg product) per unit product) and specific pollutant loads (pollution load (e.g., gr/kg product) per unit product) should be calculated. Furthermore, such specific consumption values calculated for the facility should be compared with reference values reported in BREF documents and inefficiencies in water use should be identified. The points requiring water efficiency practices should be determined and appropriate water efficiency measures (BATs) should be specified. Also, a cost-benefit analysis should be conducted considering potential savings/reductions and capital and O&M costs. In this invited plenary speech, industrial cleaner production studies and water control measures planned or already implemented in full-scale were presented. Case studies and success stories from Turkish industries were discussed. Such studies and projects included various industrial sectors with different NACE codes.

Keywords: Best available techniques, cleaner production, efficiency, wastewater, water.

ACCURATE AND SWIFT PREDICTION OF URBAN WIND ENVIRONMENTS AND POLLUTANT DISPERSION

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Abstract

The accurate and swift prediction of building wind environments and pollutant dispersion is essential for fostering healthy and comfortable outdoor spaces. While Computational Fluid Dynamics (CFD) provides detailed forecasts for outdoor airflow and pollutant movement, its high cost restricts its widespread use. Additionally, the accuracy of current turbulence models can be compromised by significant errors. The ever-changing nature of outdoor wind direction and speed further complicates the prediction of wind and pollutant distribution in urban areas.

This paper first proposed a two-stage CFD-graph neural network (GNN) framework for efficient steady-state prediction of airflow around buildings. A CFD solver provides the initial state, and then a GNN directly corrects the CFD outputs towards a high-fidelity target in a single prediction step, bypassing the flaws normally generated by Reynolds averaged Navier-Stokes equation (RANS) modelling. We used large-eddy simulations (LES) to generate results for GNN model training data. The proposed method was thus distinguished from previous GNN applications, which were unsteady RANS surrogates that are still constrained by RANS inaccuracy. By applying the trained GNN models to predict airflow, turbulence, and contaminant dispersion for a cluster of buildings in a city center, the GNN prediction predicted the results very close to experimental data and LES predictions. The accuracy was much higher than RANS modelling.

By using the polynomial chaos expansion method, this paper also show how to approximate velocity and concentration distributions around buildings by expanding orthogonal polynomials with wind direction and wind speed as input variables. We quantified the uncertainty with varying wind conditions on air velocity and pollutant concentration. The polynomials of velocity and pollutant concentration with wind condition obtained by this method can achieve very good accuracy. This method allows for quick calculations of velocity and concentration results, providing the distributions of velocity and concentration with respect to wind conditions. It enables direct and rapid prediction of air velocity and pollutant concentration, avoiding the need for repeated simulations due to varying wind conditions and thus improving computational efficiency. This approach provides more comprehensive information about pollution dispersion in actual urban environments.

In both cases, we can reduce the computing cost significantly from 10 times to a few thousands of times, depending on the geometry, grid number used, and accuracy accepted. This study enhances the performance of numerical prediction of airflow and contaminant dispersion around buildings by the two methods. The two methods have shown strong generalizability, which allows for quick and accurate calculations. The two methods have great potential for use in practice.

ADDRESSING CLIMATE CHANGE: THE ROLE OF CARBON CAPTURE AND STORAGE (CCS) AND THE NEED FOR COLLECTIVE ACTION

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Abstract

Carbon dioxide (CO₂) is fundamental to sustaining life on Earth, but its current excessive levels are driving rapid and unprecedented changes in global temperatures and ecosystems, occurring at a pace about 12,000 times faster than natural geological rates. This keynote speech aims to elevate public awareness about climate change by presenting scientific evidence and examining carbon capture and storage (CCS) as a potential mitigation technique. The objective is to uncover the root causes of climate change, with a particular emphasis on the role of CO₂ emissions resulting from fossil fuel combustion.

The data reveals that annually, fossil fuel burning releases approximately 60 times more carbon into the atmosphere than natural systems can manage. These emissions arise from two primary sources: addressable and unaddressable. Addressable sources, which are stationary, include power plants and refineries that convert fossil fuels into electricity and produce everyday items like plastics, medicines, and cosmetics. In contrast, unaddressable sources are non-stationary emitters, such as vehicles (cars, planes, ships, and trains), which account for the bulk of CO₂ emissions. Once CO₂ is released into the atmosphere, recapturing it is exceptionally challenging. Although only 40% of this CO₂ remains airborne, the rest is absorbed by terrestrial and oceanic systems, altering ocean chemistry, disrupting ecosystems, and contributing to environmental changes. This 40% is a significant driver of accelerated global warming, as CO₂ is transparent to UV radiation from the sun but absorbs infrared radiation emitted by the Earth's surface, thereby trapping heat. This increase in surface temperature leads to alterations in vegetation, habitats, and ecosystems, gradually impacting human lives.

It is crucial to recognize that climate change is fundamentally linked to our carbon consumption, which has historically contributed to the comfortable lifestyles humans enjoy today. While the exact consequences of climate change on human lives remain uncertain, proactive measures are necessary. CCS offers a feasible, albeit partial, solution to this crisis by capturing CO₂ emissions from large stationary sources like industrial facilities. Deep saline formations can potentially store CO₂ for up to 10,000 years, but CCS faces significant challenges, including high costs and complex long-term monitoring requirements to prevent CO₂ leakage. Moreover, converting CO₂ into stable carbonates is a gradual process that may take thousands of years. In conclusion, while CCS is a valuable tool in the fight against climate change, it is not a standalone solution. Mitigating climate change requires a collective effort, including practical actions such as reducing electricity consumption, adopting energy-efficient technologies, preventing deforestation, and shifting toward cleaner energy sources. These measures, in combination with CCS, are essential to effectively address this global challenge.

significant environmental, economic and social benefits, such as reduction of operating costs, reduction of ecological damage and improved company image. The CP approach has become increasingly popular since the mid-1990s.

In parallel with the increasing population and industrialization, available water resources on a global scale are also decreasing rapidly. While the industrial water use in less developed countries has a share of 10-30% in total water use, this rate varies between 50 and 80% in

industrialized countries. Developing strategies for the sustainable use of water sources in industries is necessary and compulsory. Integrated approaches such as CP and water control measures can provide effective results in reducing water consumption in industries. In addition to water use, wastewater amount and wastewater pollution loads can also be reduced with water efficiency practices. With such practices, not only water consumption and wastewater generation can be reduced in industrial facilities, but also energy consumption, chemical use, environmental discharge and emissions, and production costs can be diminished. Efficiency studies should be carried out not only for water but also for other inputs such as chemicals, energy, and raw materials in the industrial facilities. In this way, higher level of technical, economic and environmental benefits can be achieved in reducing resource use and improving environmental performance in industrial facilities. Water Efficiency Feasibility Study for a specific industrial facility may basically include following sections: characterization of the facility, current water use and pricing, process-based and other water use points, examination of relevant sectoral best available techniques (BAT) reference (BREF) documents and reports of similar facilities related to water use, potential reductions in water use and wastewater production, identification of the current status, determination of the sectoral BATs to improve water efficiency, and cost-benefit analysis.

Various steps for assessing water efficiency in industries are summarized as following: preparation of data collection and onsite survey forms, analyzing related sectoral BREF documents, field studies and data collection, water efficiency and water balance calculations, current status analysis, comparison of the specific water consumption values of the facility with those reported in BREF documents, determination of potential savings/reductions, determination of final BAT list to be implemented, evaluation of the savings/benefits to be achieved by the implementation of the final BAT list, economic/financial assessments, and lastly implementation. Within the scope of current status analysis; water use and wastewater generation points should be determined, specific water consumptions (water consumption (for example L/kg product) per unit product mass/volume/piece etc.), specific wastewater amounts (wastewater generation (L/kg product) per unit product) and specific pollutant loads (pollution load (e.g., gr/kg product) per unit product) should be calculated. Furthermore, such specific consumption values calculated for the facility should be compared with reference values reported in BREF documents and inefficiencies in water use should be identified. The points requiring water efficiency practices should be determined and appropriate water efficiency measures (BATs) should be specified. Also, a cost-benefit analysis should be conducted considering potential savings/reductions and capital and O&M costs. In this invited plenary speech, industrial cleaner production studies and water control measures planned or already implemented in full-scale were presented. Case studies and success stories from Turkish industries were discussed. Such studies and projects included various industrial sectors with different NACE codes.

Keywords: Best available techniques, cleaner production, efficiency, wastewater, water.

CHALLENGES AND OPPORTUNITIES IN AVIATION: SUSTAINABLE AVIATION FUELS AND ELECTRIFIED AIRCRAFT PROPULSION

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Abstract

The transportation sector, with all its dependent components, is currently attempting to implement radical policies towards environmental sustainability. The aviation industry is one of the largest sources of greenhouse gas (GHG) emissions, which increase based on the amount of petroleum-derived fuel. The increasing liquid fuel demand of aircrafts has pushed for more environmentally friendly and sustainable sources along with further technological advancements. The aviation industry faces significant challenges such as fuel costs and environmental and energy security issues arising from the use of fossil fuel. Currently, there are many strategies to increase energy efficiency while combating environmental problems, including sustainable fuel solutions and innovative battery technologies. Alternative fuels are attractive because they help address energy and environmental challenges and advance sustainable aviation. They have the potential to improve air quality and slow down global climate change while expanding access to local energy resources by diversifying fuel sources. Alternative fuels can also contribute to price and supply stability and help energize economic development in rural communities. Electrification and decarbonization of aircrafts offer a number of benefits, including reduced energy consumption, lower greenhouse gas emissions, lower noise levels compared to conventional aircrafts, and more reliable electrical subsystems. However, current production rates of sustainable aviation fuel (SAF) technologies can only meet a fraction of the market size of the commercial aviation industry. Similarly, short-range all-electric aircrafts offer great potential for reducing environmental impacts, but will require significant improvements in battery technologies to remain cost competitive. The use of alternative fuels and emission-reducing electric aircrafts in the aviation industry will support emerging economies by maximizing the use of existing infrastructures. However, implementing these strategies requires global planning and some of these technologies require infrastructural revisions in order to maintain the same level of safety at all destinations with the alternative solutions. At this point, while SAFs used in commercial aircrafts offer a long-term, environmentally friendly solution, battery technologies need to be further developed in terms of safety and reliability. In addition, the investigation of operational parameters of batteries such as energy density, weight, operating temperature, and battery recycling and the analysis of environmental impacts and emissions from the production of battery technologies to the recycling of batteries are necessary to understand the environmental impacts of this latest proposed solution more comprehensively and to address the current negative consequences of such technologies in the aviation industry. While current projections show that the dependence on liquid fuels in the aviation sector will continue to increase, it is assessed that alternative methods such as electrification and hydrogen, which are much more costly and require additional safety procedures and major infrastructure changes, will not be feasible in the near future. Overall, sustainable aviation must be achieved on the condition that flight safety is at the forefront for both cargo and passenger transportation while cost and environmental benefits are taken into account.

COAL PYROLYSIS STUDIES: APPLICATION TO IN-SITU SUPERHEAT STEAM HYDROGEN PRODUCTION

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Abstract

Hydrogen is promising as a potential alternative energy source that can replace fossil fuels. The most common hydrogen production method is pyrolysis. In this study, pyrolysis experiments of 4 coal samples (Missouri, Wyoming, Colorado, and Illinois) were carried out to determine weight loss by thermogravimetric analysis (TGA) and measurement of off-gas composition by gas chromatography (GC) for H₂, or mass spectrometry (MS) for light hydrocarbons, C1-C4. Results are intended to support the concept that in-situ pyrolysis of coal by superheat steam can be a source of hydrogen, along with hydrocarbon components which can be used for providing heat to drive the process with excess going into pipeline.

Keywords: Hydrogen production, In-situ coal recovery; Coal pyrolysis; Superheat steam stimulation

1 INTRODUCTION

One of the primary candidates for the replacement of fossil fuels is hydrogen. However, hydrogen does not typically occur in large quantities in the molecular form, so it must be produced by any of various processes. The Department of Energy has summarized four methods to produce hydrogen¹. These are: natural gas reforming, biomass gasification, biomass-derived liquid reforming, and solar thermochemical hydrogen. For the reforming processes, carbon dioxide is a byproduct, and since this is classified as a greenhouse warming gas, various methods are being considered to prevent its venting into the atmosphere, such as deep well injection. The DOE Project “Hydrogen Shot”² seeks to produce hydrogen for 1\$ per kg within 1 decade.

The application of this work is to support the concept of in-situ pyrolysis of coal for production of hydrogen and lighter hydrocarbons of value. The hydrogen economy is in need of a source of hydrogen without attendant carbon dioxide production, other than electrolysis of water, which to date, is not a widely deployed technology. Among other

considerations in this study are the retention of carbon in the formation along with sulfur so that this method does not inject these associated pollutants into the atmosphere. Although various gases can be injected into the formation to carry heat from the surface, steam is characterized by a high specific heat, compared to other gases and hence, can convey more energy to the formation at a given temperature than many other choices. And a major component of energy in superheated steam occurs in the liquid phase so that heat exchange is well known and practiced.

TGA, MS, and GC were used to help identify hydrogen content and hydrocarbon species of the gaseous products from various coal samples during pyrolysis. Coal composition varies significantly depending on the type, formation, moisture, etc. The most abundant element is carbon, and the typical ratio of C/H is around 1/1 which implies that hydrogen is around 8% by mass, but because of other components, e.g., moisture, sulfur, nitrogen, oxygen, ash, then a more typical composition of hydrogen is around 6%, notwithstanding the hydrogen content in moisture. Adding complication, is that water can be associated with coal, either as free water

which evaporates at lower temperatures, or associated water which typically is liberated somewhere in the range of 200 °C - 300 °C. Along with production of hydrogen by coal pyrolysis, a significant quantity of methane is also expected, along with a modest production of C2-C4. Other typical components of coal include nitrogen, oxygen, sulfur, and ash. Although the occurrence of these components can confound recovery of marketable gases, the undesirable constituents, e.g., sulfur and coke remain mostly underground. Heavy crude oils, subject to pyrolysis conditions, have been shown to produce free hydrogen³. Previous studies of pyrolysis of shale oil have also shown that some shales, e.g., Pennsylvanian formation shales in eastern Kansas, result in a high level of hydrogen evolution under pyrolysis conditions⁴.

A conceptual schematic, illustrating how an in-situ process to recover hydrogen and methane in marketable quantities, is shown in Figure 1.

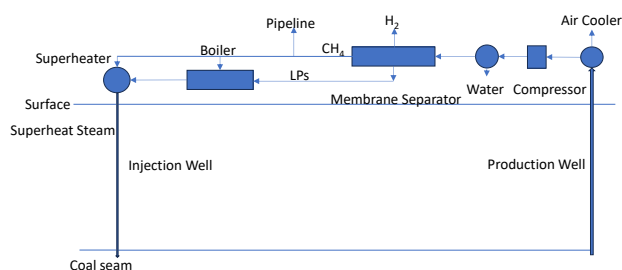


Figure 1. Idealized schematic of H₂ recovery system

In Figure 1, hydrogen is shown to be separated from methane by membrane, which is a well demonstrated technology⁵. It is anticipated that separation will not be 100% but trace contamination of either stream is not an expected problem.

In this study, pyrolysis experiments of Missouri, Wyoming, Colorado, and Illinois coals samples were carried out to determine weight loss by Thermogravimetric Analysis (TGA) and measurement of off-gas composition by gas chromatography for H₂, or mass spectrometry for light hydrocarbons, C1-C4. The samples were subjected to in situ pyrolysis at the specified temperatures and the results were compared.

2 EXPERIMENTAL DETAILS

Four different coal samples were provided by Energy Analyst, LLC and were pulverized using a mortar and pestle prior to analysis. Preliminary thermal analysis was carried out in

a Thermogravimetric Analyzer (TGA; NETZSCH STA 449 F3 Jupiter) from room temperature to 900 °C at a rate of 20 °C/min under argon with a purge flow of 100 ml/min. This was to establish the anticipated pyrolysis temperature range to be used in experiments to follow.

To determine the gasses evolved during pyrolysis of the various coal samples, 0.5-2 g of pulverized coal was loaded into an alumina boat which was placed in a quartz process tube within a tube furnace (Lindberg/BLUE Eurotherm) and a nitrogen purge was established with a flow of 178 ml/min (135 ml/min at STP) using a mass flow controller. Once all air had been flushed from the system (at least 15 mins) the tube furnace was heated from room temperature to 500 °C or 600 °C at a rate of 5 °C/min and held at the maximum temperature for 3 hours.

During the entire pyrolysis experiment, gaseous compositions were measured using a Gas Chromatograph (GC; Agilent Technologies 3000A Micro GC) and a Mass Spectrometer (MS; Hiden Analytical QGA) both of which sampled the gas stream exiting the process tube (See Figure 2). The GC was calibrated using a certified calibration gas mixture (purchased from MESA Specialty Gases) containing 100 ppm each of various hydrocarbons by volume, and a hydrogen/argon gas mixture containing 2% hydrogen by volume (Matheson Trigas).

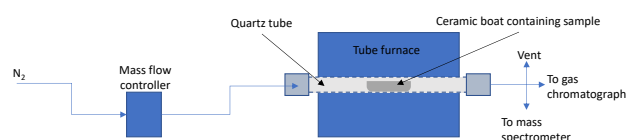


Figure 2. Schematic of tube furnace experimental setup

Gas flow rates for purge gases were established using a bubble meter and were corrected to Standard Temperature and Pressure (STP) for use in the calculation of product flow rates. Raw data from the GC (i.e., concentration of a species) was converted into a flow rate of the species based on the flow rate and concentration. Numerical integration of the resulting curve of flow rate versus time gave an absolute amount of the species, which was normalized against mass of coal sample to give a yield of the species in liters of gaseous species per kilogram of coal (L/kg) at STP.

3 RESULTS AND DISCUSSION

Figure 3 summarizes the TGA data for all four coal samples, measured under identical conditions, and with similar masses.

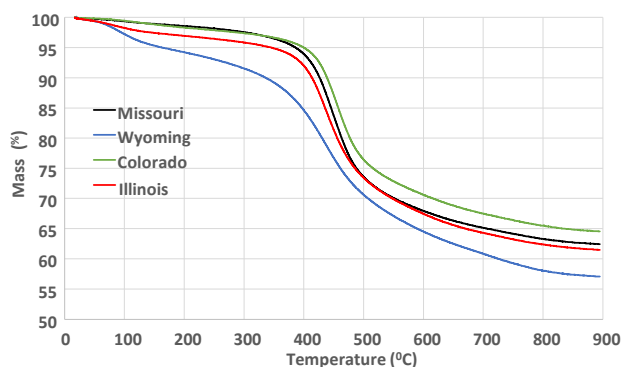


Figure 3. TGA plots for all coal samples measured under argon (100 ml/min) with a heating rate of 20 °C/min

The major mass loss for each coal sample occurs between 400 and 600 °C, and it was decided to investigate pyrolysis at two temperatures in this range: 500 and 600 °C.

The Missouri coal showed the least difference in mass loss between the two techniques, suggesting it is the least dependent on time at temperature. The greatest mass loss was shown by the Wyoming coal sample which may be attributed largely to its high-water content, as shown by the MS data recorded during tube furnace runs. The coal samples from Colorado and Missouri showed similar mass loss profiles, with the lowest mass loss below 400 °C of all the coals tested; this observation may be attributed to the relatively small amounts of water and light hydrocarbons detected during the tube furnace runs.

3.1 Evolved Gas Analysis

Results show the calculated flow rates of hydrogen and the major light hydrocarbon species evolving from the coal samples during each tube furnace run as determined from the GC data. Flow rates are reported as liters of gas per minute per kilogram of coal (L/min/Kg). To provide a work-around, a run was conducted under a helium carrier gas which allowed estimation of methane yield from the GC data for one sample.

For the MS data, only the signals corresponding to water (mass 18), hydrogen (mass 2) and methane (mass 16) are plotted; higher hydrocarbons tend to fragment prolifically in

the mass spectrometer under electron bombardment, and thus are not representative of the true gas composition. The MS data analysis shown water evolution from most coals occurs in two or more stages; one below 300 °C, and one or more at higher temperature (above 350 °C for the Illinois coal, and closer to 450 °C for the other coals). Common to all coal samples is a dominant hydrogen peak that occurs slightly after the major hydrocarbons are released.

The hydrogen envelope extends throughout the isothermal period and drops to zero quickly once the furnace temperature begins to cool. The trends in integrated volumetric hydrocarbon evolution for all coal samples was typically $\text{CH}_4 > \text{C}_2\text{H}_x > \text{C}_3\text{H}_x > \text{C}_4\text{H}_x$. Wyoming coal had a significantly larger fraction of ethylene which evolved early in the heating process, beginning around 150 °C.

4. CONCLUSIONS

All coal samples were characterized by thermogravimetric analysis and were subsequently subjected to pyrolysis under inert gas purge with analysis of evolved gases by mass spectrometry and gas chromatography. Water, hydrogen, and light hydrocarbons (C1 – C4) were the principal evolved species that were tracked. Water was not quantified but contributes significantly to the low temperature mass loss of most coal samples. Hydrocarbons typically begin evolving between 350 and 400 °C, although a few instances of lower-temperature release of ethylene were noted. Hydrogen evolution peaked at slightly later times than the hydrocarbons, and remained at a measurable level until the end of the pyrolysis period and the furnace began to cool, regardless of whether the pyrolysis temperature was 500 or 600 °C. The hydrogen evolution peak was so large for the coal samples pyrolyzed at 600 °C that the GC detector became saturated. Two runs were repeated using smaller quantities of coal to bring the hydrogen level down to a quantifiable level.

The MS traces were examined for any of the expected forms of sulfur which might be in the gaseous products, and none were found.

From these results, it can be surmised that in-situ of coal by high temperature gas injection (superheated steam, for example), may warrant further study as a vast potential source of

hydrogen, necessary to fuel the future hydrogen economy.

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ADDITIVE MANUFACTURING OF VESSELS FOR HYDROGEN STORAGE

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Abstract

This work presents an analysis of available literature and future prospects for producing hydrogen storage vessels using additive manufacturing technologies. Various materials and technologies are explored independently and in unison to arrive at the best combination of strength, storage efficiency, impermeability as well as safety. Additive manufacturing technologies currently available are found to be capable of producing the required material properties as well as the customization needed for modular operation, where the capacity of said vessels are tailored to the needs of the end users and proposed applications. Operating under high pressure also paves the way for 3D printed high pressure storage vessels that can also be utilized for compressed air energy storage applications, which adds to the appeal and novelty of using additive manufacturing for physical energy storage purposes.

Keywords: High pressure vessels; additive manufacturing; 3D printing; hydrogen storage; compressed air energy storage

NOVEL INTEGRATED HYDROGEN LIQUEFACTION PROCESS USING PHOTOVOLTAIC PANELS AND DIFFUSION ABSORPTION REFRIGERATION

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Abstract

This research explores a hybrid hydrogen liquefaction configuration that integrates a combined heat and power system, photovoltaic cells, diffusion absorption refrigeration, and waste heat recovery. The system is specifically designed and analyzed under the climatic conditions of Seoul, South Korea. Furthermore, these cascade refrigerating systems have the requisite cooling and liquefaction capabilities-helium and hydrogen refrigerants. The specific energy consumption is a very challenging issue when it comes to hydrogen storage through liquefaction. Waste heat recovery from various industries can help reduce the power consumption in hydrogen liquefaction cycles. This study utilizes waste heat from the power plant to provide refrigeration within the diffusion absorption refrigeration cycle. The developed integrated structure needs 9 MW of power and supplies this amount from solar energy and photovoltaic panels. By Aspen HYSYS V12.1 software and PVsyst 7.3.1 software for the design of photovoltaic panels, simulated the developed integrated structure. Also, the diffusion absorption refrigeration integrated structure generates 50 TPD of liquid hydrogen. The research aims to assess the performance and efficiency of this integrated system within the unique environmental context of Seoul, which includes significant solar radiation and the availability of waste heat from various industries. The findings of this study could contribute to improving hydrogen liquefaction methods and the use of renewable energy resources in regions with similar climatic conditions. To supply the cycle power, out of 3 modules of AXITEC AC-550MBT and 157 inverters Canadian Solar CS-125KTL have been used. Additionally, the highest and lowest of performance ratio were 89.6% in January and 79.2% in August, respectively. The highest and lowest of available energy were 3726.8 in September and 3304.6 MWh in February, respectively. As well as the maximum and minimum losses due to mismatch were recorded in September and February in the amount of 83.80 and 72.78 MWh, respectively. Also, the specific power consumption in the structure is 4.320 kWh/kgLH₂.

Keywords: Hydrogen, solar energy, photovoltaic panels, process integration, waste heat recovery.

1 INTRODUCTION

The increasing energy consumption has led to the growing global initiative focused on reducing the adverse environmental and economic impacts associated with energy use [1,2]. Hydrogen (H₂) definitely does represent a viable alternative to fossil fuels because of versatility in production of electricity and its potential integration within current natural gas systems [3,4]. In recent decades, H₂ has received wide attention as a potential cleaner fuel with the aim of mitigating greenhouse gas (GHG) emissions [5]. However, the steps involved in its production, storage, and transportation have received wide recognition as fairly challenging and expensive [6,7]. When H₂ burns, it is water vapor that is released and includes a large amount of energy [8,9]. Even

though there are advantages to liquid hydrogen (LH₂), its production is highly problematic due to issues such as specific energy consumption (SEC) and boil-off gas (BOG), which create many complications while trying to produce it [10]. Yang et al. [11] proposed a new process for producing LH₂ coupled with energy storage, accompanied by 3E analysis for technical feasibility and economic viability estimations of the process. Their results gave an overall exergy efficiency (EXE) of 53.2%, a SEC use of 7.25 kWh/kgLH₂, and a round-trip efficiency (RTE) of 58.9%. Yin et al. [12] conducted an analysis and optimization of H₂ liquefaction processes. The results showed that their study gave an overview of the recent progress regarding design and optimization of H₂ liquefaction processes. The

SEC was found to range between 5-8 kWh/kgLH₂ while EXE ranges between 40%-60%. Ghorbani et al. [13] proposed a new approach for a liquid carbon dioxide (CO₂) energy storage system configured for power production by solar energy. Their results showed that the net power produced by the combined system to be 7.872 MW for Tehran, Iran. Besides, EXE was computed to be 83.84%, while the cost of major product was estimated at 8.55 US\$/kWh. Taghavi et al. [8] presented an integrated process for H₂ liquefaction with renewable energy sources and liquid air cold energy recovery (LACER) for pre-cooling of the H₂. From here, an economic analysis gave a payback period of 4.249 years, while the production cost for the LH₂ was 5.432 USD/kgLH₂ and an additional value of 1.567 US\$/kgLH₂. Jouybari et al. [14] developed a configuration for the integrated system that includes waste heat recovery (WHR) and a Kalina power generation unit in H₂ liquefaction. Results showed that it gave an EXE of 23.59% with a SEC of 7.405 kWh/kgLH₂, produced 22.34 kg/s of LH₂, and generated a power rating of 595.6 MW. Mehrpooya et al. [15] proposed a novel H₂ purification process using diffusion absorption refrigeration (DAR). The results obtained showed the overall exergy destruction rate to be 45.764 kW, while irreversibility in the air cooler contributed 32%. The amount of thermal energy input to the refrigeration unit was 16.81 kW. The sensitivity analysis presented that while increasing the H₂ content by 36%, the energy consumption increased by 2.2% and EXE criterion 1 decreased by 2.6%. Berrada et al. [16] provided in-depth reviews of H₂ production using solar energy and photovoltaic systems, with a great deal of emphasis on the economic and socio-political aspects of H₂ production in Morocco. This research work estimated the cost of H₂ production in Morocco to be in the range of 3.49 to 5.96 US\$/kg. Karimi et al. [17] proposed an innovative process for H₂ production and liquefaction powered by solar power. The system is powered by both an organic Rankine cycle (ORC) and a thermoelectric generator while processing a considerable 6400 kg of LH₂ per hour. As indicated in the study, the liquefaction cycle had an SEC of approximately 5.72 kWh/kgLH₂, while their measured energy efficiency value for the H₂ production section was 16.64%.

Gençer et al. [18] described an original concept whereby solar thermal H₂ production is linked to

integrated coproduction processes using solar energy. Their model proved that if the coproduction process is combined with solar thermal H₂ production and power generation, there will be an improvement of up to 11% in EXE compared to conventional routes. Bamisile et al. [19] offered a thermo-environmental study for the concentrated photovoltaic thermal (CPVT) system, which was integrated with a Kalina power cycle for multi-generation and H₂ production. The results got from these two new multigeneration setups showed that configuration 1 could have an energy efficiency as high as 68.73%, while configuration 2 reached 70.08%. Besides, integration of the Kalina power cycle with CPVT increased electricity production by 14.15%. Mousavi et al. [20] suggested a cogeneration system driven by parabolic trough collectors (PTC) generating solar energy, with an ORC and DAR systems in the layout. Exergy destruction in the PTC field was maximum, 31.80 kW out of 67.89 kW for the total system; the EXE for the PTC and the whole system was 55.23% and 67.89%, respectively. It provided the required power and cooling of 10.76 kW and 44.55 kW, respectively, using 80.76 kW and 364.30 kW in thermal energy from the DAR and ORC systems, respectively. Moreover, nighttime make-ups for the energy demands were achieved through a battery bank and phase change material (PCM). To create a more sustainable and cost-efficient H₂ liquefaction process, there is increasing interest in harnessing solar energy, photovoltaic panels (PV), and WHR as alternative energy sources. In this paper, a design for a H₂ liquefaction system using WHR, solar energy, and PV technology in Seoul, South Korea, is presented. The process was modeled using Aspen HYSYS V12.1, and the PV system was designed with PVsyst 7.3.1.

2 PROCESS DESCRIPTION

Liquid hydrogen is considered one of the cleanest and most environmentally friendly sources of energy because it would result in completely no emissions when used, making it a zero-emission source of energy. However, for the storage and transportation purposes of gaseous H₂ to be feasible, the liquefaction process becomes important. This is because large storage tanks are needed in the gaseous state that makes the storage and transportation of H₂ in this state to be difficult and expensive. However, liquefaction advantages such as the production of LH₂, which can be more

easily stored and transported. However, the ortho- H_2 to para- H_2 conversion badly affects the process of the H_2 liquefaction cycle. Normally, H_2 contains 25% para- H_2 and 75% ortho- H_2 . During liquefaction, this conversion is extremely necessary since ortho- H_2 continues to be unstable at a temperature near absolute zero, and in case it is not converted to para- H_2 while storing, some difficulties or energy loss may be noted. Hence, its optimization is important and necessary for controlling and optimizing the H_2 liquefaction process so that it may achieve better efficiency without losing energy. Ultimately, LH_2 is not only feasible as a source of sustainable and clean energy but is also foreseen to be resilient in supply where clean and reliable energy is required in such remote and inaccessible places. This creates a particular interest in these contexts due to its ease of storage and transportation [10].

This research gives an innovative H_2 liquefaction system that eliminates multi-component refrigerants with reduced specific energy consumption by the combination of WHR and DAR. Solar energy is used to waive the supply of energy to the liquefaction cycle. Waste heat is supplied to the absorption refrigeration cycle, which produces cooling for H_2 precooling. A proposed approach combining an integrated cooling cycle with solar energy has the potential to make a breakthrough in H_2 liquefaction where extensive solar resources are available, such as Seoul in South Korea.

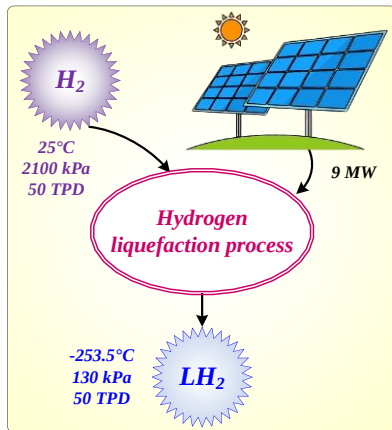


Figure 1. The block flow diagram (BFD) of the integrated structure of the hydrogen liquefaction process.

Considering that South Korea has the largest concentration of factories and huge waste heat from those industries, with excellent solar irradiance, the effectiveness of this new system is

bound to be very high. Figure 1 shows the block flow diagram (BFD) for the integrated scheme designed for H_2 liquefaction. Also, Figure 2 shows the process flow diagram (PFD) for the integrated scheme designed for H_2 liquefaction.

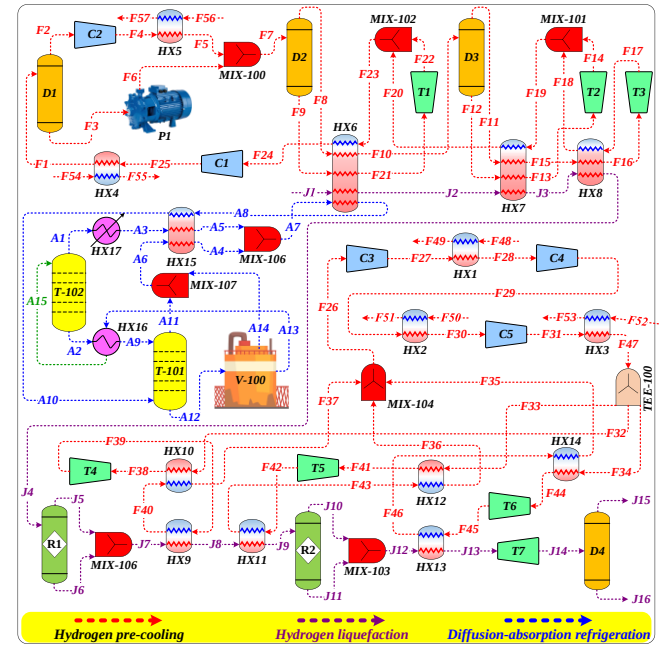


Figure 2. The process flow diagram (PFD) of the integrated structure of the hydrogen liquefaction process. Modified from ref. [1]

The developed integrated structure needs 9 MW of power and supplies this amount from solar energy and PV. Solar energy, WHR, and DAR are utilized in the process of H_2 liquefaction. PV installed in Seoul, the capital city of South Korea, are used to provide the required power for the H_2 liquefaction system. Seoul is situated in the northwest region of the country and is bordered by Paju to the north, Incheon to the west, Gyeonggi Province to the south and east, and the Han River to the southeast. The approximate PV power potential in Seoul is 1400 kWh/kWp per year, and the average solar horizontal irradiation is 1500 kWh/m² [21]. With growing global demands on energy, renewable sources of energy become critical in today's world energy scene. In this context, the most prominent among such contributions is solar energy. The solar cell, otherwise known as a photovoltaic cell, is at the heart of any solar power technology and converts sunlight into electrical energy by the photovoltaic effect [22]. The International Energy Agency defined some key performance metrics that are useful for on-grid PV systems power plant

feasibility studies. Of importance is the final system yield, Y_F -a quantity that measures on-grid energy production over some period. Quantitatively, it may be expressed as the total output of AC energy by an on-grid PV system divided by its maximum STC power rating [23].

$$Y_F = \frac{E_{AC}}{P_{PV}} \quad (1)$$

The final yield of a PV system is defined as the amount of electrical energy generated, in kWh/kWp, which provides an indication of the continuous generation of electricity with respect to the rated capacity of the system.

E_{AC} reflects the AC electricity generated per unit of DC input. The peak power output, P_{PV} , is the maximum power under ideal conditions, while the reference yield, Y_R , is the ratio between in-plane solar radiation and the array's reference irradiance under STC [24].

$$Y_R = \frac{H_t (kWh m^{-2})}{G_o (kW m^{-2})} \quad (2)$$

$$Y_A = \frac{E_{DC}}{P_O} \quad (3)$$

$$PR = \frac{Y_F}{Y_R} \quad (4)$$

Y_A provide the DC energy produced by a PV system per kWh of rated power per kWp under STC. Performance ratio (PR) is a measure of the ratio of the system final yield to its reference yield.

The total energy loss and array absorber loss can be calculated through Eqs. 5 and 6 as the difference between reference yield and array yield respectively [25].

$$L = Y_R - Y_F \quad (5)$$

$$L_C = Y_R - Y_F \quad (6)$$

Eq. 7 gives inverter efficiency computed from, which divides the AC power output by the inverter by the DC power output of the PV array. Eq. 8 is used to calculate the efficiency of a PV system, which is obtained by multiplying the efficiency of the PV module by the efficiency of the inverter [26].

$$\eta_{inv} = \frac{P_{AC}}{P_{DC}} \quad (7)$$

$$\eta_{system} = \eta_{PV} \times \eta_{inv} \quad (8)$$

3 SIMILATION AND DESIGN

The design and simulation of PV were performed using the PVsyst 7.3.1 software. The weather conditions of Seoul, the capital of South Korea, were considered for the simulation. Seoul is geographically located at latitude 37.532600 (37° 31' 57.3600" N), longitude 127.024612 (127° 1' 28.6032" E), and is 38 m above sea level, situated in the northwest region of the country. It shares borders with Paju to the north, Incheon to the west, and Gyeonggi Province to the south and east. The Han River flows along the southeastern boundary of the city. The movement path of the sun and the shading loss of Seoul city for one year are shown in Figure 3.

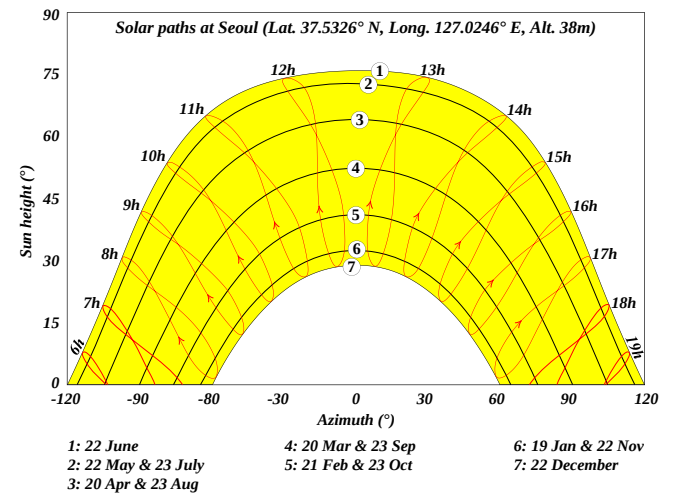


Figure 3. The solar paths at Seoul.

4 RESULTS AND DISCUSSION

The operational specifications of the solar PV utilized in the hybrid configuration developed are enumerated in Table 1.

Table 1. The operational specifications of the solar PV.

Specification	
Electrical performance under standard test conditions (*STC: irradiance 1000 W/m ² , module temperature 50°C)	
Maximum operating power (P_{max})	8885 (kW)
Highest power voltage 20°C (V_{mpp})	640 (V)
Highest power current STC (I_{mpp})	15948 (A)

Open circuit voltage -10°C (V_{oc})	896 (V)
Short circuit current STC (I_{sc})	17272 (A)
Electrical performance at Nominal operating cell temperature (*NOCT: irradiance 1054 W/m ² , module temperature 50°C)	
Maximum operating power (P_{max})	9347 (kW)
Highest power voltage 20°C (V_{mpp})	640 (V)
Highest power current GMax (I_{mpp})	16822 (A)
Open circuit voltage -10°C (V_{oc})	896 (V)
Short circuit current GMax (I_{sc})	17272 (A)
Module characteristics	
Length × Width × depth (mm)	1476 × 983 × 35
Weight (kg)	17
Number of Module	49944 (2081 strings of 24 modules in series)
Manufacturer	Hyundai
Description and details	Hyundai_HIS_S200SF
Inverter characteristics	
Length × Width × depth (mm)	2600 × 2080 × 800
Weight (kg)	1550
Number of Inverter	18
Manufacturer	Hyundai
Description and details	Hyundai_HPC_500HL

To model the PV unit and supply its energy needs, it is important to examine the geographical features and meteorological conditions of the site. In this research, a fixed-tilted panel was employed for the model, with an average monthly horizontal solar irradiation of 34 ° angle that was considered

the slope angle of PV units.

In Figure 4, a comparison is made between the monthly yield and energy production of both the reference model by [23] and the proposed model.

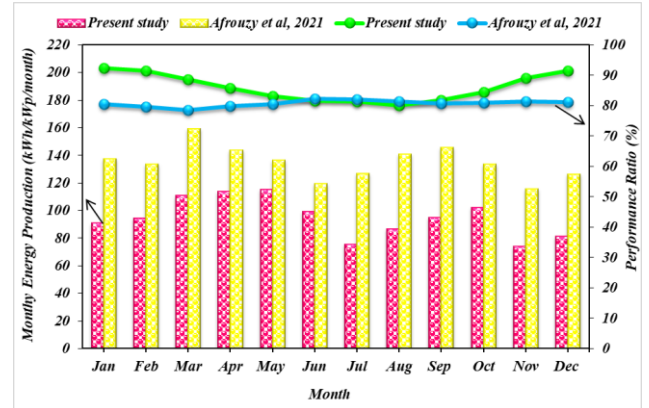


Figure 4. Comparing monthly yield and energy production of the reference [23] and proposed model.

Figure 5 depicts the average monthly temperature and solar irradiation in a typical year for Seoul.

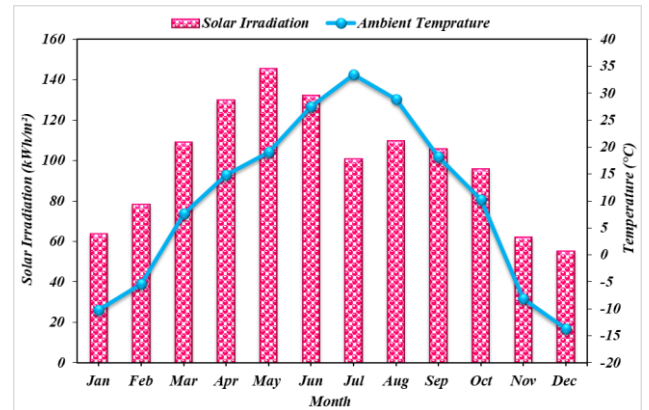


Figure 5. Monthly average ambient temperature and solar irradiation in a typical year in Seoul.

Based on the data shown in Figure 6, the average monthly horizontal global radiation in Seoul varies from 55.30 kWh/m² in December to 145.4 kWh/m² in May.

Additionally, the warmest month of the year is July with an average temperature of 33.5 °C, while December is the coldest month with an average temperature of -13.7 °C.

On average, the environmental temperature in Seoul throughout the year is 12.54 °C. In Figure 6, the PR, energy produced by the array, and energy injected into the grid are illustrated.

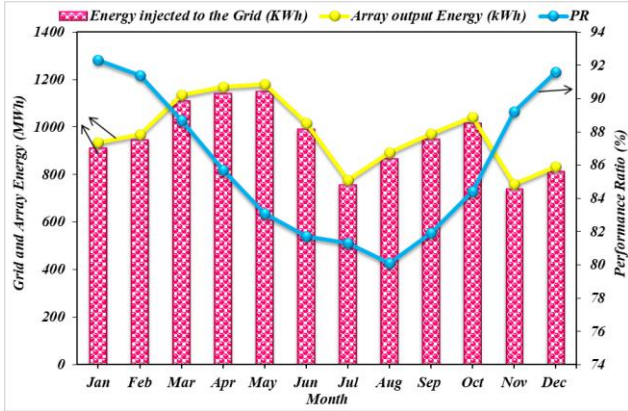


Figure 6. Monthly array energy production and energy injected into the grid and PR.

Throughout the year, various systems showed monthly fluctuations in solar energy injection, as seen in Figure 6. The PR for January was the highest at 92.3%, whereas it was lowest in August, at 80.1%. The average PR for the year was 85.7%. May recorded the highest available energy at 1150 MWh, while July recorded the lowest at 756 MWh, possibly because of higher global solar irradiance on tilted planes during different months. Figure 7 depicts the PV unit and collection losses, along with the productive energy generated.

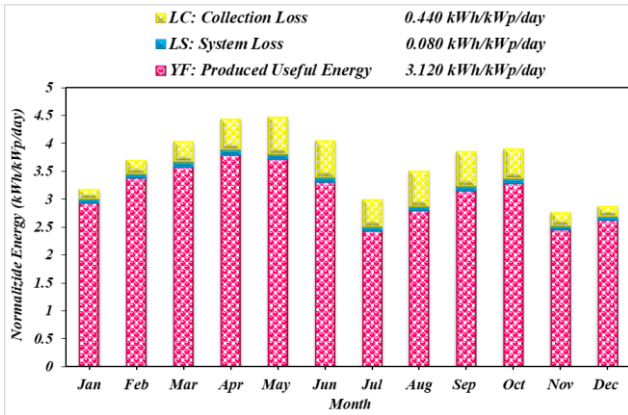


Figure 7. Normalized energy per month.

PV panels absorb solar energy, which subsequently undergoes a reduction in energy through absorption losses, before being routed to inverters. These inverters then distribute the resulting energy into the grid as beneficial energy. In a typical year in Seoul, Figure 8 shows the system's, array's, and inverter's efficiencies. Electricity can be generated using PV panels over a broad range of optical frequencies. However, since they are incapable of capturing the entire spectrum of sunlight, a significant amount of solar energy remains unutilized.

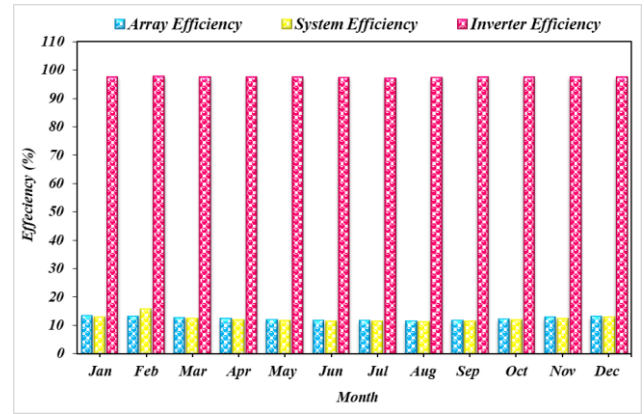


Figure 8. System, array, and inverter efficiencies in a typical year in Seoul.

Based on simulations, Figure 9 illustrates the losses incurred by the PV system throughout the year.

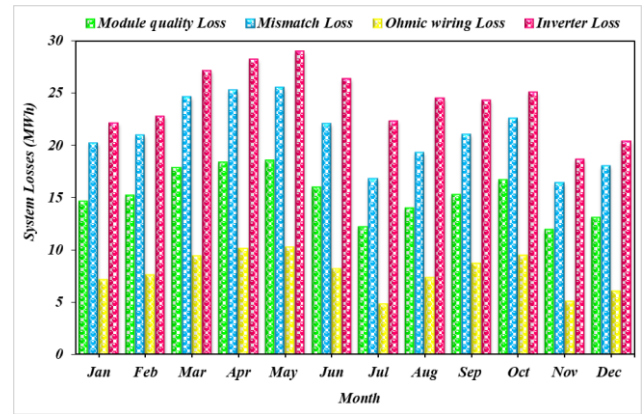


Figure 9. Diagram of system losses over the whole year in Seoul.

The findings indicate that the incorrect selection of cable size and length can lead to a direct impact on ohmic wiring loss, resulting in an average annual loss of 93.78 MWh. Additionally, the average annual loss attributed to module quality was found to be 183.4 MWh. The maximum and minimum losses due to mismatch were recorded in May and July the amount of 25.51 MWh and 16.79 MWh, respectively.

5 CONCLUSION

This paper proposes a new integrated scheme for an H₂ liquefaction system that combines PV, DAR, and WHR, optimized for the climatic conditions of Seoul, South Korea. This configuration integrates solar energy, supplying the required 9 MW of power to feed the liquefaction process, and significantly improves

the whole efficiency of the system. Results show that the system produces 50 TPD of LH_2 with an SPC of 4.32 kWh/kg LH_2 . It can be noted that through baseline design strategies integrating WHR and DAR with solar energy, energy efficiency is improved considerably, reflected in its high exergy efficiency reaching 67.89%. To supply the cycle power, out of 3 modules of AXITEC AC-550MBT and 157 inverters Canadian Solar CS-125KTL have been used. The highest PR was in January at 89.6%, while the lowest one was 79.2% in August. Its energy generation performance has also been quite strong; the highest available energy was at 3726.8 MWh during September, and the lowest was during February with 3304.6 MWh. As well as the maximum and minimum losses due to mismatch were recorded in September and February in the amount of 83.80 and 72.78 MWh, respectively. It adds extremely useful insights into the potential of renewable energy integration in H_2 liquefaction processes for developing a sustainable and cost-effective solution for H_2 production and storage, especially in regions with rich solar resources. The findings have implications for implementing such systems in industrially dense and solar-rich areas, such as Seoul, to rapidly propel the H_2 economy through mitigated dependence on fossil fuels and environmental impacts. Further work will seek to optimize components of the system while gaining experience in the scalability of this approach in different geographic contexts to enhance global H_2 production capacities.

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DIRECT USE OF OXYGEN AND HYDROGEN PRODUCED BY ELECTROLYSIS IN AN INDUSTRIAL NATURAL GAS BURNER

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Abstract

Electrolysis systems are of great importance in terms of green hydrogen production today. While hydrogen production is carried out from water with these systems, oxygen atoms are also released. In this study, experiments were carried out on an industrial natural gas burner with a maximum power of 100 kW. Instead of storing the H₂ and O₂ gases that will emerge as a result of a standard electrolysis process, it was simulated that they were fed directly to the natural gas boiler. The burner power was kept constant as 33 kW in the experiments. First of all, the effect of 10% H₂ by volume was added to the fuel and the boiler outlet temperature was investigated. In addition, the oxygen enrichment performance of the hydrogen-added fuel was tested by adding additional O₂ to the inlet air. In the numerical study, the experimental data were first verified. The results obtained showed that H₂ addition increased the combustion chamber outlet temperature under all O₂ conditions. In addition, a critical change of 28.5 - 31% O₂ occurred in both natural gas combustion and H₂ addition cases. After this interval, the combustion chamber outlet temperature decreased.

Keywords: Methane, Hydrogen, Oxygen Enrichment

1 INTRODUCTION

Natural gas is a fuel with a low carbon/hydrogen ratio, almost all of which consists of methane gas. Since it has the lowest carbon ratio among hydrocarbon fuels found in nature, its usage rate is high. Despite this, researchers are looking for ways to reduce CO and CO₂ emissions resulting from the carbon content of natural gas. The most prominent issue in this regard is Hydrogen energy. Researchers are conducting intensive studies for Hydrogen energy. These studies include starting from the production stage of Hydrogen, storage, transportation and combustion. All of these stages involve different difficulties and need to be solved. In the literature, Methane gas is used in many studies

to represent natural gas. There are many studies aiming to burn Methane gas as a mixture with Hydrogen and achieve low emissions.

Alabas et al. [1] enriched methane fuel with both hydrogen and oxygen in their study. The study results showed that both O₂ and H₂ increases reduced CO emissions. On the other hand, H₂ addition reduced NO_x emissions, while oxygen enrichment increased them. Zhang et al. [2] investigated the oxygen enrichment of methane flame for high compression ratio condition. The results showed that oxygen enrichment greatly increased the flame propagation speed. In addition, it was seen that the increase in oxygen ratio also supported the formation of flame. Cai et al. [3] investigated the effect of different O₂ ratios on methane flame combustion speed and

Markstein length under high pressure. The results showed that oxygen enrichment greatly increased the laminar combustion speed. On the other hand, oxygen enrichment decreased Markstein length and made it unstable due to hydrodynamic instabilities. Xu et al. [4] investigated the NO formation and heat transfer structure of Methane/Hydrogen mixtures under MILD combustion conditions in their study. The results showed that hydrogen addition caused an increase in Damköhler number. On the other hand, in cases where the hydrogen content is high, MILD combustion has given results. When the studies in the literature are examined, there are examples where methane fuel is enriched with Hydrogen and Oxygen. Most of these studies are pilot burners. Despite this, there are deficiencies in the studies carried out on an industrially used burner.

2 METHODOLOGY

The numerically validated combustion chamber is shown in Figure 1 [5]. First, methane combustion was carried out at different O₂ ratios in the burner from which the experimental data were taken. The boiler outlet temperature at the end of combustion was obtained under all O₂ conditions. The validated experiments were carried out in the laboratory of Dr. Isabel Amezcua, Department of Energy Engineering, Polytechnic University of Madrid. The results obtained were submitted to Fuel journal and are under peer review after revision.



Figure 1. Combustion Chamber

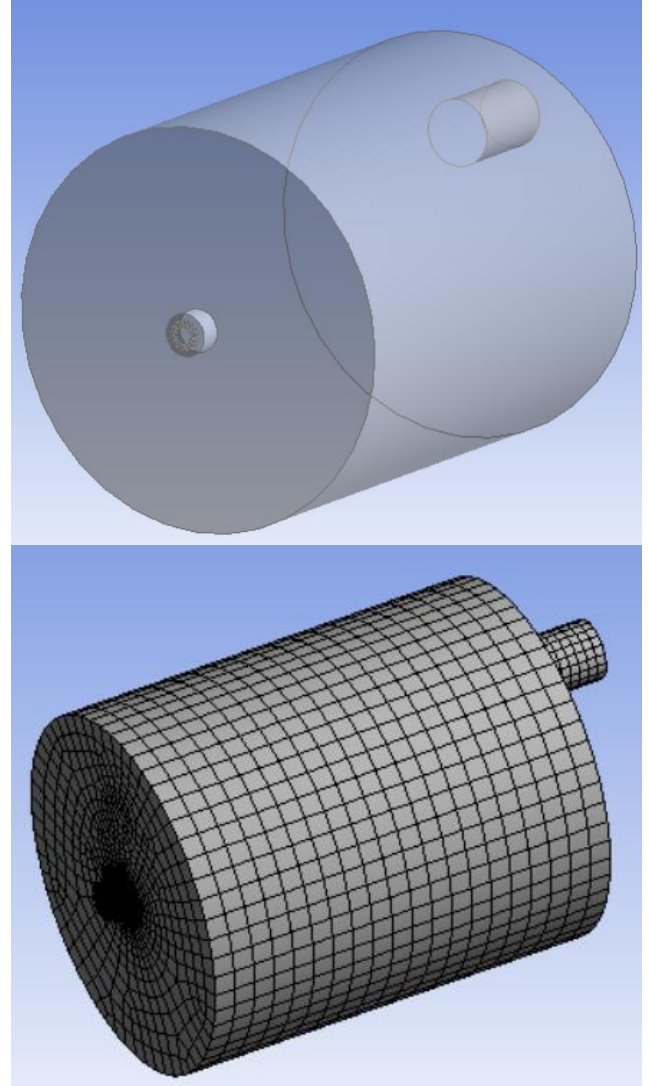


Figure 2. Combustion chamber model and mesh structure used in the study

The model combustion chamber and mesh structure used in the current study are presented in Figure 2. Modeling was performed on a single piece simulating the entire combustion chamber. Ansys Fluent CFD code, which is available in Erciyes University infrastructure, was used for all computational reactive analyses. In order to ensure that further modeling is acceptable, exhaust temperature values obtained at 100% methane and O₂ levels in different oxidizers were verified with experimental temperature values. For this purpose, the initial design parameters used for verification and all cases examined in this study are given in Table 1.

In this way, it was aimed to reveal the effect of H₂ addition on the combustion performance of the gas turbine. The total heat load provided during this process was kept constant.

Table 1. Numerical analysis parameters

Definition	Value/Parameter	Unit
Inlet Turbulent Intensity	8	%
Thermal Power	33	kW
Equivalence Ratio	0,83	---
Convective heat transfer coefficient	30	W/m ² .K
Wall Thickness of the Combustor	0,002	m
Solver	Pressure-Based	---
Spatial Discretization	Second Order Upwind	---
Gradient	Least Squares Cell Based	---
Pressure	Presto	---
Mesh Nodes	338269	---
Mesh Elements	318768	---

3. RESULTS AND DISCUSSIONS

In this numerical study, firstly the verification of the experimental data was done. Figure 3 presents the graph where the experimental data was verified numerically. As can be seen from the graph, similar values were obtained in the boiler outlet temperatures at almost all O₂ ratios. In addition, the boiler outlet temperature change as a result of the O₂ change drew a similar curve. This shows that the burner was verified.

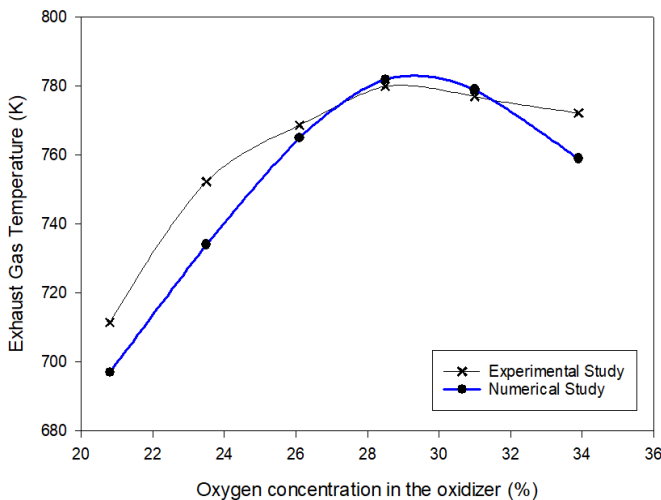


Figure 3. Numerical Verification

In the innovative part of the study, a scenario was simulated where Hydrogen and Oxygen gases resulting from electrolysis were fed to the burner at the same time. The flame temperature data obtained in this case are shown in Figure 4. The study results clearly show that the addition

of Hydrogen increases the combustion chamber exit temperature. At all O₂/N₂ ratios, boiler exit temperatures were higher in the H₂ added fuel. On the other hand, a similar change in the temperature increase trend occurred after 28.5% O₂ ratio and decreased after 31% O₂.

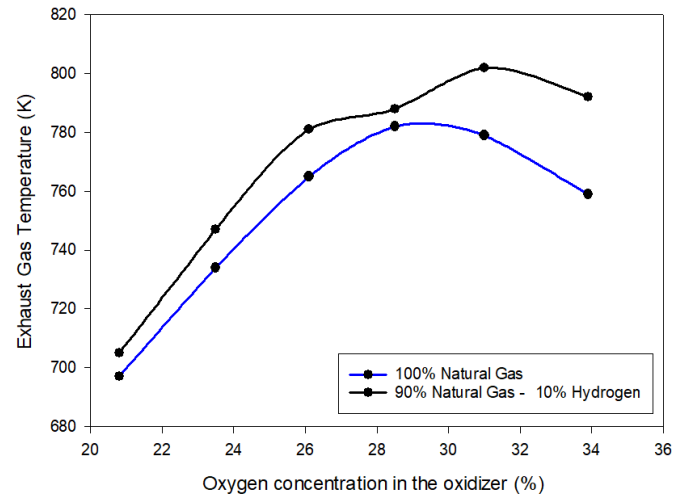


Figure 4. Effect of H₂ and O₂ addition on combustion chamber outlet temperature

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EFFICIENT PHOTOCATALYST OF A BINARY P-N HETEROJUNCTION, AG₃PO₄/CU₂O FOR DEGRADATION OF ENDOSULFAN AND HYDROGEN EVALUATION

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Abstract

In this work, the binary p-n heterojunction was fabricated and the band alignment at the interface of the individual semiconductor in photocatalyst materials, Ag₃PO₄/Cu₂O was thoroughly studied to know the superior charge separation and migration capability in photocatalytic behavior of fabricated materials. A simple wet chemical process followed by a hydrothermal fabrication strategy was incorporated for the development of the binary p-n Ag₃PO₄/Cu₂O hetero structures. The tunable band structure of individual semiconductors with the work function (ϕ), witnessed a band bending at the space charge region. The bending at the interface induces a carrier concentration gradient and manifests a rectifying current transport diode. The fabricated p-n heterostructures and carrier migration between n-type Ag₃PO₄ and p-type Cu₂O were verified by different morphological and physicochemical methods. The band banding at the interface, leading to a narrow depletion region, favors the tunneling of electron-hole pairs through a Z-scheme carrier transport mechanism. The electron-hole pair movement was further confirmed by considering the band edge position after contact, photocatalytic scavengers, and the radical trapping experiment. The Ag₃PO₄/Cu₂O p-n heterojunction photocatalyst manifested a 737.4 $\mu\text{mol g}^{-1}\text{h}^{-1}$ of H₂ generation and 91% endosulfan degradation efficiency, which are 12 and 9 times higher than that of pure Ag₃PO₄. The p-n heterojunction photocatalyst displayed a higher current density with electron-hole migration efficiency, synergistically enhancing the catalytic activity through the interfacial space charge junction.

Keywords: Semiconductor, Photocatalysis, p-n heterojunction, Band bending, Water Splitting, Endosulfan

EFFECT OF SLUDGE RETENTION TIME (SRT) ON BIOREGENERATION OF POWDERED ACTIVATED CARBON LOADED WITH PARACETAMOL

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Abstract

In this study, the bioregeneration of powdered activated carbon (PAC) loaded with analgesic and anti-inflammatory drug, paracetamol (PAR) was investigated at three different sludge retention times (SRTs). In the scope of bioregeneration of PAC loaded with PAR which operated in batch system, a five stage experimental set-up was carried out such as abiotic adsorption, abiotic desorption, bioregeneration process, post-adsorption, and adsorption onto activated sludge. Parallel to bioregeneration studies, biodegradation studies of PAR for control reactor have been carried out. According to the results obtained from bioregeneration experiment, the bioregeneration efficiencies of PAR were found to be 17.3% at the SRT of 10 days, 26.3% at the SRT of 30 days, and 20.1% at the SRT of 60 days. These results show that optimum SRT is 30 days for bioregeneration. The bioregeneration of PAR was affected by both desorption and extracellular enzymes.

Keywords: Adsorption; Paracetamol (PAR); Powdered Activated Carbon (PAC); Desorption; Bioregeneration; Extracellular enzyme

INTRODUCTION

Studies on the treatment of pharmaceuticals have shown that many of these substances cannot be completely removed by conventional activated sludge systems and membrane bioreactor (MBR) (Verlicchi et al., 2012; Kim et al., 2014). However, high sludge retention time (SRT) can increase metabolism and degradation capacity because of increase in microbial diversity. Also, the residence time of the micropollutants can be increased with activated carbon added biological treatment. Activated carbon can be regenerated from the activated carbon surface by bioregeneration. This study aims to investigate the effect of SRT on bioregeneration of PAC loaded with PAR. Bioregeneration is carried out by desorbing organic pollutants which adsorbed into activated carbon pores by the concentration gradient and extracellular enzymes and consuming them cometabolically by bacteria (Aktaş and Çeçen, 2007).

MATERIAL AND METHODS

Adsorption and desorption studies with PAR

Adsorption and desorption studies with PAR were performed in 100 mL flasks shaken at 150 rpm and 25°C. Desorption process was continued by changing the purified water until the concentration of the desorbed PAR reached to 0.1 mg/L.

Bioregeneration experiment

Bioregeneration of PAC was evaluated using a methodology consisting of five experimental steps. At the adsorption step, 1 g of PAC was loaded with 200 mg/L PAR. In the bioregeneration experiments, 500 mg of acclimated activated sludge taken from the control MBR which was operated at three different SRTs (10, 30 and 60 days) by the hospital wastewater was contacted with saturated PAC. Glucose and minerals were added to the reactor. In the post-adsorption step, PAR adsorption experiment was carried

out using the mixture of activated sludge and PAC which taken from bioregeneration reactor. In order to determine the sorption properties of sludge, 500 mg of the activated sludge was contacted with PAR (200 mg/L). Post adsorption and sorption experiments were performed by adding paraformaldehyde to prevent the activity of activated sludge. PAR concentration was determined using UV-absorption at 244 nm.

Bioregeneration was calculated based on the ratio between the equilibrium adsorption capacities of fresh and bioregenerated activated carbons (Klimenko et al., 2003) as follows:

$$\text{Bioregeneration (\%)} = 100 * Q_{\text{reg}} / Q$$

Eq.1

where Q_{reg} and Q are the equilibrium adsorption capacities of regenerated and fresh activated carbon, respectively.

RESULTS AND DISCUSSION

Adsorption and desorption of PAR

The removal efficiency of PAR (C_0 : 50 mg/L) at optimum conditions (PAC: 0.15 g, t: 24 h) was found to be 99.7%. The cumulative desorption efficiency was determined as 26.3%.

Calculation of bioregeneration

Table 1 presents the bioregeneration efficiencies which were calculated at each SRTs. The highest bioregeneration efficiency was obtained at the SRT of 30 days, and the lowest bioregeneration efficiency was at the SRT of 10 days. The reason was thought that the enzyme activity of biomass at SRT of 30 days was higher than the SRTs of 10 and 60 days. The results showed that the SRT was an important factor affecting bioregeneration of PAC.

Table 1. Bioregeneration efficiencies of PAC loaded with PAR at each SRTs.

SRT	10 days	30 days	60 days
Bioregeneration amount (mg/g)	26.6	40.7	30.6
Bioregeneration efficiency (%)	17.3	26.8	20.1
Bioregeneration with concentration gradient (mg/g)	17.3	17.3	17.3
Concentration gradient efficiency (%)	11.3	11.4	11.4
Bioregeneration with enzymes (mg/g)	9.3	23.4	13.3
Enzymes activity efficiency (%)	6.0	15.4	8.7

ACKNOWLEDGEMENTS

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**MICROPLASTIC (POLYSTYRENE) TOXICITY ON AQUATIC PRIMARY PRODUCER
NOSTOC MUSCORUM AND EFFECT OF CARBON DEPRIVATION ON POLYSTYRENE
FILM BREAKDOWN**

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Abstract

Polystyrene microplastic is categorized as an emerging pollutant. Indiscriminate use of microplastic-loaded articles contaminates our environment that cause reduction in primary and secondary productivity of the ecosystems. In extreme conditions it may lead to complete collapse of the ecosystems. Therefore, in the present study, effect of polystyrene (film form & dissolved form) was studied on the growth and biochemical constituents of aquatic primary producer (*Nostoc muscorum*) along with their potential to degrade polystyrene under carbon deprivation. The dissolved form exhibited higher free radical-mediated toxicity than the film form. The pigment (chlorophyll, carotenoids, and phycobilin) and protein exhibited reduction, but the oxidative defence enzymes and proline increased to provide resistance.

Ubiquitous distribution, high persistence and the deleterious impact of microplastic in the environment need global attention for bioremediation. In that effort, it was observed that the reduction in carbon source in the nutrient medium prompted *Nostoc muscorum* to derive its carbon supply from polystyrene film that reduced microplastic concentration in the medium and its toxic effect. The formation of a higher number of holes in polystyrene film under 50% C deprivation than 100% C supply suggested polystyrene film degradation and release of chemicals, mainly carbon, utilised in cyanobacterial growth.

Keywords: Microplastic. Polystyrene. *Nostoc*. oxidative stress. Carbon deprivation.

QUANTIFYING THE CORRELATION BETWEEN CO₂ EMISSIONS AND RENEWABLE ENERGY INDICATORS

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Abstract

This study investigates the correlation between CO₂ emissions and some renewable energy metrics using Pearson's correlation analysis, focusing on only Germany. The results declare that depending on renewable energy production increases, CO₂ emissions decrease significantly, this is interfaced with correlation coefficients between -0.950 and -0.956, highlighting a strong negative relationship (one increases the other decreases). However, the same interface is not correct for the economic metrics related to carbon damage and CO₂ emissions because the correlation between them is much weaker at -0.057, proposing that contrary general belief, economic factors play complex role in emissions reduction needs to research.

This study emphasizes that can not be neglected importance of renewable energy in tackling climate change, highlighting that using of renewable technologies are very important for achieving significant reductions in CO₂ emissions in Global perspective. The study calls for continued support and policies that promote renewable energy adoption to effectively combat global warming.

Keywords: CO₂ Emissions, Renewable Energy, Correlation Analysis, Climate Change Mitigation, Policy Support.

1 INTRODUCTION

The global conformance towards renewable energy is a solution as a critic strategy for mitigating climate change. Interpreting the relation between CO₂ emissions and renewable energy is essential for shaping national/international policies and strategies aimed at decreasing carbon footprints. This literature review demonstrates the results from various studies that examine this linkage, focusing on the nature and strength of the correlation, as well as the inferences for policy and application.

Many studies have documented a strong inverse correlation between renewable energy adoption and CO₂ emissions. For instance, [1] found that increased deployment of renewable energy technologies, particularly wind and solar, is associated with significant reductions in CO₂ emissions in both developed and developing countries. Similarly, [2] observed that renewable energy sources contribute to lowering carbon emissions by replacing fossil fuels in electricity generation.

The interest of government policies in supporting renewable energy and focusing to

reduce CO₂ emissions has been surveyed in numerous studies. According to [3], countries with strong policy frameworks, such as subsidies for renewable energy and carbon taxes, show a more marked decrease in CO₂ emissions. [4] also underlined the importance of regulatory support, noting that policy-driven renewable energy adoption is a important issue in achieving emissions reduction goals.

Technological advancements in renewable energy technologies have been important in improving their efficiency and reducing costs, therefore being helpful greater adoption. [5] reported that developments in solar photovoltaic (PV) technology have significantly reduced the costs and increased the deployment of solar energy, making support to a reduction in emissions. [6] emphasized smart grid technologies in integrating renewable energy into the grid and the role of battery storage, therefore stabilizing energy supply and reducing reliance on fossil fuels.

The influence of renewable energy on CO₂ emissions varies across sectors and regions. [7] declared that in locations with abundant renewable resources, such as solar and wind, the correlation with CO₂ emissions is stronger.

However, [8] focused that in transport and industry sectors, this correlation is weaker than the other sectors, as transport and industry sectors have been to transition to renewable energy sources slowly.

Economic considerations, including mostly investment in renewable energy infrastructure, also play an important role in the analyzed correlation. [9] pointed out that countries with higher levels of investment in renewable energy infrastructure have seen more major reductions in CO₂ emissions. In another study, [10] discussed the challenges faced by low-income countries in financing renewable energy projects, which barriers their effective ability to reduce emissions.

The literature continuously shows a high correlation between renewable energy and CO₂ emissions, proving the potential of renewable energy as a crucial strategy for climate change mitigation. However, the capacity of this correlation is influenced by various different factors, technological advancements, policy frameworks, regional dynamics, and economic situations. Future research should continue to explore these dynamics, focusing on how to overcome districts to renewable energy adoption in different situations and enhance the effectiveness of policies aimed at reducing CO₂ emissions.

The aim of this study is to make a new correlation analysis for seven different data (Electricity production from renewable sources, excluding hydroelectric (% of total); Electricity production.

2 METHODS

2.1 Data Collection and Preparation

The data used in this analysis was sourced from a comprehensive dataset containing various series related to renewable energy indicators and CO₂ emissions. Specifically, the dataset included:

Series 1: Electricity production from renewable sources (excluding hydroelectric)

Series 2: Renewable electricity output

Series 3: Renewable energy consumption

Series 4: Adjusted savings from carbon dioxide damage

Series 5: Financial metrics related to carbon damage

Series 6: Total adjusted savings

Series 7: CO₂ emissions

The data was structured in a multi-year format, with each series representing a time series of values [11].

2.2 Data Formatting and Cleaning

The dataset was first formatted as natural logarithm. When original continuous data does not follow the bell curve, it can be log converted this data to make it as “normal” as possible, thus making the statistical analysis results from this data more valid.

Then dataset was cleaned to ensure accuracy and completeness. This involved:

Removing non-numeric columns: Columns not pertinent to the analysis, such as series names and metadata, were excluded.

Handling missing data: Missing values, if any, were addressed using standard data imputation techniques or were excluded from the analysis to prevent skewing the results.

2.3 Istatistical Analysis

The primary analytical method used was Pearson's correlation coefficient. This statistical measure quantifies the linear relationship between two continuous variables, providing both the strength and direction of the association.

Pearson's Correlation Coefficient (r): The coefficient values range from -1 to 1, where:

- **+1** indicates a perfect positive linear relationship.
- **-1** indicates a perfect negative linear relationship.
- **0** indicates no linear relationship.

The formula for Pearson's correlation is:

$$r = \frac{\sum(x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum(x_i - \bar{x})^2 \sum(y_i - \bar{y})^2}}$$

(1)

Where:

r is correlation coefficient,

x_i and y_i are the individual sample points for the two variables,

$\bar{x}$ and $\bar{y}$ are the means of the respective variables.

3 RESULTS

The findings demonstrate a strong, negative connection between renewable energy use and CO₂ emissions. This means that as renewable

energy increases, CO₂ emissions tend to decrease significantly. However, the relationship between financial measures of carbon damage and renewable energy is less clear, indicating that other factors are likely involved.

Overall, this research emphasizes the important role of renewable energy in reducing carbon emissions. To maximize its impact, continued support and investment are crucial. Further studies should delve deeper into the factors driving these relationships and consider the influence of technology and policy.

Table 1. Correlation Between Series

Between	Correlation
Series 1 and Series 7	-0.950
Series 2 and Series 7	-0.946
Series 3 and Series 7	-0.953
Series 4 and Series 7	-0.956
Series 5 and Series 7	-0.057
Series 6 and Series 7	-0.927

In Table 1, these negative correlation values indicate an inverse relationship between Series 7 and the other series. Notably, Series 5 and Series 7 have a much weaker correlation compared to the other pairs.

To understand how the data changed over time, it was examined each series year by year, looking for patterns like steady increases, decreases, or seasonal fluctuations. Visualizing this data through graphs helped us clearly see these patterns.

It was found that most of the data (Series 1, 2, 3, 4, 6, and 7) showed a consistent upward trend from 1992 to 2014. Figure 1 demonstrates this trend:

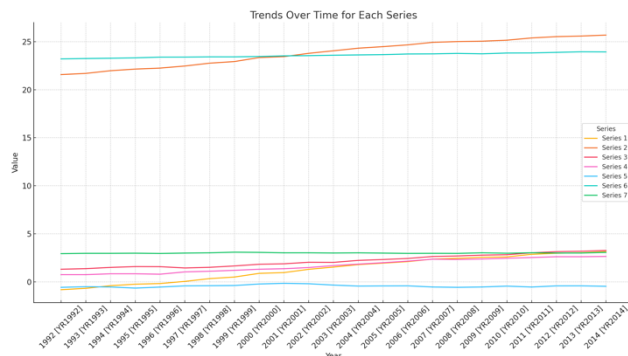


Figure 1. Trend Over Time for All Series

Series 5 appears relatively flat with some fluctuations, suggesting little to no consistent trend.

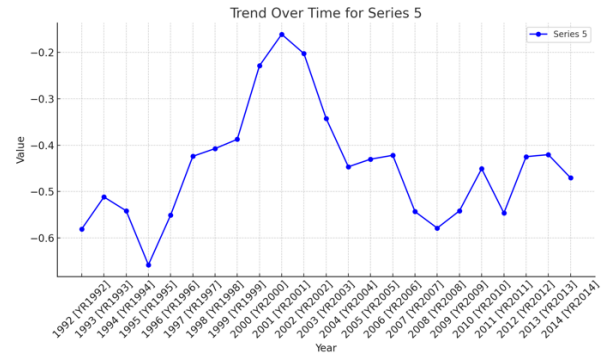


Figure 2. Trend Over Time for Series 5

The Figure 2 shows the trend over time for Series 5. Key observations include:

The series initially declines from 1992 to approximately 1995 before steadily rising to a high point around 2001. Following this peak, the data experiences ups and downs, without a clear upward or downward direction.

This pattern suggests that Series 5 experienced significant changes, especially in the early 2000s. Further investigation could reveal the factors contributing to these fluctuations.

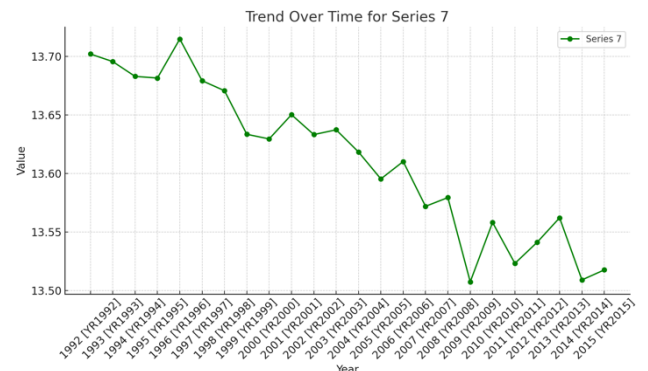


Figure 3. Trend Over Time for Series 7

Figure 3 shows a relatively stable trend for Series 7 over time, with slight fluctuations. The values seem to hover around the mean with minor variations.

There are several other methods and approaches to analyze the relationship between CO₂ emissions and renewable energy indicators. There are some other examples in the literature: For instance, [12] investigated the relationship between renewable energy and CO₂ emissions in Spain and Portugal. They found similarly high negative correlations, particularly in wind and solar energy sectors, where emission reductions were significant as renewable energy adoption increased. Their results align with the findings in

this study, underscoring that the deployment of renewable energy technologies contributes to substantial reductions in carbon emissions, particularly in electricity generation.

The study by [13] on the United States further supports these conclusions, where they observed that regions with strong policy support for renewable energy, such as California, show a marked decrease in CO₂ emissions. However, they noted that the effectiveness of renewable energy adoption varies by state, with some areas still reliant on fossil fuels. In contrast, this study's results demonstrate a consistent reduction in emissions across Germany, suggesting that Germany's more unified national policies may be more effective in driving widespread emission reductions.

[14] explored renewable energy in Germany and Sweden and found similarly strong correlations, with both countries benefiting from extensive investments in wind and solar energy. However, their study also emphasized the role of hydropower in Sweden, which contributes significantly to their overall renewable energy output. Germany's energy landscape, as examined in this paper, focuses less on hydropower and more on solar and wind, indicating that renewable energy strategies vary significantly between nations but still lead to comparable emissions reductions.

In a study of Brazil and Mexico, [15] found that the impact of renewable energy on emissions reduction was less pronounced than in European countries. They attributed this to the slower pace of renewable energy adoption in the industrial and transportation sectors. While the overall trend in Brazil and Mexico aligns with the findings of this study, the weaker correlation coefficients suggest that these countries face additional challenges, such as economic and infrastructural barriers, which Germany may not encounter to the same extent.

Lastly, [16] examined Australia and New Zealand, finding that renewable energy adoption has significantly reduced CO₂ emissions in the electricity sector. However, like in Germany, their research indicates that other sectors, such as transportation and heavy industry, have been slower to transition to renewables, thus limiting the overall potential for emissions reduction. This finding aligns with the weaker correlation between financial metrics and CO₂ emissions observed in this study, indicating that economic

factors and sector-specific adoption play crucial roles in the overall effectiveness of renewable energy policies

4 CONCLUSION

In this study six different correlation analyses are made. These analyses show important evidence of a strong negative relationship between CO₂ emissions and six key renewable energy indicators for data of Germany. The high negative correlation coefficients (-0.950 to -0.956) declare that used more of renewable energy sources, such as waste, solar, wind and hydropower, is related with significant reductions in CO₂ emissions. These strong relationships encourage the issue that give more place to renewable energy in production of electricity is one of the most suitable strategy for mitigating climate change. However, there is a relatively weak correlation got in Series 5 proofs that the financial impact of carbon damage may not directly relate with CO₂ emissions, focusing the requirement for a more extra examining of economic factors. Furthermore, it was emphasized the important not to ignore role of renewable energy in reaching sustainable environment and highlights the requirement for continued investment and policy support for energy sector in this study. In a near future, researcher should explore the underlying dynamics driving these correlations and assess the impact of additional variables such as technological developments and regulatory frameworks.

In future studies, by using a combination of alternative methods, researchers will gain a more comprehensive understanding of the dynamics between CO₂ emissions and renewable energy, providing robust and actionable insights.

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HARNESSING MACHINE LEARNING FOR SURROGATE MODELING AND CIRCULAR CARBON ECONOMY: MULTI-OBJECTIVE OPTIMIZATION IN CO₂-TO-METHANOL CONVERSION

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Abstract

Converting carbon dioxide (CO₂) into methanol holds immense potential for combating climate change and building a circular economy. However, optimizing this complex process has been hindered by classical modeling methods. This research introduces a novel approach that combines the power of artificial intelligence (AI) with advanced optimization techniques to revolutionize methanol production. By employing machine learning models, specifically Gaussian Process Regression (GPR) and Artificial Neural Networks (ANN), accurately predict key process outcomes. Trained on data from a physical-based simulator, these models enable identification of optimal operating conditions (Reaction temperature, pressure, H₂ to CO₂ feed ratio, purge gas stream, temperature and pressure of flash separator) utilizing Non-dominated Sorting Genetic Algorithm II (NSGA-II). The approach successfully generates Pareto-optimal solutions, balancing maximizing CO₂ conversion, methanol production rate, and methanol yield, leading to a significant improvement in process efficiency. This study not only demonstrates the effectiveness of AI in optimizing complex chemical processes but also offers a promising pathway towards a sustainable future fueled by renewable methanol.

Keywords: Methanol synthesis, artificial intelligence, machine learning, optimization, carbon capture, circular economy

CALCULATION OF GLOBAL WARMING POTENTIAL OF CONVENTIONAL AND ORGANIC CHARDONNAY GRAPE PRODUCTION

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Abstract

Agriculture is both directly impacted by the effects of climate change and contributes to its progression. Therefore, assessing the environmental impacts of current agricultural practices is crucial to achieving sustainability goals.

This study aims to calculate the global warming potential of the only organic producer and the only conventional producer of Chardonnay grapes in Cappadocia Region, Türkiye. The global warming potential analysis was carried out through inventory studies and the measurements taken during the 2018 and 2019 production seasons. Inputs affecting the global warming potential in the study include fossil fuel consumption, animal manure use, equipment and machinery production, and electricity consumption for irrigation. The results show that to produce 1 kg of Chardonnay grapes, the average global warming potential for 2018 and 2019 is 2.027 kg CO₂ equivalent/kg for the organic producer and 2.120 kg CO₂ equivalent/kg for the conventional producer.

The CO₂ emissions from fossil fuel use, which contribute the most to the global warming potential of organic farming, are CH₄ and N₂O emissions released product and use of fertilizer for conventional farming that contribute the most to the global warming potential.

Keywords: Global Warming, Organic Agriculture, Conventional Agriculture, Chardonnay

1 INTRODUCTION

Agriculture is the cornerstone of food production [1]. As agricultural practices shifted due to technological advancements, increased productivity, market demands, and the use of mechanization. Modern techniques and large-scale production led to the adoption of industrial agriculture to meet growing food demands and provide economic benefits. Consequently, input usage and energy consumption in agriculture increased, bringing various environmental problems including global climate change.

Agriculture is directly affected by the consequences of climate change. Extreme weather events, shifting seasons, excessive heat, and droughts due to changes in climate lead to decreases in yield and product quality. According to estimates by the United Nations, a 30% reduction in agricultural production is expected by 2050, indicating a move towards a global food crisis [2]. However, agriculture itself

is one the biggest contributors to global warming [3]. Today, 10-12% of the greenhouse gases released into the atmosphere originate from agricultural production.

The contribution of agricultural activities to global warming primarily arises from the emissions of CO₂, CH₄, and N₂O into the atmosphere. Practices such as leaving the soil surface exposed through repeated tillage, using fossil fuel-powered agricultural equipment, and the extraction and consumption of fossil fuels in the production of machinery, fertilizers, and pesticides, all result in increased CO₂ emissions and contribute to climate change [4].

Certain food groups continue to be produced using traditional methods; however, advancements in production technologies are increasingly integrating mechanization into these practices. Grape cultivation, a major agricultural activity in the Cappadocia region, has been practiced since the dawn of civilization. While

the region is known for its diverse grape varieties, Chardonnay has recently gained prominence due to its versatility, diverse flavor profiles, adaptability to various winemaking techniques, compatibility with a wide range of foods, and enduring popularity as a preferred white wine [5]. In the Cappadocia Region, currently two wine producers cultivate Chardonnay grapes. However, no study has investigated these production systems and their environmental impacts and global warming potential.

This study aims to calculate the global warming potential of the only organic producer and the only conventional producer of Chardonnay grapes in Cappadocia Region, Türkiye and recommend solutions to decrease the environmental impact of grape cultivation in the region.

2 MATERIALS AND METHODS

Study Area

The study focuses on Chardonnay grape production in the Cappadocia region, Türkiye, specifically examining the impact of global warming on grape production for both organic and conventional wine producers in the area. All production methods were monitored through field surveys, and the environmental impact of production was determined based on the survey data.

The organic and conventional producers of Chardonnay wine in the region were chosen for the purpose of the study.

The organic producer (O.F.) is in Kayseri and operates a diverse agricultural farm approximately 50 km from Cappadocia. This farm practices organic agriculture and produces both domestic and international wine grapes. The vineyards are situated 1050 meters above sea level, with coordinates at 38°79'14" north latitude and 35°26'42" east longitude. The land has an 8.5% slope and covers approximately 27 decares. The age of the vines ranges from 14 to 35 years.

The conventional producer (C.F.) is located in the Ürgüp region of Cappadocia. This producer cultivates local grape varieties like Emir as well as international varieties such as Chardonnay.

The land has a 7% slope and covers approximately 85 decares. The vines were planted in 2001 and are relatively younger. The vineyards are also situated 1050 meters above sea level.

Surveys and Impact Analysis

Detailed surveys were carried out to understand the production systems of both farmers for the 2018 and 2019 production years. Figure 1 shows the processes for grape production.

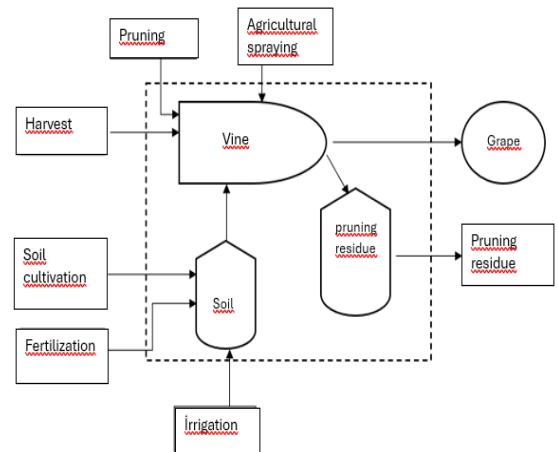


Figure 1. Processes for grape production.

All inputs and outputs were determined through the surveys and global warming impact as CO₂ equivalent was calculated using the emission factors presented in IPCC guidelines [6] (Figure 2).

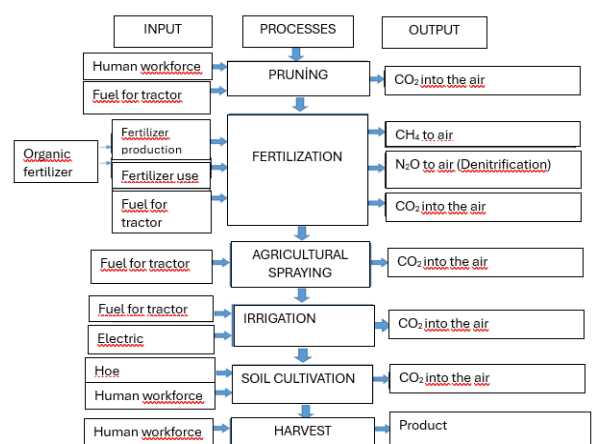


Figure 2. Inputs and outputs of processes.

Functional unit for this study was 1 kg of Chardonnay grape and 1 ha of agricultural area and system borders was from cradle to farm gate; only the environmental impacts of the grape production process in the vineyard were

assessed; the transportation to the winery and the wine production process were not considered.

3 RESULTS AND DISCUSSION

Table 1 shows the averages of two years (2018 and 2019) CO₂, CH₄, N₂O releases to the atmosphere due to fossil fuel and electric consumption, two major contributions to the global warming potential when the functional unit is 1 kg of produced grape.

Table 1. CO₂, CH₄ and N₂O releases to the atmosphere due to fossil fuel and electric consumption. Functional unit is 1 kg of grape.

		O.F. 1 kg grape/ CO ₂ eq.kg	C.F. 1 kg grape/ CO ₂ eq.kg
Fossil Fuel	CO ₂ to air (kg)	0.30	0.22
	CH ₄ to air (kg)	0.30	1.50
	N ₂ O to air (kg)	0.18	0.69
Electricity	CO ₂ to air (kg)	0.007	0.010

According to the study results, to produce 1 kg of Chardonnay grapes, the global warming potential effect is 2.027 kg CO₂ eq./kg for the organic farming producer and 2.120 kg CO₂ eq./kg for the conventional farming producer, based on the averages for 2018 and 2019.

Table 2 shows the averages of two years (2018 and 2019) CO₂, CH₄, N₂O releases to the atmosphere due to fossil fuel and electric consumption, two major contributions to the global warming potential when the functional unit is 1 ha of agricultural area.

Table 2. CO₂, CH₄ and N₂O releases to the atmosphere due to fossil fuel and electric consumption. Functional unit is 1ha of agricultural area.

		O.F. 1 ha / CO ₂ eq.kg	C.F. 1 ha/ CO ₂ eq.kg
Fossil Fuel	CO ₂ to air (kg)	1726	576
	CH ₄ to air (kg)	420	3150
	N ₂ O to air (kg)	247	1799
Electricity	CO ₂ to air (kg)	8.04	31.03

To produce 1 kg of Chardonnay grapes, the O.F. has the highest CO₂ emissions from fossil fuel use, accounting for 76% of the total. The producer's agricultural activities, such as irrigation, soil cultivation, and pesticide application, involve significant fuel consumption. For the C.F., CH₄ emissions to the air account for 1.50 kg CO₂ equivalent/kg with a 62% share, and N₂O emissions account for 0.69 kg CO₂ equivalent/kg with a 29% share. The storage and use of organic fertilizers contribute significantly to CH₄ and N₂O emissions. For both producers, electricity consumption was the lowest input.

According to these results, for the C.F., the highest inputs for global warming potential per unit area and weight of the product are CH₄ and N₂O emissions. The emissions resulting from the storage and use of organic animal manure increase the global warming potential. For the O.F., the highest input for global warming potential per unit area and weight of the product comes from CO₂ emissions due to fossil fuel use. The producer's extensive use of tractors in agricultural activities contributes to higher emissions.

4 CONCLUSION

For the conventional farming (C.F.) producer, the total global warming potential averages 5,555.5 kg CO₂/ha over the two production years. For the organic farming (O.F.) producer, the average is 1,377.5 kg CO₂/ha over the two years. The main contributor to the global warming potential for the conventional producer is the CH₄ emissions from organic fertilizer production. For organic producers, the highest input comes from CO₂ emissions due to fossil fuel consumption. The lowest input value for both producers is emissions from electricity consumption.

As a result of the research on global warming potential, it was found that both producers implement numerous agricultural activities with high inputs. Among these activities, soil cultivation and fertilization are identified as having the most significant environmental impact. These direct soil activities are not only important for the economic lifespan of the vines but also pose environmental issues if performed carelessly. Reducing the negative effects of soil cultivation and fertilization on the environment and human health can be achieved by applying alternative solutions that protect soil health and the ecosystem. Two such alternative solutions that are gaining increasing attention and application today are mulching and cover cropping.

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EXPERIMENTAL STUDY OF A SOLAR ASSISTED STORAGE SYSTEM FOR SHELF-LIFE ENHANCEMENT OF TOMATOES

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Abstract

Fruit and vegetables are rich in essential nutrients for proper human growth and good health. Harvested Fruit and vegetables deteriorate quickly as they continue metabolic activities due to higher moisture content. Both growers and customers have significant challenges in preserving fresh fruit and vegetables to extend their storage life. The shelf-life of fruit and vegetables can be prolonged through providing low temperature and high relative humidity. In this regard, a solar assisted storage system is developed with locally available materials like bricks, cement, and sand (etc). The system is experimentally evaluated by storing green mature tomatoes. The storage system was able to decrease inside temperature by 9-11°C as compared to outside conditions and maintained relative humidity above 90%, with 84% average cooling efficiency.

Keywords: Fruit and vegetables, passive cooling, solar-assisted storage system, performance evaluation, physicochemical analyses.

1 INTRODUCTION

Harvested fruit and vegetables are valuable food sources but have a short shelf-life due to ongoing metabolic processes such as respiration and transpiration. These processes in harvested perishable products are caused due to higher moisture content (60-95%) [1], [2]. In respiration, nutritional contents in products break down into metabolites, carbon dioxide, water, and energy by utilizing outside oxygen. The process of respiration mainly depends upon surrounding temperature. Transpiration is the loss of water contents from products and mainly depending on surrounding relative humidity [3][4]. Both respiration and transpiration rate play an important role in storage of perishable fruit and vegetables at farm. The rate of process in products mainly depends on external environmental factors such as, relative humidity, temperature, air velocity, and air composition etc. [5], [6]. These processes may not be stopped but can be slowed down through providing favourable environment [5], [6]. Fruit and vegetables start decaying immediately after harvesting. Post-harvest losses of fruit and vegetables in developing countries are reported to be 30-50% [7]. These losses are often due to a lack of efficient storage options at the farm level [8], [9]. Refrigeration is one of the methods available for storage of fruits and vegetables at farm. Storage through refrigeration is costly, energy-intensive, and harmful to the environment

as well [10]. Small/marginal-scale farmers often sell their products at a low price to middlemen to avoid losses due to inadequate storage facilities. In this regard, a low-cost and environment friendly solar assisted passive storage system (SAPS) based on passive evaporative cooling is developed to avoid such postharvest losses at farm. It works on the principle of natural process of evaporation as given in Figure (1). Ambient heat moves from outside brick wall having high temperature to wet evaporative media through conduction and convection. Inside respiratory heat of stored products also moves to evaporative media (sand). The wet evaporative media releases inside and outside absorbed heat through evaporation from surface of evaporative media, consequently cooling is produced in the storage system [11], [12]. Solar assisted passive storage system can be used to store tomatoes, brinjals, potatoes, mangoes, leafy green vegetables, chilies, and cauliflowers at farm for some days [13], [14], [15], [16], [17], [18]. In this study, solar assisted storage system is developed and evaluated by storing green mature tomatoes.

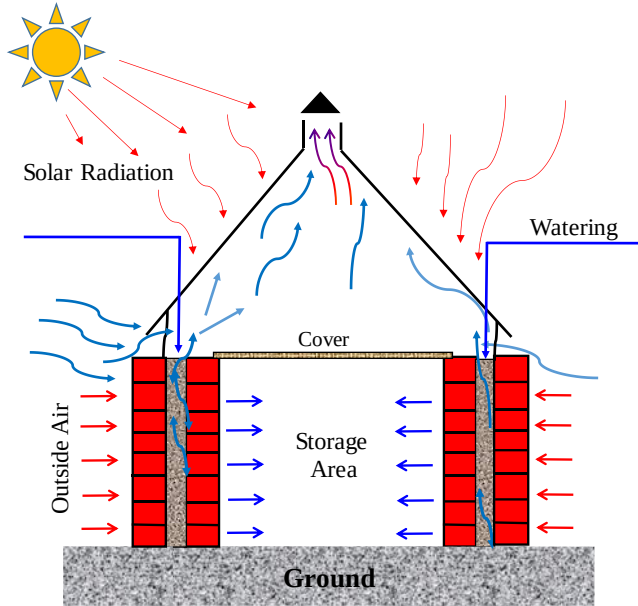


Figure 1 Schematic view of SAPS

2 MATERIALS AND METHOD

2.1 Experimental Site

The solar-assisted passive storage system was developed at Department of Agricultural Engineering, Bahauddin Zakariya University (30°15'49"N, 71°30'35"E) Multan, Pakistan. Locally available materials i.e., kiln bricks, sand, and cement were used for its development. The inner and outer walls of SAPS were made with local available bricks. It is constructed in rectangular shape having 4.94 m³ total space for storage of products according to the need of smallholding/marginal farmers to store their products at remote farms. The 6-inch (0.15m) space between the two erected brick walls was filled with an evaporative media (sand). The overhead cover of the storage system was made with jute cloths and bamboo sticks. Water was added daily to evaporative media to keep it wet based on the porosity. Moreover, a solar chimney of 1.22 m height was installed on storage system to improve the air ventilation over the surface of evaporative media. Initially, 20kg of tomatoes were stored inside and outside of storage system for testing.

2.2 Cooling Performance of SAPS

The cooling performance of developed storage system was determined by measuring the inside and outside relative humidity and temperature over the storage period. The relative humidity and temperature of outside and inside of the storage system were recorded by digital sensors. The wet-bulb temperature (T_{wb}) was calculated using the following Equation (1) as described by [19].

$$T_{wb} = T \tan^{-1} \left(0.151977 * \frac{\sqrt{RH + 8.313659}}{\sqrt{RH + 8.313659}} \right) + \tan^{-1} (T + RH) - \tan^{-1} (RH - 1.676331) + 0.00391838 \left(\sqrt[3]{RH} \right) \tan^{-1} (0.023101 RH) - 4.686035 \quad (1)$$

The cooling performance of developed storage system was calculated by Equation (2) as described by [20].

$$\text{Cooling efficiency} = \frac{T_{db} - T_{SAPS}}{T_{db} - T_{wb}} \times 100 \quad (2)$$

where, T_{db} , T_{SAPS} and T_{wb} are outside dry bulb temperature, temperature inside the storage system, and wet bulb temperature of outside air, respectively.

2.3 Physicochemical Analyses

Physicochemical analyses of physiological weight loss (PWL), visual appearance (VA) and titratable acidity (TA) were performed to check the freshness of stored tomatoes. Analyses performed on 1st, 3rd, 5th, 7th, 9th, 11th, 13th, and 15th day of storage. The initial and final weight of stored tomatoes were measured with weighing balance, used to measure the percentage of physiological weight loss. The titratable acidity of tomatoes was calculated by using Equation (3) described by Pinheiro et al. [22].

$$TA = \frac{\text{ml (NaOH)} \times \text{M of NaOH} \times \text{kc}}{\text{sample used in ml}} \times 100 \quad (3)$$

where, kc is the acid factor for tomatoes (0.084).

3 RESULT AND DISCUSSIONS

3.1 Cooling Performance

The change in relative humidity and temperature during storage of tomatoes are shown in Figure (2). The difference of temperature between outside conditions and inside of system was measured 11°C and average relative humidity difference was measured 45% inside of storage system. In a similar study, Shitanda et al. [23] evaluated a 27m³ size storage system that reduced 11°C temperature and increase 38% relative humidity than ambient condition. Davalo et al. [24] reported the temperature difference of 13.24 °C and 41% a relative humidity between inside and outside the 8m³ storage system. However, lab-scale storage systems was able to reduce temperature in range

10-15 °C and maintain relative humidity above 90% [9], [11], [25], [26], [27]. In this study, the average cooling efficiency of 84% was measured. In similar other study for commercial-scale storage system [24], who reported 78% cooling efficiency. While, the cooling efficiency of lab-scale storage systems were observed higher (about 90%) as compared to commercial storage system [13], [25], [28].

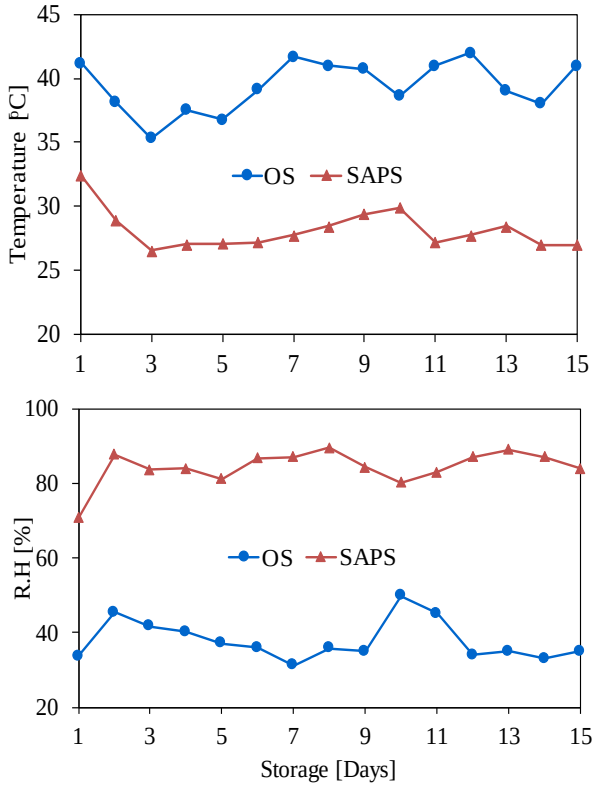


Figure 2 Temperature and Relative Humidity Profile

3.2 Physicochemical Analyses

Physiochemical Analyses performed on regular intervals of storage days. Loss of water contents from harvested agricultural products is a major cause of postharvest deterioration in term weight loss, economic loss and visual compositional change [30]. Two equal weights of tomatoes were stored in solar assisted storage system and outside condition. The weight loss of stored tomatoes in percentage is given in Figure (3). During storage interval, PWL was measured 10.6% and 87.5% for tomatoes stored in SAPS and outside conditions, respectively on 15th day of storage. Results are in coresponding to study [31], reported 10.25% weight loss after 21 days for tomatoes stored such a storage system. Other similar study [32], reported PWL of 11.96% after 12 days for ripe tomatoes stored in storage system.

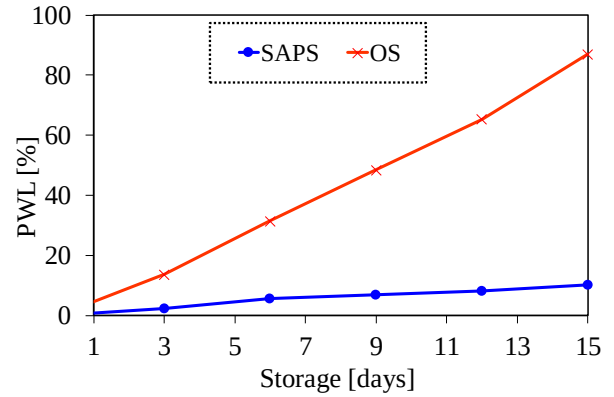


Figure 3 PWL for stored tomatoes

The tomatoes stored outside of storage system deteriorate rapidly as compared to inside stored tomatoes. The rapid declining pattern of acidity shown in Figure (4) was observed in outside stored products. It was due higher respiration rate to convert acid contents in tomatoes into soluble solids in rapid ripening due to environmental conditions [17], [33], [34]. Titratable acidity declined from 0.64 to 0.44 for tomatoes stored inside the system after 15 days. On the other hand, titratable acidity rapidly decreases from 0.64 to 0.16 for tomatoes stored outside of the system after 15 days. Results were related to other study [34], which reported 0.25 titratable for outside stored tomatoes after 12 days. Titratable acidity results concluded that the acidity level declined earlier in tomatoes stored in OS condition due to a higher respiration rate as compared to those stored in solar-assisted storage system [34], [35].

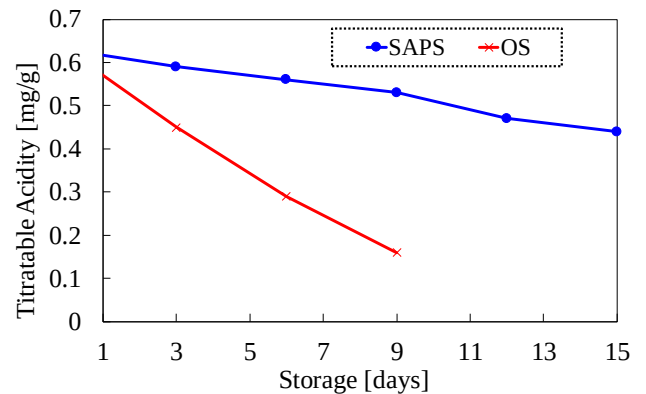


Figure 4 Acidity declining in stored tomatoes

The visual appearance of stored tomatoes inside and outside of storage system is given in Figure (5). Tomatoes stored in outside condition decayed/spoiled earlier as compared to those stored in solar assisted storage system. It was because faster respiration and transpiration rate in tomatoes stored outside. Outside warm and dry

conditions enhance the decaying rate due to microorganism activity [36].



Figure 5 Visual appearance of tomatoes stored in outside and SAPS on 15th day.

4 CONCLUSIONS

Inside temperature of solar assisted passive storage system was reduced about 11°C than outside air temperature. The relative humidity was enhanced about 45%, correspondingly. The average cooling efficiency was measured as 85%. Low temperature and higher humidity (above 80%) provide a favorable condition to store tomatoes at farm level for some days. The maintained inside conditions slow down the respiration/ transpiration rate and lead to extending the shelf-life of tomatoes. The OS stored tomatoes were not useable after 6 days, while SAPS stored tomatoes were remained fresh even after 15 days.

ACKNOWLEDGEMENTS

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THERMODYNAMIC ANALYSIS OF SOLAR TOWER BASED INTEGRATED SYSTEM FOR POWER PRODUCTION

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Abstract

Renewable energy systems are gaining traction in the face of fossil fuel depletion and escalating environmental concerns. This study unveils a promising future with its thermodynamic analysis of a solar tower-based integrated system that not only generates power but also produces hot water. The system's main components-a solar tower plant, a heat storage unit, and Rankine and organic Rankine cycles-work in harmony to achieve an overall energy efficiency of 58.37% and an exergy efficiency of 52.49%. These impressive figures demonstrate the potential of the solar tower plant and power production cycles, with heat storage units, to enhance the system's performance by destructing 9421 kW of exergy. The system's power and hot water production capacity is equally impressive at 7162 kW and 5185 kW. To further underscore the system's potential, parametric analyses have been conducted to explore the effects of the solar tower system's varying reference temperature and working fluid temperature.

Keywords: Solar energy, solar tower plant, thermal energy storage, integrated system, thermodynamic analysis.

1 INTRODUCTION

As the globe struggles with the environmental and economic issues related to the use of fossil fuels, the global energy landscape is changing dramatically [1]. Investigating and implementing sustainable and clean energy alternatives is necessary due to the negative impacts of greenhouse gas emissions and the depletion of non-renewable energy resources. Solar energy is unique among renewable energy technologies because of its abundance and capacity to supply a significant amount of the world's energy needs [2]. One of the more well-known technologies in concentrated solar power (CSP) is the solar tower system, which has become a highly effective way to capture solar energy [3]. These systems focus sunlight onto a central receiver atop a tower using a field of mirrors called heliostats. This thermal energy can be used for various applications, including electricity generation and hot water production.

Integrating solar tower systems with other renewable energy technologies and thermal energy storage units offers an avenue for enhancing overall system efficiency and reliability [4]. By storing excess thermal energy, the system can provide a continuous energy supply even during

periods of low solar irradiance, thereby addressing one of solar energy's critical limitations.

This study proposes a comprehensive thermodynamic analysis of a novel solar tower-based integrated system designed for combined power and hot water production. The integrated system comprises a solar tower plant, a thermal energy storage unit, and an Organic Rankine Cycle (ORC) plant. The system's performance is evaluated using energy and exergy analyses to determine efficiency and destruction rates. In addition, parametric analysis is performed to see the effects of the reference temperature and the working fluid temperature of the solar power plant.

Through this analysis, we aim to demonstrate the viability and efficiency of the proposed integrated system in using solar energy for multiple applications.

2 SYSTEM DESCRIPTION

Figure 1 demonstrates the schematic diagram of the solar tower-based integrated system and flows operating inside the designed system. The heliostats reflect sunlight onto the central receiver at the top of the tower.

Then, the central receiver absorbs the concentrated solar energy and heats the working fluid, which is

NaNO₃/KNO₃. Then, heat energy is stored in the storage unit if solar irradiance is high and excess thermal energy exits. Then, flow 6 exits the heat exchanger of the Rankine cycle to transfer its heat energy for power production. Excess heat energy from the Rankine cycle is sent to the organic Rankine cycle via flow 7. ORC uses isobutane as a working fluid to produce power. Two condensers are integrated into the turbines of each power cycle, producing hot water.

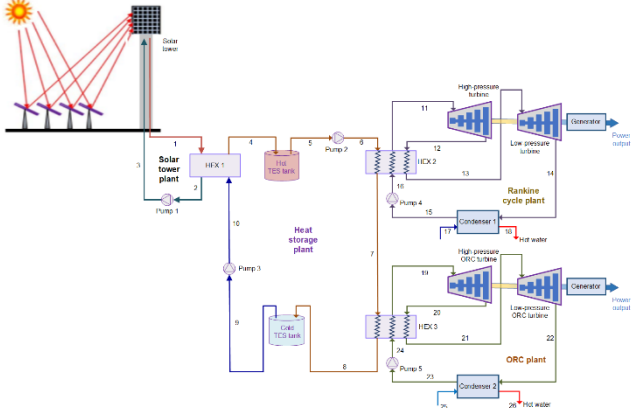


Figure 1. The schematic diagram of the solar tower based integrated plant

Table 1. Inlet and design indicators for integrated plant modelling.

Indicator	Value
Reference temperature, T_o	25 °C
Reference pressure, P_o	101.3 kPa
Working fluid of solar tower plant	NaNO ₃ /KNO ₃
Solar tower inlet temperature, T_3	435 °C
Solar tower inlet pressure, P_3	120 kPa
Solar tower exit temperature, T_1	575 °C
Solar tower exit pressure, P_1	100 kPa
High pressure turbine inlet temperature, T_{11}	225 °C
High pressure turbine inlet pressure, P_{11}	1000 kPa
Low pressure turbine inlet temperature, T_{13}	225 °C
Low pressure turbine inlet pressure, P_{13}	700 kPa
Working fluid of ORC plant	Isobutane
High pressure ORC turbine inlet temperature, T_{19}	174 °C
High pressure ORC turbine inlet pressure, P_{19}	2798 kPa
Low pressure ORC turbine inlet temperature, T_{21}	174 °C
Low pressure ORC turbine inlet pressure, P_{21}	1395 kPa

Isentropic performance of high pressure turbine, η_{HPT}	0.90
Isentropic performance of low pressure turbine, η_{LPT}	0.90
Isentropic performance of high pressure ORC turbine, η_{HPOT}	0.80
Isentropic performance of low pressure ORC turbine, η_{LOPT}	0.80

3 THERMODYNAMIC ANALYSIS

The integrated system, as well as its sub-systems and components, are analysed using the energy and exergy analyses. The mass, energy, entropy, and exergy balance equations are written as [5]:

$$\sum \dot{m}_i - \sum \dot{m}_e = 0 \quad (1)$$

$$\sum \dot{m}_i h_i + \sum \dot{Q}_i + \sum \dot{W}_i - \sum \dot{m}_e h_e - \sum \dot{Q}_e - \sum \dot{W}_e = 0 \quad (2)$$

$$\sum \dot{m}_i s_i + \sum \left(\frac{\dot{Q}}{T} \right) + \dot{S}_{gen} - \sum \dot{m}_e s_e = 0 \quad (3)$$

$$\sum \dot{m}_i ex_i + \dot{E}x_i^Q + \dot{E}x_i^W - \sum \dot{m}_e ex_e - \dot{E}x_e^Q - \dot{E}x_e^W - \dot{E}x_d = 0 \quad (4)$$

The sub-expressions i and e are the inlet and outlet conditions. Also, $\dot{m}$, $\dot{W}$ and $\dot{Q}$ are the rates of mass flow, work, and heat transfer, respectively. h and s are the specific enthalpy and entropy. $\dot{E}x^Q$ and $\dot{E}x^W$ are the heat transfer and work exergy rates as given below:

$$\dot{E}x_Q = \left(1 - \frac{T_o}{T} \right) \dot{Q} \quad (5)$$

$$\dot{E}x^W = \dot{W} \quad (6)$$

The flow exergy defined in Eq. (4) is described as:

$$ex = ex_{ph} + ex_{ch} \quad (7)$$

Moreover, ex_{ph} is written as:

$$ex_{ph} = (h - h_o) - T_o(s - s_o) \quad (8)$$

The chemical exergy of gas mixture is written as [6]:

$$ex_{mix}^{ch} = \sum x_k ex_{ch}^k + RT_o \sum x_k \ln(x_k) \quad (9)$$

where x_k and ex_{ch}^k shows molar fraction and standard chemical exergy. The exergy destruction rate can be defined as:

$$\dot{E}x_d = T_o \dot{S}_{gen} \quad (10)$$

The energy and exergy efficiencies are used to analyse the performance of the solar tower based integrated plant. Hence, the energy and exergy efficiency equations can be described as given below:

$$\eta = \frac{\text{Useful energy output in product}}{\text{Energy input}} \quad (11)$$

$$\psi = \frac{\text{Exergy output in product}}{\text{Exergy input}} \quad (12)$$

4 RESULTS AND DISCUSSION

In this part of the study, to evaluate the designed solar energy-based integrated plant, thermodynamic and parametric analyses are performed.

Table 2. Useful outlets of integrated plant turbines.

Outputs	Value
High pressure turbine power production rate, $\dot{W}_{HPT}$	4196 kW
Low pressure turbine power production rate, $\dot{W}_{LPT}$	1695 kW
High pressure ORC turbine power production rate, $\dot{W}_{HPOT}$	877 kW
Low pressure ORC turbine power production rate, $\dot{W}_{LPOT}$	394 kW
Total power production rate	7162 kW
Hot water production rate	5185 kW

Table 2 highlights the power production capabilities of the various turbines within the integrated plant and its hot water production capacity. The high-pressure and low-pressure turbines, both in the primary system and the ORC plant, collectively contribute to a significant power output of 7162 kW. Additionally, the system's ability to produce 5185 kW of hot water demonstrates its multifaceted utility in providing electrical and thermal energy, making it a highly efficient and versatile solution for renewable energy applications.

Table 3. Energy and exergy efficiencies and exergy destruction rates of integrated plant and its sub-plants.

Integrated plant and its sub-plants	Energy efficiency	Exergy efficiency	Exergy destruction rate (kW)
Solar tower plant	0.6163	0.5724	1821
Heat storage plant	0.7819	0.7485	953
Rankine cycle plant	0.3906	0.3614	4332
ORC plant	0.1614	0.1243	2315
Integrated plant	0.5837	0.5249	9421

Table 3 presents the energy and exergy efficiencies and exergy destruction rates for the integrated plant and its sub-plants. The overall energy efficiency of the integrated plant is 58.37%, while its exergy efficiency is slightly lower at 52.49%, reflecting the inherent inefficiencies in converting all available energy into valuable work. The solar tower plant, a critical system component, has an energy efficiency of 85.26% and an exergy efficiency of 39.34%, indicating substantial exergy destruction primarily due to high-temperature thermal processes. The thermal energy storage unit exhibits an energy efficiency of 78.38% and a relatively low exergy efficiency of 24.18%, emphasizing significant losses during energy storage and retrieval. The ORC plant, responsible for converting thermal energy into electrical power, achieves an energy efficiency of 28.84% and an exergy efficiency of 60.52%, showing its effectiveness in utilizing available exergy. Exergy destruction rates for the integrated plant and its sub-plants highlight areas of improvement, with the solar tower plant and thermal energy storage unit contributing 1821 kW and 953 kW, respectively, to the overall exergy destruction. This analysis underscores optimizing each component to enhance the integrated system's performance.

4.1 Parametric analyses

In this part of the study, two parameters, the reference temperature and the working fluid

temperature of the solar tower plant, are chosen to see their effects on system performance and production rates. In energy generation systems, the reference temperature generally plays a crucial role on system performance. As the reference temperature increases, irreversibilities occurring in energy conversion processes reduce. This leads to higher exergy efficiencies. As seen in Figure 2, the exergy efficiencies of all sub-plants and the integrated plant improve with increasing reference temperature from 0 °C to 40 °C.

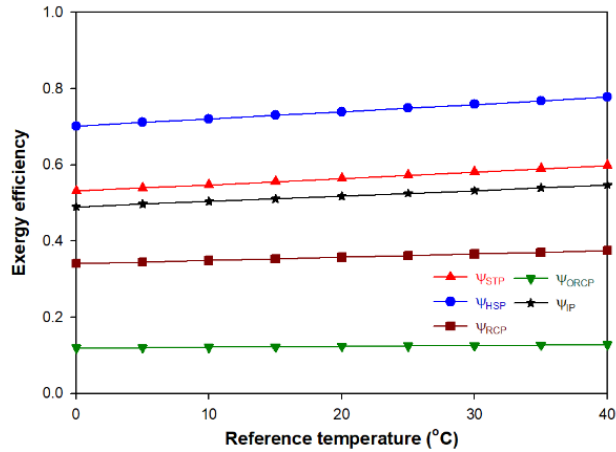


Figure 2. The effect of the reference temperature on exergy efficiencies of sub-plants and the overall plant

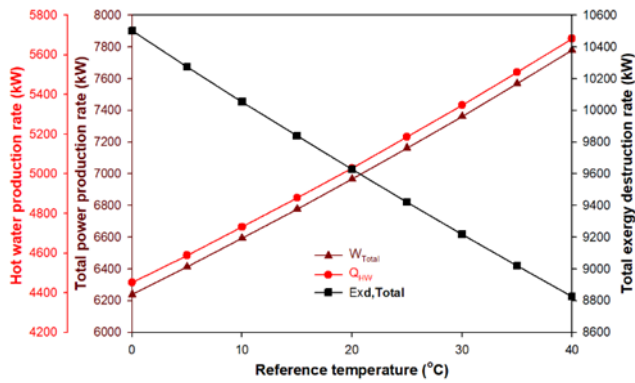


Figure 3. The effect of the reference temperature on production rates and the total exergy destruction

According to Figure 3, the total power production of the integrated plant increases from 6200 kW to 7800 kW as the reference temperature increases. Similarly, hot water production rises from 6300 kW to 7900 kW with increasing temperature. Hence, exergy destruction rates decrease from 10400 kW to 8800 kW. This production rate improvement occurs primarily because the higher reference temperature plays a crucial role in reducing heat losses to the surroundings. This leads to higher exergy efficiencies and higher

production rates, underscoring the significance of the reference temperature in the system's performance.

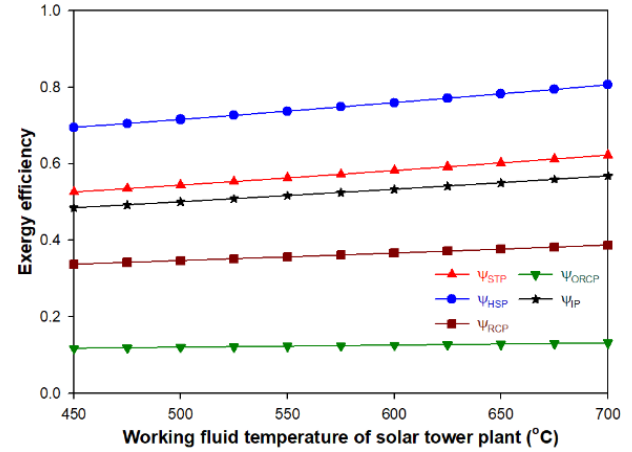


Figure 4. The effect of the working fluid temperature of solar tower plant on exergy efficiencies

The second parameter is the working fluid temperature of the solar power plant. Figure 4 presents its effect on exergy efficiencies. As the figure shows, the exergy efficiencies of all sub-plants and the integrated plant increase due to higher energy input to the system.

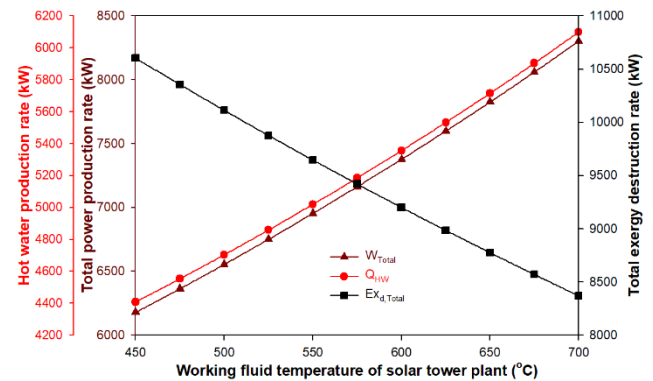


Figure 5. The effect of the working fluid temperature of solar tower plant on production rates

Figure 5 presents the power and hot water production rate change concerning increasing working fluid temperature. As seen from the figure, working fluid temperature is essential in improving production rates and decreasing exergy destruction rates. These parameters will be helpful to solar power plant design.

5 CONCLUSIONS

This study presents a comprehensive thermodynamic analysis of a solar tower-based integrated system designed for combined power and hot water production. The system's

performance was evaluated using energy and exergy analyses, providing insights into its efficiency and potential areas for improvement. The integrated plant achieved an overall energy efficiency of 58.37% and an exergy efficiency of 52.49%, demonstrating its capability to harness solar energy for multiple applications effectively. The high efficiency of the solar tower plant, with an energy efficiency of 85.26%, underscores its critical role in the system. However, the relatively lower exergy efficiency of 39.34% indicates significant room for optimization, particularly in high-temperature thermal processes. The thermal energy storage unit, with an energy efficiency of 78.38% and an exergy efficiency of 24.18%, also presents opportunities for enhancing performance, especially in minimizing exergy losses during storage and retrieval. Exergy destruction rates identified in the analysis emphasize critical areas for improvement. The solar tower plant and thermal energy storage unit, contributing 1821 kW and 953 kW to the overall exergy destruction, respectively, are prime candidates for optimization efforts to reduce irreversibilities.

In conclusion, the proposed solar tower-based integrated system demonstrates significant potential for sustainable and efficient energy production. By optimizing the components with

the highest exergy destruction rates, the system's overall performance can be further enhanced. This study contributes valuable insights into the design and operation of integrated renewable energy systems, paving the way for more efficient and sustainable energy solutions in the future.

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A SOLAR-POWERED COMBINED PLANT BASED ON SUPERCRITICAL CO₂ BRAYTON CYCLE FOR POWER, HEATING, AND HYDROGEN GENERATION; ENERGETIC AND ENERGETIC PERFORMANCE INVESTIGATION

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Abstract

This study focuses on a comprehensive thermodynamic analysis of power, heating, and hydrogen production by a combined system based on a parabolic dish collector. The system is mainly composed of a parabolic dish solar collector, a supercritical CO₂ Brayton cycle with an intercooler, and a PEM electrolysis unit. This system is investigated in terms of energy and exergy efficiency methods and many parametric analyses are performed to determine the changes in system performance. As a result of the analysis, the net electricity generation capacity of this system is calculated as 449.2 kW while the net heat load is determined as 2127 kW. Also, the system's green hydrogen production capacity is 0.0006152 kg/s. As a result, the total energy and exergy efficiencies of this system are determined as 36.19% and 17.22%.

Keywords: Energy, exergy, combined system, solar, green hydrogen, power,

1 INTRODUCTION

The rapid increase in the world population, technological developments, and the rise in living standards have led to a global increase in energy demand. A large portion of the increasing energy consumption is still met by traditional energy sources. However, the limited reserves of fossil fuels and their use causing many environmental problems such as global warming, climate crisis, increased CO₂ emissions, and ecological pollution, have made the use of renewable and sustainable energy sources such as wind, biomass, solar, and geothermal more critical.

Among renewable energy sources, solar energy stands out due to its lower cost and ease of access. Solar energy is collected using various collectors such as flat plate type, parabolic trough type, vacuum tube type, and parabolic dish type. One of the most effective ways to obtain high-temperature heat from solar energy is by using concentrating solar technology. Parabolic dish solar collectors, which belong to this group, can be used in various climatic conditions and provide efficient energy conversion by continuously tracking the sun

throughout the day. Parabolic dish collectors can be integrated with various power generation systems such as the Brayton cycle, organic Rankine cycle (ORC), Stirling engine, and supercritical carbon dioxide (sCO₂) based closed Brayton cycle.

To reduce the cost of solar power plants, improving the performance of the energy conversion system is of great importance. In recent years, supercritical carbon dioxide Brayton systems have attracted significant attention due to their higher thermal performance. In the supercritical Brayton cycle, environmentally friendly, abundant, and non-toxic carbon dioxide is used as the working fluid. Around the critical point, the thermophysical properties of CO₂ show sharp nonlinear changes. This reduces the compression work of the supercritical Brayton cycle, thereby increasing the efficiency of the cycle. The critical temperature of CO₂ is 30.98°C and its critical pressure is 7.38 MPa. CO₂ becomes less compressible in regions near the critical point.

In the literature, various supercritical Brayton system configurations are available: recuperation system, recompression system, partial cooling system, reheating system, inter-cooling system,

Briefly, PDSC absorbs energy from the sun to meet the necessary energy demand of the plant. A thermal energy storage system is also included to maintain necessary heat energy during nighttime. The storage system consists of hot (HST) and cold storage tanks (CST). The sCO₂ Brayton cycle is designed for electricity generation and is composed of six components: compressor, gas cooler, intercooler, heater, heat exchanger, and turbine. After the rejection of some amount of the heat energy to HEX1, sCO₂ continues its flow and assists the other sub-cycles in the order of HEX2 (hydrogen production). The hydrogen production system is a well-known process with the PEM electrolyzer in which freshwater is split into hydrogen and oxygen.

2.1 Thermodynamic investigation

To perform the thermodynamic examination, some assumptions are made, and in line with these assumptions, mass, energy, entropy, and exergy equilibriums should be considered separately. For any system, in its most general form, these equilibrium equations can be written as follows [6-7]

The energy and exergy balance formulation for the proposed model are presented in Table 2.

Table 2. Energy Balance Equations Table

Components	Energy Balance Equations
Com1	$\dot{m}_6 h_6 + \dot{W}_{C1} = \dot{m}_7 h_7$
Comp2	$\dot{m}_8 h_8 + \dot{W}_{C2} = \dot{m}_9 h_9$
Turbine 1	$\dot{m}_{10} h_{10} = \dot{m}_{11} + \dot{W}_{T1}$
HEX 1	$\dot{m}_4 h_4 + \dot{m}_9 h_9 = \dot{m}_5 h_5 + \dot{m}_{10} h_{10}$
HEX 2	$\dot{Q}_{in} + \dot{m}_{20} h_{20} = \dot{m}_{21} h_{21}$
Pump	$\dot{m}_1 h_1 + \dot{W}_p = \dot{m}_2 h_2$
Turbine 2	$\dot{m}_{11} h_{11} = \dot{W}_{T2} + \dot{m}_{12} h_{12}$
PEM	$\dot{W}_{PEM} + \dot{m}_{22} h_{22} = \dot{m}_{23} h_{23} + \dot{m}_{26} h_{26}$
Exergy Balance Equations	
Com1	$\dot{E}x_6 + \dot{W}_{C1} = \dot{E}x_7 + \dot{E}x_{D,C1}$
Com2	$\dot{E}x_8 + \dot{W}_{C2} = \dot{E}x_9 + \dot{E}x_{D,C2}$
Turbine 1	$\dot{E}x_{10} = \dot{E}x_{11} + \dot{W}_{T1} + \dot{E}x_{D,T1}$
Turbine 2	$\dot{E}x_{11} = \dot{E}x_{12} + \dot{W}_{T2} + \dot{E}x_{D,T2}$
HEX1	$\dot{E}x_4 + \dot{E}x_9 = \dot{E}x_5 + \dot{E}x_{10} + \dot{E}x_{D,HEX1}$

$$\dot{m}_i = \dot{m}_e$$

$$(1)$$

$$\dot{Q}_i + \dot{W}_i + \sum \dot{m}_i h_i = \dot{Q}_e + \dot{W}_e + \sum \dot{m}_e h_e \quad (2)$$

$$\sum \left(\frac{\dot{Q}}{T} \right)_{in} + \sum \dot{m}_i s_i + \dot{S}_{gen} = \sum \left(\frac{\dot{Q}}{T} \right)_e + \sum \dot{m}_e s_e \quad (3)$$

$$\dot{E}x_{Qin} + \dot{E}x_{Win} + \sum \dot{m}_i ex_i = \dot{E}x_{Qe} + \dot{E}x_{We} + \sum \dot{m}_e ex_e + \dot{E}x_{des} \quad (4)$$

The performances of the entire system can be defined as follows:

$$\eta_{overall} = \frac{\dot{W}_{net} + \dot{Q}_{heating} + (\dot{m}_{H_2} LHV_{H_2})}{\dot{Q}_{solar}} \quad (5)$$

$$\psi_{overall} = \frac{\dot{W}_{net} + \dot{E}x_{heating} + (\dot{m}_{H_2} LHV_{H_2})}{\dot{E}x_{solar}} \quad (6)$$

The parameters accepted in this study are given in Table 1.

Table 1. Plant design limitations

Parameter	Value
T1 isentropic efficiency	85, %
T2 isentropic efficiency	85, %
Pump efficiency	88, %
Compressor efficiency	88, %
PEM efficiency	56, %
Reference temperature	25, °C

HEX2	$\dot{E}x_{Q,in} + \dot{E}x_{20} = \dot{E}x_{21} + \dot{E}x_{D,HEX2}$
Pump	$\dot{E}x_1 + \dot{W}_p = \dot{E}x_2 + \dot{E}x_{D,P}$
PEM	$\dot{E}x_{22} + \dot{W}_{PEM} = \dot{E}x_{23} + \dot{E}x_{26} + \dot{E}x_{D,PEM}$

3 RESULTS AND DISCUSSION

The proposed study focuses on the comprehensive thermodynamic analysis of the solar energy-based combined plant for clean power, heating, and hydrogen generation. For this aim, the effect of the solar radiation (G_b) on the net power, heating, and hydrogen production is examined and charted in Figure 2. By increasing the G_b from 600 to 800 W/m^2 , the power and heating rates increase. Also, the hydrogen generation load rises.

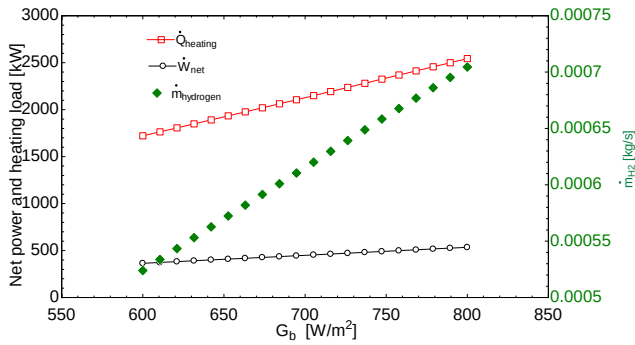


Figure 2. A diagram of the effect of solar radiation on the beneficial crops

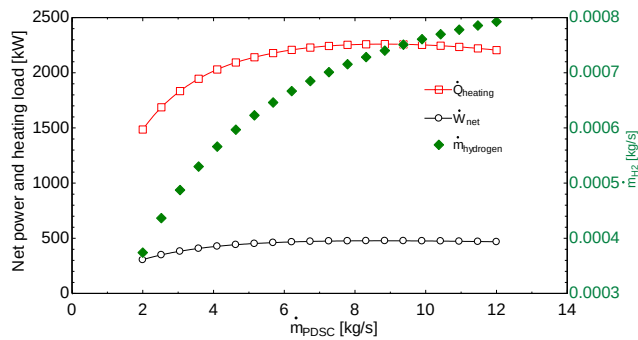


Figure 4. Effect of the PDSC mass flow rate on the system products

Figure 5 shows the influence of the PDSC mass flow rate on the developed system's energetic and exergetic performance indicators. This chart shows the rise in the PDSC mass rate leads to an increase in the energy and exergy efficiency of the developed model.

Figure 3 indicates the effect of G_b on the developed system's performance rates. With the increase of the G_b value, both the energy and exergy efficiency of the entire system has increased, as the system reaches higher values and the useful products obtained have increased.

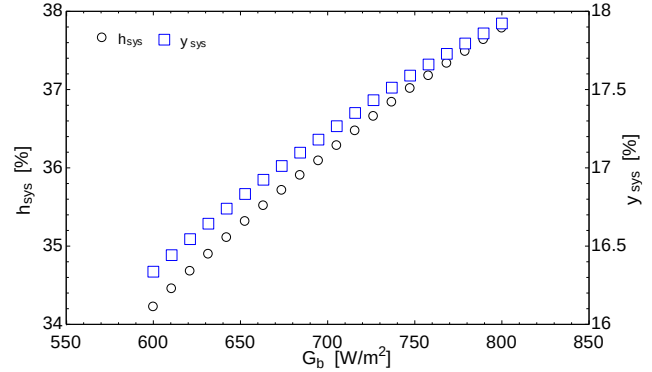


Figure 3. Performance rate of the modeled plant versus different G_b value

Figure 4 examines the influence of the PDSC mass flow rate on the system products. As can be shown in the graph, the rise in mass rate has a linear effect on the goes-up power, heating, and hydrogen rates. Overall, it can be concluded that the rise in fuel mass had a positive effect both in the system

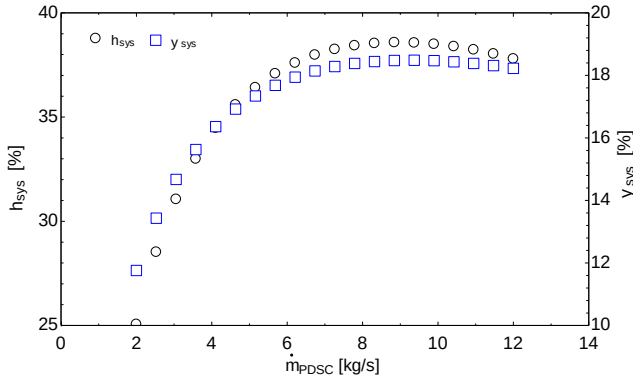


Figure 5. Impact of the PDSC mass flow rate on the system performance rate

Figure 6 investigates the relationship between compressor compression ratio and system performance changes. With increasing the compression ratio, the system can generate more beneficial crops and then the system performance increases. It can be determined that the rise in the compression ratio had a positive effect on the system efficiency up to a critical value. However, when this critical value is exceeded, net electricity production becomes negative due to the higher power consumed by the compressor and therefore system performance may be adversely affected.

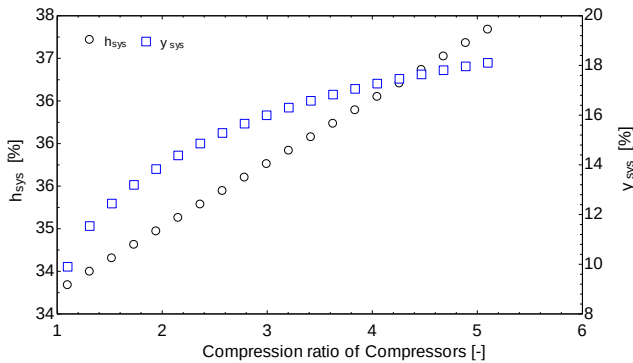


Figure 6. Variation of system efficiency with different compressor compression ratio

The thermodynamic analysis case results of the developed model are presented in Table 3. As indicated the net power rate is 449.2 kW and the hydrogen generation capacity is computed as 0.0006152 kg/s, respectively. Overall system efficiency is determined as 36.19%.

Table 3. The values of the components in the proposed system

Components	Value	Unit
$\dot{W}_{C1}$	123.8	kW
$\dot{W}_{C2}$	71.11	kW
$\dot{W}_{T1}$	410	kW
$\dot{W}_{T2}$	360.6	kW

$\dot{W}_{net}$	449.2	kW
$\dot{Q}_{heating}$	2127	kW
$\dot{m}_{H_2}$	0.0006152	kg/s
η_{sys}	36.19	%
ψ_{sys}	17.22	%

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PARAMETER EXTRACTION AND OPTIMISATION OF A SOLAR CELL USING MATLAB: A THEORETICAL PERSPECTIVE

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ABSTRACT

When examining a solar cell, it is crucial to identify the electrical characteristics also referred to as parameters that elucidate its performance, across various conditions. These parameters play a role in comprehending and enhancing the solar cell's efficiency. This paper presents a technique for extracting and optimising these parameters using MATLAB. The process commences with collecting real world solar cell data specifically focusing on their current-voltage behaviour under varying conditions such as temperature fluctuations and different lighting conditions. This data is essential for characterising and modelling the solar cell performance.

Following data collection, a model is selected to depict the cell's behaviour. This article employs the single-diode model due to its blend of complexity and precision. This model incorporates parameters like photocurrent (I_{ph}), diode saturation current (I_o), series resistance (R_s), shunt resistance (R_{sh}) and diode ideality factor (n). Equations governing this model are formulated, laying the groundwork for analysis.

Using MATLAB a function is developed to simulate the current-voltage behaviour based on these parameters. The crux of this parameter extraction process involves employing optimization techniques to minimize disparities, between simulated results and actual experimental data. The MATLAB function 'lsqcurvefit' is used to optimize (that is, minimize the difference between the simulated and actual data) the extracted parameters.

Subsequently, the obtained parameters are validated by comparing the I-V curves and assessing factors like fill factor and efficiency metrics. This thorough process does not only help in determining parameters but also provides valuable insights into solar cell effectiveness paving the way, for enhanced design and optimization opportunities.

Keywords: Parameters, MATLAB, Diode model, Optimisation

1 REAL-WORLD DATA COLLECTION

1.1 Current-Voltage (I-V) Characteristics

I-V Essential data for extracting metrics like efficiency (η), fill factor (FF), open-circuit voltage (V_{oc}), and short-circuit current (I_{sc}) can be obtained from experimental I-V curves. These parameters are important measures of a solar cell's performance and are affected by several variables that must be considered in practical settings [1]-[3]. In the sections that follow, we go over the following variables that affect a solar cell's performance: temperature changes, light and dark conditions, and irradiance levels.

1.2 Irradiance Levels

The amount of power per unit area that is received as electromagnetic radiation from the sun is known as irradiance. Watts per square meter, or W/m^2 , is the standard unit of measurement. To comprehend how solar cells behave under various sunshine intensities, testing solar cells at varied irradiance levels is essential. The generated current is directly impacted by irradiance; that is, as irradiance rises, the short-circuit current (I_{sc}) rises proportionately [4].

The relationship between short-circuit current (I_{sc}) and irradiance (G) is given by:

$$I_{sc} = I_{sc,ref} \left(\frac{G}{G_{ref}} \right) \quad (1)$$

where $I_{sc,ref}$ is the short-circuit current at the reference irradiance G_{ref} (usually 1000 W/m²) [5].

Irradiance also impacts the open-circuit voltage (Voc). The relationship between Voc and irradiance (G) can be expressed as:

$$V_{oc} = V_{oc,ref} + \frac{nkT}{q} \ln \left(\frac{G}{G_{ref}} \right) \quad (2)$$

where:

- $V_{oc,ref}$ is the open-circuit voltage at the reference irradiance G_{ref} ,
- n is the ideality factor of the diode,
- k is Boltzmann's constant,
- T is the absolute temperature,
- q is the charge of an electron [6].

A common set of Standard Test Conditions (STC) includes an irradiation of 1000 W/m². To fully assess the cell's performance, testing at various levels, such as low light (200 W/m²) and strong light (1200 W/m²), is required because real-world conditions frequently differ [7].

1.3 Temperature Variations

A solar cell's open-circuit voltage (Voc) and short-circuit current (Isc) are both strongly impacted by temperature.

1.3.1 Impact on Open-Circuit Voltage

The open-circuit voltage (Voc) declines with temperature in most solar cells. Rising temperatures cause a decrease in bandgap energy and an increase in recombination rates. Voc and temperature (T) have the following relationship:

$$V_{oc}(T) = V_{oc,ref} - \beta(T - T_{ref}) \quad (3)$$

where:

- $V_{oc}(T)$ is the open-circuit voltage at temperature (T),
- $V_{oc,ref}$ is the open-circuit voltage at the reference temperature (T_{ref}),
- β is the temperature coefficient of the open-circuit voltage, typically around -2 mV/°C for silicon solar cells [8].

1.3.2 Impact on Short-Circuit Current

The short-circuit current (Isc) typically increases with rising temperature since the photocurrent is less affected by temperature changes, as the voltage. The connection between Isc and temperature is not straightforward, but it can be influenced by changes in the saturation current (Io) due to temperature. The effect can be estimated by:

$$I_{sc}(T) \approx I_{sc,ref} (1 + \alpha(T - T_{ref})) \quad (4)$$

where:

- $I_{sc}(T)$ is the short-circuit current at temperature (T),
- $I_{sc,ref}$ is the short-circuit current at the reference temperature (T_{ref}),
- α is the temperature coefficient of the short-circuit current, typically positive [9].

To completely define the thermal sensitivity of the cell, experimental data collection should therefore include measurements at both increased and decreased temperatures, typically spanning from -20°C to 80°C.

1.4 Light and Dark Conditions

To distinguish between photovoltaic effects and leakage currents, solar cells must be tested in both light and dark conditions. The information regarding the power generating capabilities of the cell is provided by the I-V curve when it is lighted. At the maximum power point (MPP), the power output (P) is determined by:

$$P_{max} = V_{mp} \times I_{mp} \quad (5)$$

In contrast, dark I-V measurements reveal information about the solar cell's diode characteristics and leakage pathways. The dark I-V characteristics can be described by the Shockley diode equation:

$$I = I_0 (e^{\frac{qV}{nkT}} - 1) \quad (6)$$

where I_0 is the saturation current, q is the charge of an electron, n is the ideality factor, k is Boltzmann's constant, and T is the temperature. Shunt resistance and other non-ideal behaviours that may have an impact on cell performance can be identified and measured with the aid of these dark conditions [3], [10].

2 SELECTING A MODEL

The accuracy and complexity of the single-diode model are balanced, making it the recommended model [11]. Under typical working conditions, the single-diode model performs satisfactorily; nevertheless, in low solar radiation, it frequently exhibits deteriorated behaviour [12]. Nonetheless, some studies use a second diode (also known as the double-diode PV model) to address the impact of charge carrier recombination losses in the depletion area [13]. The single-diode model consists of these elements:

- Photocurrent (Iph): This current is generated by the incident light on the solar cell

and is directly proportional to the intensity of the sunlight.

- Diode Saturation Current (I_o): This represents the recombination and leakage current in the solar cell, which occurs when the diode is in reverse bias.

- Series Resistance (R_s): This resistance is due to the movement of current through the internal components of the solar cell, including the semiconductor material and the metal contacts.

- Shunt Resistance (R_{sh}): This resistance is due to the leakage current paths parallel to the solar cell's pn junction, which can occur due to manufacturing defects or impurities.

- Diode Ideality Factor (n): This factor reflects the deviation of the diode's behaviour from the ideal. It considers the recombination mechanisms in the solar cell and typically ranges from 1 to 2.

The single-diode model is a robust and trustworthy tool for analysing the current-voltage behaviour under diverse conditions because it accurately represents the fundamental physical processes that occur within the solar cell.

3 DEFINING THE MODEL EQUATIONS

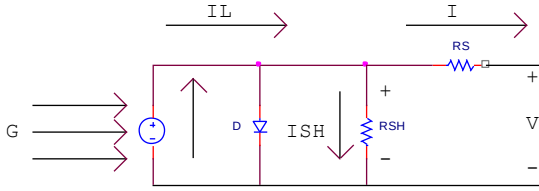


Figure 1. Equivalent circuit of solar cell

To simulate a solar cell's electrical behaviour, a nonlinear p-n junction can be used as a model [14]. A mathematical model is built using equations that depict the relationship between the inputs and outputs of the solar cell to comprehend these characteristics. As shown in Figure 1, the most basic equivalent circuit for a solar cell is made up of a current source that is connected in parallel with a diode.

The equation governing the single-diode model is given by [15]:

$$I = I_{ph} - I_o \left(e^{\frac{V+IR_s}{nV_T}} - 1 \right) - \frac{V+IR_s}{R_{sh}} \quad (7)$$

Where:

- I : Current.
- V : Voltage.

- I_{ph} : Photocurrent.

- I_o : Diode saturation current.

- R_s : Series resistance.

- R_{sh} : Shunt resistance.

- n : Ideality factor.

- V_T : Thermal voltage ($k_B T/q$).

4 PARAMETER EXTRACTION AND OPTIMISATION USING MATLAB

To simulate the solar cell behaviour, the MATLAB code defines and applies a single-diode model, optimizing model parameters to fit experimental current-voltage (I-V) data. The first two functions defined are one for computing the current using the single-diode model and another for calculating the root mean square error (RMSE) between the experimental and simulated data. The script reads data from a CSV file (see Table 1), preprocesses it, and eliminates any missing values. The I-V curves, both experimental and fitted, are then plotted under various conditions (see Figure 2). To guarantee a satisfactory fit, the model parameters are optimized using the MATLAB function 'lsqcurvefit' and an RMSE check. Important solar cell characteristics are collected and shown in Table 2, including efficiency, fill factor (FF), maximum power point (MPP), open-circuit voltage (Voc), and short-circuit current (Isc). A power vs. voltage (P-V) characteristic plot (Figure 3) for each condition and a 3D plot (Figure 4) illustrating the relationship between I-V characteristics, temperature, and light intensity are additional visualizations.

Table 1. Sample experimental current-voltage (I-V) data

Condition	V	I	Temp	LI
Condition1	0	0.5	25	1000
Condition1	0.1	0.48	25	1000
Condition1	0.2	0.45	25	1000
Condition1	0.3	0.4	25	1000
Condition1	0.4	0.35	25	1000
Condition1	0.5	0.25	25	1000
Condition1	0.6	0.1	25	1000
Condition2	0	0.55	30	800
Condition2	0.1	0.52	30	800
Condition2	0.2	0.5	30	800
Condition2	0.3	0.45	30	800
Condition2	0.4	0.38	30	800
Condition2	0.5	0.3	30	800
Condition2	0.6	0.15	30	800
Condition3	0	0.6	20	900

Condition3	0.1	0.58	20	900
Condition3	0.2	0.55	20	900
Condition3	0.3	0.5	20	900
Condition3	0.4	0.42	20	900
Condition3	0.5	0.32	20	900
Condition3	0.6	0.18	20	900

Where:

V: Voltage.

I: Current.

Temp: Temperature.

LI: Light Intensity.

Table 2. Key solar cell extracted parameters

Condition	Efficiency	FF	Pmax	Imp	Vmp	Voc	Isc
Condition1	32.532	0.32532	0.14	0.35	0.4	0.8607	0.5
Condition2	45.128	0.45128	0.152	0.38	0.4	0.6124	0.55
Condition3	45.285	0.45285	0.168	0.42	0.4	0.61831	0.6

Table 3. Optimised parameters

Iph	Rp	Rs	n	Io
0.3958	463.9725	0.0420	0.9491	7.807e-13

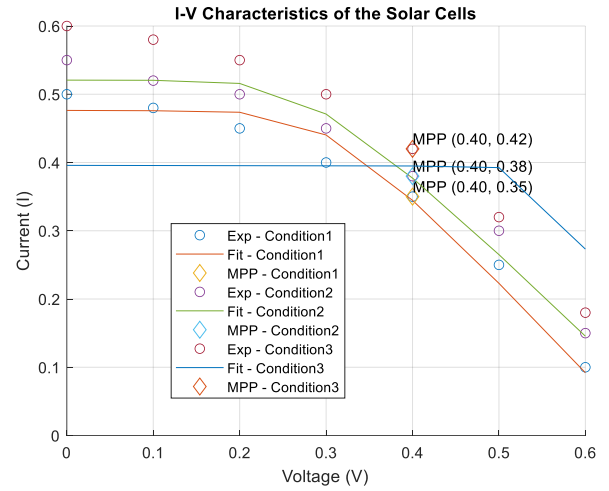


Figure 2. I-V Characteristics of the Solar Cell

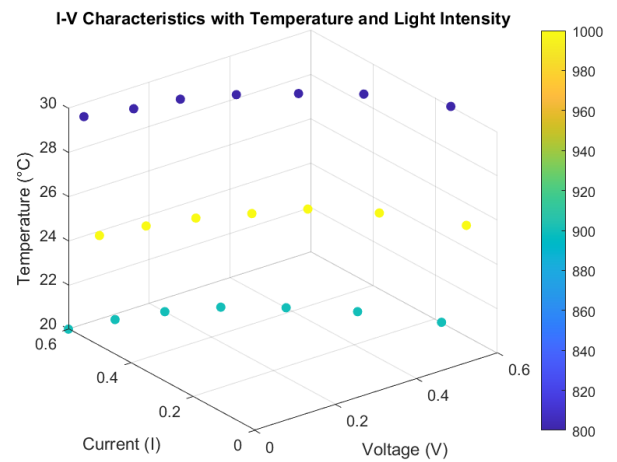


Figure 3. I-V Characteristics of the Solar Cell with Temperature and Light Intensity

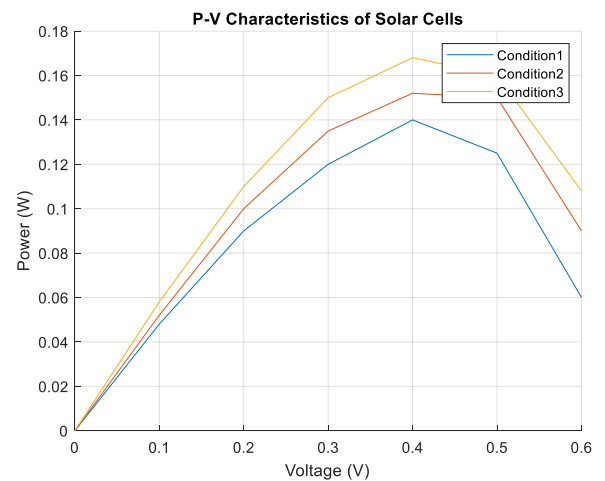


Figure 4. P-V Characteristics of the Solar Cells

5 CONCLUSIONS

The conclusions derived from the extracted and optimised single-diode model parameters can offer important information on the

characteristics and performance of the solar cells under study. The study that was done for this publication led to the following results.

A thorough evaluation of the solar cell performance is provided by the single-diode model's optimized and extracted parameters. The short-circuit current (I_{sc}) and open-circuit voltage (V_{oc}), which represent the maximum current and voltage capacities of the cell, respectively, are important indicators. The optimal operating parameters for maximum efficiency are shown by the maximum power (P_{max}), voltage (V_{mp}), and current (I_{mp}) at maximum power. The efficiency percentage and the fill factor (FF) demonstrate how well the cell performs overall and how well it converts sunlight into electrical energy. Furthermore, optimal parameters that shed light on the internal properties and quality of the solar cell include saturation current (I_0), ideality factor (n), series resistance (R_s), shunt resistance (R_p), and photocurrent (I_{ph}). A low root mean square error (RMSE) indicates a well-fitting model that accurately represents experimental data and aids in optimizing and enhancing solar cell performance.

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PREDICTING SOLAR CELL TEMPERATURE ON SOILED SURFACES USING MACHINE LEARNING AND THERMAL ANALYSIS: IMPLICATIONS FOR ENERGY PRODUCTION

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Abstract

Soiling on solar photovoltaics causes significant losses in transmittance and lead to temperature rise in solar cells. This phenomenon results in significant power losses on solar cells due to both the reduction in solar irradiance incident on the solar cell as well as the power drop due to thermal impacts. To comprehensively understand the effects of dust particles on solar cell performance and temperature, it is crucial to delve into their physical and thermal properties. This study investigates using machine learning techniques in conjunction with thermal analysis to forecast solar cell temperatures on soiled surfaces. Focusing on the physical and thermal properties of dust, including density, size, thermal conductivity, and specific heat, the study aims to understand their influence on the thermal behavior of solar cells. ANSYS steady-state thermal analysis and Computational Fluid Dynamics (CFD) were used to simulate the impact of various dust characteristics on solar cell temperature following a set of designed experiments. The SST k- ω turbulence model was implemented together with the discrete phase model for predicting fluid flow and dust motion respectively. Exploratory data analysis was performed to analyse the significance of each of the variables used in the modelling process and select the best variables for predictive modelling. A random forest approach was employed in the modeling strategy to construct a predictive model. The outcomes were integrated into energy simulations to assess the effects of diverse dust physical and thermal properties on energy production, specifically concentrating on solar cell temperature and transmittance reduction. The developed predictive model exhibited high accuracy, as demonstrated by a coefficient of determination (R^2) of 0.973 and a Mean Absolute Percentage Error (MAPE) of 2.31°C. Average energy losses attributed to thermal effects on soiled solar cells were reported to be up to 4.5% excluding the normal cell temperature rise on clean solar cells. Notably, the study shows the importance of predicting soiled solar cell temperature due to its substantial impact on energy costs attributable to thermal losses. Furthermore, the research is instrumental in determining an optimal cleaning schedule tailored to each combination of dust characteristics, thereby enhancing the efficiency of solar energy systems. The results demonstrate the significant role dust thermal and physical properties play in shaping solar cell thermal characteristics. Moreover, the study showcases that random forests serve as a viable method for temperature prediction on soiled solar cells.

Keywords: Machine Learning, Solar Cell Temperature, Dust Characteristics, Random Forest, Energy Production.

TREATMENT OF DYEING INDUSTRY WASTEWATER: A COMPARISON BETWEEN THE UV/PEROXYDATE AND UV/PERSULFATE PROCESSES

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Abstract

Generation of anion sulfate radicals and hydroxyl radicals by UV/Persulfate and the UV/Peroxydate processes have been successfully studied to degrade Ponceau S dye. Under [PS]=0.06 mM; [H₂O₂]=2 mM; [$S_2O_8^{2-}$]=2 mM, the UV/Persulfate process was effective ($k_{app}=0.163 \text{ min}^{-1}$) than the UV/Peroxydate process ($k_{app}=0.054 \text{ min}^{-1}$). The lack of dissolved oxygen, the excess of hydrogen peroxide (H₂O₂) dosage at 2 mM, and the alkaline pH of 10.01 significantly reduced the UV/Peroxydate efficiency. The scavenging effect of the hydro-genocarbonates and nitrates on the PS dye degradation by the UV/Persulfate process was significant, whereas chlorides had a slight influence. The composition of seawater in chlorides, sulfates, carbonates, and bromides decreased the photoactivity of the studied processes. The presence of phenol showed that the reactive affinity of the hydroxyl radicals is more superior to the anion sulfate radicals. The UV/Persulfate process achieved 82.35% of chemical oxygen demand removal against 59.56% for the UV/Peroxydate in about 100 min. This study demonstrated that the UV/Persulfate process is a viable option for PS dye degradation.

Keywords: advanced oxidation processes, anion sulfate radical, chemical oxygen demand, hydroxyl radical, UV/H₂O₂, UV/ $S_2O_8^{2-}$

$$VT^n = C \quad (1)$$

where, V is the cutting speed and T is the tool life. The model constants n and C depend on the tool and work material pair.

Citation of the references should be made within square brackets. For example, book reference [1] and other references [2,3] are listed at the end of the paper.

COMPARISON OF DIFFERENT SPATIAL INTERPOLATION TECHNIQUES FOR ESTIMATING AREAL PRECIPITATION IN TÜRKİYE

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Abstract

In this study, we investigated performance of the different interpolation techniques for estimating the spatial distribution of precipitation over Türkiye. The analysis was based on precipitation data collected during 1980-2020 period at 237 stations. The methods used included inverse distance weighted (IDW), local polynomial interpolation (LPI), ordinary kriging (OK), empirical Bayesian kriging (EBK), ordinary co-kriging (UCK), and geographically weighted regression. Cross-validation is applied to evaluate the performance of interpolation methods. Correlation coefficient (R), mean error (ME), and root mean square error (RMSE) were used as performance measures. The results indicate that MGWR and GWR were the optimal methods with the lowest RMSE and ME and the highest R values for interpolating the precipitation over Türkiye. The techniques that considered geographical characteristics (i.e., elevation) (MGWR, GWR, UCK) performed better in representing the spatial variations of the average annual precipitation.

Keywords: Precipitation, Spatial Interpolation, Performance Evaluation

1 INTRODUCTION

Precipitation is the most significant component of the water cycle. An in-depth understanding of climatic variables, particularly precipitation, is essential for managing water resources for municipal, industrial, and agricultural purposes. Precipitation on the land surface is directly measured by using ground-based instruments such as rain gauges installed on specific locations. Although more recently satellite- or radar-based measurements for precipitation, which provide better spatial representation, have become available, gauge-based data are still imperative for hydrological and meteorological studies for validating satellite- or radar-based data and conducting long-term data analysis as well [1, 2].

Unfortunately, gauge-based precipitation data have also some drawbacks [3]. As these data are collected at particular locations, they are only representative of the locations they are collected. Usually, the distribution of rain gauges over a region is irregular and they are located in populated areas, which causes an additional challenge when an accurate estimate of average precipitation over a surface is required. Moreover, the presence of strong winds can also

introduce errors with the measured rainfall amounts. Due to the increasing use of spatial analysis in climatology and hydrology, the estimation of areal precipitation has become crucial. [4].

The aim of this study is two-fold. First is to apply different spatial interpolation techniques to estimate average annual precipitation over Türkiye. The second is to assess performance of the selected interpolation techniques by employing by using the cross-validation methods. in estimating the spatial variations of the average annual precipitation over the country.

2 MATERIAL AND METHODS

In the study, precipitation data collected during the 1980-2020 period at 237 meteorological stations operated by the State Meteorological Service were used in the analysis. The selected stations are presented in Figure 1. The stations were dispersed almost evenly over Türkiye.

The interpolation techniques that we used to estimate the areal precipitation, included inverse distance weighted (IDW), local polynomial interpolation (LPI), ordinary kriging (OK), empirical Bayesian kriging (EBK), ordinary co-kriging (UCK) and geographically weighted

regression (GWR). Correlation coefficient (R), mean error (ME) and root mean square error

(RMSE) verification metrics were used to assess each technique's performance.

Below we described the techniques used.

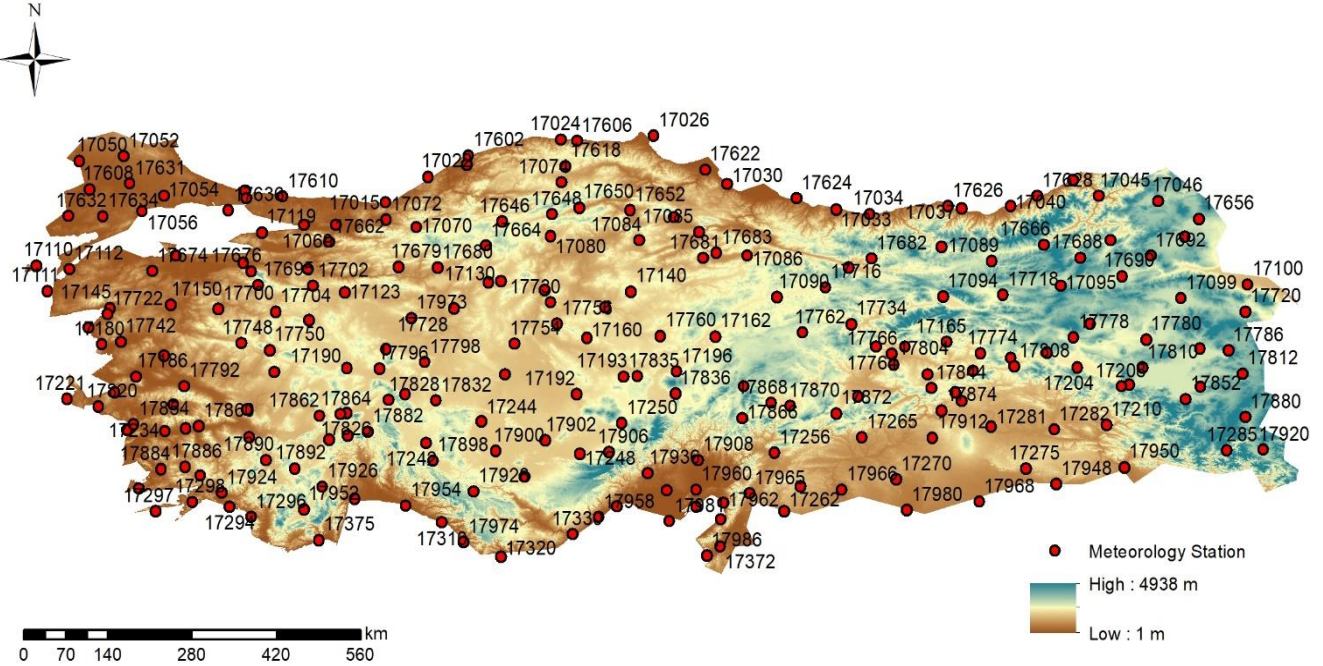


Figure 1. Locations of meteorology stations and topographical characteristics of Türkiye

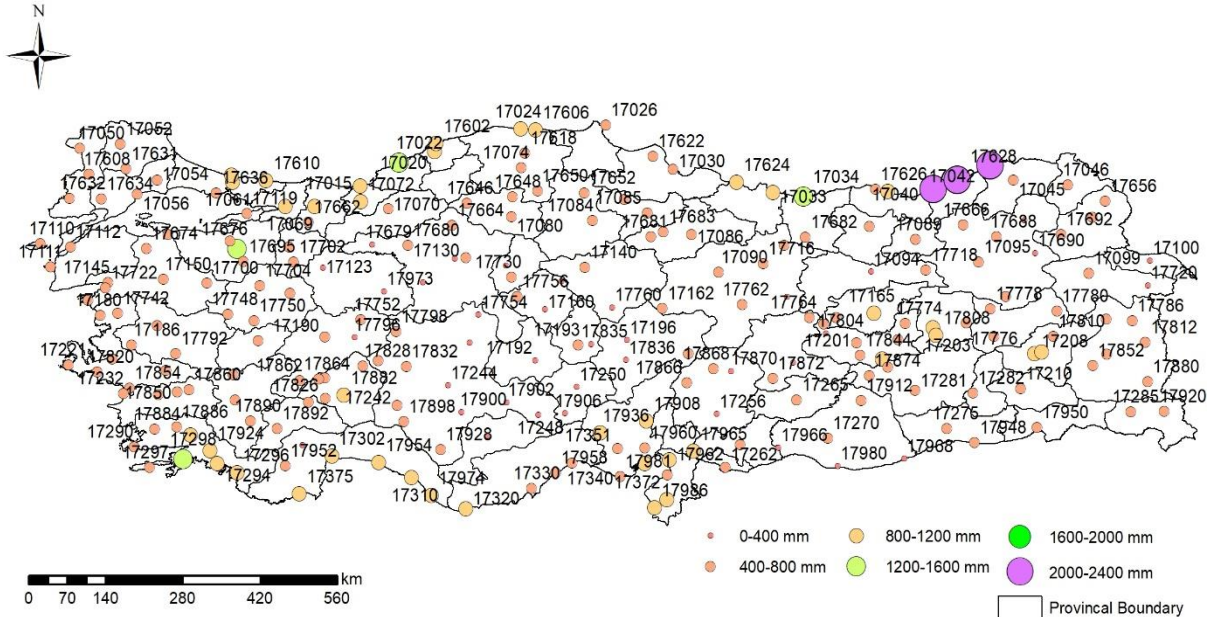


Figure 2. Average annual precipitation for the 1980-2022 period in these stations

2.1 Inverse Distance Weighting

Inverse Distance Weighting (IDW) is one of the most widely used interpolation techniques in spatial data analysis [5, 6]. This technique estimates the value of an unknown point using the values of known points and the distances to these known points. In this technique, a weighting inversely proportional to the distance was used when estimating the value of a point. This approach amplifies the effect of nearby points, while the effect of distant points is

reduced. In the IDW method, first, the coordinates of known points and the measurement values at these points are collected. The weight is calculated for each known point. The weight is determined according to the inverse of the distance between the known point and the point to be estimated. The value of the unknown point is calculated as the weighted average of the known points.

2.2 Local Polynomial Interpolation

Local Polynomial Interpolation (LPI) uses polynomials on a small subset of known points around an unknown point to estimate the value of that point and has been applied for interpolation of precipitation data [5]. LPI aims to determine the trends and patterns in the dataset by using a polynomial determined around each estimated point. The degree of the polynomial can be different and often it is selected based on the characteristics of the dataset, e.g. complexity. In this technique, first, the known points around the point to be estimated are determined. Using these points, a polynomial formula with a certain degree is acquired. Then, the value of the point to be estimated is calculated using this polynomial. This process is repeated for each estimated point, and all the estimates are performed using local polynomials. LPI provides better results if the dataset is heterogeneous and has different trends in different regions. However, the disadvantages of LPI are its the high computational cost and the need to choose the polynomial degree accurately.

2.3 Ordinary Kriging

Kriging is a technique, widely used in the analysis of geographical data including precipitation [7, 8]. In this technique, first, the variability of precipitation with distance is examined. This step involves a calculation of the correlation between the distance between data points and the values are analyzed using graphs called variograms. The variogram data obtained are arranged to fit a specific mathematical model. These models include different variogram models such as spherical, exponential and Gaussian. Based on the selected variogram model, weights are calculated for each of the known data points and using these weights, values at the unknown points are estimated. Different types of kriging techniques are available. In this study, one of the kriging techniques we selected is ordinary kriging (OK). OK is a method which can be used when the mean of the variable does not show a significant trend over space [9]. In this technique, we tried different variogram models and determined that the Gaussian model provided the best results.

2.4 Empirical Bayesian Kriging

Empirical Bayesian Kriging (EBK) is another kriging method implemented in this study. This

method assumes that there may be variations in different subsections of the data set and continuously updates the model parameters by taking these variations into account [8]. The first step in the EBK method is to collect the coordinates of known points and the measurement values at those points. Then, the model parameters determined by classical kriging methods are applied to different subsections of the data set and are continuously updated. In this process, variations and uncertainties are calculated for each subsection. Using the updated model parameters, the values of unknown points are calculated with the weighted average method and the estimates in each subsection are weighted according to their reliability. Finally, the obtained estimates are evaluated and their accuracy is analysed. The advantages of EBK include obtaining more reliable estimates, automatically updating the model parameters and having a wide range of applications. It also performs well when the data variation is high and there are dissimilarities in different parts of the dataset [10]. EBK typically outperforms better with higher data complexity. However, EBK is a method that requires complex calculations and has a high computational cost.

2.5 Ordinary Co-kriging

Co-kriging is a method that uses secondary variables to improve the estimation of the primary variable of interest [11]. In this study, we considered altitude as the representation of the geographic variations in the estimation of precipitation data. The co-kriging method optimizes the variogram model that defines the spatial correlation of both primary and secondary variables. This requires fitting appropriate variogram models to experimental variograms and correctly modeling the cross variograms that measure the spatial correlation between primary and secondary variables. In this study, the ordinary co-kriging method (OCK) was applied. With OCK, we tried different variogram models and determined that the Gaussian model provided the best results.

2.6 Geographically Weighted Regression (GWR)

Geographically Weighted Regression (GWR) is a spatial analysis technique that improves traditional regression models by accounting for spatial heterogeneity [12]. Traditional regression

models are based on the assumption that there is a homogeneous relationship between dependent and independent variables. In contrast, GWR considers that the relationship between variables may vary spatially. This method provides a better representation of the local patterns and processes by generating local coefficients for each location. In the GWR application, we optimized several parameters to enhance model performance. For bandwidth, we applied fixed bandwidth with Gaussian kernel type. We used the cross-validation criterion to evaluate and compare different parameter settings.

2.7 Multiscale Geographically Weighted Regression (GWR)

Multiscale Geographically Weighted Regression (MGWR) is an extension of GWR. GWR technique assumes that the spatial scale is fixed for all processes, and a single optimal bandwidth is found for the processes. In contrast, MGWR assumes that different spatial scales can be used for different processes, and a bandwidth vector is used whose elements represent the spatial scales of different processes [13]. In the MGWR application, we applied fixed bandwidth with Gaussian kernel type. We also used the cross-validation criterion to evaluate and compare different parameter settings.

3 RESULTS AND DISCUSSION

In this study, we used data from 237 stations. Average annual precipitation in the 237 stations for the 1980-2020 period varied between 264 mm and 2321 mm, and the average for 237 stations was 628 mm (Figure 2). The highest precipitation was recorded at Artvin/Hopa station no. 17042 located in northeastern Türkiye, and the lowest precipitation occurred at Iğdır/Merkez station no. 17100 in eastern Türkiye. In general, we observe that precipitation is higher in the coastal regions compared to central and eastern regions that locate at higher elevations.

For each interpolation method used for optimize the results by setting the different options for model parameters. The results obtained (Figure 3) with different techniques were compared based on R, ME, and RMSE (Table 1).

The RMSE values for different techniques were in the order of MGWR<GWR<EBC<OCK<OK<LPI<IDW. The ME values showed a similar order for ME. The order based on R was MGWR>GWR>EBC>OCK>OK>LPI>IDW.

Overall, the minimum RMSE and ME and maximum R were obtained with MGWR and GWR. Also, the performances of GWR and MGWR were comparatively better than other others. MGWR and GWR consider spatial non-stationarity while examining the relationships between variables. This allows better representations of local variations in model parameters and improves performance [13, 14].

Table 1. Comparison of Different Techniques

Interpolation Method	R	ME	RMSE
Inverse Distance Weighted (IDW)	0.74	71.51	192.02
Local Polynomial Interpolation (LPI)	0.79	93.57	174.25
Ordinary Kriging (OK)	0.79	90.03	174.07
Empirical Bayesian Kriging (EBK)	0.81	81.02	169.05
Ordinary Co-kriging (OCK)	0.80	86.67	173.6
Geographically Weighted Regression (GWR)	0.96	-17.77	82.05
Multiscale Geographically Weighted Regression (GWR)	0.98	8.54	50.45

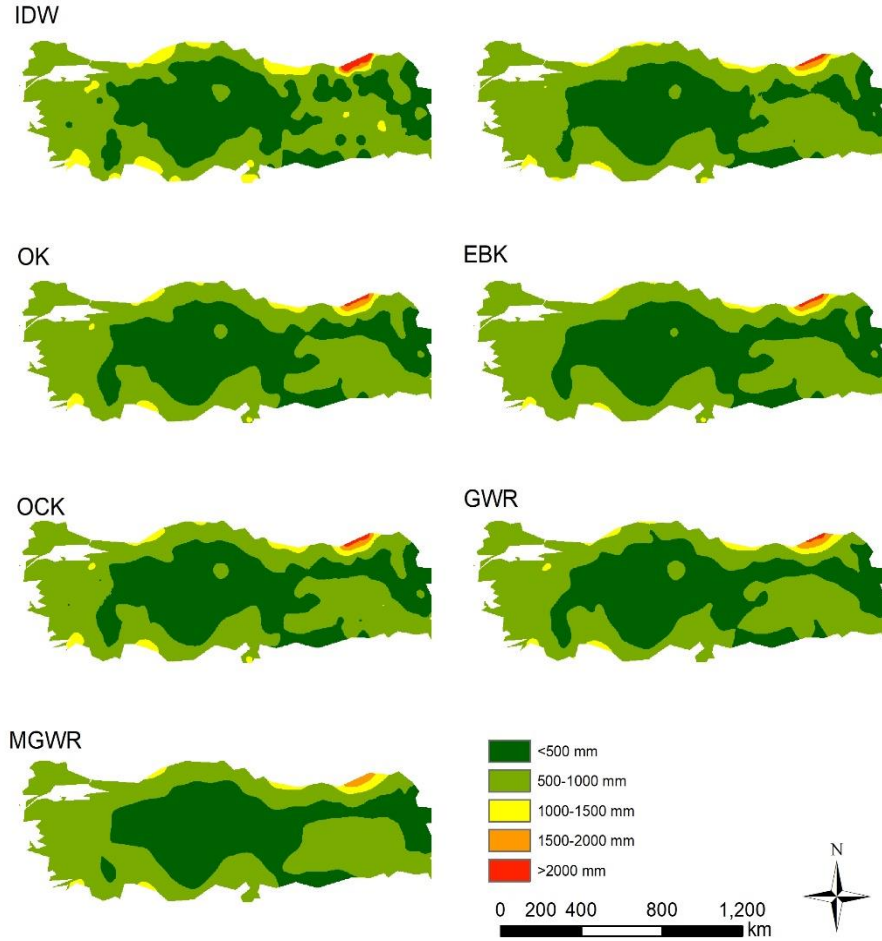


Figure 3. Distribution of precipitation over Türkiye with different interpolation methods

In this study, we confirmed that precipitation is dependent on regional geographical characteristics over Türkiye [7, 15]. The techniques that considered elevation as the input (OCK, GWR, MGWR) generally provided better result. One exception to this was EBK, which performed better than OCK, but still provided poorer performance compared to GWR and MGWR.

4 CONCLUSIONS

In this study, we examined the performance of different techniques for estimating areal precipitation over Türkiye. The results showed that MGWR and GWR yielded better performance than others. In the future, we will consider other geographical and environmental variables to allow increase in explanatory power of the models. We can also use data from other sources such as radar and satellite data, to provide better estimates.

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TOXICITY EVALUATION OF RAW AND TREATED CHROME TANNING WASTEWATER BY POWDERED MARBLE ADSORPTION WITH A BIOTEST ORGE AND LETTUCE

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Abstract

Wastewater from chrome tanning contains large amounts of organic and inorganic compounds, including toxic substances such as chromium salts. The toxicity of raw and treated wastewater using biosorption was assessed through a germination test using lettuce seeds. The results showed that chrome tanning wastewater is phytotoxic, and this phytotoxicity initially manifests by inhibiting germination (acute toxicity of tannery wastewater) and decreasing plant emergence rates in the later period (chronic toxicity). The slight reduction in toxicity, even after a high removal of chromium (up to 99%), suggests that the toxicity of chrome tanning is not solely due to chromium but also to high levels of chloride, which contribute to this toxicity. In contrast, the sulfate ions present in the effluent do not seem to have an inhibitory effect on the germination of barley and lettuce seeds at the concentrations found.

Keywords: Chrome tanning, Bio sorption, Bioassays, Toxicity.

STRAIN EFFECTS IN TYPE I AND TYPE II COLLOIDAL CORE/SHELL QUANTUM DOTS FOR ENERGY STORAGE

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Abstract

Accurate theoretical models and detailed numerical simulations of the impact of strain on the structural, electronic and optical properties of nanoscale semiconductor heterostructures are crucial for accurately prediction of their potential in fabricating nanodevices for energy applications. In this work, a second nearest neighbour sp^3s^* tight binding and eight band $k \cdot p$ effective mass approximation is used to determine the strain effects on the electronic band structure properties of nanoscale spherical CdSe and ZnSe based core/shell semiconductor heterostructures, considering variations in the core and shell dimensions and growth temperature. Calculations carried out on the spherical core/shell Type I and Type II heterostructure quantum dots (QDs) suggest a parabolic decrease (increase) in core bandgaps in CdSe/CdS, CdSe/ZnS, ZnSe/CdS and ZnSe/ZnS quantum dots as core (shell) diameter increases for a fixed shell (core) diameter. The proposed model can be a good design tool for simulating nanoscale core/shell quantum dots for energy applications.

Keywords: CdSe and ZnSe core/shell quantum dots, Interface strain, Second nearest neighbour 2NN sp^3s^* tight binding model, 8-band and 2-band $k \cdot p$ effective mass approximations.

1 INTRODUCTION

Fabrication of semiconductor nanocrystals (NCs) with different compositions by using the colloidal chemical technique allows the combination of more than one semiconductor as a core/shell heterostructure. This structure has been used extensively to control the electronic structure of semiconductor quantum dots (QDs) in the form of Type-I, Type-II and quasi type-II structures. In a Type-I structure, the charge carriers are confined in core by the large band offsets of conduction and valence bands of the shell material. In a Type-II structure, there is separation of excited electrons and holes into either the core or shell by a staggered band structure.

Reliable theoretical modelling and precise numerical calculation of interface strain effects on electronic and optical properties of nanoscale core/shell Type I and Type II heterostructures are crucial for accurately prediction of their potential in fabricating nanodevices for energy storage applications. The electronic band structure of low dimensional semiconductor devices are often calculated by using: (i) First principle ab-initio methods, such as density functional theory (DFT)

[1], (ii) Empirical methods, such as local/nonlocal empirical pseudopotential method [2], or (iii) *tight binding method* (also known as the linear combination of atomic orbitals (LCAO) method) [3], and $k \cdot p$ method [4].

In this work, interface strain effects on the electronic properties of core/shell Type I and Type II CdSe/CdS(ZnS) and ZnSe/CdS(ZnS) nanoscale heterostructures are studied by using semiempirical second nearest neighbour 2NN sp^3s^* tight binding model and eight band $k \cdot p$ effective mass approximation. Thermoelastic model is used to determine interface strain effects on the electronic and optical properties of spherical CdSe/Cd(Zn)S (Type-I) and ZnSe/CdS (Type-II) core/shell QDs as a function dimensions, composition.

2 CALCULATION METHODS

2.1 NN sp^3 tight binding model

In the semiempirical tight binding model one assumes that the valence electrons are tightly bound to their nuclei as in the free atom. Anion and cation atoms are brought together until their separations become comparable to the lattice

constant of semiconductors, at which point their wave functions will overlap. In the Slater-Koster formalism [3], the wave function $\psi_{\alpha k}$ is written as linear combination of atomic orbitals $\varphi_{\alpha}(k)$

$$|\psi_{\alpha k}\rangle = \sum_{\alpha} u_{\alpha} |\varphi_{\alpha}(k)\rangle = N^{-1} \sum_i e^{i \cdot k \cdot r_i} |\varphi_{\alpha}(r - r_i)\rangle, \quad (1)$$

where $\mathbf{r}$ is the position of electron with respect to origin of coordinate system in real space, $\mathbf{k}$ is the wave vector, N is the number of atoms, and $\mathbf{r}_i$ is the crystal lattice site. The energy state is given by the eigenvalue of linear matrix equation

$$\sum_{\beta} [H_{\alpha\beta}(k) - S_{\alpha\beta}(k)E] u_{\beta} = 0, \quad (2)$$

where α is cation s (p) orbital and β is anion s (p) orbital and u_{β} is the wave function coefficient.

The Bloch functions are orthogonal so that the overlap matrix $S_{\alpha\beta} = \langle \varphi_{\alpha}(k) | \varphi_{\beta}(k) \rangle$ is an identity matrix. E is eigenvalue

and $H_{\alpha\beta} = \langle \varphi_{\alpha}(k) | H | \varphi_{\beta}(k) \rangle$ is the (2x2)

Hamiltonian matrix. The on-site and off-site atomic energies

$E_{sa}, E_{sc}, E_{pa}, E_{pc}$ and $E_{ss}, E_{xx}, E_{sa}, E_{sc}, E_{pa}, E_{pc}, E_{xy}$

dominate the acceptable features of electronic band structure. The interface strain will modify the off-site tight binding (TB) matrix elements with respect to their unstrained values and are often determined by assuming that they obey the Harrison Scaling rule [5]:

$$V_{ll'm}(\varepsilon) = V_{ll'm}(a/a_0)^{-\eta_{ll'm}} \quad (3)$$

where $V_{ll'm}(\varepsilon)$ and $V_{ll'm}$ are the strained and bulk value of interaction potential for anion and cation atoms. The exponents $\eta_{ll'm}$ are determined to reproduce the strain dependent band structure of relevant semiconductors under hydrostatic pressure, namely the volume deformation potential $a_{gl} = -B(\partial E_{gl}/\partial P)$ of corresponding band gaps E_{gT}, E_{gL} and E_{gX} at symmetry points.

2.2 k·p effective mass approximation

The k·p effective mass approximation can be used to calculate the energy states in nanoscale semiconductor heterostructures. Kane's parabolic two band *k·p approximation* [6] can be effectively used for a qualitative understanding of quantum confinement and strain effects on conduction and valence band edges of quantum dots and nanowires. In Kane's *k·p* theory, the electronic states are expanded in a finite set of Bloch states close to an extremum k_0 of band structure inside

the Brillouin zone, with spin-orbit interaction effect is considered which leads to following expressions for conduction and valence band energy levels [7].

$$E_c(k) = -\frac{E_g}{2} + \frac{\hbar^2 k^2}{2m_0} + \frac{E_g}{2} \left(1 + \frac{\hbar^2 k^2 (E_g + \Delta)}{2m_{cv}^* E_g (E_g + 2\Delta/3)} \right)^{1/2} \quad (4a)$$

$$E_v(k) = -\frac{E_g}{2} + \frac{\hbar^2 k^2}{2m_0} - \frac{E_g}{2} \left(1 + \frac{\hbar^2 k^2 (E_g + \Delta)}{2m_{cv}^* E_g (E_g + 2\Delta/3)} \right)^{1/2} \quad (4b)$$

where $E_g = E_c(0) - E_v(0)$ is the unperturbed band gap and Δ is the contribution of spin-orbit interaction to band gap and conduction and valence band energies.

The quantum size effect in core region of spherical core/shell nanostructures is given by the dispersion relation with $|k| = 2\pi/d$, where d is the core diameter. One can expand square root term in Equations (4a) and (4b) by using the Binomial approximation as $(1+x)^{1/2} = 1+x/2$ and write the following equation for core bandgap

$$E_g^{nc} = E_g^{bi}(\varepsilon_i) + \frac{2\pi^2 \hbar^2}{m_{cv}^* d^2} \delta_{sp} \left(1 - \frac{2\pi^2 \hbar^2}{m_{cv}^* d^2} \delta_{sp} \right) \quad (5)$$

where $\delta_{sp} = (E_g^{bi}(\varepsilon_i) + \Delta_i) / (E_g^{bi}(\varepsilon_i) + 2\Delta_i/3)$ is the correction factor which considers the spin-orbit interaction contribution to quantum confinement and $E_g^{bi}(\varepsilon_i)$ is strain dependent bulk bandgap and the correction factor δ_{sp} is close to unity for wide bandgap semiconductors such as GaAs and ZnSe ($E_g \gg \Delta$). We recently have shown that the correction factor effects on quantum confinement is between 5% to 8% for wide gap III-V and II-VI compounds. However, δ_{sp} is larger than unity for narrow bandgap semiconductors for which bandgap is nearly equal to or smaller than spin-orbit energy ($E_g \approx \Delta$). δ_{sp} increases the quantum confinement about 20% for InAs and GaSb narrow gap semiconductors.

Since the first proposal of using two band *effective mass approximation* [8, 9] to calculate core bandgap, other theoretical models have been

developed over the years. The eight-band model is an extension of the four-band model with the spin-orbit coupling, which is introduced as a perturbation, together with the $k \cdot p$ term. One minimizes the number of parameters by using the following Hamiltonian.

$$H = \frac{p^2}{2m_0} + V(r) + \frac{\hbar^2 k^2}{2m_0} + \frac{\hbar k \cdot p}{m_0} + \frac{\hbar}{4m_0 \sigma^2 c^2} (\sigma \times \nabla V) \cdot (\hbar k + p) \quad (6)$$

Matrix elements with eigenfunctions $u_{n,0\uparrow}$ and $u_{n,0\downarrow}$ are generated from $H_{mn} \equiv \langle u_{m,0} | H | u_{n,0} \rangle$.

3 RESULTS AND DISCUSSION

3.1 Calculations by 2NN sp^3s^* tight binding and 8-band $k \cdot p$ models.

Figures 1 and 2 show the comparison of energy band structure of bulk CdSe, ZnSe, CdS, and ZnS semiconductors calculated by using the 2NN sp^3s^* tight binding and 8-band $k \cdot p$ models. As can be seen from Table 1, bandgaps calculated by using the 2NN sp^3s^* TB model and 8-band $k \cdot p$ model are in excellent agreement.

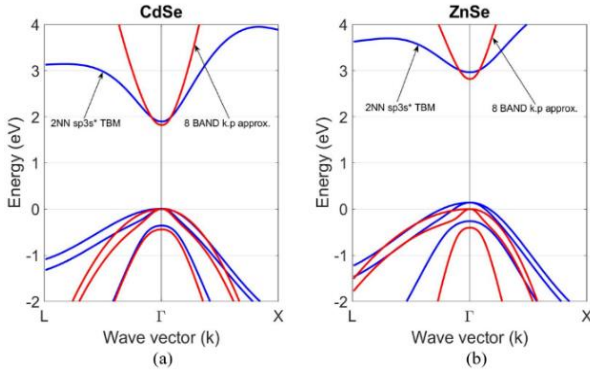


Figure 1. Band structure of (a) CdSe and (b) ZnSe bulk semiconductors obtained by using 2NN sp^3s^* tight binding model and 8 band $k \cdot p$ approximation

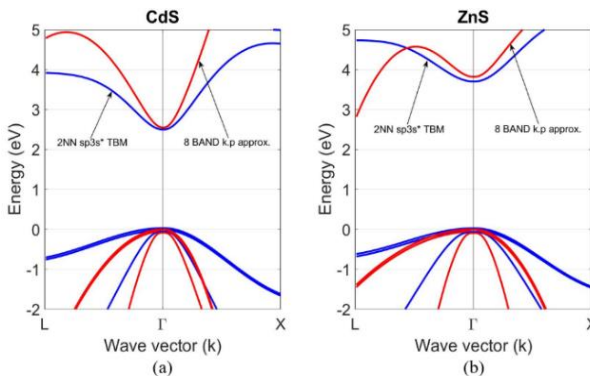


Figure 2. Energy band structure of (a) CdS and (b) ZnS semiconductors obtained by using 2NN sp^3s^* tight binding

model and 8 band $k \cdot p$ approximation

We should point out that the bulk model calculations do not consider the effects of core and shell dimensions and difference between linear thermal expansion coefficients, elastic constants, and finally the effect of spin-orbit splitting of constituents in the computation of interface strain in quantum dots.

3.2 Strain effect on core QD bandgap

The continuum elasticity theories do not fully consider the effect of dimensions, alloy composition, difference between linear thermal expansion coefficients, free thermal expansion of lattice constants and anisotropy of elastic constants of semiconductors forming microscale planar and nanoscale core/shell heterostructures. It is well known that group IV elemental and groups III-V and II-VI compound semiconductors tend to expand due to ΔT temperature rise during crystal growth and still retain their original crystal structure [10]. Therefore, one must consider the effects of lattice thermal expansion of constituent semiconductors and thermal strain across the heterointerface developed during crystal growth which contribute to interface strain due to local mechanical stress.

Table 1. Calculated band gaps of bulk CdSe, ZnSe, CdS and ZnS semiconductors (in eV) at 0 K

	2NN sp^3s^* Tight binding model	8-band $k \cdot p$ approximation
CdSe	1.899	1.823
ZnSe	2.824	2.823
CdS	2.503	2.552
ZnS	3.702	3.820

Exciton energy in Type I CdSe/Cd(Zn)S core/shell quantum dots is result of the direct transitions of exciton pairs inside the core, hence, $E_g^{nc}(d) = hc / \lambda_{\max}$ gives exciton energy of core. Here c is the speed of light, h is the Planck's constant and $\lambda_{\max}$ is wavelength at which the absorption of the nanoparticle is maximum. In ZnSe/CdS (type-II), hole is confined to core and electron to shell, resulting in indirect transition from shell conduction band minimum to core valance band maximum. Bandgaps in Type I and Type II core/shell QDs are calculated by using the 2-band effective mass approximation proposed by Brus [9]

$$E_g^{nc} = E_g^b + \frac{2\hbar^2\pi^2}{m_{cv}^*d^2} - \frac{3.572e^2}{\epsilon_\infty d} - \frac{0.124e^4}{\hbar^2 m_{cv}^* \epsilon_\infty^2} \quad (7)$$

where E_g^b is the bulk direct bandgap. The second term gives the kinetic energy of electron-hole pair, the third term belongs to Coulomb interaction and the last term determines the correlation energy between electrons and holes. Here, $m_{cv}^* = (m_e^* m_h^*) / (m_e^* + m_h^*)$ is the reduced effective mass of electron-hole pair. m_e^* and m_h^* are the effective masse of free electrons and holes, and ϵ_∞ is the optical dielectric constant of bulk semiconductor ($m_e^* = 0.16m_0$, $m_h^* = 0.75m_0$ and $\epsilon_\infty = 5.9\epsilon_0$ for ZnSe and $m_n^* = 0.13m_0$, $m_p^* = 0.43m_0$ and $\epsilon_\infty = 6.2\epsilon_0$ for CdSe in bulk [11]).

When a core/shell QD heterostructure is synthesized from two semiconductors with dissimilar physical properties, there will be a potential barrier in the conduction band and potential step in the valence band at core/shell interface. According to the continuum elastic theory [12], the uniaxial component of biaxial strain tensor splits the heavy-hole, light-hole and split-off valence band edges relative to the average valence band edge. The hydrostatic component of the biaxial strain tensor will cause a shift in the conduction and valence energy band edges relative to their unstrained values.

To emphasize the importance of the structural and elastic properties of constituents in strain modelling across the spherical core/shell quantum dots it is necessary to incorporate the thermal and interface strains produced by the resistance of the medium to thermal expansion [13]. In spherical coordinates, the stress-strain relations (Hooke's law) are written as

$$\epsilon_{rr} = \frac{1}{E}(\sigma_{rr} - \nu(\sigma_{\theta\theta} + \sigma_{\varphi\varphi})) + \alpha\Delta T \quad (8a)$$

$$\epsilon_{\theta\theta} = \frac{1}{E}(\sigma_{\theta\theta} - \nu(\sigma_{rr} + \sigma_{\varphi\varphi})) + \alpha\Delta T \quad (8b)$$

$$\epsilon_{\varphi\varphi} = \frac{1}{E}[\sigma_{\varphi\varphi} - \nu(\sigma_{rr} + \sigma_{\theta\theta})] + \alpha\Delta T \quad (8c)$$

where ϵ_{ij} and σ_{ij} are the Cartesian strain and stress components, respectively. E and ν are the elastic moduli, respectively. The second term ($\alpha\Delta T$) in Equation (8) is the thermal strain due to temperature change ΔT . Here $\epsilon_{rr} = \epsilon_r$ is the radial and $\epsilon_{\theta\theta} = \epsilon_{\varphi\varphi} = \epsilon_t$ are tangential strains with corresponding stresses $\sigma_{rr} = \sigma_r$ and

$\sigma_{\theta\theta} = \sigma_{\varphi\varphi} = \sigma_t$. In the absence of body forces, the equilibrium equation is written as [13]

$$\frac{d\sigma_r}{dr} + \frac{2}{r}(\sigma_r - \sigma_t) = 0 \quad (9)$$

which can be solved by using the following boundary conditions: (i) stress is continuous across interface ($\sigma_{ir}(a) = \sigma_{mr}(a) = -P_i$), (ii) there is no stress outside core/shell structure $\sigma_{mr}(b) = P_o = 0$, and (iii) tangential strain has a lattice mismatch discontinuity at interface, so that *shrink fit condition* [13] is

$$\begin{aligned} |r(\epsilon_{m\theta} - \epsilon_{i\theta})|_{r=a} &= a\epsilon_{im} \\ &= a(a_i - a_m)/a_m \end{aligned}$$

(10)

where a is the radius of the core region.

Solution of Equation (10) in core region, subject to boundary conditions (i), (ii) and (iii), yields $\sigma_{ir} = \sigma_{i\theta} = \sigma_{i\varphi} = \sigma_i = -P_i$. Substituting these results into Equations (8a), (8b), and (8c) one finds the radial and tangential components of the interface strain in core region

$$\epsilon_i = \frac{(1-2\nu_i)\sigma_i}{E_i} + \alpha_i T = -\frac{(1-2\nu_i)P_i}{E_i} + \alpha_i T \quad (11)$$

where $\epsilon_i = \epsilon_{ir} = \epsilon_{i\theta} = \epsilon_{i\varphi}$. Solving Eq. (9) in shell region, one finds radial and tangential stresses

$$\sigma_{mr} = \frac{a^3 b^3 (P_o - P_i)}{(b^3 - a^3)r^3} + \frac{a^3 P_i - b^3 P_o}{(b^3 - a^3)} \quad (12a)$$

$$\sigma_{m\theta} = \sigma_{m\varphi} = -\frac{a^3 b^3 (P_o - P_i)}{2(b^3 - a^3)r^3} + \frac{a^3 P_i - b^3 P_o}{(b^3 - a^3)}$$

When $b \gg a$ and $P_o = 0$, Eqs. (12) reduce to $\sigma_{mr} = -P_i(a/r)^3$, $\sigma_{m\theta} = \sigma_{m\varphi} = P_i(a^3/2r^3)$.

Substituting Equations (12a) and (12b) in Equations (8a), (8b) and (8c) at $r=a$ with $P_o = 0$, radial and tangential strains on the shell side is written as

$$\epsilon_{mr} = \frac{P_i((1-2\nu_m)a^3 - (1+\nu_m)b^3)}{E_m(b^3 - a^3)} + \alpha_m T \quad (13a)$$

$$\epsilon_{mt} = \frac{P_i((1-2\nu_m)a^3 - (1+\nu_m)b^3)}{E_m(b^3 - a^3)} + \alpha_m T \quad (13b)$$

where $\epsilon_{mt} = \epsilon_{m\theta} = \epsilon_{m\varphi}$ is the tangential component of interface strain in the shell region. Combining

Equations (13a) and (13b) with Equation (11), contact pressure at core/shell interface becomes

$$P_i = \frac{2E_i E_m [1 - (\alpha/b)^3] [\varepsilon_{im} + (\alpha_i - \alpha_m)T]}{C + 2D (\alpha/b)^3} \quad (14)$$

where constants C and D are given as

$$C = [(1 + \nu_m)E_i + 2(1 - 2\nu_i)E_m]$$

$$D = [(1 - 2\nu_m)E_i - (1 - 2\nu_i)E_m].$$

On substitution of Equation (14) into Equation (11), one finds the strain acting on core side of the interface. Substitution of Equation (14) into Equations (13a) and (13b), one finds the strain acting on the shell side of the interface. Using the so called statistical thermodynamic model [14], shift in bandgap as a function of pressure and temperature is given as

$$\delta E_{gi} = \Delta C_{ip}^0 T (1 - \ln T) - \frac{a_{gi}}{B} \left(1 - \frac{P_i}{2B} - \frac{(1+B')P_i^2}{3B^2} \right) P_i \quad (15)$$

where E_{gi} is the bulk bandgap at 0 K, the logarithmic term is the contributions due to the lattice vibration. The third term represents the core/shell interface strain effect, respectively. $a_{gi} = -B(\partial E_{gi} / \partial P)$ is the bandgap deformation potential at $i = \Gamma, L, X$ symmetry points of core in bulk. B is bulk modulus and $B' = \partial B / \partial P$. ΔC_{ip}^0 is the standard state heat capacity of reaction for the formation of electron-hole pair and it is obtained by fitting Equation (15) to the measured bandgap of bulk semiconductor at any temperature (e.g., 300 K) and constant pressure.

Figure 3 shows the effect of core diameter on core bandgap shifts of CdSe/ZnS, CdSe/CdS, ZnSe/ZnS, and ZnSe/CdS core/shell QDs with fixed shell (core) diameter at 300 K. They are calculated by using 2NN $sp3s^*$ TB model, including spin-orbit coupling.

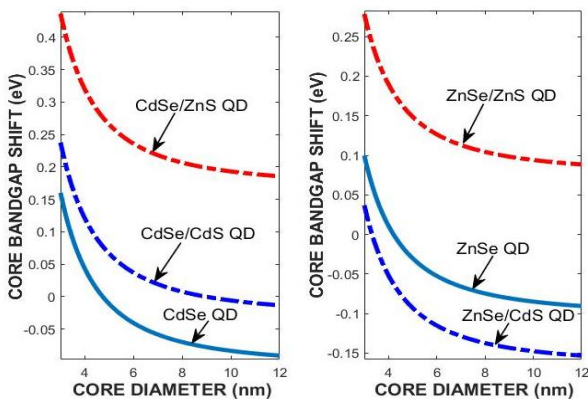


Figure 3. Core diameter effects on core bandgap shifts in CdSe/ZnS, CdSe/CdS (left) and ZnSe/ZnS, ZnSe/CdS (right) core/shell QDs calculated by using 2NN $sp3s^*$ TB model.

Figure 4 shows the effect of core diameter on core bandgap shifts of CdSe/ZnS, CdSe/CdS, ZnSe/ZnS, and ZnSe/CdS core/shell QDs with fixed shell (core) diameter at 300 K. They are calculated by using the 8-band $k.p$ approximation.

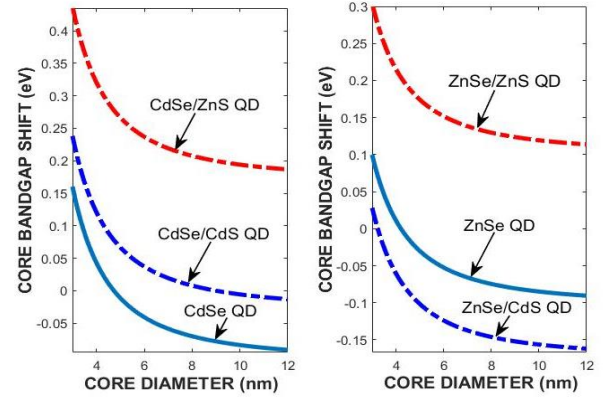


Figure 4. Core diameter effects on core bandgap shifts in CdSe/ZnS, CdSe/CdS (left), ZnSe/ZnS, ZnSe/CdS (right) core/shell QDs calculated by using 8-band $k.p$ approximation.

Comparison of Figures 3 and 4 indicate that both 2NN $sp3s^*$ TB model and 8-band $k.p$ approximation predict that linearly increasing core diameter (with fixed shell diameter) yield parabolic decreasing effect on the shift in the core band gap of CdSe/ZnS(CdS) and ZnSe/ZnS(CdS) core/shell heterostructure QDs with fixed shell diameter.

Figure 5 shows the effect of shell diameter on core bandgap shifts of CdSe/ZnS, CdSe/CdS, ZnSe/ZnS, and ZnSe/CdS core/shell QDs with fixed core diameter, calculated by using the 2NN $sp3s^*$ TB model, including spin-orbit coupling.

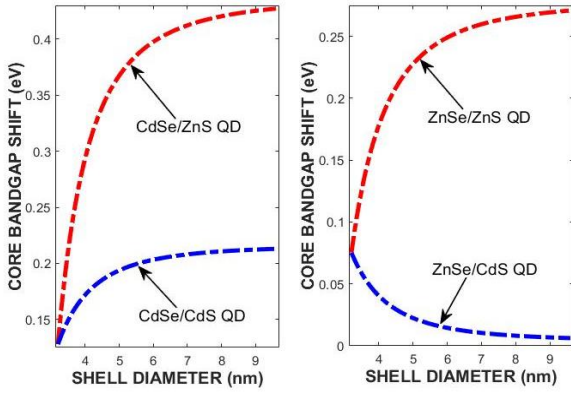


Figure 5. Shell diameter effects on core bandgap shifts in CdSe/ZnS, CdSe/CdS (left), ZnSe/ZnS, ZnSe/CdS (right) core/shell QDs calculated by using 2NN $sp3s^*$ TB model

Figure 6 shows the effect of shell diameter increase on the shift in the core bandgap of CdSe/ZnS(CdS) and ZnSe/ZnS(CdS) core/shell heterostructure QDs with fixed core diameter, calculated by using the 8-band $k.p$ approximation.

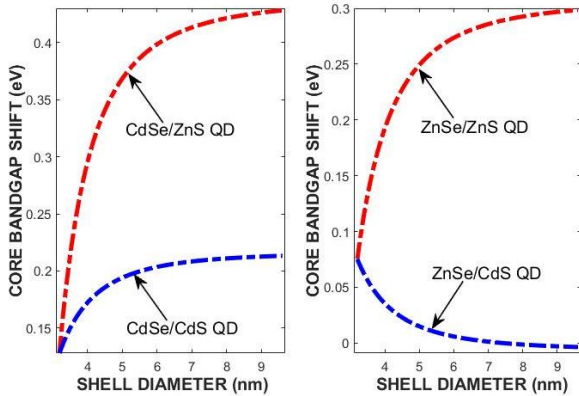


Figure 6. Shell diameter effects on core bandgap shifts in CdSe/ZnS, CdSe/CdS (left), ZnSe/ZnS, ZnSe/CdS (right) core/shell QDs calculated by using 8-band $k.p$ approximation

Comparison of Figures 5 and 6 indicate that both 2NN $sp3s^*$ TB model and 8-band $k.p$ approximation predict parabolic increase in the core bandgap of CdSe/ZnS (CdS) and ZnSe/ZnS core/shell heterostructure QDs. However, both theories predict parabolic decrease of the core bandgap shift in ZnSe/CdS core/shell heterostructure QDs. This is because of the shell diameter on the change of the sign in the thermoelastic hydrostatic strain across the ZnSe/CdS heterointerface.

When one of the constituents of nanoscale core/shell heterostructures is a semiconductor alloy (e.g., CdSe/CdZnS, ZnSe/ZnCdS), the

composition variation of structural properties of alloy constituent (CdZnS or ZnCdS) will alter the sign and modify the magnitude of the interface strain across the core/shell interface. Therefore, in addition to mismatches between lattice constants and thermal expansion coefficients, it is important to include the composition contribution to the interface strain effects on electronic properties of microscale planar and nanoscale core/shell heterostructures prior to any device fabrication. The composition dependent strain effect on core lattice constant of spherical binary/ternary core/shell heterostructure will be in a way that is not seen in microscale planar geometry. Modified virtual crystal approximation [15, 16] can be implemented in the thermoelastic model [17] to study alloy effects on strain and in turn on lattice constant, band gaps and band offsets in binary/ternary (ternary//binary) core/shell QDs. We plan to explore this issue in further theoretical work.

4. CONCLUSION

The effect of the interface lattice mismatch induced strain on the core bandgaps in ZnSe/ZnS, CdSe/Cd (Zn)S type-I and ZnSe/CdS type-II core/shell semiconductor heterostructures was evaluated by using second nearest neighbour (2NN) $sp3s^*$ tight binding model and eight band $k.p$ effective mass approximation. Calculations show a parabolic decrease (increase) in core bandgap shifts as core (shell) diameter increases for a fixed shell (core) diameter and a parabolic increase (decrease) in core bandgap shifts as shell (core) diameter increases for a fixed core (shell) diameter in CdSe/ZnS (CdS) and ZnSe/ZnS core/shell heterostructure QDs. However, both theories predict parabolic decrease of the core bandgap shift in ZnSe/CdS core/shell heterostructure QDs. This is because of the shell diameter on the change of the sign in the thermoelastic hydrostatic strain across the ZnSe/CdS heterointerface. Predictions suggests that proposed model can be a good design tool for simulation of nanoscale core/shell quantum dots for energy storage applications. We plan to explore the composition dependent strain effect in the ternary/binary core/shell heterostructure quantum dots as further work.

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DESIGN OF AN EFFECTIVE BRAKING SYSTEM FOR ELECTRIC VEHICLES

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Abstract

Given the ever-increasing demand for more efficient modes of transporting people, goods, and services that are also built around the preservation of our environment for future generations, there is an imposition on these new modes of transportation to have efficient, cost-effective, and energy-saving means of bringing about a reduction in vehicular-speed or halt in a manner that best protects the driver, the vehicle, its passengers, as well as other road users. The braking-system proposed in this study is a synergistic combination of the widely used Anti-lock braking system-ABS, which is based on the principles of preventing vehicle sliding, and the Regenerative braking system-RBS, which has gained popularity with its use in electric cars. A major focus of this paper is the integration of both braking-systems, which included Fuzzy Logic Control and Simulink. The integration of both braking-systems was accomplished through two novel control strategies that considered the intentions of the driver as well as the surrounding conditions when determining the most-efficient way to reduce vehicle speed when braking was required. In this paper, an electric vehicle was used as the mode of transportation to properly demonstrate the conservative-energy conversion from kinetic energy to electrical energy achieved by the Regenerative braking-system.

Keywords: Fuzzy Logic Controller, Simulink, Anti-lock Braking System, Regenerative Braking System

1 INTRODUCTION

As electric vehicles have gained popularity and acceptance in recent years because of their environmentally friendly operation, they necessitate the development of an advanced braking system that allows for short braking distances, manoeuvrability while braking, and the reduction of heat energy dissipated to the environment when the brake callipers clamp on the rotating tires. This braking system should also include a mechanism for energy conservation, which converts the lost heat energy into a form that is valuable to the vehicle, such as electrical energy, for example.

The purpose of the paper is to propose the design of an energy conserving braking system for use in Electric Vehicles. The usage of an electric vehicle in this design is justified by the fact that the primary goal of regenerative braking systems is to save energy by preventing it from being wasted during the conversion of kinetic

energy to electrical energy. It is directly related to the vehicle's speed and the frequency with which the RBS is used that the amount of electrical energy generated and fed to the batteries to charge them is increased. For example, the higher the current vehicle velocity when the brakes are applied (when the brake pedal is pressed) and the more frequently the brakes are used, the greater the amount of electrical energy is generated to charge the batteries.

Automobiles often use a friction-type braking system, which is comprised of a collection of mechanical, hydraulic, and electrical components that are actuated by friction. As a result, when the brakes are applied, the pads or shoes that contact the brake drums or rotor convert kinetic energy into thermal energy via friction. Brakes work by converting the kinetic energy of the vehicle into heat energy. As a result, brakes are a device for switching between

different forms of energy. The pedal, booster, master cylinder, combination valve, lines for the flow of brake fluid, emergency brakes, disc brakes, and drum brakes are the essential components of a basic automotive braking system.

The disc system or the drum system are the two types of friction type braking systems used in automobiles, and the system used is determined by the function that the vehicle is needed to do. The disc brake operates by applying pressure to a pair of pads against a revolving disc, causing the rotational motion to be retarded because of the friction between the pads and the disc [1]. The drum brake consists of brake shoes with friction material lining attached to them that are pressed against the inner surface of a drum that rotates in conjunction with an axle, so producing friction. When the friction occurs, the kinetic energy of the drum and connected wheel is converted to heat energy, which slows the rotation of the drum and attached wheel [2]. The disc brake system is preferred over the drum brake system because it provides greater stopping performance owing to its higher efficiency in heat dissipation and because it recovers more quickly after being submerged in liquid. They are, however, constructed from ceramic composites to provide greater heat endurance, resulting in higher manufacturing costs and a restricted use to exotic vehicles. Because of its all-in-one construction, which makes it simpler to replace when repair work is required, the drum brake has a lower manufacturing cost and a lower maintenance cost than other types of brakes. They may also be used as parking brakes since they are self-energizing, unlike disc brakes need specific parking brake devices to be used as parking brakes [3].

A braking system was developed for a three-wheeled battery electric vehicle, according to [4], with the goal of lowering the vehicle's speed using friction force and preventing the vehicle from rolling when it comes to a complete stop. When there is induced friction, it causes the vehicle's motion to be stopped by converting the vehicle's motion energy into heat energy. The heat energy is subsequently released into the surrounding environment. The vehicle is comprised of two independently actuating braking systems, each of which is equipped with

an activator (caliper), a single command control lever, and command transmission cables, among other components. One system is responsible for the front wheels, while the other is responsible for the back wheels. The rear wheels, on the other hand, are equipped with an activator for each individual wheel, which is controlled by the same command control as the front wheels. Because the brakes on the right and left wheels are balanced, it is feasible to operate both braking systems at the same time without having to remove either hand from the steering wheel. During the vehicle construction process, the efficacy of the braking systems was evaluated by placing the driver on a 20 percent inclination to test the brakes. Each braking system was designed to be engaged independently of the others to assist keep the car stationary.

In electric vehicles, the loss and subsequent wastage of kinetic energy in the form of heat energy to the surrounding environment occurs during the braking action, which is performed using conventional braking involving the contact of the moving wheels with frictional rubber pads or brake liners to stop the vehicle [5] wrote an article on converting the mechanical energy of a car, as well as the heat that would have been lost during braking, into electrical energy using a system known as "Regenerative braking," which transforms the motor used to power electric vehicles into a generator whenever a significant deceleration of the vehicle is required; the electrical energy obtained is then used to charge the batteries that power the vehicle. Afterwards, actual braking is accomplished by channelling all the amassed momentum or kinetic energy into the generator, resulting in the vehicle coming to a controlled and slow stop.

According to studies on how rapid braking affects a car's unbalance and, therefore, accidents, the wheels lose their manoeuvrability when the traditional braking system locks them in a fixed position [6]. As a result, the anti-lock braking system (ABS) was created to prevent the brakes from being locked while the vehicle is being driven. With the ABS, the driver has complete control over his or her vehicle by preventing it from locking its wheels in sudden braking situations under any road conditions and at any speed, allowing him or her to easily get out of the car with a simple manoeuvre by turning the steering wheel light slightly while

the vehicle is skidding. The Brake Control Module, an electronic control device that is used in anti-lock braking systems, regulates the number of rotations made by each wheel. It brings the wheels to a halt by delivering commands to the wheels to activate and deactivate brake callipers at extremely short intervals of roughly twenty times per second, thereby stopping the wheels.

In a study on the Anti-lock braking system (ABS), its methods, and its superior technology to prevent vehicles from skidding off the road [7]. A safety system in vehicles that regulates wheel slide so that the maximum amount of friction is received during braking and that the steering stability is maintained is known as the anti-lock braking system (ABS).

An intelligent electronic control system, according to [8] is used in an anti-collision system for four-wheelers to decrease collisions with other vehicles. To minimize the amount of damage caused by a collision, this system applies the brake and extends the bumper from its original position, among other things. Among the key components of the paper are an infrared transmitter and receiver circuit, as well as a control unit and a pneumatic bumper system. It makes use of an infrared sensor to detect colliding objects such as obstacles, humans, or vehicles within one foot of the bumper. A feedback signal is sent to the control unit, which activates the solenoid valve, which sends compressed air from the compressor connected to it at one end to the two pneumatic cylinders connected to it at the other end, allowing the bumper to be extended from its original position by a specified distance. Additionally, when the proximity sensor determines that the vehicle is traveling at a speed greater than 80km per hour, a signal is transmitted to both the control unit and the pneumatic bumper activation system, activating the system. By pushing the brake pedal, the driver may also bring the car to a complete stop. This device protects the car before a collision occurs and enhances the reaction time of the vehicles' braking systems, allowing them to maintain a safe distance between them. We can gain control of an overspeeding automobile in a short amount of time by using this approach.

According to [9], the Anti-lock Braking System (ABS) is a component of active safety systems

that assist drivers in coming to a safe stop during panic braking while maintaining the vehicle's stability and steerability. Although the RBS is disabled at a safe (low) deceleration threshold in favor of the ABS, this is not always the case. Because of this safety margin, much less energy is recovered than would be feasible if both RBS and ABS were allowed to function at the same time. The integration of regenerative braking system RBS and friction brakes may increase the energy economy of a vehicle by allowing for more frequent energy recuperation activations, which are particularly important under high deceleration demands. With four, two, and one Electric Machines EM, the primary goal of this doctorate project is to create and execute novel wheel slip control systems with torque blending strategies for diverse vehicle topologies utilizing different EM configurations. The combination of the two brake actuators will increase the braking performance as well as the overall energy efficiency of the vehicle in the future. ABS is also enabled by pure EM in some circumstances when the regenerative brake torque is adequate.

2 METHODOLOGY

The proposed design is an energy conserving braking system for use in Electric Vehicles. The design incorporates an Anti-lock braking system (ABS) as well as a regenerative braking system (RBS) for maximum conversion of the energy generated into useful energy. The main objective is to design an energy conserving braking system for use in electric vehicles.

The design would incorporate an Anti-lock braking system (ABS) as well as a regenerative braking system (RBS) for maximum conversion of the energy generated into useful energy.

In the design of this paper, the following methods are done to achieve an efficient braking system for the EV;

- Two Control strategies methods (Fuzzy Logic Control and Simulink) were implemented.
- In the FLC, two conditions of braking torque efficiency were used to satisfy the design
- FLC design was used to determine the best braking system at different scenarios and simulated for graphical results

- Develop a mathematical Model for the ABS and RBS to be required for the Simulink Control Strategy
- The Model simulated using MATLAB Simulink incorporates alternating between the two braking systems.

2.1 Fuzzy Logic Controller Design Model

Fuzzy controllers are based on rule bases and membership functions for their design aspect. They are effective because they consider grey areas of design aspects. Fuzzy controllers are more robust and easier to implement as compared to classical control schemes. This is the main reason why fuzzy controller schemes are implemented in artificial intelligence papers because they cover the grey area aspects of design.

In this paper, fuzzy controller is proposed with two inputs; vehicle speed and inter-vehicle distance, and one output; brake force, to create a safety distance between vehicles under different circumstances which ranges both extremes of speed and distance (too much and too little).

The fuzzy logic design consists of inputs, the Mamdani-Fuzzy inference engine, from which output is obtained. The output is the brake force and is defuzzied using the centroid method.

2.2 Membership Functions

It is very important we implement the membership function in the fuzzification and the defuzzification steps of the FLC because it must perform evaluation of the non-fuzzy input values to the fuzzy linguistics terms and vice versa. More so, the membership function implemented to measure these linguistic terms. Below are the membership function of the inputs and the output values showing their respective ranges.

Variable Speed –

The distance moved by the car before coming to a stop after hitting the brake is the actual braking distance, and it changes with each increase in speed.

Then, the vehicle speed is divided from 0 to 10 m/s into 5 different ranges as follows:

- Too slow (0-2 m/s), Triangular.
- Slow (1-4 m/s), Triangular.
- Optimum (3-6 m/s), Triangular.
- Fast (5-8 m/s), Triangular.

- Too Fast (7-10 m/s), Triangular.

Variable Distance –

The most important factor when it comes to braking distance is how fast you are going. There is a direct relation to speed, and when your car will come to a complete stop once you hit the brakes. To put it simply, the faster you are going in your car, the longer your braking distance will be

We divide the distance range from 0-10 m to three sub ranges, very close(V_{cls}), close, and far. The inter-vehicle distance is classified as follows:

- Very close distance (0-2 m), Triangular.
- Close distance (2-4 m), Triangular.
- Optimum (4-6 m), Triangular
- Far distance (6-8 m), Triangular.
- Very far distance (8-10 m), Triangular.

Output Braking Torque –

Now for the output membership function, The Output is regarded as the Braking Torque that brings the car to a halt after all the input parameters have been fed into the system.

Brake torque is essentially the power of the braking system.

For Anti-lock braking system, the brake caliper acts on the disc at a certain distance from the hub center, known as the effective radius. The force exerted by the caliper, multiplied by the effective radius of the system equals the brake torque. Increasing either the force applied by the caliper, or the effective radius results in increased brake torque.

For Regenerative braking, the current vehicular speed is diffused as the rotary kinetic energy of the wheels is instead used to drive the motor, bringing about a speed decrease and eventual halt. The brake torque is then obtained as a function of the rotary kinetic energy.

The membership functions are classified as.

- Decrease large (0-20Nm),
- Decrease Small (20-40Nm),
- No Braking Torque (40-60Nm),
- Increase Small (60-80Nm),
- Increase Large (80-100Nm).

2.3 Design Rules base

Therefore, the fuzzy rules for training with an IF-THEN condition and a conclusion used for this design is shown in Table 1 and Figure 1 below.

2.4 Condition of Design

- The Regenerative Braking System is more efficient at a shorter distance and low Speed
- The Anti-Lock braking system is more efficient at a longer distance and high speed.

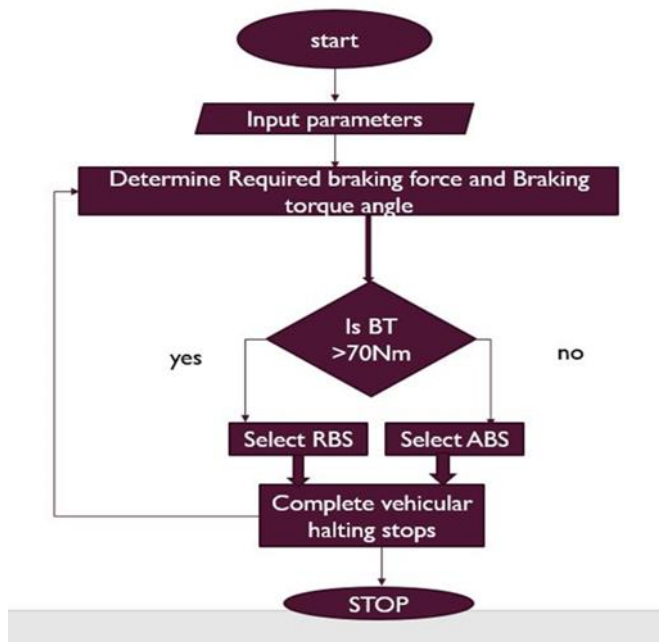


Figure 1. Flowchart Design of Fuzzy Logic Controller Model

Table 1. Fuzzy Rule based training

S/N	INPUT		OUTPUT
	Variable_ Distance	Variable_ Speed	Braking_ Torque
1	VERY CLOSE	TOO SLOW	ITS
2	VERY CLOSE	SLOW	ITS
3	VERY CLOSE	OPTIMUM	DTS
4	VERY CLOSE	FAST	ITG
5	VERY CLOSE	TOO FAST	ITG
6	CLOSE	TOO SLOW	ITS
7	CLOSE	SLOW	ITS
8	CLOSE	OPTIMUM	ITS
9	CLOSE	FAST	ITS
10	CLOSE	TOO FAST	ITG
11	OPTIMUM	TOO SLOW	DTG
12	OPTIMUM	SLOW	DTS
13	OPTIMUM	OPTIMUM	DTS
14	OPTIMUM	FAST	ITS
15	OPTIMUM	TOO FAST	ITS
16	FAR	TOO SLOW	DTS
17	FAR	SLOW	DTS
18	FAR	OPTIMUM	DTS
19	FAR	FAST	ITS
20	FAR	TOO FAST	ITS
21	VERY FAR	TOO SLOW	NBT
22	VERY FAR	SLOW	NBT
23	VERY FAR	OPTIMUM	NBT
24	VERY FAR	FAST	DTS
25	VERY FAR	TOO FAST	ITS

2.5 Simulink Design Model

The deceleration of an Electric Vehicle EV having the Anti-lock braking system only means that the kinetic energy already generated in the vehicle is being converted into thermal or heat energy through the action of friction. Research shows that in urban driving, about one third to half of the energy required for the operation of a vehicle is consumed in braking. The regenerative braking system on electric vehicles however converts this kinetic energy instead into electrical energy which can be stored in batteries for reuse in propelling the vehicle during the driving cycle. Therefore, improving fuel economy while reducing emissions that contribute to air pollution.

This paper aimed at implementing the less complex parallel regenerative system while still efficiently conserving and converting the energy

into a useful form for the Electric Vehicle. This seamless less complex integration of both ABS and RBS is to be achieved through a novel control strategy that considers the object to be collided with, its distance to the Electric Vehicle, and the choice of the driver on what braking system to employ to bring about the safe and fast halting of the vehicle while allowing for its manoeuvrability during the braking process. The control strategy involves affixing an ultrasonic sensor to the front of the Electric Vehicle to detect obstructions that could cause collisions, as well as installing a rotary-type potentiometer at the brake pedal to calculate the angular displacement of the pedal. The vehicles manufacturer would have a preset threshold for the brake pedal's angular displacement set for "normal braking conditions", such that when the angular displacement of the pedal is more than this threshold, emergency braking is needed and the braking system to be used is the Anti-lock braking system. This process is monitored and controlled by an Overall Control Unit whose block diagram and flowchart are given below;

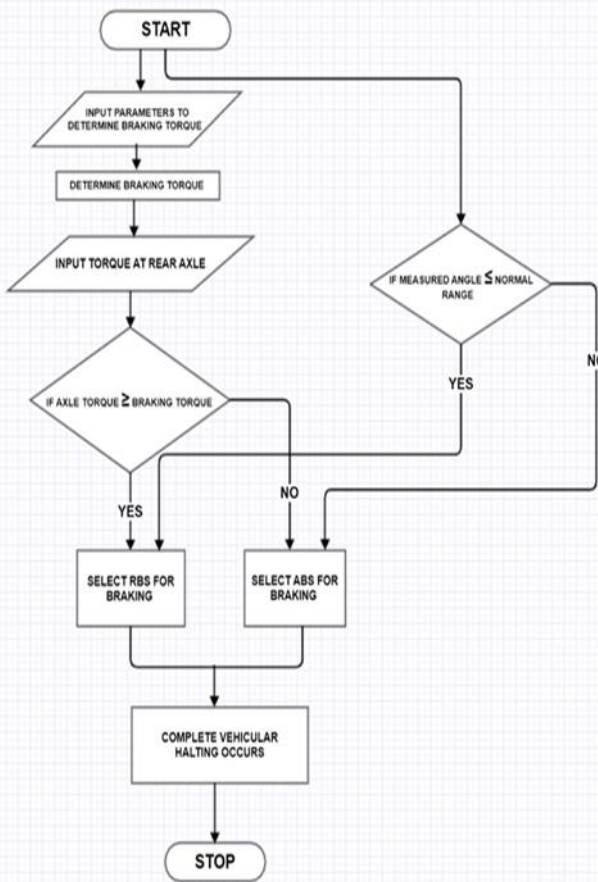


Figure 2. OCU Flowchart

2.6 Mathematical Modelling

The Anti-lock braking system is modelled mathematically by considering the third vehicle dynamics of the Electric Vehicle below.

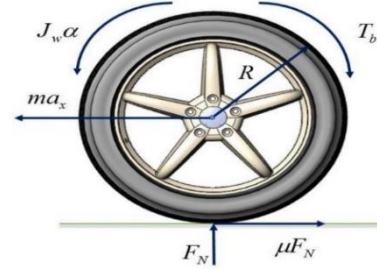


Figure 3. Third vehicle model

Applying Newton's second law of motion to the free body diagram showed above gives the dynamic model equations of the systems motion in linear (x) and vertical (y) directions respectively;

$$\therefore \dot{v}_x = -\mu \times \frac{F_N}{m} \quad (1)$$

$$\therefore \dot{v}_x = -\mu \times g \quad (2)$$

$$\therefore \dot{\omega} = \frac{\mu \times R \times F_N - T_b}{J_w} \quad (3)$$

$$\dot{\lambda} = \frac{-\mu \times F_N \left[\frac{(1-\lambda)}{m} + \frac{R^2}{J_w} \right] + \frac{R}{J_w \times v_x} \times T_b}{\lambda} \quad (4)$$

$$\mu(\lambda, v_x) = [C_1(1 - e^{-C_2\lambda}) - C_3\lambda]e^{-C_4v_x} \quad (5)$$

The regenerative braking torque of the regenerative braking system is offered by the electric motor during the deceleration processes, and is modelled below;

$$\lambda = \frac{(v_x - \omega) \times R}{v_x} \quad (6)$$

$$\dot{\omega} I_w = \mu F_N R + \frac{C_D A v_x^2 R}{21.15} - T_b \quad (7)$$

$$m_o \dot{v}_x = \frac{C_D A v_x^2}{21.15 v_x} + \mu F_N \quad (8)$$

According to the phase plane theory, combining (6), (7), and (8) gives the optimal braking torque that drives the wheel slip ratio to the ideal value fleetly below;

$$T_{bo} = \frac{\mu I_w}{r_n} \left[\left(\lambda - \frac{v_x - \omega R}{v_x} \right) + \left(\frac{m_o R^2}{I_w} + \frac{C_D A v_x^2 R^2}{21.15 \dot{v}_x I_w} + \frac{\omega R}{v_x} \right) \right] \quad (9)$$

The object distance to the sensor can be calculated below;

$$L = \frac{1}{2} \times T \times C \quad (10)$$

The braking torque needed to bring the Electric Vehicle to rest is calculated below;

$$F = ma \quad (11)$$

$$a = \frac{v^2}{2L} \quad (12)$$

$$T = F \times r \quad (13)$$

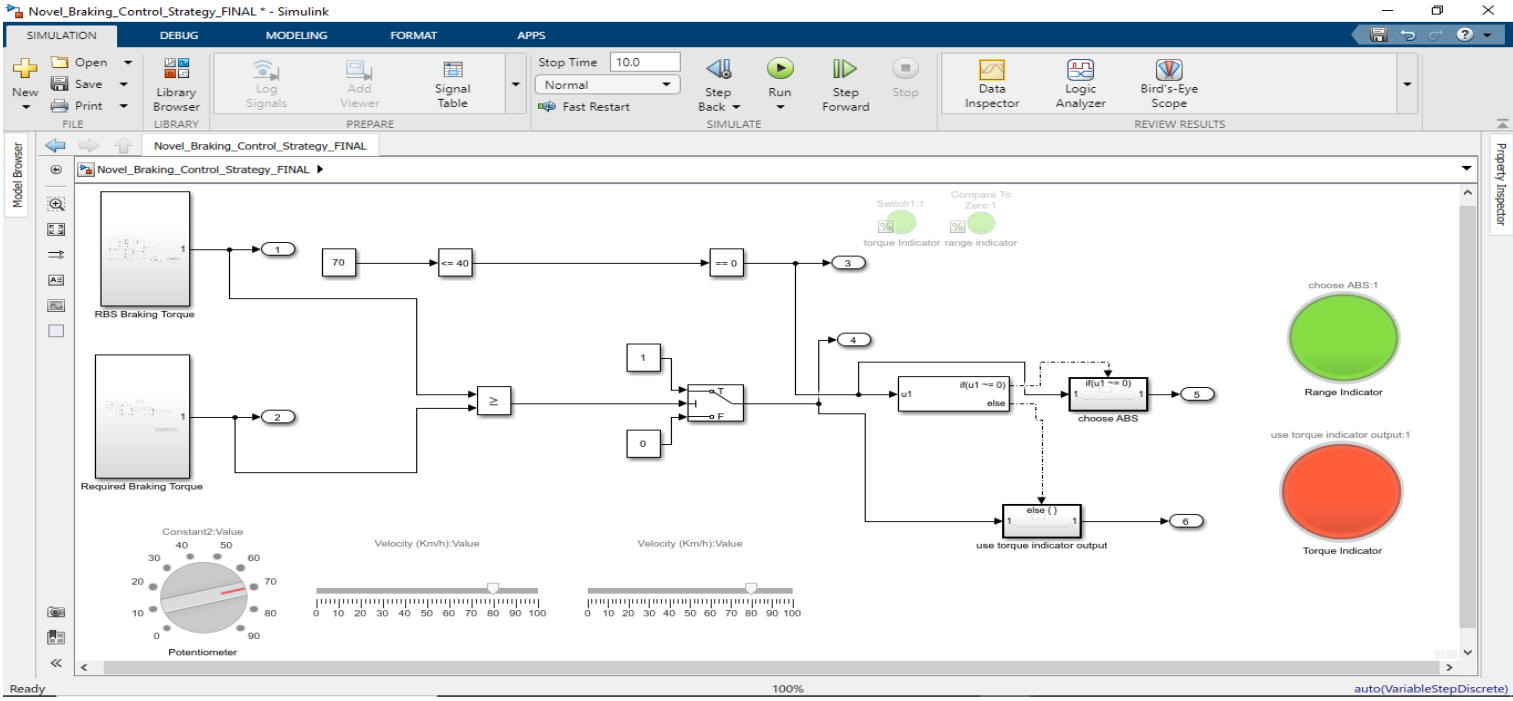


Figure 4. Simulation of Novel Control Strategy (OCU)

3 RESULTS

3.1 Defuzzification

To evaluate the Rule base and compute it for result, a scenario is taken as applicable to the design condition. In a scenario whereby the distance is close, and speed is slow, the defuzzification value is expected to have more than 70 Nm as the braking torque.

This hypothesis is tested in the rule viewer, having 2.01 meters as braking distance, that is the distance from object to vehicle, and a speed of 0.985m/s, the braking torque force exerted to halt the car was 74.7Nm.

Now this satisfies the condition that such a scenario, the Regenerative force is best used as the braking system to halt the car and in turn, such enormous energy force is converted to electric energy for the electric vehicle.

It is agreeable that this scenario is applicable to an electric vehicle in a traffic especially a heavy traffic, where the vehicle would have to be halted several times.

This gives an advantage to the electric vehicle and proves the essence of the existence of electric vehicles.

The plot from the rules is given below.

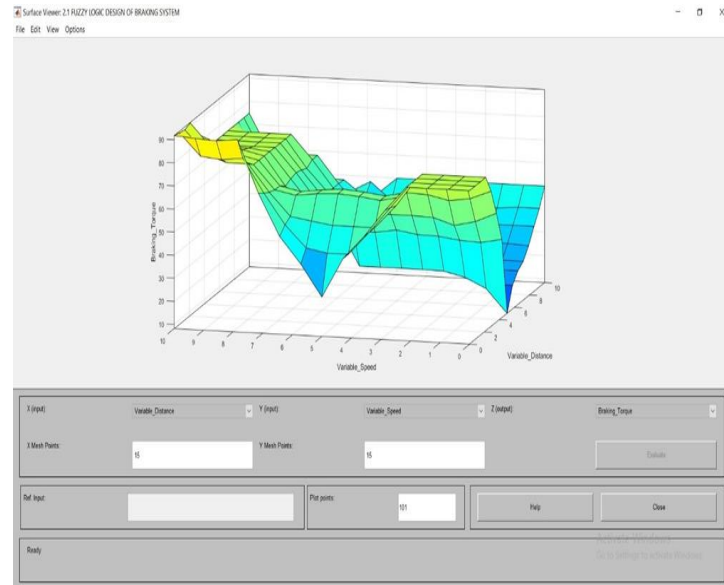


Figure 5. Flowchart

4 DISCUSSION

To verify the Simulink control strategy alongside its effectiveness in bringing about speed reduction to avoid collision, simulations and analysis in MATLAB Simulink software environment were conducted using parameters given in the table below.

Table 2: Table of Parameters

Parameter	Character	Value	Unit
Wheel Radius	R	0.25	m
Initial	V_x	0 – 100	km/h

Velocity			
Moment of Inertia	I_w	1.13	kgm^2
Vehicle Mass	M	350	kg
Acceleration due to gravity	G	9.81	m/s^2
Coefficient of Air Resistance	C_D	0.75	-
Frontal Area	A	4	m^2
Object Distance	L	100-200	m

Assuming a brake pedal angle range to be measured by the potentiometer $0 - 40^\circ$ as the operating range for the driver's intent to use the Regenerative Braking System, such that anything more than $(40^\circ \leq \theta \leq 90^\circ)$ signifies the driver's intent to use the Anti-lock Braking System.

Two sliders are provided to simulate the Electric Vehicle's speedometer, providing velocity values ranging from 0 – 100 km/h to the system.

The system's output is obtained by reading the light combinations of two Lamps labelled Range Indicator and Torque Indicator having either green or red colours. The information is represented in Table 3 below.

Table 3: Table showing meaning of Lamp colours

Range Indicator	Torque Indicator	Braking System to be Used
Red	Green	Regenerative Braking System
Green	Red	Anti-lock Braking System
Red	Red	Anti-lock Braking System

The parameters are inserted in the simulations such that the ultrasonic sensor output (object distance) is varied from 50m to 200m for different surface types to obtain Braking torque information, as well as verify the performance, accuracy, and effectiveness of the system. The results are presented in the table below;

Table 4: MATLAB SIMULINK Table of Simulation Results

Object Distance (m)	Surface Type	Velocity (km/h)	Pedal Position ($^\circ$)	Required Braking Torque (Nm)	RBS Braking Torque (Nm)	Lamp Colour	Decision (Braking System)
50	Dry Asphalt	40	25	108.20	117.22	R – Green T – Red	RBS

Table 4 above shows the simulations for the Electric Vehicle moving at an assumed velocity of 40km/h, driving on dry asphalt with its brake pedal being pressed with an angle of 25° so as to bring the Electric Vehicle to rest within 50m, also highlighting the required braking torque to bring the Electric Vehicle to rest, the braking torque to be provided by the RBS, and the Overall decision of the system in terms of Lamp colours.

Table 5: MATLAB SIMULINK Table of Simulation Results

Object Distance (m)	Surface Type	Velocity (km/h)	Pedal Position ($^\circ$)	Required Braking Torque (Nm)	RBS Braking Torque (Nm)	Lamp Colour	Decision (Braking System)
200	Wet Asphalt	67	45	75.89	91.13	R – Green T – Red	ABS

Table 5 above shows the simulations for the Electric Vehicle moving at an assumed velocity of 67km/h, driving on wet asphalt with its brake pedal being pressed with an angle of 45° to bring the Electric Vehicle to rest within 200m, also highlighting the required braking torque to bring the Electric Vehicle to rest, the braking torque to be provided by the RBS, and the Overall decision of the system in terms of Lamp colors.

From the table above it can be seen that the system correctly determines what braking system to use based on the current conditions such that the determination and selection process follows the stipulated operation, it is also seen that for various values of road type, velocity, and object distance the RBS was able to provide more than the required braking torque to bring the Electric Vehicle to rest, indicating that not only is the RBS capable of recharging the Electric Vehicles' batteries, it is also very efficient in braking the vehicle before it reaches or collides with the upcoming obstacle.

5 CONCLUSION

The braking system proposed in this paper is a synergistic combination of the widely used Anti-lock braking system, which is based on the principles of reducing vehicle skidding, and the semi-recent Regenerative braking system, which has gained popularity since being implemented in electric vehicles. Integrating both braking systems became the focus of this paper, which was accomplished using different control strategies that considers the intentions of the driver as well a variety of environmental factors to determine the most efficient way to bring the vehicle down to required speed reduction. In the paper, an electric vehicle is used to properly demonstrate the conservative energy conversion (from kinetic energy to electrical energy) by the Regenerative braking system, as the terrains through which electric vehicles travel require only modest vehicular speeds. As can be seen from the report, both the speed of the vehicle and the frequency with which the RBS is used directly influence how much electrical energy is generated and fed into the batteries. Since electric vehicles are normally driven at modest speeds and have a speed gauge ranging from 0 to 100 km/h, they do not produce enough current to overcharge the batteries. This is only assumed for the design of this paper. This is due to the environments in which they operate and the functions they perform. As a result, the extra kinetic (Rotary) energy that would have been turned into electrical energy and squandered because of the high speed of automobiles is not even acquired in the first place.

Future publications on automotive braking systems should take into consideration pneumatic-powered antilock braking systems, since substantial work and study has already been done on hydraulic-powered antilock braking systems. Other persons interested in participating in similar articles should keep in mind that the resilience of a system's design is not a significant predictor of the system's performance, but rather the efficacy of the system.

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HIGHLY EFFICIENT TENG SYSTEM DECORATED WITH BIOMASS MATERIAL INTO THE SILICONE

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Abstract

The idea of generating electrical energy from mechanical energy is of great importance due to the abundance and constant waste of this energy in daily life. Triboelectric Nanogenerators (TENG) have recently emerged as a highly efficient, cost-effective, and simple technology with the potential to solve this problem. Biomass-derived materials offer promising opportunities to improve the performance and versatility of triboelectric devices due to their abundance, renewability, and biocompatibility. In this study, we have attempted to increase the electrical generation capacity of a TENG with vertical contact separation mode by doping biomass-derived materials into silicone. According to our results, the maximum voltage and power results are measured as 550 V and 184 mW, respectively.

Keywords: TENG, Energy, Biomass, Carbon

1 INTRODUCTION

Triboelectric nanogenerators (TENG) are a recently discovered energy-harvesting technology that converts various types of mechanical energy into electrical energy by combining contact electrification and electrostatic induction [1]. Electricity generation in TENGs occurs when two dielectric layers of different polarities come into contact with each other and are electrostatically charged. The outer parts of these two layers are covered with a conductive layer and these conductive layers are connected to each other with a conductive wire to ensure electron flow [2].

Apart from portable devices and sensor technologies, TENGs have applications in many fields including human gestures, wind energy, wave energy, internet of things, and other ambient motions [3,5,6,7].

TENGs have different modes such as vertical contact separation mode, lateral sliding mode, single electrode mode, and freestanding triboelectric layer mode [8,9,10,11]. Among these modes, the vertical contact separation method is distinguished from other modes due to its high efficiency and durability.

Many types of materials have been used in this technology to date. Thanks to the progress in material science, the number of materials to be

used is increasing day by day. These materials are listed in a table called the triboelectric series according to their tendency to exchange electrons. In this table, tribo-positivity increases as you go up and tribo-negativity increases as you go down. To achieve the highest efficiency in TENGs, materials should be chosen far apart from each other. In the extant literature, polyvinylidene fluoride (PVDF)[12], fluorinated ethylene propylene (FEP) [13], polyvinyl chloride (PVC)[14], polyimide (PI) [15], polydimethylsiloxane (PDMS) [16] and polytetrafluoroethylene (PTFE) [17] have been employed as tribo-negative materials, whereas polyamide (PA) [18], natural polymers [19] and metal [20] have been utilized as tribo-positive materials.

This study examined the impact of varying weight ratios of torrefied pine sawdust on the performance of TENG systems. In the course of the experiment, a TENG system with vertical contact separation mode was utilized. The maximum peak output voltage of the silicon/copper TENG system doped with torrefied pine sawdust was obtained at a doping ratio of 7.5 wt%. At this doping ratio, the output voltage of the silicon/copper TENG system was found to be 2.75 times that of the pure silicon/copper TENG system.

2. Material and Method

2.1 Fabrication of TENG

The project team utilized a 3D printer to produce the layers utilized as support in the TENG system from a Poly Lactic Acid (PLA) polymer. The dimensions of the layers were determined to be 100 x 100 x 5 mm. Holes were drilled from the center of the layer's wall thickness to the midpoint of the surface. The cables were then inserted into the holes and fixed to the contact point of the conductive electrodes with solder. A pneumatic system was employed to move the layers. Moreover, the frequency can be modified through the use of a sensor system.

The dielectric layers intended for use in the TENG system were produced via the doctor blade method. In this method, different ratios of torrefied pine sawdust (2.5%, 5%, 7.5%, and 10% by weight) were added to 15 g of silicone, and the resulting mixtures were mixed until a homogeneous solution was obtained. Subsequently, the mixture was coated as a thin layer on an aluminium foil substrate utilizing a 100 mm × 100 mm × 5 mm mold with a doctor blade. Subsequently, the silicone-based samples were subjected to a curing and drying process, which was conducted overnight.

Figure 1 shows the output voltages of TENGs fabricated with torrefied pine sawdust doped silicon and copper materials as dielectric layers under the load resistance of a measuring device with an internal resistance of 10 MΩ. The peak output voltages of the TENG systems fabricated with pure silicon, 2.5 wt%, 5 wt%, 7.5 wt%, and 10 wt% torrefied pine sawdust doped silicon were measured as 200 V, 400 V, 480 V, 550 V, and 450 V, respectively. As illustrated in the figure, the highest output performance was achieved with a doping rate of 7.5%. This value is equivalent to 2.75 times that of pure silicon.

Conclusion

In conclusion, to enhance the performance of the TENG system constructed with silicon and copper, we introduced different weight rates of torrefied pine sawdust into the tribo-negative material silicon. The results demonstrated that the highest output performance was achieved at a doping ratio of 7.5 wt%. As a result of this doping process, an increase in output performance of the TENG system by a factor of 1.75 was observed in comparison to the performance of a system comprising pure silicon.

ACKNOWLEDGEMENTS

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layer on an aluminium foil substrate utilizing a 100 mm × 100 mm × 5 mm mold with a doctor blade. Subsequently, the silicone-based samples were subjected to a curing and drying process, which was conducted overnight.

3. Result and Discussion

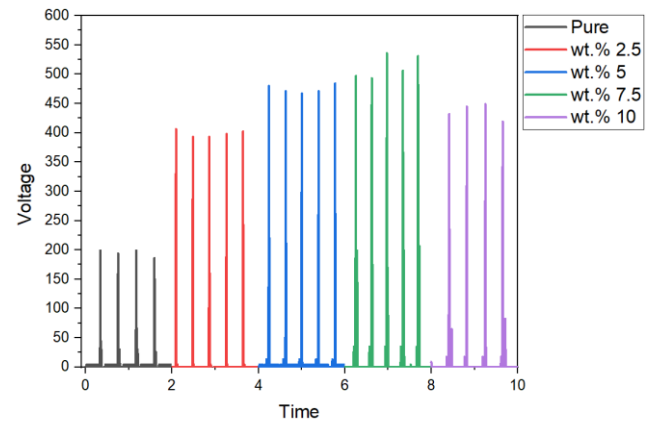


Figure 1. The output voltage of the TENG models under a load resistance of 10 MΩ

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IMPLEMENTATION OF A REAL-TIME POWERTRAIN TEST BENCH FOR FUEL CELL ELECTRIC VEHICLES

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Abstract

Test systems and processes are vital for fuel cell electric vehicles (FCEVs). Risks arising from the explosive nature of the hydrogen element, efficiency problems, applicability to vehicles, functional issues, etc. should be tested in FCEV design before or during production. This study aims to realize a real-time test system for all electrical tests and performance analyses of the powertrain system of FCEVs, which are among today's new and trending technologies. In this system, which is realized in real-time with LabVIEW, monitoring, control, and testing of the FCEV powertrain system consisting of fuel cell, battery, motor driver and BLDC motor can be performed. The system's performance under different loads and electrical operating conditions can be monitored and reported. We have developed an effective test bench for studying and conducting tests on FCEVs. This software can examine the operating logic of FCEVs, test processes, the implemented test system, the technologies used, and the performance of electrical and electronic equipment.

Keywords: FCEV, Hydrogen Safety, Fuel Cell, Powertrain, Energy Management

1 INTRODUCTION

In today's world, increasing environmental concerns and limited reserves of fossil fuels are increasing the interest in renewable and sustainable energy sources day by day. In this context, hydrogen energy stands out as a clean and efficient energy source of the future. Hydrogen can play an important role in reducing the carbon footprint because it produces only water vapor as a result of combustion and does not release harmful emissions into the environment [1].

The use of hydrogen in energy production has the potential to create a major revolution, especially in the automotive sector. The development of hydrogen vehicle technology offers significant opportunities in terms of both environmental sustainability and energy security. In particular, it highlights electric vehicles (FCEVs) using fuel cells due to their significant reduction in vehicle weight and high power density [2].

Testing and evaluation processes are critical for the widespread and safe integration of FCEV technology. Various tests are conducted to evaluate the performance, safety, and durability of hydrogen vehicles. These tests cover a wide range of areas, from the efficiency of fuel cells to the safety of hydrogen storage systems.

In a study on the subject [3], in-depth information is provided on the design, working principles and use in vehicles of hydrogen fuel cells. The advantages, disadvantages, and application areas of hydrogen fuel cells are examined. It examines the emission characteristics of hydrogen-fueled internal combustion engines and discusses strategies to reduce NOx emissions in particular.

A report by the US Department of Energy [4] provides information on the development and dissemination of hydrogen fueling infrastructure. Current data on the future of the hydrogen economy and current projects are presented. In a study on the basic principles of fuel cells [5], comprehensive research is conducted on their types and working mechanisms. The theoretical basis and practical applications of hydrogen fuel cells are discussed.

There are also studies focusing on Proton Exchange Membrane (PEM) fuel cells, providing theoretical information and practical applications [6-8]. In these studies, a detailed review of fuel cell technology is made.

A paper [9], that provides a comprehensive assessment of the future of the hydrogen economy, addresses hydrogen production, storage, and use in detail.

One of the standards investigated [10] defines bubble emission techniques used for hydrogen leakage tests. It provides information about leakage tests, which are critical for the safety of hydrogen vehicles.

This study examines FCEV types and test processes. Focusing specifically on the energy management system of a working fuel cell vehicle, a real-time test system was developed with LabVIEW. The purpose of this application is to collect data from the relevant sections of the hydrogen vehicle, control the energy management, and operate the powertrain system in accordance with the desired criteria.

2 ELECTRICAL TESTS FOR FCEVS

Hydrogen vehicles are vehicles that are powered by electric motors and generate electricity using hydrogen fuel. Various test processes are applied to ensure the safety, performance, and efficiency of the electrical components of these vehicles. Electrical test processes cover the electrical circuits from the vehicle's battery systems to the electric motors and are generally applied at every stage of the production process. Electrical test procedures for hydrogen vehicles are given below.

Battery Capacity Test: It is important to accurately determine the capacity of batteries used in hydrogen vehicles. This test is performed to verify the nominal capacity of the battery and to ensure the expected performance. The battery is discharged to a certain current to measure its capacity and check its compliance with the specifications [11].

Charge/Discharge Tests: Charge/discharge tests are performed to simulate the charge and discharge cycles of battery packs. These tests are important in determining battery performance and life. Batteries are subjected to a specific charge/discharge profile to examine their behavior and evaluate the continuity of their performance [12].

Electric Motor Efficiency Tests: The efficiency, energy consumption, and performance of electric motors used in hydrogen vehicles are important. Therefore, efficiency tests are performed by applying various loads to electric motors. The power loss, temperature increase, and other performance metrics of the motor are measured and evaluated according to the specified standards [13].

Power Electronics Tests: Power electronic components are used to control and direct

electric current in hydrogen vehicles. Proper operation of these components is critical to the safety and performance of the vehicle. Power electronic tests are performed to verify the performance of inverters, converters, and other electronic components [14].

Electrical Insulation Tests: Electrical insulation tests are performed to verify that the insulation between different electrical circuits of the vehicle is intact. In these tests, the insulation resistance is measured and the insulation level is evaluated according to certain standards. Electrical insulation tests help reduce the risk of short circuits in the vehicle [13].

The advantages of electrical testing procedures for hydrogen vehicles are given below:

- **Safety:** Electrical tests ensure the safety of the vehicle's electrical systems and help prevent electrical failures.
- **Performance:** Correctly performed tests help optimize the vehicle's electric motor and battery system performance.
- **Longevity:** Electrical tests ensure that the vehicle's electrical components have a long life and that failures are detected and repaired in advance.

Electrical testing processes in hydrogen vehicles are critical to the safety, performance, and durability of the vehicle. Proper testing ensures that hydrogen vehicles operate safely and effectively.

3 DEVELOPED TEST BENCH

In the study, the LabVIEW MyRIO data acquisition card was used to control the fuel cell and battery-powered electric motor system and to acquire electrical data. The single-line diagram of the developed system is shown in Figure 1.

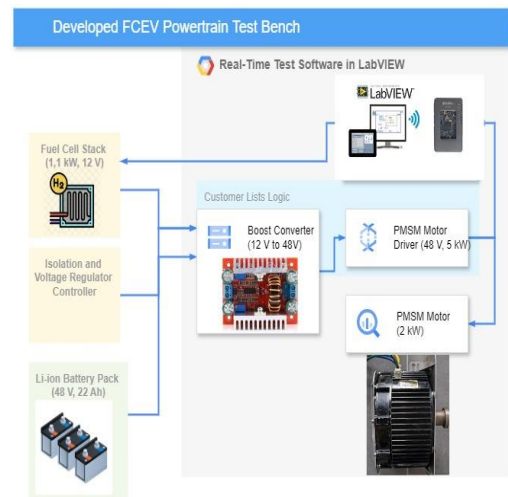


Figure 1. Developed test bench powertrain

The device's real-time data processing capabilities and wide I/O support ensured that the system operated with high performance and reliability. The fuel cell and battery features shown in Figure 1 are given below.

- **Fuel Cell:** The system uses a fuel cell that can produce 1.1 kW of power. Fuel cells convert the chemical energy of hydrogen into electrical energy.
- **Boost Converter:** The fuel cell operates at 12V voltage and this energy is increased to 96V using a boost converter.
- **Li-ion Battery Pack:** The system uses a battery with a voltage of 96V and a capacity of 22Ah. This battery performs energy storage and power balancing tasks. The battery meets the energy requirements of the system and provides support for sudden energy needs.
- **PMSM Motor:** The 48 V, 5 kW, 3-phase PMSM motor shown in Figure 2 was used in the test system.

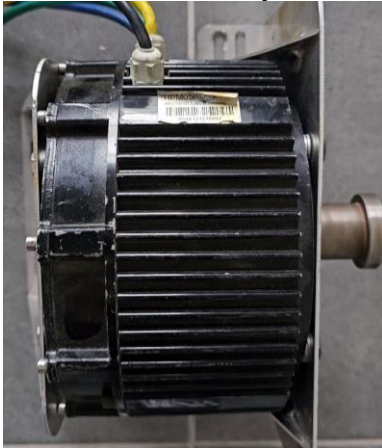


Figure 2. PMSM Motor used in the test system

The Boost Converter is used to increase the 12V voltage from the fuel cell to 96V. This converter makes the low-voltage energy produced by the fuel cell compatible with the battery voltage, thus providing the necessary energy to the motor drivers and motors. Figure 3 shows the system interface for the case where the fuel cell is used as a power source and the PMSM Motor is driven.

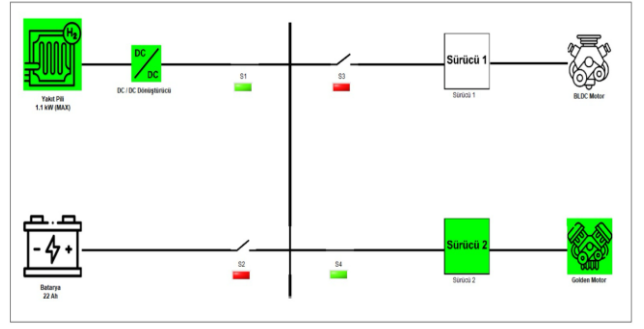


Figure 3. Fuel Cell and PMSM System interface in the motor operating state

Figure 4 shows the system interface for the situation where the fuel cell and battery are used as power sources and the PMSM Motor is driven.

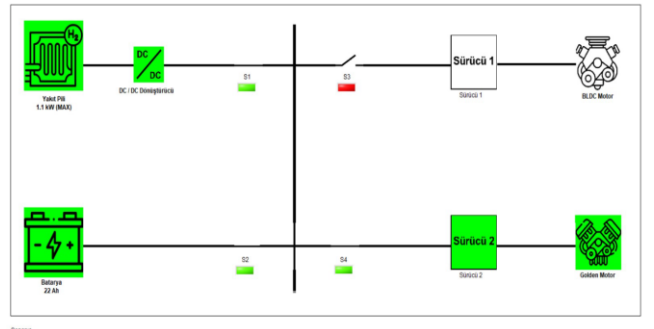


Figure 4. Interface with Fuel Cell, Battery, and PMSM Engine in working condition

4 RESULTS and CONCLUSION

The results obtained from the study are given below.

- Safety and Efficiency:** The developed test system evaluated all the parameters required to ensure the safe and efficient operation of hydrogen vehicles.
- Energy Management:** Tests conducted on the energy management systems of hydrogen vehicles have enabled the fuel cells to be evaluated with the energy management system. This has enabled the vehicle to consume energy efficiently and exhibit maximum performance.
- Software and Algorithm Developments:** The LabVIEW-based software and algorithms used ensured that the test system was flexible and user-friendly. The ability to collect and

analyze real-time data increased the accuracy and reliability of the tests.

The technologies used in this study provided efficient and reliable operation of the electric motor system powered by a combination of fuel cells and batteries. The integration of LabVIEW and myRIO increased the control and data processing capabilities of the system and provided a user-friendly interface. Fuel cell and battery technologies played a critical role in energy management and storage, while the boost converter optimized energy conversion. The combination of these technologies contributed significantly to the successful implementation of the study.

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A STUDY ON THE DETERMINATION OF STORAGE PERFORMANCE IN BATTERIES WITH DIVERSE CHARACTERISTICS OF ENERGY OBTAINED FROM SOLAR/WIND HYBRID RENEWABLE ENERGY SYSTEMS

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Abstract

The presented paper aims to determine the performance of energy storage with batteries for solar/wind hybrid renewable energy systems. In line with this aim, a hybrid energy system combines two wind turbines (WT) with different nominal powers and two different types of solar panels (PV). There are four distinct scenarios (PV1+WT1, PV1+WT2, PV2+WT1, PV2+WT2). In addition, the storage capacity of distinct battery types (Sodium-ion battery, Lead-acid battery, and Lithium-ion battery) in the hybrid system with different potentials was investigated. Since the potential of wind and solar energy varies according to meteorological data and geographical location, a case study is conducted to implement the suggested system in Kayseri province. Firstly, the energy production and levelized cost of electricity were calculated and compared. And then the energy storage capacities were calculated for different types of batteries. The results reveal the impact of the integration of battery types with different energy storage capacities on system performance as well as the determination of the highest capacity and lowest cost energy storage.

Keywords: Energy Storage, Solar, Wind, Renewable Energy, Hybrid System

ACTIVATED CARBON PRODUCTION FROM CHESTNUT SHELLS FOR ENERGY STORAGE AND CONVERSION APPLICATIONS

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Abstract

Today, the limited availability of energy resources has increased the demand for renewable and sustainable energy sources. One of the most effective technologies in clean and sustainable sources is hydrogen production based on water electrolysis. Due to the high cost and scarcity of Pt group metals, which have low overpotentials to provide large cathodic current densities for the most efficient hydrogen evolution reaction (HER), studies on carbon-based alternatives from naturally abundant elements have increased as low-cost alternatives to these electrocatalysts. Biocarbon-based materials offer a good alternative to commercial carbon materials with their high surface areas, porous structures, low costs, and environmentally friendly properties. Transition metal nanoparticles as the catalyst's core and nonmetal doping into the carbon skeleton, in particular, can increase the catalytic activity of carbon-based catalysts by varying the electronic state density of carbon and creating new HER active sites. In this paper, chestnut shells, which are abundantly available as a biomass source, have high carbon content and low cost, and the potential of activated carbon produced from these shells for energy applications has been investigated. Within the scope of the study, activated carbon production from chestnut shells was carried out by chemical activation method and the obtained sample was comprehensively characterized by physicochemical analyses such as RAMAN, XRD, BET, FE-SEM EDX, FT-IR, and electrochemical tests such as CV and LSV. This study has successfully elucidated the structural properties and crystal structure of the CS-AC/Cu sample through rigorous experimentation and analysis.

Keywords: Activated carbon, Chestnut shell, Biomass, Chemical activation, Electrochemical analysis.

DEVELOPMENT OF AN IOT-BASED PREDICTIVE MAINTENANCE SYSTEM FOR PV POWER PLANTS CONSIDERING DUST CUMULATIVE INDEX

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Abstract

Photovoltaic (PV) power plants have an important place among sustainable energy sources. However, the efficiency of these plants can be negatively affected by various environmental factors. The most important of these factors is dust. Dust accumulation covers the surface of solar modules, reducing light transmittance and thus causing significant losses in energy production. In this study, an IoT-based system for dust estimation was developed to minimize the effects of dust in PV power plants and increase energy efficiency. In the study, parameters such as module temperature, current, power, radiation, ambient temperature, and ambient humidity were measured in real-time and data was collected from various sensors. With the help of this data, the dust cumulative index (DCI) of the system was calculated. The obtained DCI parameter was used to determine the degree of dust on the surface of solar modules and the frequency of cleaning. The developed system also includes a low-cost solar power plant remote monitoring system. This system offers significant advantages in both economic and environmental terms by allowing users to remotely monitor the performance and maintenance requirements of the modules and also contributes to the development of smart maintenance strategies in solar power plants.

Keywords: PV Power Plant, Energy Efficiency, Dust Cumulative Index, IoT, Predictive Maintenance

1 INTRODUCTION

One of the factors affecting the efficiency of solar power plants is surface dust accumulation. Systems that measure and classify the dust accumulation on PV modules can significantly reduce maintenance costs and increase efficiency [1]

A study [2] that allows the development of more efficient cleaning strategies for concentrated solar power plants (CSP), was aimed to minimize production losses due to pollution. It was found that the average pollution rate for horizontal fixed mirrors was 0.12 pp/d in low dust seasons and 0.22 pp/d in high seasons. Two-year meteorological measurements were extended to ten years using autoregressive time series models, and thus the pollution rates of the heliostat field were estimated.

In another study [3], the effectiveness of the electrostatic cleaning method was evaluated to reduce dust losses in photovoltaic (PV) modules. A folding grid mechanism equipped with copper conductors was used in the study. Three main

variables were investigated: voltage, dust density, and cleaning time. The findings show that voltage is the most important factor determining the cleaning performance. It was observed that the cleaning efficiency increased as the voltage increased. In the cleaning operations performed for 3 minutes at 30 g/m² dust density, 2.5 kV, 3 kV, and 3.5 kV voltages provided 59.52%, 71.39%, and 83.36% cleaning efficiency, respectively.

In a similar study [4], the effect of dust accumulation on the efficiency of photovoltaic (PV) modules was investigated experimentally. In the study, it was observed that dust accumulated on the module surface reduced the amount of radiation reaching the cells and caused losses in the energy conversion rate. In the experimental study, the energy generation values of a clean module and modules with 5-day, 1-month, and 6-month dust accumulation on their surfaces, respectively, were compared. The results showed that dust accumulation seriously reduced the module efficiency; 5-day dusting caused 5.26%,

1-month dusting caused 28.49% and 6-month dusting caused 78.38% energy production loss.

A block model was proposed to simulate the dusting effect in the Matlab Simulink environment [5]. The results show that the proposed model provides 4.34% more accurate predictions than previous models.

IoT-based studies have also been conducted with dust estimation [6-8]. In these studies, the design of a low-cost, expandable, and easy-to-use device that measures and records environmental parameters for solar energy systems is discussed.

In this study, an IoT-based system for dust estimation has been developed to minimize the effects of dust in solar energy plants and to increase energy efficiency. In the study, parameters such as module temperature, current, power, radiation, ambient temperature, and ambient humidity were measured in real-time and data was collected from various sensors. With the help of these data, the dust cumulative index (DCI) of the system was calculated. The obtained DCI parameter was used to determine the degree of dust on the surface of solar modules and the frequency of cleaning.

2 METHODOLOGY

Another method can be used instead of a pyranometer to measure solar radiation in a region. This alternative method is based on measuring the temperature (TP) and short-circuit current (ISC) values of a photovoltaic module. The short-circuit current of a photovoltaic module is directly proportional to the amount of radiation to which the module is exposed and the temperature of the module, and this relationship is expressed by Equation (1) below. With this equation, the amount of radiation can be calculated directly without using a radiation meter [9].

$$I_{sc} = \frac{I_{SCREF} \times G}{G_{REF}} \times (1 + \alpha(T_p - T_{MREF})) \quad (1)$$

In this case, T_{MREF} represents the reference temperature of the photovoltaic module (25°C), while G_{REF} indicates the reference radiation amount falling on the module (1000 W/m²). α represents the temperature coefficient of the short-circuit current found in the technical specifications of the module, and I_{SCREF} represents the short-circuit current of the module under reference conditions. As a result of the arrangements made using Equation (1), Equation (2) was formulated, which expresses the radiation amount falling on the photovoltaic module with the short-circuit

current and temperature values of the module. This new equation allows calculation using the current and temperature values of the module to determine the radiation amount. [10].

$$G = \frac{I_{sc} \times G_{REF}}{I_{SCREF} (1 + \alpha(T_p - T_{REF}))} \quad (2)$$

To calculate the amount of radiation falling on the photovoltaic module using Equation (2), the temperature and short-circuit current of the module must be measured. In order to perform this measurement, a photovoltaic module based on single-crystal silicon technology with a power of 200 W was preferred. As a result of measuring the environmental parameters, the amount of energy that the photovoltaic module used will produce was determined. The mathematical model, which can be used from the information provided in the catalog of the module for energy calculation and is preferred due to the ease of the calculation process, is specified in Equation (3). In this approach, it is mandatory to measure the amount of radiation and temperature to which the module is exposed to determine the maximum energy production capacity of the photovoltaic module.

$$P_M = \frac{P_{MREF} \times G}{G_{REF}} (1 + \gamma(T_p - T_{REF})) \quad (3)$$

In this case, the symbol γ represents the maximum output power temperature coefficient of 0.041 specified in the technical specifications of the photovoltaic module, while P_{MREF} represents the maximum output power of 200 W obtained under the reference conditions specified in the datasheet of the module.

$$DCI[\%] = \frac{P_T}{P_M} \quad (4)$$

DCI is dust cumulative index; P_T output power of PV module; P_M output power of PV module in clean condition.

3 DEVELOPED IoT-based SYSTEM

This study employs an experimental approach to enhance the efficiency of solar module systems and to better understand maintenance requirements. The research involves comprehensive data collection through various sensors connected to the solar modules, real-time monitoring, and analysis of this data.

During this process, critical parameters such as the current passing through the solar module, module temperature, ambient temperature, and humidity are measured. The raw data collected is then enhanced and expanded through various

processing techniques. Figure 1 shows the general structure of the system.

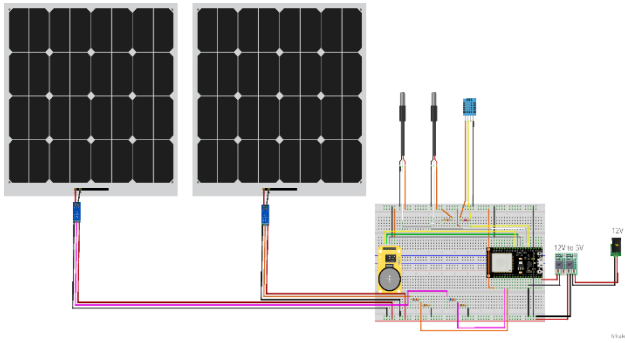


Figure 1. The general structure of the system

The basic components of the system consist of two solar modules, two ACS712 sensors for current measurement, two DS18B20 sensors for temperature measurement, one DHT11 sensor for ambient temperature and humidity measurement, one DS3231 real-time clock module for time control, and one ESP32 WROOM-32U microcontroller module. In addition, a voltage regulator circuit that converts 12 volts to 5 volts is also available. In this study, the dust rate index was obtained by dividing the output power values of a regularly cleaned PV module by dusted PV module accumulation. Figure 2 shows the experimental system.

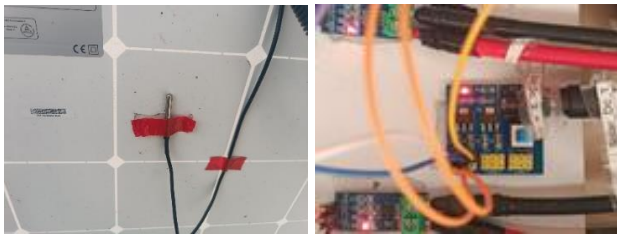


Figure 2. Experimental setup

3.1. Development of data recorder with ESP32 WROOM-32U

The ESP32 WROOM-32U, developed by Espressif Systems, is a high-performance microcontroller unit. This advanced microcontroller stands out with its dual-core processor and low power consumption. Supporting wireless communication technologies such as Wi-Fi and Bluetooth, the ESP32 is an ideal choice for IoT (Internet of Things) projects. Additionally, it caters to a wide range of applications with features such as expandable memory options, various GPIO (General Purpose Input/Output) pins, and analog signal processing

capabilities. Figure 3 shows the data recorder block diagram.

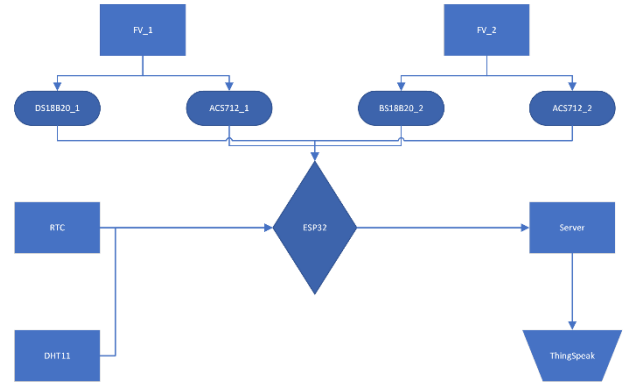


Figure 3. Data Recorder Block Diagram

The fundamental components of the system include two solar modules, two ACS712 sensors for current measurement, two DS18B20 sensors for temperature measurement, one DHT11 sensor for ambient temperature and humidity measurement, a DS3231 real-time clock module for time control, and an ESP32 WROOM-32U microcontroller module. Additionally, a voltage regulator circuit is present to convert 12V to 5V. This system is designed to monitor the energy produced by the solar modules and to measure environmental conditions. The 12V coming from an external power source is converted to 5V through the voltage regulator, which is necessary for the operation of the ESP32 microcontroller module and other sensors.

3.2. Instant data viewing and tracking with ThingSpeak

ThingSpeak is an analytics and visualization platform designed for IoT (Internet of Things) applications. This platform is used to collect, store, analyze, and visualize data from various sensors and devices. Users can manage real-time data streams and perform various calculations on this data, such as calculating averages, minimums, and maximums, or identifying complex relationships and trends using this data. ThingSpeak also supports powerful mathematical analysis tools like MATLAB, allowing users to perform in-depth data analysis and advanced data processing operations.

4 RESULTS and CONCLUSION

The temperatures of the solar modules are measured using DS18B20 digital temperature sensors. These sensors are known for their high accuracy in temperature measurement, and due to these features, it is possible to record the temperature changes of the modules with

precision. The measured temperatures of the two different modules, 'Panel Temperature_1' and 'Panel Temperature_2,' are included in the dataset. These temperatures are a critical parameter that can directly affect the efficiency of the modules.

To assess the impact of weather conditions on the performance of solar modules, ambient temperature and humidity are also measured. These data are obtained using a DHT11 sensor. This sensor is capable of measuring both temperature and humidity and stands out for its economical and user-friendly nature. The 'Ambient Temperature' and 'Ambient Humidity' data are used to analyze the effects of environmental conditions on module performance. Figure 4 shows the variation of output power from clean and polluted PV modules.

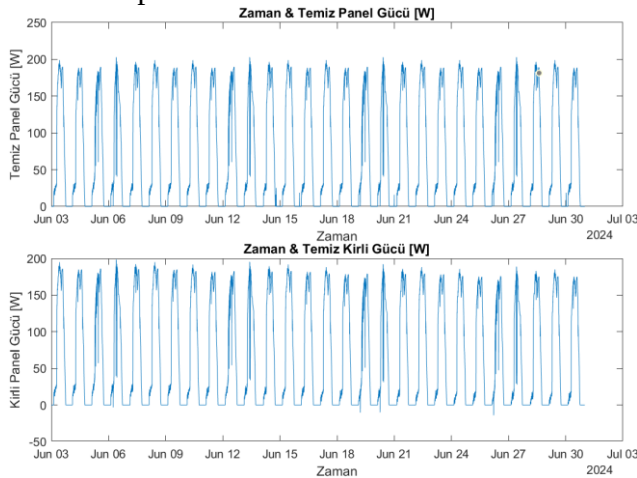


Figure 4. Variation of output power from clean and polluted PV modules

Finally, the current values from the solar modules are measured using ACS712 current sensors. These sensors use the magnetic field principle to accurately detect current values and collect data through two different channels, 'Panel Current_1' and 'Panel Current_2.' This current data directly indicates the electrical production capacity of the modules and is of great importance in instantly monitoring system performance.

The dataset created with the data obtained from these sensors is a valuable resource for detailed monitoring of the performance of solar module systems. Data analysis can be used in various applications such as increasing system efficiency, determining maintenance needs, and predicting potential failures in advance. The Dust Cumulative Index (DCI) change obtained from the system is shown in Figure 5.

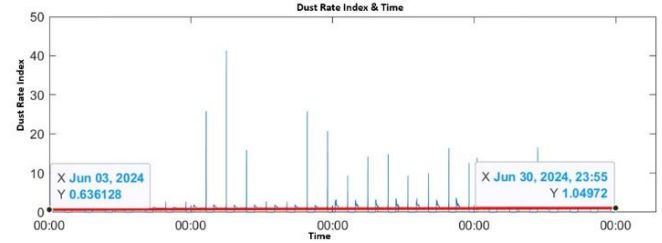


Figure 5. Dust Cumulative Index (DCI)

The parameters that can be calculated through data analysis and included in the monitoring system are the maximum output power, irradiance, and dust rate index. The DCI is an important tool for determining the maintenance periods of the modules and increasing their efficiency. The developed system allows users to remotely monitor the performance and maintenance requirements of modules, providing significant advantages both economically and environmentally, and contributing to the development of smart maintenance strategies in solar power plants.

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EFFECT OF VARIOUS HYDROGEN INJECTION ANGLES ON ENGINE PERFORMANCE AND EMISSIONS

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Abstract

There are a number of advantages that hydrogen offers over traditional fossil fuels when it comes to engine fuel. In comparison to traditional fuels, hydrogen offers clean combustion, low ignition energy, a wide flammability range, a greater flame speed, minimum diffusion risk, and a high energy density. This study examines the impact of different hydrogen injection angles on the emissions and performance of an engine. The computational fluid dynamics method is applied to examine hydrogen injection performance in diesel engines with commercial software. Performance parameters, combustion pressure, temperature inside the combustion chamber and heat release rate, together with the emissions parameters CO and NO_x are investigated. The highest combustion pressure is determined at 30° and 45° spray angles. The maximum temperatures for hydrogen injection angles of 15°, 30°, and 45° were found as 1330 K, 1335 K, 1290 K, respectively. At a 30% hydrogen injection angle, combustion and emissions were found to be optimal.

Keywords: Diesel engine, Hydrogen injection, Combustion performance, Emissions

1 INTRODUCTION

Hydrogen as a fuel for engines has several distinguishing features that make it an appealing alternative to standard fossil fuels. Hydrogen supplies clean combustion and has high energy density, wide flammability range, higher flame speed than conventional fuels, low diffusion risk and low ignition energy. Hydrogen engines are a promising technology for lowering emissions and shifting to more sustainable energy sources. However, there are storage, infrastructure, and production constraints that must be addressed before widespread use can occur.

Nowadays, internal combustion engines remain the most efficient machinery fuelled by fossil fuels. The burning of fossil fuels in diesel engines produces hazardous pollutants. National and international institutions have implemented various laws minimize these emissions. To avoid problems with diesel engines and

minimize the greenhouse effect, we must develop new alternative energy forms and technologies. Most of the techniques used to minimize emissions in diesel engines affect engine performance. Thus, several strategies have been developed to boost performance using selected optimization criteria and design parameters while reducing emissions in diesel engines [1].

Hydrogen can be used directly as a fuel in compression ignition (CI) engines. Due to its high compression ratios, hydrogen significantly improves thermal efficiency. Due to its low cetane number and high autoignition temperature, hydrogen is not suitable for direct use in CI engines [2]. Therefore, hydrogen can be utilized as an additional fuel in diesel engines. Researchers have focused on hydrogen fuel and its effects in recent years, as the addition of hydrogen to diesel fuel improves engine performance and reduces significant pollutant emissions.

Menea et al. [3] investigated the optimal combination of injection characteristics including injection timing, pressure, and variable valve lift for a hydrogen injection system. The analysis results revealed that NO_x emissions and combustion performance rose, while the release of CO₂ decreased. Bayramoglu and Yilmaz [1] look for new hydrogen injection strategies on diesel engines with estimation of emissions and performance. The paper revealed that precise determination of injection timing together with the optimum amount of hydrogen brings crucial improvement in engine performance and emissions. Li et al. [4] investigated the impact of split hydrogen injection rates on hydrogen distribution, emissions, and combustion. CO, HC, and NO_x emissions were estimated numerically using various injection proportions.

In this study, effects of various hydrogen injection angles are investigated on an engine in terms of performance and emissions.

2 METHODOLOGY

Within the scope of the investigation, the combustion analyses are performed using the diesel engine listed in Table 1.

Table 1. Diesel Engine Specification [5,6]

Specification	Value and specs
Engine Type	Caterpillar 3400
Bore x Stroke	137 x 165.1
Number of nozzles	6 x 0.23
Inlet valve closing angle	190.3
Exhaust valve opening angle	505.3

The combustion process analyses are carried out on a single-cylinder four-stroke diesel engine. The hydrogen injection approaches are depicted in Figure 1. In the

analyses, 15°, 30° and 45° injection angles are compared leaving other engine properties constant. Diesel fuel was mixed with hydrogen at a mass ratio of 10%.

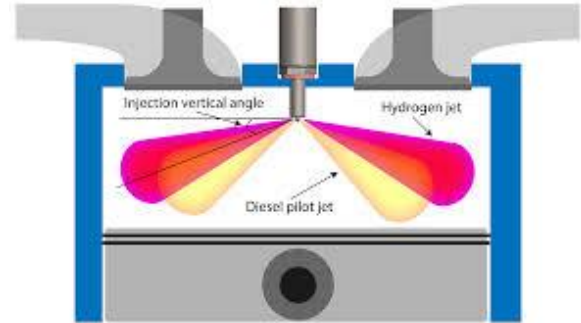


Figure 1. Direct injection of hydrogen and diesel

Diesel engine combustion analyses were carried out by CFD method with Ansys Forte software [7]. In the combustion analysis, the chemical kinetic mechanism was provided by Chemkin software and a chemical reduction mechanism containing a total of 35 species and 173 reactions was used [1,8]. The combustion chamber flow conditions are turbulent and RNG k-epsilon turbulence model is used [9].

3 RESULTS AND DISCUSSION

In this study, the CFD method is applied to examine hydrogen injection in diesel engines with commercial software. Performance parameters, combustion pressure, temperature inside the combustion chamber and heat release rate, together with the emissions parameters CO and NO_x, have been estimated for the specified diesel engine.

3.1 Performance parameters

Fig. 2 and 3 demonstrate combustion chamber pressure and temperature, respectively.

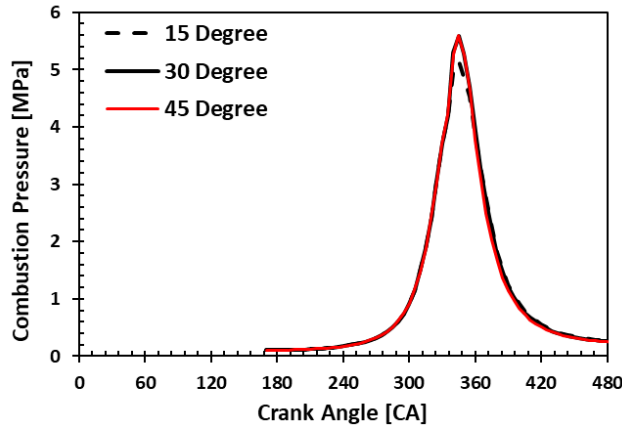


Figure 2. Combustion pressure

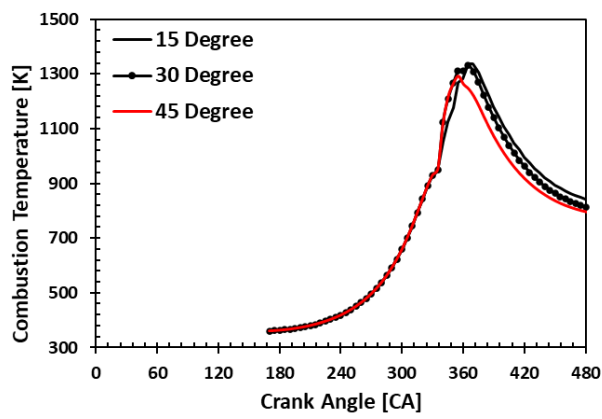


Figure 3. Combustion Temperature

One can clearly see that with increasing injection angle, pressure increases inside the combustion chamber. However, unlike this case, it is observed that the temperature does not show the same characteristic in the combustion chamber. This can be explained by the fact that combustion occurs earlier with increasing injection angle.

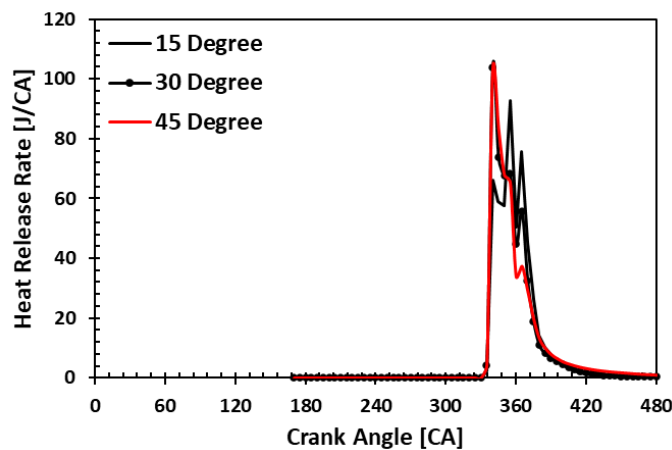


Figure 4. Heat release rate (HRR)

Fig. 4. shows the heat release rate change inside the combustion chamber with respect to the crack angle. As seen in the combustion pressure graph (Fig. 2), heat release also started at earlier crank angles and rates reached their peak at approximately 350° CA.

3.2 Emission Parameters

Figs. 5 and 6 compare CO and NO_x emission parameters with respect to crank angles, respectively. Minimum CO emissions are achieved at a 15° hydrogen injection angle. It is indeed negatively contributed to CO emissions by increasing the hydrogen injection angle.

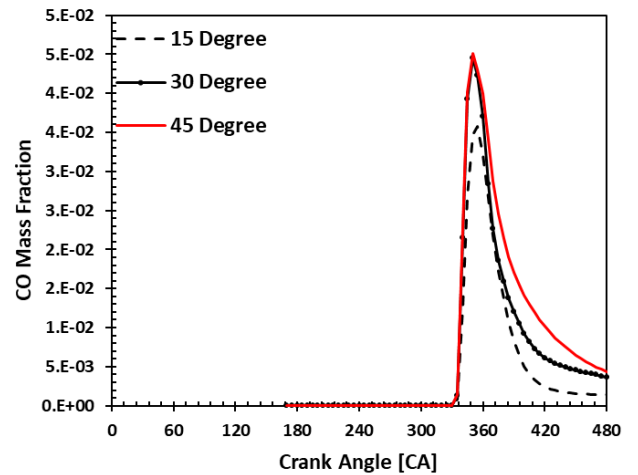


Figure 5. CO Emissions

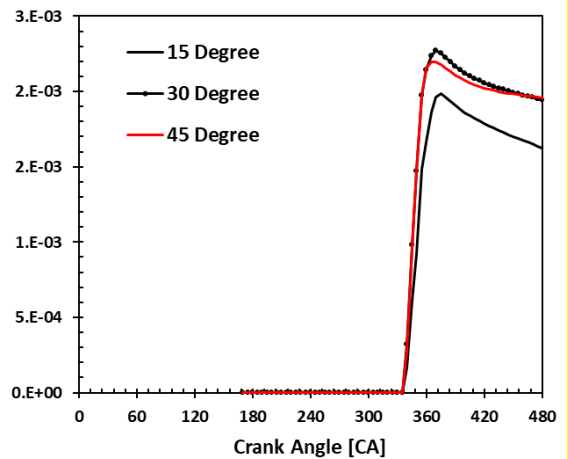


Figure 6. NO_x Emissions

In Fig. 6, it is clearly observed that maximum NO_x emissions have been observed in the hydrogen injection angle of 30°. This indicates that the hydrogen injection angle needs to be carefully adjusted to keep NO_x emissions at the desired level.

CONCLUSIONS

In this study, diesel (90%) and hydrogen (10%) injected engine numerically is investigated for 15°, 30° and 45° injection angles. The combustion and emission characteristics are analyzed at low, intermediate and high hydrogen injection angles. The findings can be summarized as follows:

- The highest combustion pressure is determined at 30° and 45° spray angles.
- It is around 5.5 bar for injection angles of 30° and 45°, and 5.2 bar for 15° injection angle.
- The maximum temperatures for hydrogen injection angles of 15°, 30°, and 45° were found as 1330 K, 1335 K, 1290 K, respectively.
- Minimum CO emissions are achieved at a 15° hydrogen injection angle.
- Maximum NO_x emissions have been observed in the 30° hydrogen injection angle.

At a 30% hydrogen injection angle, combustion and emissions were found to be optimal. This is due to the more homogeneous mixing of the spray into the piston bowl. In future studies, the effect of both diesel and hydrogen injection on combustion and emissions at different injection angles can be investigated.

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INVESTIGATION OF THE EFFECT OF USING BORON ADDITIVE IN AN INTERNAL COMBUSTION ENGINE USING GASOLINE AS FUEL

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Abstract

In today's vehicles, engine parts overheat because they operate at high speeds and produce too much power, and as a result of this heating, the amount of wear on the engine parts increases as the lubricating oils lose their properties. Too much wear affects engine performance. In this study, the effect of boron additive on lubricating oil was investigated using gasoline as fuel in a Lombardini LGW 523 brand 2-cylinder water-cooled engine. The experiments were carried out in 4 stages. The engine oil was maintained and started, and experiments were carried out. Then, the engine was operated for 50 hours in different operating positions and the experiments were repeated. At the end of this study, the engine maintenance was performed and boron additive was added to the engine oil and these experiments were repeated. In this study, energy analysis was applied to the data obtained and the effect of boron additive was examined.

Keywords: Energy, power, combustion, emission

1. Introduction

Due to insufficient lubrication of the moving parts of motor vehicles during startup and at high speeds, a complete oil film layer does not form between the parts and the engine parts overheat. Reaching high temperatures causes wear of moving parts. While this reduces engine life and engine performance, fuel consumption also increases. As fuel consumption increases, emissions also increase. When engine oil is used for a long time, it loses its oil properties and overheats, causing wear. Various additives are added to engine oil in order to reduce or eliminate these negative effects. One of these additives is boron additive.

Some studies on this subject in the literature are as follows.

Akbiyik et al. performed performance and exhaust emission experiments on a 2-cylinder, 4-stroke Lombardini LGW 523 engine with fuel mixtures consisting of gasoline, natural gas and methanol. The experiments were carried out at a constant

engine speed of 3000 rpm and at 4 different torque values. They made energy and exergy analyzes in line with the data obtained from these experiments. As a result of the energy and exergy analyses, it was observed that energy and exergy efficiencies increased in all fuel types with increasing torque values. The best engine performance, lowest specific fuel consumption and best emissions were obtained when using a mixture of gasoline and 50g/h natural gas[1].

Doğan et al. carried out the performance and exhaust emission tests of a single-cylinder, 4-stroke spark ignition engine at different engine speeds using fuel mixtures consisting of gasoline and ethanol. They examined their environmental behaviour by performing energy and exergy analyzes in line with the data obtained from these tests. In this study, the highest efficiency, highest engine power and lowest fuel consumption for all fuels were obtained when the engine speed was 2500 rpm. It has been determined that with the addition

of ethanol to fuel mixtures, there is a significant decrease in exhaust emissions, and thermal efficiency and exergy efficiency decrease. It has been determined that environmental and economic costs increase as the ethanol ratio increases in fuel mixtures consisting of gasoline and ethanol. It has been stated that the optimum ethanol ratio in fuel mixtures from an economic and environmental perspective is between 30% and 40%. It has also been stated that if the ethanol content is more than 50%, engine power will decrease and fuel consumption will increase [2].

Lee et al. performed experiments using various ignition timings and excess air ratios in a hydrogen fueled spark ignition engine. Energy and exergy analyzes were carried out by developing zero-dimensional two-zone modeling to obtain in-cylinder properties. The results showed that with the same excess air ratio, the exergy analysis results were similar to the energy analysis results, such as increased exhaust exergy loss and decreased heat transfer exergy loss due to delaying the ignition timing. It has been shown that the irreversibility of hydrogen combustion increases by delaying the ignition timing. It was determined that the heat transfer exergy loss increased from 27% to 31%, the exhaust exergy loss decreased from 20% to 15%, and the irreversibility was maintained at approximately 10%. It has been stated that irreversibility is maintained due to the balance between increase and decrease in irreversibility [3]. Patil et al. performed experiments at three different engine speeds (1500rpm, 2500rpm, 3500rpm) using gasoline-ketone blended fuels in a three-cylinder, 4-stroke, spark ignition engine. In line with the data obtained from these experiments, energy and exergy analyses, entropy production and sustainability evaluations were made. For the tested fuels, higher brake thermal efficiency and exergy efficiency were obtained at 2500 rpm engine speed compared to other engine speeds. It has

been stated that the mixture obtained by adding 10% ketone to gasoline has energy, exergy and sustainability evaluations comparable to commercial gasoline. In this study, it was determined that the exergy destruction rate for gasoline was lower than gasoline-ketone mixtures. Among the fuel mixtures tested, it was determined that 70% gasoline and 30% ketone blended fuel had 21% lower carbon monoxide and nitrogen oxide emissions than commercial gasoline at 2500 rpm engine speed [4].

Üstün et al. carried out the performance and exhaust emission tests of a single-cylinder, 4-stroke and spark ignition engine. They performed engine tests with fuel mixtures consisting of gasoline and waste fusel oil at full load and at different engine speeds. In line with the data obtained from these experiments, energy, exergy and exergy-based economic analyzes were carried out. It has been determined that as the proportion of waste fusel oil in fuel mixtures increases, CO, HC and nitrogen oxide emissions decrease and CO₂ emissions increase. As the ratio of fusel oil in fuel mixtures increased, fuel consumption increased, engine power and useful work from the engine decreased. In line with the energy and exergy analyses, it has been determined that thermal efficiency and exergy efficiency decrease as the proportion of waste fusel oil in fuel mixtures increases. Adding waste fusel oil to fuel mixtures increased exergy destruction. The increase in exergy destruction increased the formation of entropy. Increasing the waste fusel oil ratio reduced the unit cost of useful work exergy of fuel mixtures. In all fuel mixtures, increasing engine speed decreased thermal efficiency and exergy efficiency [5].

Yeşilyurt et al. performed performance and exhaust emission experiments with alternative fuels obtained by adding different oxygen fuel additives to gasoline in a spark ignition engine. They evaluated the data obtained from the experiments in terms of thermodynamics and economics. Ethanol, methanol, ethyl acetate, methyl

acetate and terpineol were added to gasoline at a rate of 15% by volume. Experiments were carried out at different engine loads and at a constant speed of 1500 rpm. In the experiments, increasing engine load caused exergy losses to increase and the unit cost of engine power exergy values to decrease. In the study, the highest exergy efficiency was found to be 19.58% for gasoline at 100% engine load. It was observed that the fuel mixture using 15% terpineol showed a better

performance in terms of energy and exergy than other mixtures [6].

2. MATERIAL AND METHOD

2.1. The experimental setup

Experimental setup; It consists of engine, dynamometer, fuel consumption measurement systems, emission device, computer and fuels (gasoline and natural gas). The schematic view of the experimental setup is given in Figure 1.



Figure 1. Schematic view of the experimental setup

Testing operations were carried out in accordance with the TSE 1231 "Internal Combustion Engines Inspection and Test Principles" standard. A 505 cc, 2-cylinder, 4-stroke, spark ignition, water-cooled Lombardini LGW 523 MPI engine was used in the experiments. The maximum torque of the test engine is 34 Nm and the maximum power is 15 kW.

Torque and power values of the Lombardini LGW 523 experimental engine were measured with an electric dynamometer. The natural gas flow rate used in the engine was determined with an Alicat M 100 SLPM gas flow meter. The

gasoline consumption amounts of the engine were determined with a liquid mass flow meter. The amount of exhaust gas was determined by the Federal emission device.

2.2. Test method

Test procedures are used in accordance with the TSE 1231 "Internal Combustion Engines Inspection and Test Principles" standard. Measurements with gasoline fuel were made at the beginning and after operating the engine at different loads for 50 hours. Boron was added to engine oil and the same experiments were repeated.

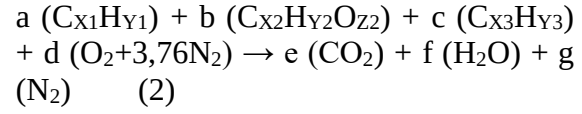
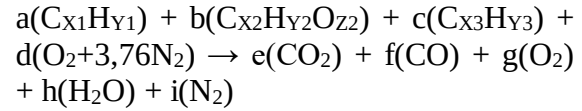
Before the experiments, the test engine was operated at idle until it reached the regime temperature. After the engine reached the regime temperature, the load was gradually increased to the maximum load value with an electric dynamometer and the engine was tested at the determined torques.

After changing the engine oil and filters, performance, fuel consumption and emission tests were performed at full load at 3000, 3500, 4000 and 4500 rpm. The engine was operated for 50 hours under different loading conditions (30 hours at 100% load, 10 hours at 50% load, 10 hours at 25% load). The experiments were repeated.

The experiments were repeated by changing the engine oil and filters and adding 10% boron additive to the engine oil. The experiments were repeated after the engine was operated at different loads for 50 hours.

2.3. Thermodynamic analysis

The first law of thermodynamics is based on the protection of energy and emphasizes that energy cannot be created or destroyed. For this reason, first law analysis is performed to determine the energy inputs and outputs in the system. The second law of thermodynamics analyzes the entropy generation and ability to do work to understand the true energy potential of systems. Except in reversible systems, exergy is not conserved like energy. Some of the exergy is destroyed due to its irreversibility in the system, and some is ejected around the system boundary [35-36]. Engine energy and exergy analyzes are calculated with combustion products obtained from combustion reaction equations. In this direction, the combustion reaction of the test fuel in the form given in the literature for multi-fuel combustion was calculated according to Eq. (1), and the complete combustion equation is also given in Eq. (2) as follows:



The following assumptions are made for the engine energy and exergy analysis:

- Engine is running in steady state,
- It is assumed that there is no water vapor in the combustion air and an ideal gas mixture consisting of 21% oxygen and 79% nitrogen,
- Exhaust gas is an ideal gas mixture,
- Potential and kinetic effects of inlet mass flow (combustion air and fuel) and outlet mass flow are neglected,
- For the overall performance of the engine, the entire engine system is taken as the control volume, for the in-cylinder analysis only the cylinder control volume is selected,
- HC and unburned fuels are negligible in the calculations due to the small amounts in the exhaust gas emissions are accepted.

2.3.1 Energy analysis

Energy is supplied to the system in the form of fuel. This energy is in the form of crankshaft work, heat transfer to the atmosphere for cooling, energy carried by the exhaust gases. As predicted by the first law of thermodynamics, the energy balance equation for the current motor system can be written from Eq. (3) to Eq. (5) as follows :

$$\begin{aligned} \sum \dot{E}_{in} &= \sum \dot{E}_{out} \\ \dot{E}_{in} &= \dot{E}_{fuel} \\ \dot{E}_{out} &= \dot{E}_W + \dot{E}_{ex} + \dot{E}_{loss} \end{aligned}$$

In Eq. (3), $\dot{E}_{in}$ represents total ingoing energy, $\dot{E}_{out}$ represents total outgoing energy, in Eq. (4) $\dot{E}_{fuel}$ states total chemical energy of the fuel which enters the system and in Eq. (5) $\dot{E}_W$ states generated effective power, $\dot{E}_{ex}$ states the

energy of exhaust gases and $\dot{E}_{loss}$ states the loss of energy in the system. $\dot{E}_{fuel}$, $\dot{E}_W$, $\dot{E}_{ex}$ and $\dot{E}_{loss}$ are calculated from Eq. (6) to Eq. (10) as follows:

$$\begin{aligned}\dot{E}_{fuel} &= \dot{m}_{fuel} H_U \\ \dot{E}_W &= \frac{2\pi M n}{60 \cdot 1000} \\ \dot{m}_{ex} &= (\dot{m}_{fuel} + \dot{m}_{air}) 0.98 \\ \dot{E}_{ex} &= \dot{m}_e \varepsilon_t \\ \dot{E}_{loss} &= \dot{E}_{fuel} - \dot{E}_{ex} - \dot{E}_W\end{aligned}$$

Assuming that the exhaust gas exits with a 2% loss, the exhaust mass is found by subtracting the losses from the sum of the mass flow rates of the air and fuel [40]. The thermal efficiency of the system is calculated according to the first law of thermodynamics as given in Eq. (11):

$$\eta = \frac{\dot{E}_W}{\dot{E}_{fuel}}$$

RESULTS

In this study, performance and emission tests were carried out using gasoline fuel at the beginning and after 50 hours of operation, and the same experiments were carried out by adding boron to engine oil. In order to determine the exact effect of boron additive, fuel energy must be determined and compared. Energy analysis was performed in four ways: fuel energy, effective shaft power energy, exhaust energy and total energy loss. Fuel energy; It represents the maximum energy that the fuel used in the engine can provide. Effective shaft power energy shows the energy used from the output shaft of the engine. Exhaust energy refers to the energy released through the exhaust. Total energy losses are the difference between these three values and represent unusable energy. Most of the total energy losses occur from exhaust and energy released to the environment through heat transfer. The energy lost through heat transfer can be reduced by insulating the combustion chamber walls. When the figures are

examined, energy values increase as the speed increases. When the fuel energies at 3000 rpm were examined, the highest fuel energy was calculated as 32,234 kW in 50 hours with boron gasoline. In experiments conducted without boron, fuel energy decreased by 5.8% after 50 hours. In boron experiments, fuel energy increased by 7.6%. There was a 5.5% decrease in effective spindle power without boron and a 0.3% decrease with boron. There was a 1.1% decrease in exhaust energy without boron and a 1.5% increase with boron. Lost energy was reduced by 6.4% without boron and increased by 11.9% with boron. Although the boron additive gave good results in the initial experiments at 3000 rpm, the amount of fuel used and the amount of lost energy increased as the operating time increased. When the fuel energies at 3500 rpm were examined, the highest fuel energy was calculated as 35.062 kW in 50 hours with boron gasoline. In experiments conducted without boron, fuel energy decreased by 5.4% after 50 hours. In experiments with boron, fuel energy increased by 6.5%. There was a 2.4% decrease in effective spindle power without boron and a 1.6% decrease with boron. There was a 2.2% decrease in exhaust energy without boron and a 1.6% increase with boron. There was a 7% decrease in lost energy without boron and an 11.1% increase with boron. Although the boron additive gave good results in the initial experiments at 3500 rpm, the amount of fuel used and the amount of lost energy increased as the operating time increased. When the fuel energies at 4000 rpm were examined, the highest fuel energy was calculated as 42,160 kW at the start without gasoline boron. In experiments conducted without boron, fuel energy decreased by 1.4% after 50 hours. In experiments with boron, fuel energy decreased by 1.0%. There was a 0.6% increase in effective spindle power without boron and a 1.5% decrease with boron. There was a 2.5% decrease in exhaust energy without boron and a 3.9%

decrease with boron. Lost energy was reduced by 2% without boron and by 0.6% with boron. In the results at 4000 rpm, boron additive gave good results in the initial and 50 hour end experiments. When the fuel energies at 4500 rpm were examined, the highest fuel energy was calculated as 45,800 kW at the start without gasoline boron. In experiments conducted without boron, fuel energy decreased by 2.5% after 50 hours. In experiments with boron, fuel energy

increased by 0.3%. There was a 1.9% decrease in effective spindle power without boron and a 2.1% decrease with boron. There was a 2.8% decrease in exhaust energy without boron and a 4.3% decrease with boron. Lost energy was reduced by 2.6% without boron and increased by 1.5% with boron. In the results at 4500 rpm, boron additive gave good results in the initial and 50 hour end experiments.

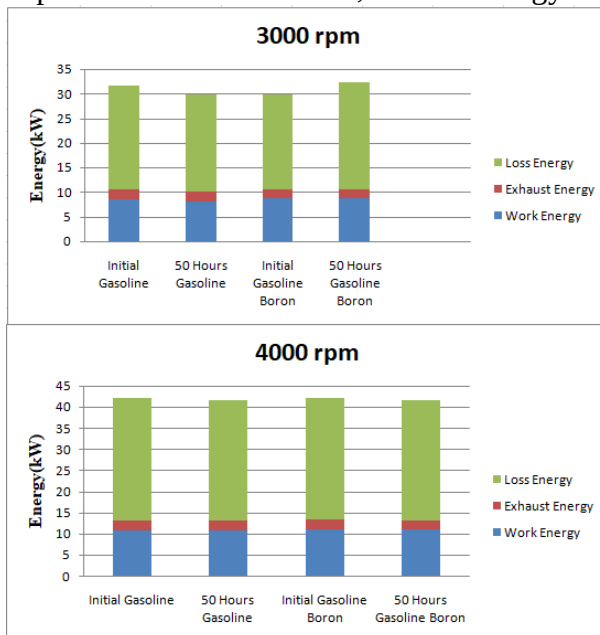


Figure 2.Energy distribution at different speeds

Thermal efficiency is also expressed as the first law efficiency of thermodynamics. As it can be seen, the highest thermal efficiency of the engine was achieved in the study with the least total energy loss. The highest thermal efficiency values were obtained at 3500 rpm. Thermal efficiency

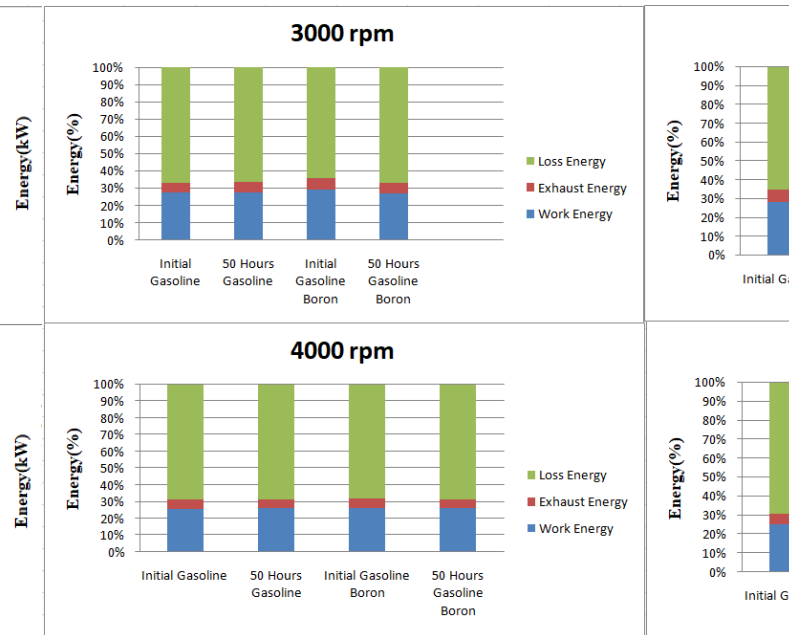


Figure 3.Energy rates at different speeds

values are slightly higher at all cycles at 50 hours in experiments conducted without boron. In experiments conducted with boron, the values at the end of 50 hours are lower.

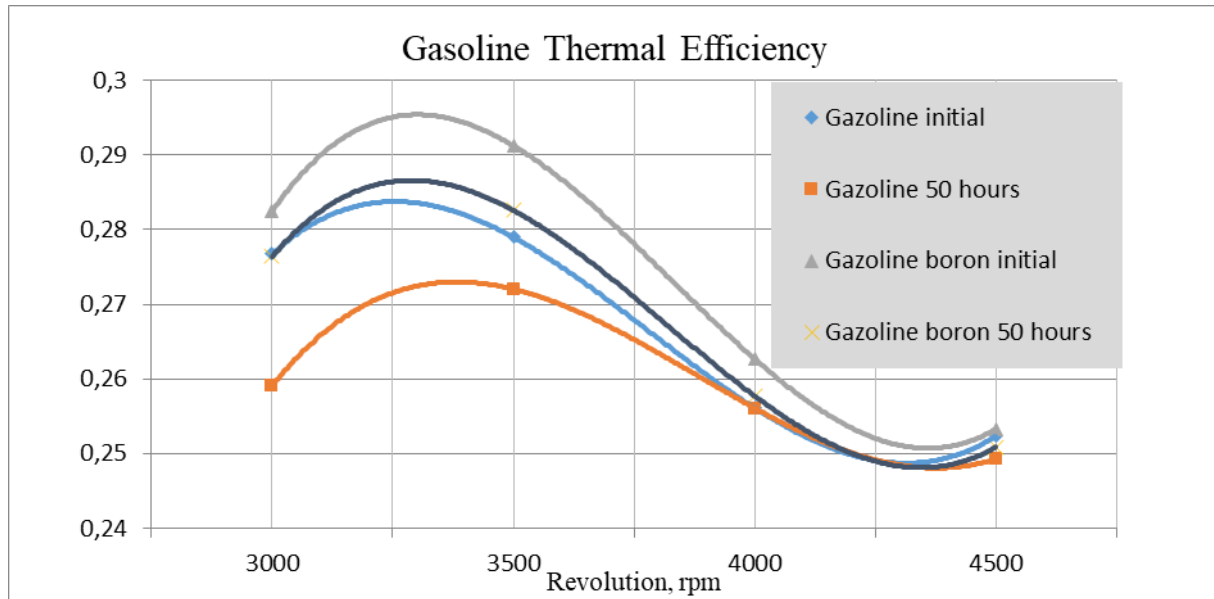


Figure 4.Speed dependent thermal efficiency

4.CONCLUSION

In the energy analysis made using gasoline fuel, boron additives and speed increase were beneficial as the engine started to get harder. Although it gave good results in the initial experiments at low speeds of 3000 and 3500 rpm, it had a negative effect on long-term operation. In experiments conducted with boron, the values at the end of 50 hours are lower. Thermal efficiency values are higher in experiments conducted with boron.

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EXPERIMENTAL STUDIES ON A FREEZER WITH PARTIAL-LOADED CONDITIONS

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Abstract

Food safety during a power outage is crucial to preventing foodborne illnesses. This study provides practical and applicable experimental findings on spatial and temporal temperature variations within a commercial freezer, which are directly relevant to the design and operation of commercial freezers. Eight experiments were carried out with four loading scenarios and two freezer set points. The study not only yields pull-down and rise-up times of the M-packages but also evaluates the performances of the partially loaded freezers. The results, represented in terms of the 1st-Law and 2nd-Law performance indicators such as COP and entropy generation fractions, have direct implications for the design and operation of commercial freezers, making the findings immediately useful for professionals in the field.

Keywords: partial-loaded freezer, experimental study, refrigeration cycle

1 INTRODUCTION

Power outages can severely impact food sustainability, posing potential risks to food safety and the food supply chain. Freezers play a crucial role in preventing food waste by allowing food to be stored for extended periods. However, power outages can disrupt this chain, leading to a rise in the internal temperature of freezers and the potential thawing of frozen food. Especially during long-term outages, food thawing is inevitable and causes food to lose its quality and freshness. In addition, refreezing thawed food can increase food safety risks and allow microorganisms to grow rapidly. Therefore, it is essential to be prepared for power outages and minimize their adverse effects. Contingency plans should be made, alternative energy sources or generators should be used, and the temperature of freezers should be checked during the outage.

Alhamid et al. conducted parametric experiments on a household refrigerator using R600a to evaluate various loading scenarios with M-packages and optimize system performance based on exergetic indicators, such as exergy destruction rate and relative irreversibility [1]. Their study

identified 43 grams as the optimal refrigerant charge. The results showed the relative irreversibilities of the system components under this optimal configuration: 77.52% for the compressor, 1.836% for the condenser, 19.8% for the capillary tube, and 0.8473% for the evaporator.

Similarly, Babarinde et al. developed an experimental setup to compare the performance of household refrigerators using R600a and LPG as refrigerants [2]. Their detailed exergy analyses, based on experimental measurements, assessed the systems' first-law and second-law efficiencies. The findings indicated that the pull-down durations for R600a and LPG-based refrigerators were 240 minutes and 210 minutes, respectively. For the LPG refrigerator, the evaporation temperature and exergy efficiency were -14°C and 45%, while for the R600a refrigerator, these values were -12°C and 42%, respectively. The study concluded that substituting R600a with LPG improved system performance, as evidenced by enhanced exergetic performance metrics such as reduced irreversibility and increased exergy efficiency.

Recent research has also addressed food safety in freezers, emphasizing the importance of proper freezer management for maintaining food quality. Holsteijn and Kemna investigated how technological advancements in household refrigeration could mitigate food waste, a significant issue in the EU [3]. Their study suggests optimizing refrigerator design can substantially reduce food waste by minimizing quality loss and spoilage. Currently, most refrigeration appliances are designed with a single temperature setting of approximately 4°C for perishable foods, which is considered a compromise rather than an optimal preservation condition. The study advocates for ideal preservation temperatures ranging from -1°C to +17°C, depending on the type and condition of the food products. Implementing these optimal temperatures could potentially extend the shelf life of food items by two to three times, thereby significantly reducing the likelihood of spoilage.

Regarding frozen foods, Brown et al. estimated that UK consumers discard over 630,000 tonnes of ‘freezable’ food annually, with a value of up to £2.3 billion, primarily due to expired ‘use by’ dates or perceived spoilage [4]. This food could be preserved through freezing, but research indicates that consumers often lack clarity on the suitability of various products for home freezing. The study, which included a review of literature and online sources, found that while most products are deemed suitable for freezing, there is inconsistent advice and significant variability in reported storage durations. The review was supplemented by an experimental assessment to address the energy implications of increased freezer use, demonstrating that the benefits of preserved food and the reduction in food waste far outweigh the associated energy costs and carbon dioxide emissions. Mercier et al. thoroughly analyzed recent advancements in time-temperature management along the food cold chain [5]. Their review underscores the importance of maintaining precise temperature control throughout the food supply chain to ensure safety and quality. The article explores various technological innovations for monitoring and controlling temperature variations, including advancements in temperature sensors, data loggers, and real-time tracking systems. Additionally, it assesses the impact of these technologies on reducing food spoilage,

extending product shelf life, and enhancing traceability.

2 MATERIAL & METHOD

2.3 System Description

This study experimentally evaluated the freezer’s dynamic behavior under four loading conditions and two temperature set points. Measurements included pull-down and rise periods in the indoor environment and the cycle properties, such as the pressure and temperature of the refrigerant. The freezer’s technical specifications are provided in Table 1.

Table 1. Technical specifications of the freezer [6]

Cooling system	Static
Refrigerant	R600a
Capacity	196 L
Daily energy consumption	0.613 kWh/day
Width	54 cm
Height	145.7 cm
Depth	57.5 cm
Number of compartments	5

The freezer has a storage capacity of 196 liters and is divided into five compartments (Figure 1a). It operates with a cooling cycle charged with 42 grams of isobutane (R600a). The freezer is equipped with six flat plate evaporators, and air circulation is achieved through buoyancy forces.

The temperature variations were obtained by placing thermocouples on the inner/outer surfaces of the freezer and the inlet/outlet sections of the components that make up the cooling cycle. In addition, pressure measurements were carried out at the compressor inlet/outlet and condenser outlet sections to determine the pressures in the refrigeration cycle. T-type thermocouples were used for temperature measurements. Test packages, called M-packs, are used to simulate food as a thermal load in the case of a real user. The chemical content of M-packets consists of 23.2% oxy-ethyl-methyl cellulose, 72.5% water, and 4.3% sodium chloride. The dimensions of the M-packs used in the experiments are 100 mm × 50 mm × 100 mm (Width × Height × Depth), and their freezing point is around -5°C. Figure 1b presents a visual of the experimental loading condition.

Figure 2 illustrates the placement of test packages in the loaded freezer experiments with 40 M-packages. The test packages are marked with two different coloring codes. Thermocouples are placed in the test packages marked in red and are located at the center of each shelf. The test packages marked in blue were used solely for thermal loading, and no temperature measurements were taken for these. Figure 2 also details the loading scenarios and the naming conventions for the thermocouples that measure the temperatures of the load packages.



(a)



(b)

Figure 1. Unloaded and loaded freezer

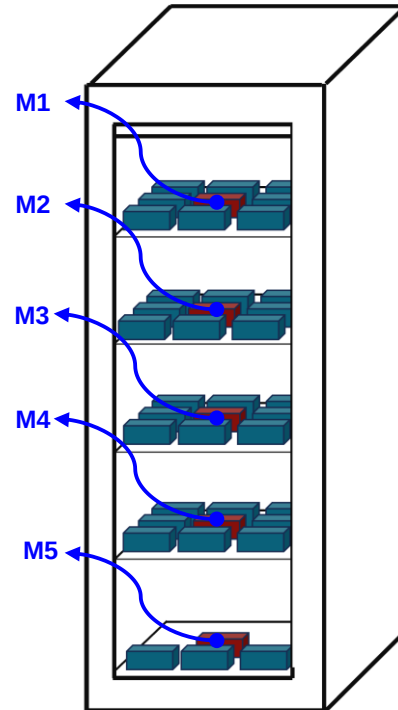


Figure 2. M-package arrangement with thermocouple positions (40 M-packages)

3.3 Data Reduction

Temperature (38 locations) and pressure (3 locations) measurements were carried out during the experiments. The first and second law calculations were performed using these measured values to determine the system component

capacities and the system's coefficient of performance (COP) values. The energy balance equations for the system components under steady-state operating conditions are defined as follows:

$$\begin{aligned} q_{\text{condenser}} &= \dot{m}(h_{\text{in}} - h_{\text{out}})_{\text{condenser}} \\ q_{\text{evaporator}} &= \dot{m}(h_{\text{out}} - h_{\text{in}})_{\text{evaporator}} \\ \dot{W}_{\text{compressor}} &= \dot{m}(h_{\text{out}} - h_{\text{in}})_{\text{compressor}} \end{aligned}$$

The enthalpy values of the R-600A fluid at the inlet and outlet of the system components were calculated using temperature and pressure data from the COOLPROP plugin. An in-house MATLAB code developed for this purpose allows for the automatic generation of T - s and p - h diagrams and component capacities. After determining the capacities of the system components, the COP values for the 1st and 2nd laws were calculated using the following equations:

$$\text{COP} = \frac{q_{\text{evaporator}}}{\dot{W}_{\text{compressor}}}$$

$$\text{COP}_{\text{II}} = \frac{\text{COP}}{\text{COP}_{\text{Carnot}}}$$

Further, entropy balance equations were defined for all components to evaluate the entropy productions.

$$\begin{aligned} \dot{S}_{\text{gen,cond}} &= \dot{m}(s_{\text{out}} - s_{\text{in}})_{\text{cond}} + \frac{q_{\text{condenser}}}{T_{\text{ambient}}} \\ \dot{S}_{\text{gen,evap}} &= \dot{m}(h_{\text{out}} - s_{\text{in}})_{\text{evap}} - \frac{q_{\text{evaporator}}}{T_{\text{freezer}}} \\ \dot{S}_{\text{gen,comp}} &= \dot{m}(s_{\text{out}} - s_{\text{in}})_{\text{comp}} + \frac{q_{\text{loss}}}{T_{\text{ambient}}} \end{aligned}$$

4 RESULTS & DISCUSSION

Freezer experiments were conducted in two set points labeled Set-2 and Set-3. The experiments utilized 24, 40, and 60 M-Packages to assess the effect of loading conditions on temperature variations and the thermodynamics performance indicators. The scenarios were labeled as follows: 0 for the unloaded condition, 1 for the 24 M-Package, 2 for the 40 M-Package, and 3 for the 60 M-Package.

Figure 2 shows the time-wise evolution of the compartment temperatures for the unloaded freezer for Set-3. The temperature reaches the set point at around 2 hours. After 14 hours, the

power-outage scenario is tested. The critical temperature for the M-packages is -4°C . It takes almost 1 hour to reach the limit temperature for the unloaded condition.

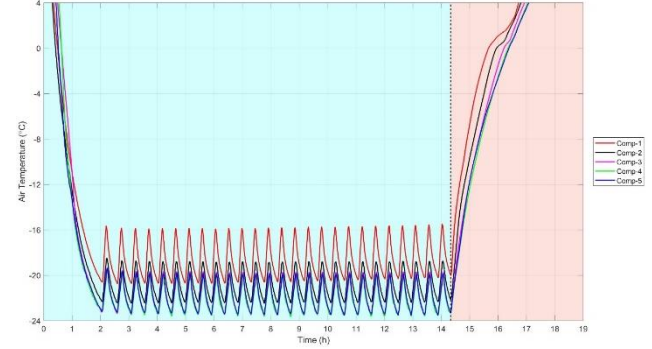
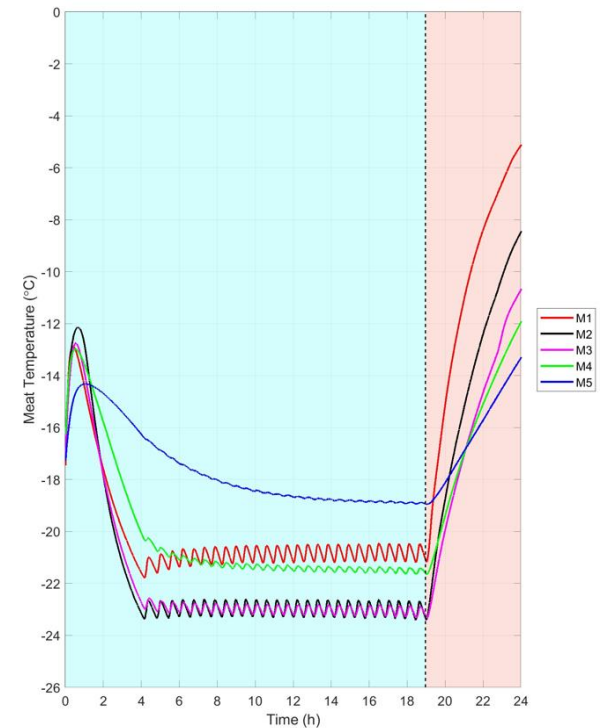
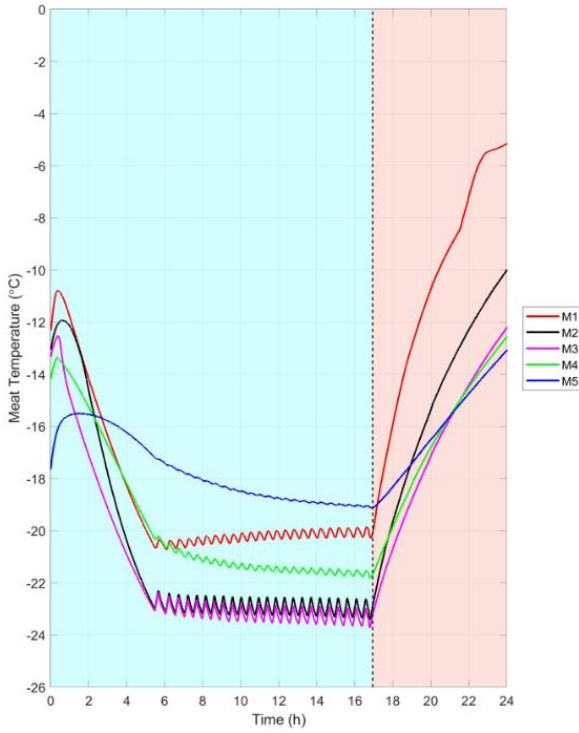


Figure 2. Unloaded freezer pull-down and power outage conditions (Set-3)

Figure 3 illustrates the M-package temperature variations for pull-down and rise-up experiments with 24 and 40 M-packages for Set-2. 24 M-packages corresponds to almost 12.5% of the internal freezer's volume. It takes nearly 5 hours to reach the M-packages temperature to reach the limit temperature. When the M-package volume fraction was increased to 20.84% in Set-2, corresponding to 40 test packages, temperature preservation time was extended to 7 hours. One should also notice that the pull-down duration increases from 4 to 5 hours by increasing the number of M-packages from 24 to 40.



(a) 24 M-packages



(b) 40 M-packages

Figure 3. Loaded freezer pull-down and power outage conditions (Set-2)

Eight power outage experiments were conducted with the loaded freezer, featuring three different loading scenarios and two thermostat set temperatures. Figure 4 illustrates the pull-down durations (PD) and time it took for the test packages to reach the critical temperature of -4°C in each experiment, i.e., rise-up duration (RU). In Set-2, which used 6.12% of the freezer's internal volume with 24 test packages, the test packages remained undeteriorated for 5 hours and 10 minutes. In Set-3, using the same internal volume and 24 test packages, preservation duration is obtained as 6 hours and 26 minutes. For Set-2, where the internal volume was increased to 10.2% with 40 test packages, the preservation time was extended to 7 hours and 35 minutes. In Set-3, with the same internal volume and 40 test packages, the test packages were preserved for 9 hours and 14 minutes. In Set-2, with 60 test packages occupying 15.30% of the freezer's internal volume, the test packages were maintained for 9 hours and 40 minutes without deterioration. In Set-3, with the increased internal volume and 60 test packages, the preservation time reached 12 hours and 57 minutes.

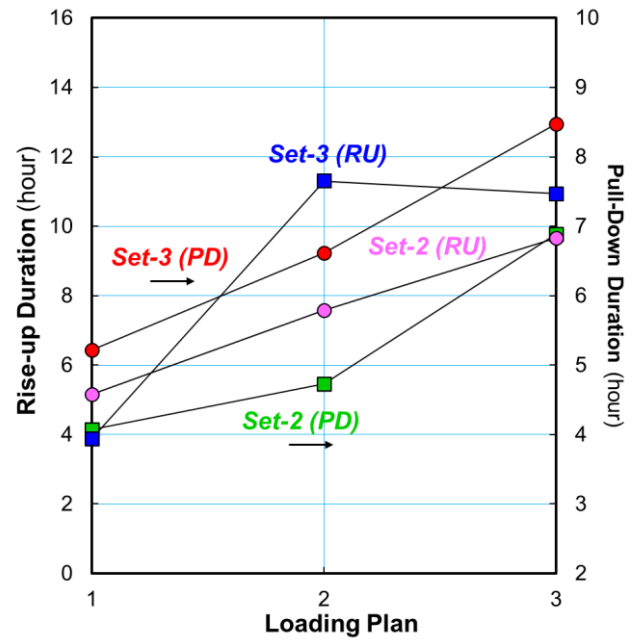
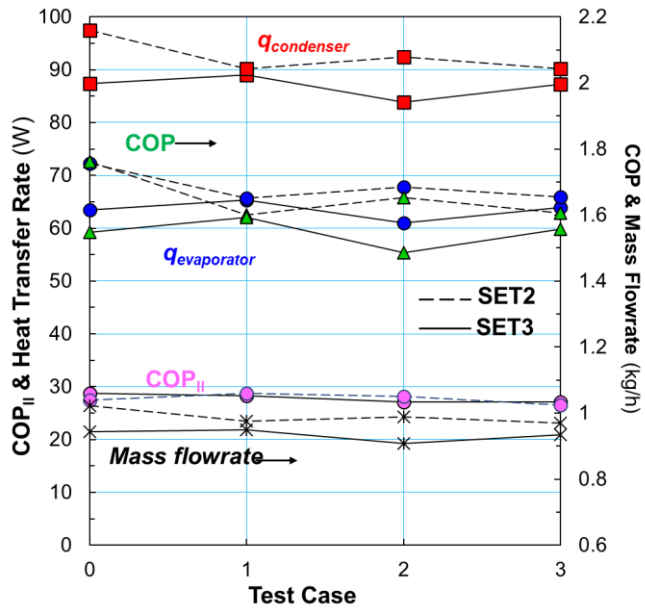
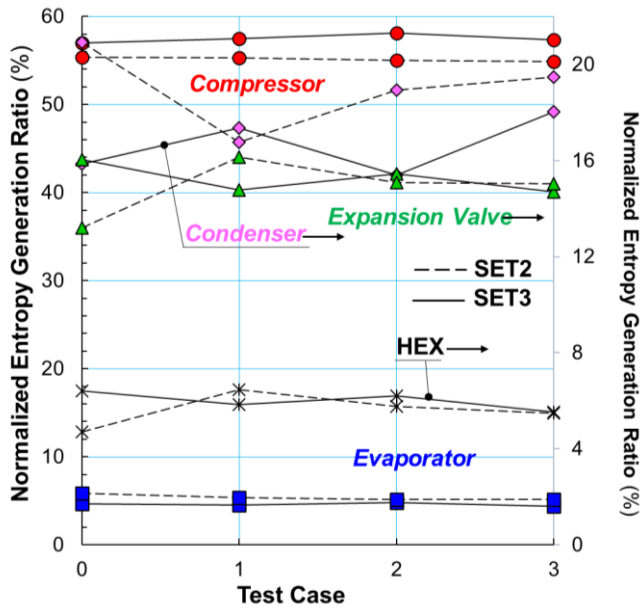


Figure 4. Unloaded freezer pull-down and power outage conditions (Set-3)

Figure 5 summarizes the performance indicators of eight experiments, two for the unloaded freezer and six for the loaded freezer. Comparative results include the 1st law and 2nd law COPs, heat transfer capacities of the evaporator and condenser, and the normalized entropy generation rates in each component. It is noted that reducing the set temperature decreases the condenser and evaporator capacities and also decreases the 1st law COP, yet the 2nd law COP is not significantly influenced by the set point of the freezer. Reducing the set-point increases the share of compressor and condenser in the entropy production. No trend is observed regarding the influence of loading condition on the system indicators. Only the 2nd law COP reduces as the number of M-packages increases.



(a)



(b)

Figure 5. The freezer's performance indicators depend on the set point and loading scenarios

5 CONCLUSIONS

Power outages pose a significant threat to food safety by disrupting temperature control in commercial freezers. This study aims to investigate the impact of loading conditions and set points on temperature variations and system performance within a commercial freezer.

Key findings indicate that increasing the number of M-packages extends the time required for the freezer's internal temperature to reach the critical

point, thus improving food preservation during power outages. While reducing the set temperature generally decreases 1st law COP, condenser and evaporator capacities, however, its impact on 2nd law COP was minimal.

This research provides practical insights for the design and operation of commercial freezers, leading to improved food safety and reduced food waste during power outages. Future research could explore the impact of increased load package numbers, testing under drawered conditions, and alternative approaches to mitigate temperature fluctuations.

ACKNOWLEDGEMENTS

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DETAILED CHARACTERISTICS OF POLYCYCLIC AROMATIC HYDROCARBONS AND TOXICITY IN A DIESEL ENGINE RUNNING ON DIESEL AND BIODIESEL BLENDS WITH ALCOHOLS

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Abstract

Diesel fuel contains aromatic compounds due to its chemical structure; it emits poly-cyclic aromatic hydrocarbon (PAH) emissions that are very harmful to the environment and human health. Due to the increasing need for diesel fuel as well as a host of environmental factors, the use of biodiesel has been accepted as an alternative to diesel fuel. Additionally, higher alcohols are used as an alternative fuel in diesel engines in order to reduce the emissions of diesel fuel and to improve the fuel properties of biodiesel. Due to the increased attention on alcohols, PAH emissions need to be investigated when higher alcohols are used as alternative fuels to diesel fuel. Currently, there are very limited studies on this subject. In this study, the effects of diesel and waste oil biodiesel mixtures containing 15% n-propanol (-Pro), 15% n-butanol (-Bu), and 15% n-pentanol (-Pen) on total PAH, toxicity, and PAH distribution in a diesel engine were investigated. PAH emissions from six different fuel mixtures were detected and quantified using the analytical chemistry method. By adding high carbon alcohols to the diesel, a reduction in toxicity and total PAH emissions were obtained. In the distribution of PAH emissions of both fuels, a great reduction in the formation of heavy PAHs was achieved. With the addition of 15% higher alcohols to diesel fuel and biodiesel, total PAH emissions were determined below the Occupational Health and Safety Administration's (OSHA)-Permissible Exposure Level (PEL:0.2 mg/m³). Thus, the use of a 15% (by vol.) mixture of high carbon alcohols together with diesel and biodiesel will not cause any adverse effects in terms of environmental health and engine operating time.

Keywords: Diesel Fuel, Waste Oil Biodiesel, Higher Alcohol, Toxicity, Wetstacking; Heavier PAHs

1 INTRODUCTION

Diesel fuel quality is subject to strict regulations due to both the production process and the emissions it produces [1,2]. The decrease in oil reserves and the instability in prices has revealed the necessity of finding alternative fuels to diesel [3-5]. For these reasons, the research of fuels that can replace diesel fuel in diesel engines has been going on for many years [6]. The widespread research interest in alternative fuels has focused on fuels that can be sourced from renewable feedstock, such as biodiesel and alcohols, to

reduce the reliance on fossil fuels.[7]. The production of biodiesel from inedible raw materials makes this fuel more attractive [8]. The feedstock used in the production of biodiesel and the determination of the mixture ratio with the diesel fuel directly affect engine performance and the sustainability of the fuel [9,10]. Studies conducted in the literature to date recommend the of biodiesel with blend ratios up to 20% [11-13]. If a higher mixture ratio is used, it becomes necessary to improve the fuel properties of the mixture. One of the effective methods of improving the fuel properties of biodiesel without using additives is mixing it with bio-alcohol at a

certain rate [14-15]. In order to encourage the adoption of renewable fuels in diesel engines, the effect of the fuels on the environment can be studied by examining all the pollutant components that are formed as a result of combustion [16-19]. Bio-alcohols are much attractive than other renewable fuels, in part, because of the ability to run bio-alcohols in diesel engines and reduce emissions [17-20,21].

The use of alcohol with diesel fuel has been studied for many years [21-23]. Particularly, the advantages of high carbon alcohols over low carbon alcohols as an alternative fuel for use in compression ignition engines [24,25]. In recent years, n-propanol, n-butanol, and n-pentanol have become prominent high-carbon alcohols considered for use in diesel engines [26-29]. Examining the pollutant emissions of both biodiesel and diesel mixtures of these alcohols will increase the degree to which industries adopt alternative fuels for application in diesel engines. However, the regulated emissions of the mixtures were investigated in all studies using biodiesel and diesel together with alcohol [30,31]. In addition to regulated emissions, PAH emissions should be kept under control for the sake of human and environmental health and should also be further examined [32]. Additionally, the 17 different PAH emissions specified by the United States Environmental Protection Agency (US EPA) must be examined. The harm of these emissions in terms of human health has also been stated by International Agency for Research on Cancer (IARC). However, studies investigating PAH emissions have been limited. Karavalakis et. al [33] conducted research on the effect of low concentration palm and rapeseed oil biodiesel-diesel blends on regulated and PAH (particle-bound PAHs, nitro-PAHs, and oxy-PAHs) emissions from a car. They found that the use of different biodiesel blends does not adversely affect nitro-PAH and oxy-PAH emissions. Gowtham et al. investigated the effects of 10%, 20%, and 30% n-butanol fumigation on PAH emissions in a diesel engine [34]. Similarly, an increase in high cyclic aromatics was observed as the n-butanol ratio increased in fumigation. In the study conducted by Arias et al., the carbonyl and PAH emissions of 13% and 20% n-butanol and renewable diesel mixtures were investigated [35]. 13% n-butanol mixture emitted the highest carbonyl compound emission. Although low-ring PAH emissions were mostly detected in both

mixtures, an increase was observed in some high-ring PAHs. The effects of adding 2%, 5%, and 20% biodiesel to diesel fuel on mono- and poly-aromatic hydrocarbon emissions (MAHs and PAHs) were investigated by Correa et al [36]. The maximum reductions in MAHs and PAHs emissions were obtained as 21.1% and 17.2%, respectively, in the 20% mixture. In the study conducted by Vojtisek et al., the carcinogenic PAH emissions of 100% diesel and biodiesel at different engine loads were investigated [37]. According to the results of the research, the carcinogenic PAH emissions of diesel were found to be 4 to 20 times higher than that of biodiesel in all engine loads. In the study conducted by Guerreiro et al., carbonyl emissions of ternary mixtures were investigated by adding ethanol, biodiesel and vegetable oil to diesel fuel [38]. However, an increase in carbonyl emissions has been observed in various three-component fuel mixtures. When the overall results of the studies are evaluated together, it is seen that the addition of high carbon alcohol as a second component to diesel fuel and biodiesel will provide a more effective solution to reduce PAH emissions.

Similarly, when all the studies in the literature have been examined so far, there is still a need for studies on the detailed investigation of the PAH emissions of biodiesel or diesel and alcohol mixtures. In this study, which was carried out in order to close this gap in the literature, based on the mixture ratio of 15% on high carbon alcohols, it is aimed to improve the fuel properties of biodiesel and reduce the use of diesel fuel. Therefore, in this study, the effects of biodiesel or diesel containing 15% by volume C3, C4, and C5 alcohol mixtures on PAH emissions in an indirect injection diesel engine were investigated.

2 TEST FACILITY AND SPECIFICATION

2.1 Test Conditions and Fuels

Table 1 shows the engine properties along with the experimental test setup, including PAH sampling, in Figure 1. Engine tests were performed in an indirect-injected, four-cylinder Onan DJC diesel engine.

set at 15% in line with the EU target, as high-carbon alcohols are promising for diesel engines.

Table 1. Test Engine Properties

Six different mixtures named as BPro15, BBu15, BPen15, DPro15, DBu15, and DPen15 were formed with 15% mixing ratios of n-propanol, n-butanol, and n-pentanol. All the binary blends samples were kept for analysing the phase separation through visual observation technique for ten days. It has been observed that there was no phase separation as all the blends were transparent and stable for the duration of the tests. The waste oil biodiesel and blended fuels properties were tested using ASTM test standards and basic fuel properties were given in Table 2.

Table 2. Test Fuels Basic Properties

Items	Density (g/ml)	Lower heating value (MJ/kg)	Cetane number	Kinematic viscosity at 40 °C (mm ² /s)	Flash point (°C)	Cloud point (°C)	CFPP (°C)
Diesel	0.818	44.8	54	2.95	74	-12	-21
Biodiesel	0.855	40.5	52	4.57	126	-8.1	-13.2
n-Propanol	0.803	30.63	12	1.74	22	-	<-51
n-Butanol	0.810	33.10	17	2.23	35	-	<-51
n-pentanol	0.815	34.94	20	2.89	49	-	-40
BPro15	0.845	32.67	44.51	4.12	94.15	-11.5	-17.1
BBu15	0.846	39.34	45.60	4.03	95.45	-12.2	-18.6
BPen15	0.848	39.87	45.89	4.21	98.63	-11.2	-17.8
DPro15	0.811	42.06	44.42	2.48	44.78	-18	-22
DBu15	0.815	42.96	46.51	2.93	59.50	-18	-24
DPen15	0.8144	42.50	45.67	2.98	50.53	-18	-23

The ASTM D975 standard requires a minimum cetane number of 40 for regular diesel fuel, with typical values of 40–55. According to this, all blended fuels meet this requirement. In terms of low temperature operability, the binary blends have better cold filter plugging point (CFPP) value. This improvement increases depending on the blend ratio of C3, C4, and C5 alcohols.

2.2 PAH Sampling Procedure

PAH sampling was conducted using a warmed engine under idle conditions for a total of 3 hrs at a rate of 10 liters per minute without dilution. Each blend was tested in triplicate. Exhaust samples were filtered using a two-step process with using a 2 µm pore diameter PTFE filter paper (37 mm diameter from Pall Co.; Port Washington, NY) to collect particle-bound material. More volatile species were collected in a 50 mg/100 mg Amberlite XAD-2 resin cartridge. For isotope-dilution mass spectrometry an internal standard (2 µg 98% anthracene-d10) was added to each sample. PAH were then extracted individually

Engine type	Onan DJC Diesel Generator
Number of cylinders	4
Number of cycles	4 cycle
Fuel injection system	Indirect
Injection pressure (MPa)	13.1
Injection timing (BTDC)	18 °CA
Bore (mm)	82.55
Stroke (mm)	92.08
Displacement (cm ³)	1970
Compression ratio	19:1
Max output (kW)	12
Max speed (rpm)	1800

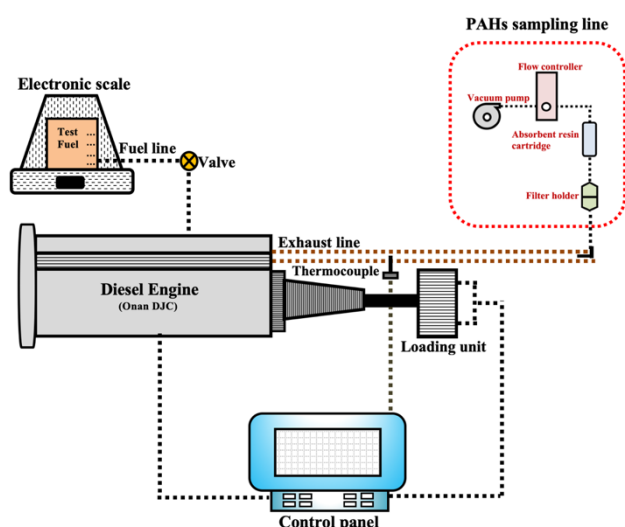


Figure 1. Test setup and PAH Sampling

The fuels used in this study included standard diesel (No:2), waste oil biodiesel, n-propanol, n-butanol, and n-pentanol. The waste oil methyl ester used in this study was produced from waste cooking oil collected from restaurants. The conversion of waste cooking oil into biodiesel was performed through the transesterification process following ASTM D6751 standard. The fatty acid composition was determined using an Agilent Technologies 6890 Network Gas Chromatograph (GC) System based on EN15779 testing standards. The ratio of saturated fatty acids was 13.28%, the ratio of unsaturated fatty acids and other fatty acid components was measured as 81.40% and 5.32%, respectively. The n-propanol (CAS No: 71-23-8), n-butanol (CAS No: 71-36-3) and n-pentanol (CAS No: 71-41-0) were obtained from Merck. The EU set a 10% target for renewable energy use in transport in 2020 and increased this target to 14% by 2030. In this context, the blend ratio was

using 5 ml of HPLC-grade hexane. Samples were washed by filtering through a 500 mg Na₂SO₄/500 mg alumina column with an additional 5ml of n-hexane. Washed samples were recovered with 50/50 vol% HPLC-grade benzene/acetonitrile and concentrated using nitrogen blowdown. Concentrated samples were frozen and kept at -80 °C before further analysis. PAHs were detected and quantified using GC-MS based on a Selected Ion Monitoring process. Further details for the GC-MS analysis are provided in Table 3; helium was the carrier gas.

Table 3. Thermal Program GC-MS

Instrument Details	GC-MS: HP 5890/5971A Column: DB5-MS
Injection Volume	1 µL
Injection Temperature	300 °C
Thermal Program	Hold 70 ° for 1 min Heat from 70-200 °C @ 70 °C/min Hold 200 °C for 2 min Heat 200-300 °C @ 7 °C/min Hold 200 °C for 10 min

The total combined uncertainty for PAH emission measurements was calculated as 1.22%. Given the inevitable variations in the PAH analysis process, the entire sample collection was performed in triplicate to ensure reproducibility. The uncertainty of all the results obtained was determined to be within the maximum range of 1.22%. In addition, because of multiple measurements, standard deviations and error bars are indicated in the relevant figures. The accuracy was checked by analyzing SRM 2975. Three different samples were analyzed, and the entire analytical procedure was tested in real situations. Values obtained were compared with data provided for certified material, within the expected range for all certified compounds.

3 RESULTS AND DISCUSSIONS

3.1 PAH Concentration in Exhaust

Figure 2 shows total PAHs of test fuels in terms of emission concentration (µg/m³). Total PAH concentrations in exhaust are given in Table 4.

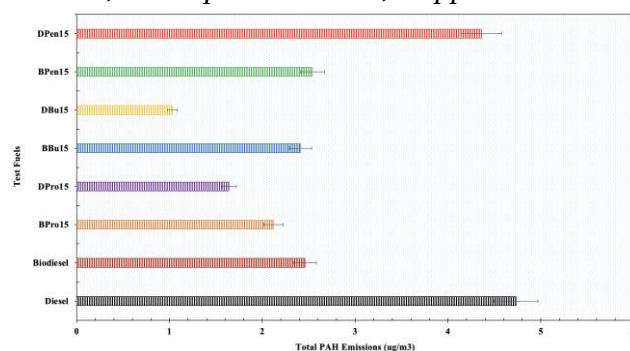


Figure 2. Total PAH Concentration

Generally, the aromatic content of a fuel is linked to the fact that fuels with aromatic components produce more PAHs than those with less aromatic content [39,40]. Since biodiesel does not contain aromatic content, PAH production is not expected to occur. There are many potential factors that can affect the formation of PAHs in the combustion chamber of a diesel engine using biodiesel, including the latent heat of evaporation (LHE) of the fuel, oxygen content, cetane number, ambient temperature and pressure, engine parameters and exhaust after-treatments [40,41].

Table 4. PAH concentration for test fuels

PAH	Number of rings	Total PAHs (µg/m³)							
		Diesel	Biodiesel	BPro15	BBu15	BPen15	DPro15	DBu15	DPen15
Naphthalene	2	1.93	0.76	1.28	1.54	1.58	0.33	0.61	1.07
Acenaphthylene	2	0.21	0.25	0.23	0.71	0.81	0.11	0.23	0.71
Fluorene	2	0.59	0.22	0.24	0.12	0.11	0.34	0.12	1.18
Phenanthrene	3	1.19	0.66	0.25	0.01	0.01	0.55	0.02	1.19
Fluoranthene	3	0.29	0.18	0.04	0.02	0.02	0.12	0.03	0.09
Pyrene	4	0.4	0.31	0.07	0.01	0.01	0.18	0.02	0.11
Benzo[a]anthracene	4	0.00*	0.01	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*
Chrysene	4	0.09	0.07	0.01	0.00*	0.00*	0.01	0.00*	0.01
Benzo[k]fluoranthene	4	0.00*	0.01	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*
Benzo[a]pyrene	5	0.01	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*

*undetected

As shown, total PAHs of biodiesel (2.46 µg/m³) significantly decreased by 48.02% compared to that of diesel fuel (4.73 µg/m³). Like biodiesel, n-propanol, n-butanol, and n-pentanol does not have aromatic content, but the aforementioned factors have caused the formation of PAHs. With the addition of -Pro, -Bu, and -Pen to biodiesel and diesel a significant reduction of 55.20%, 49.08%, 46.33%, 65.35%, 78.23% , and 7.88% in total PAH emissions were obtained for BPro15, BBu15, BPen15, DPro15, DBu15, and DPen15 compared to diesel fuel. A slight increase in total PAHs was observed for -Pen15 compared to other blended fuels. This increase in PAHs with C5 alcohol blending is likely due to the increase in evaporation enthalpy and the fuel lean zones in the combustion chamber due to the fuel borne-oxygen content [42]. Additionally, considering the

numerous possibilities for PAH formation in a diesel engine, increasing oxygen content above a certain limit may have an adverse effect on combustion and lead to a decrease in chemical reactivity which causes rearrangement of radicals in the ignition zone and more favourable radical formation for PAH occurrence [43-45]. Depending on the alcohol mixture ratio, C3 and C4 alcohols show great potential for reducing total PAH emissions [46]. By adding 15% -Pro, -Bu and -Pen alcohol to biodiesel, the effect of the improvement in fuel properties on reducing PAH emissions may increase the use of these alcohols [40].

3.2 PAH Dispersion

A large amount of PAHs are released in the diesel combustion process, depending on the number of aromatic rings. The relative dispersion of PAHs in blends is shown in Figure 3. When Figure 3 and Table 4 are examined together in the distribution of PAHs, it is observed that the distribution in all test fuels is concentrated in two- and three-rings aromatic components. The low and medium molecular weight PAHs were the predominant compounds for all blended fuels. High levels of low-rings PAHs may be due to the amount of blended fuels pyrolyzed from incomplete combustion due to the addition of alcohols [45-47]. However, five-ring aromatics were encountered at DBu15 and DPen15, which may be caused by ignition delay and low cetane number leading to the inability of -Bu and -Pen alcohol radicals to suppress the formation of five-ring aromatics in the final stage of combustion.

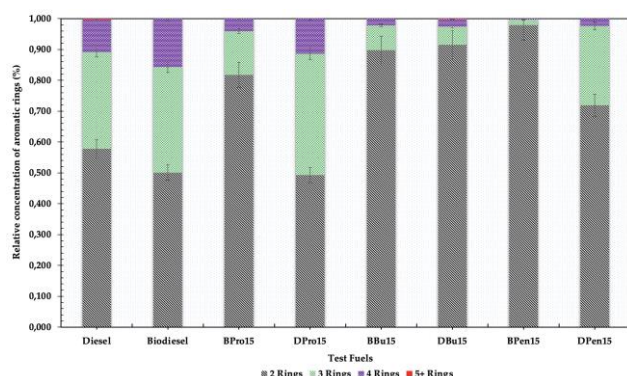


Figure 3. Relative Dispersion of PAHs

In contrast to low ring PAHs, the formation of high-ring PAHs has a more negative impact on both the environment and engine durability [47,48]. Thus, heavy molecular PAHs will

condense more easily in the exhaust valve body with the unburned fuel, causing wetstacking [30,49,50]. In this case, mixtures of BPro15, BBu15, BPen15 and DPro15 come to the forefront in terms of the absence of 5-rings aromatic compounds. Thus, it has been understood that the wet stacking problem can be avoided by using alcohol-blended fuels in diesel engines [46].

3.3 PAH Toxicity

The total carcinogenicity of PAHs that may affect human health is defined as toxic equivalent factor (TEF) values [42,51,52]. The weighted benzo[a]pyrene equivalent (BaPeq (ng/m³)) of each PAH compound was calculated based on TEF [42,53-55]. The toxicity distribution of PAH emissions is shown in Figure 4 and the toxicity BaPeq (ng/m³) concentration in the exhaust is shown in Table 5. As can be seen from the total PAH values and distribution, 16.20 BaPeq (ng/m³) was calculated due to the high PAH release of diesel fuel. On the other hand, biodiesel (2.67 ng/m³) provided an 83.49% reduction compared to diesel fuel. With the addition of -Pro, -Bu, and -Pen alcohol to diesel and biodiesel, a significant reduction in toxicity was achieved. This decrease was 93.56%, 93.09%, 93.45%, 91.38%, 86.36%, and 74.83% for BPro15, BBu15, BPen15, DPro15, DBu15 and DPen15, respectively.

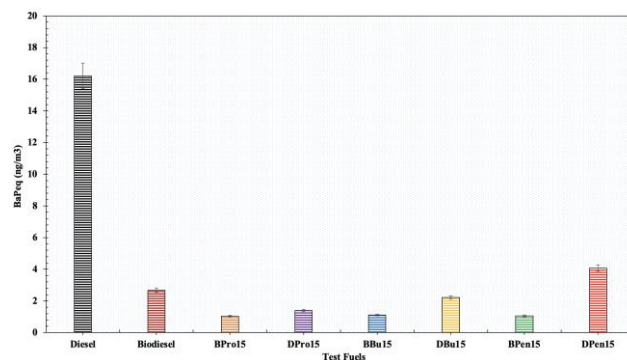


Figure 4. Toxicity of PAH emission for Test Fuels

This reduction is attributed to the presence of lower-ring aromatic compounds, especially with the addition of alcohol [54,55]. As a result, a great reduction in pollutant emissions with the addition of 15% alcohol to biodiesel and diesel fuel showed that this mixture ratio can be used safely in diesel engine.

Table 5. BaPeq concentration in exhaust

PAH	Number of rings	Toxicity BaPeq (ng/m ³)							
		Diesel	Biodiesel	BPro15	BBu15	BPen15	DPro15	DBu15	DPen15
Acenaphthylene	2	0,211	0,246	0,287	0,941	0,91	0,131	0,351	0,752
Fluorene	2	0,593	0,223	0,284	0,133	0,11	0,372	0,166	1,198
Phenanthrene	3	1,194	0,66	0,266	0,011	0,01	0,574	0,637	1,378
Fluoranthene	3	0,288	0,18	0,054	0,028	0,02	0,121	0,922	0,141
Pyrene	4	0,403	0,305	0,082	0,004	0,01	0,192	0,123	0,119
Benzo[a]anthracene	4	0	0,919	0	0	0	0,001	0	0,462
Chrysene	4	0,094	0,065	0,07	0,002	0	0,006	0,002	0,007
Benzo[k]fluoranthene	4	0,046	0,077	0	0	0	0	0	0
Benzo[a]pyrene	5	13,378	0	0	0	0	0	0,009	0,021

4 CONCLUSIONS

Due to the tightening emission regulations and the increasing demand for fossil fuels, the use of alternative fuels in diesel engines has become inevitable. It is important to determine the mixtures of biodiesel and alcohols, which are prominent for diesel engines, that can be used safely in terms of environment and human health. To this point, contrary to regulated emissions, knowing the effects of fuels with a 15% alcohol mixture ratio accepted in the literature on PAH emissions will contribute to the safe use of these fuels. In this study, PAH emissions of biodiesel and diesel mixtures containing 15% (by volume) n-propanol, n-butanol, and n-pentanol alcohols were investigated.

The main results obtained are follows;

- Compared to diesel fuel, a significant reduction was achieved in total PAH emissions for BPro15, BBu15, BPen15, DPro15, and DBu15, respectively, with the addition of higher alcohols.

- At the same time, BPro15, BBu15, BPen15, and DPro15 fuels have come to the fore in high ring aromatic component distribution because they do not contain 5 rings.

- The reduction in toxicity of BPro15, BBu15, BPen15, DPro15, DBu15 and DPen15 provided a crucial advantage for using higher alcohols with biodiesel and diesel fuel.

This study found that mixing 15% (by vol.) -Pro, -Bu, and -Pen alcohol with diesel fuel and biodiesel reduces the PAH formation mechanism. Long-term tests on different engine types to encourage the use of blends will contribute to the determination of the PAH formation mechanisms of these fuels.

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FORMATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN A DIESEL ENGINE FUELED WITH DIESEL AND BIODIESEL CONTAINING LOW CONCENTRATIONS OF C3/C4/C5 ALCOHOLS

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Abstract

Diesel engines will be used for many years in the power generation and transportation sectors. Due to their prevalence, it has become inevitable that alternative fuels will be integrated into the fuel supply chain. Biodiesel and high carbon alcohols, which have the potential to be an alternative to diesel fuel, are tested in diesel engines. For biodiesel to be used directly in a diesel engine, fuel properties need to be improved. In addition to the regulated emissions of alternative fuels, the detection of polycyclic aromatic hydrocarbons (PAHs) is very important for both environmental health and engine durability. At this stage, it is also vital to investigate the consequences of adding alcohol to diesel or biodiesel within the mixing ratios set by the European Union (EU) and the United States of America (USA). For this purpose, in this study compares the effects of the addition of n-propanol (C3), n-butanol (C4) and n-pentanol (C5) to biodiesel (B100) and diesel (D100) at a low mixing ratio of 7.5% (by volume) on PAH emissions (total PAH, PAH dispersion, and toxicity). PAH samples were meticulously processed and extensively analysed using rigorous analytical chemistry methodology (GC-MS). With the addition of higher alcohols to diesel and biodiesel, the maximum reductions in total PAH emissions were obtained in n-propanol mixtures 92.5% Diesel+7.5% Propanol and 92.5% Biodiesel+7.5% Propanol, respectively. Similarly, n-propanol mixtures have come to the fore in reducing toxicity. This can be attributed to the effect of the high latent heat of evaporation of n-propanol and the reaction caused by fatty acid radicals. Overall, the lower use of higher alcohols in biodiesel and diesel is recommended not only for reducing overall PAH emissions and toxicity, but also for heavier PAHs, which are more carcinogenic and pose a greater risk of wet stacking problems for engine durability.

Keywords: Diesel engine, Biodiesel; n-propanol, n-butanol, n-pentanol, Unregulated emissions, Wetstacking

1 INTRODUCTION

Diesel engines, one of many petroleum-based liquid fuel engines, are not only prominent in the transit and shipping sectors, but also extensively used in the power generation industry, machinery, and other industrial sectors [1,2]. Unfortunately, diesel engines operating on petroleum diesel fuel produce higher emissions of particulate matter (PM), nitrogen oxides (NO_x), unburned carbon monoxide (CO), hydrocarbon (HC), and life cycle carbon dioxide (CO₂). In fact, diesel engines are believed to be among the largest sources of NO_x and smoke pollution [3-5]. The fact that diesel

engines will be used for many years in power generation, apart from the transportation sector, necessitates the use of alternative fuels in these engines. According to the working principle of the diesel engine, biodiesel and alcohol have come to the fore as alternative fuels [4-6].

The EU set a 10% target for renewable energy use in transport in 2020 and raised this target to 14% by 2030. This figure was doubled for advanced biofuels. Biodiesel is a strong candidate as an alternative to diesel because it can be used alone or mixed with diesel fuel and also, in large part,

due to the fact that it is biodegradable and producible from renewable feedstock. However, the potential for competitiveness between biofuel production and food supply poses a risk to food availability. The potential for increased competition for the food supply and arable land make biodiesel manufactured from inedible, or waste, oils better options for use in diesel engines [5]. Due to the fuel properties of biodiesel, it is not possible to use neat biodiesel in diesel engines for a long period. To further improve the potential of biodiesel, alcohols can be easily blended with biodiesel in various percentages to improve their performance in diesel engines [6]. Active studies have been performed to study the effects to exhaust emissions and system performance from mixing biodiesel with methanol (CH_3OH), ethanol ($\text{C}_2\text{H}_5\text{OH}$) [7,8]. Unlike low-carbon alcohols, there are limited studies using high-carbon alcohols such as n-propanol, n-butanol, and n-pentanol. These alcohols have become prominent and can be used as a mixture with diesel fuel at any rate [9,10]. The majority of the current literature has similarly found that blending these alcohols with biodiesel or diesel is expected to improve fuel properties and combustion, while reducing regulated emissions such as CO, HC, NO_x [11,12].

Although regulated emissions produced from biodiesel-alcohol and diesel-alcohol blends are well documented, unregulated emissions such as polycyclic aromatic hydrocarbons (PAHs) lack extensive research. PAHs should be considered when any new fuel is being evaluated for widespread adoption in internal combustion engines because PAHs can harm living organisms and be dangerous to engine components [13-15]. PAHs are characterized as carcinogenic by both the International Agency for Research on Cancer (IARC) and the US Environmental Protection Agency (EPA) and are of grave concern [16]. Although thousands of PAHs may exist, the EPA

has identified 17 compounds of interest. Along with the toxic effects of PAHs to living organisms, these compounds have recently been investigated for their impact on engine performance [17]. Therefore, the focal point of future biofuel research must include the assessment of PAH emissions in addition to exploring the benefits and uses of biofuels. Future research in this field must also address the concern of wet stacking, which is a condition that occurs at low engine loads because of two pertinent factors: high PAH production at low combustion temperatures and low exhaust temperatures. These conditions result in condensation of PAHs on the exhaust valve stem and seizure of the exhaust valve stem in the valve guide [18-20]. Yilmaz and Davis conducted one of the only studies that have investigated this issue to date [21]; they examined PAH formation in a diesel engine fueled with diesel, biodiesel and biodiesel/n-butanol blends. The results showed significantly lower PAHs for biodiesel and blended fuels as compared to diesel fuel. It was observed that adding 10% n-butanol to biodiesel further reduced PAHs, but that fractions above 10% produced undesirable increases in PAH formation.

A review of the current body of literature shows that high-carbon alcohols have yielded promising results regarding engine performance and emissions compared to low-carbon alcohols [22]. Yet, extensive research on its viability as a suitable component of biodiesel or diesel blends is lacking. Thus, in light of the impact of biodiesel or diesel and n-propanol, n-butanol, and n-pentanol blends on PAH production, more research is needed. With this motivation, in this study, the effects of biodiesel and diesel mixtures containing 7.5% n-propanol, n-butanol, and n-pentanol on PAH (total PAH, PAH dispersion, and toxicity) emissions were comparatively investigated in order to both improve the fuel properties of biodiesel and reduce the use of diesel fuel.

purchased from Valero), waste cooking oil biodiesel, n-propanol (CAS No:71-23-8), n-butanol (CAS No:71-36-3), and n-pentanol (CAS no:71-41-0).

The waste oil methyl ester used in this study was produced from waste cooking oil collected from restaurants. The conversion of waste cooking oil into biodiesel was performed through the transesterification process following ASTM D6751 standard. While the ratio of saturated fatty

2 MATERIALS AND METHODS

2.1 Test fuels and facility

Engine tests were performed in an indirect-injected, four-cylinder Onan DJC diesel engine. The detailed specifications of the engine are listed in Table 1, and the schematic view of the engine test facility (PAHs sampling line and test facility) is given in Figure 1. The five different fuels used in this study included standard diesel (No. 2,

acids, unsaturated fatty acids and other fatty acid components were measured as 13.28%, 81.40% and 5.32%, respectively.

Biofuel usage requirements in European Union member states are planned based on the Fuel Quality Directive (FQD) and Renewable Energy Directive II (RED II).

Table 1. Technical Specifications of Test Engine

Engine type	Onan Generator
Type	DJC
Intake system	Natural aspirated
Bore (mm)	82.55
Stroke (mm)	92.08
Displacement (cm ³)	1970
Number of cylinders	4
Number of cycles	4 cycle
Compression ratio	19:1
Max output (kW)	12
Max speed (rpm)	1800
Fuel injection system	Indirect
Injection pressure (MPa)	13.1
Injection timing (bTDC)	18 °CA

In this context, the 7.5% (by vol.) blend ratio was determined by considering the type of raw material, the producible, and accessible fuel quantities. Besides diesel fuel (D100) and waste oil biodiesel (B100), binary blends of diesel (92.5%) and biodiesel (92.5%) were prepared with 7.5% n-propanol (DC3 and BC3), n-butanol (DC4 and BC4), and n-pentanol (DC5 and BC5). Test blends were obtained by the splash-blending method, which is the most common and cheapest process.

All fuel blends were miscible and stable for the duration of the tests. The specifications of the test fuels were presented in Table 2.

Table 2. Test Fuels Specifications

Items	Density (g/ml)	Lower heating value (MJ/kg)	Cetane number	Kinematic viscosity at 40 °C (mm ² /s)	Flash point (°C)	Cloud point (°C)	CFPP (°C)
Diesel	0.818	44.8	54	2.95	74	-12	-21
Biodiesel	0.855	40.5	52	4.57	126	-8.1	-13.2
C3	0.803	30.63	12	1.74	22	-	<-51
C4	0.810	33.10	17	2.23	35	-	<-51
C5	0.815	34.94	20	2.89	49	-	-40
BC3	0.848	40.01	50.01	4.37	97.2	-10.1	-16.4
BC4	0.850	40.02	50.45	4.39	98.4	-10.3	-16.6
BC5	0.851	40.73	51.09	4.41	103.5	-9.4	-15.8
DC3	0.811	43.68	51.18	2.55	45.85	-16	-21
DC4	0.815	44.19	52.10	2.80	67.23	-17	-22
DC5	0.815	44.27	52.23	2.84	62.05	-16	-22

When the fuel properties of the blended fuels are examined, it is seen that they are close to diesel fuel. A significant improvement was obtained in the cold flow parameters (cloud point and cold filter plugging point (CFPP)) of the blends with the addition of alcohol to the biodiesel. The engine operated on neat diesel for approximately ten minutes before making a switch from diesel to blended fuels, which was used as a standard procedure to mitigate cold-start effects.

2.2 PAH Sampling Procedure

The test engine was run for three hours at idle for each fuel and in triplicate to collect PAHs. PAH emissions sample collection and analysis were determined for test fuels according to EN ISO 11338-2:2003 test standard [23]. Prior to the start of the PAH collection, the engine was started and run for at least 10 min on neat diesel to minimize cold-starting effects. The undiluted exhaust was sampled at 10 lpm through a set of collection media on which the PAHs condense. Particle-

bound PAHs were collected on a 37 mm diameter, 2 μ m pore Pall Corporation (Port Washington, NY) PTFE filter, and semi-volatile PAHs were

collected in an adsorbent resin cartridge, and the two collection mediums were connected in series as shown in the Figure 1 sampling line. run in Selected Ion Monitoring (SIM). Specifications of the GC-MS system is shown in Table 3.

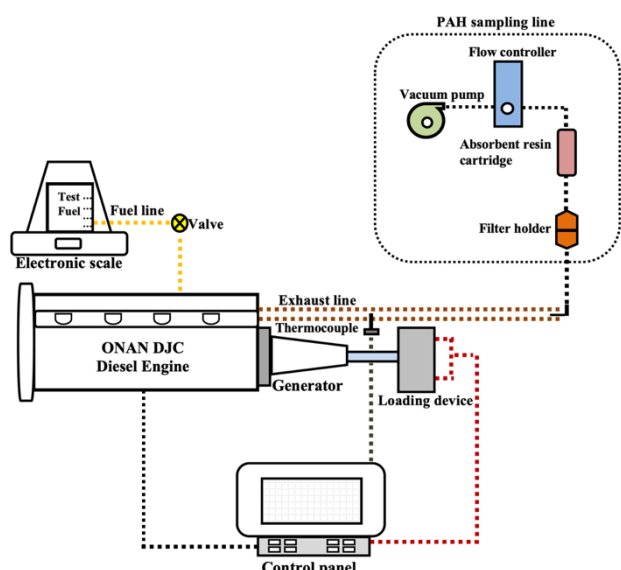


Figure 1. PAH Sampling and Test Facility

The resin cartridge was supplied by Sigma Aldrich (St. Louis, MO) and was filled with two stages of Amberlite XAD-2 adsorbent resin (50 mg/100 mg). On average, the temperature across the filter did not exceed 50 °C. The filter and cartridge after collection were then spiked with 2000 ng of anthracene- d_{10} (98%, Sigma Aldrich, St. Louis, MO) as an internal standard, and the filter and resin cartridges were extracted (separately) into 5 ml of HPLC-grade hexane (Alfa Aesar, Ward Hill, MA). The extracts were naturally aspirated through a cleanup column filled with 500 mg Na_2SO_4 /500mg alumina (Fisher Scientific, Waltham, MA). The alumina was activated at 120 °C for 24 hours prior to use. The column was washed with 5 ml of n-hexane and the PAHs were recovered by eluting with 5 ml 50/50 (vol%) benzene/acetonitrile (HPLC grade, Alfa Aesar, Ward Hill, MA).

The GC-MS analytical conditions were chosen according to the recommendations from the United States Environmental Protection Agency (US EPA) for determination of PAHs in ambient air [16]. Prior to GC-MS analysis, the samples were concentrated to 0.5 ml by N_2 blowdown under gentle heating. The solutions were then frozen at -80 °C until the sample could be analyzed. Isotope-dilution mass spectrometry was used to identify and quantify the PAHs in the samples. The specifications of the GC-MS and the program used to identify PAHs. Due to low concentrations for the analytes, the GC-MS was

Table 3. Thermal Program GC-MS

Instrument Details	GC-MS: HP 5890/5971A Column: DB5-MS
Injection Volume	1 μ L
Injection Temperature	300 °C
Thermal Program	Hold 70 ° for 1 min Heat from 70-200 °C @ 70 °C/min Hold 200 °C for 2 min Heat 200-300 °C @ 7 °C/min Hold 200 °C for 10 min

According to the World Health Organization's International Agency for Research on Cancer (IARC), and the US EPA, PAHs pose a significant risk to human health [16]. Both the IARC and EPA have specified at least 17 PAHs that are considered hazardous and possibly carcinogenic. In this study, only 10 of the 17 EPA-priority PAHs could be detected according to the detection limit. The distribution of the 10 priority PAH emissions is also shown in Table 4.

3 RESULTS AND DISCUSSIONS

The unregulated emission parameters such as change in PAH concentration, distribution, and toxicity were evaluated and compared to biodiesel and diesel fuel. Results are discussed in terms of unregulated emission parameters, with emphasis on the formation of PAHs.

3.1 PAH Concentration in Exhaust Gas

PAHs have a mixture of PAH of varying concentrations which may affect PAH dissipation differently from contamination with a single PAH. Generally, the aromatic content of a fuel is linked to the fact that fuels with aromatic components produce more PAHs than those with less aromatic content [14,17]. In order to evaluate the PAH emission of alternative fuels, total PAH emission, PAH distribution, and PAH pollutants must be analysed separately. In this context, total PAH, PAH dispersion, and PAH toxicity were evaluated and compared with alcohol mixtures of biodiesel and diesel fuel. In order to make an overall

assessment, the total PAH emissions of each fuel are considered. The PAH concentration of test fuels is given in Figure 2 and their concentrations are given in Table 4. According to Figure 2, the maximum total PAH emission was observed in diesel fuel with a concentration of $4.73 \mu\text{g}/\text{m}^3$.

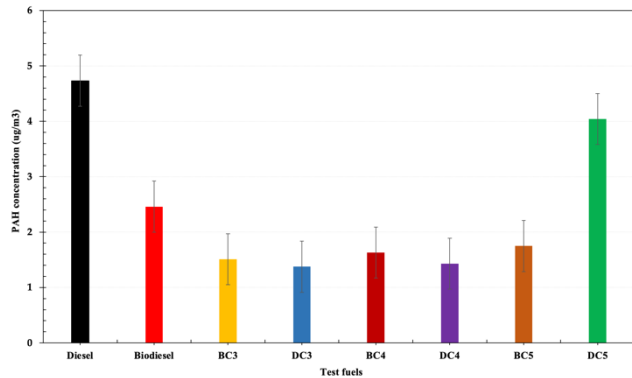


Figure 2. PAH Concentration in The Exhaust

It can also be attributed that PAHs in diesel originate from unburned diesel fuel because high temperatures favor the formation of unsubstituted aromatics and generate particles with a larger content of PAHs [24]. Additionally, there are two main ways of dealing with total PAH emissions. One is the way that PAHs in the fuel or lubricating oil are involved in the combustion process and remains there [25], and the other is the pyrosynthesis pathway where PAHs are formed or resynthesized during combustion [18]. Higher molecular weight PAHs are mainly produced during the in-cylinder combustion process, while lower molecular weight PAHs originate primarily from unburned fuel. Compared to diesel fuel, biodiesel showed a 48.02% reduction with total PAH emissions of $2.46 \mu\text{g}/\text{m}^3$. Although biodiesel is free of aromatic components, PAH formation mechanism such as Diels-Alder may be caused by combustion reactions [26-28]. According to the Diels-Alder reaction, polyunsaturated fatty esters are known to be particularly sensitive to the reactions involved in the formation of PAHs [26]. Compared to diesel, BC3, BC4, BC5, DC3, DC4, and DC5 reduced the total PAH emission by 68.09%, 65.56%, 63.02%, 70.90%, 69.79%, and 14.60%, respectively. It is understood that the PAH reducing effect of the carbon number of n-pentanol in diesel-n-pentanol mixture is weaker than the others. On the other hand, n-propanol blends performed best in reducing total PAH emissions. Like biodiesel, used alcohols do not have aromatic content, but the aforementioned

factors have caused the formation of PAHs [29-32]. Depending on the cooling of the in-cylinder temperature due to the increased alcohol content (with higher latent heat of evaporation), the engine oil residues from the previous cycle may cause PAH accumulation to be included. However, in general, with the addition of high carbon alcohol to biodiesel and diesel at this rate, a significant decrease in PAH concentration was observed. The wetstacking problem that may occur in the engine can be prevented by using 7.5% high carbon alcohols together with biodiesel and diesel fuel.

Table 4. PAH Concentration in Exhaust

PAH	Number of rings	Total PAHs ($\mu\text{g}/\text{m}^3$)							
		D100	B100	BC3	BC4	BC5	DC3	DC4	DC5
Naphthalene	2	1.93	0.76	0.81	0.73	0.81	0.228	0.35	0.512
Acenaphthylene	2	0.21	0.25	0.2	0.5	0.51	0.014	0.25	0.61
Fluorene	2	0.59	0.22	0.24	0.12	0.12	0.134	0.27	1.002
Phenanthrene	3	1.19	0.66	0.16	0.18	0.2	0.258	0.27	1.211
Fluoranthene	3	0.29	0.18	0.04	0.05	0.05	0.355	0.1	0.312
Pyrene	4	0.4	0.31	0.05	0.04	0.05	0.354	0.13	0.321
Benzo[a]anthracene	4	0.00*	0.01	0.00*	0.00*	0.00*	0.006	0.01	0.01
Chrysene	4	0.09	0.07	0.01	0.01	0.01	0.021	0.03	0.035
Benzo[k]fluoranthene	4	0.00*	0.01	0.00*	0.00*	0.00*	0.007	0.01	0.018
Benzo[a]pyrene	5	0.01	0.00*	0.00*	0.00*	0.00*	0.00*	0.01	0.011

* undetected.

3.2 Distribution of PAHs

The relative distribution of PAHs in regard to the number of aromatic rings is shown in Figure 3. Based on the molecular weight of each PAH, all 17 types of PAH compounds measured as recommended by the US EPA were analyzed in low, medium, and high molecular weight groups [16]. In this study, 10 out of 17 PAHs were detected in the test engine. Generally, most of the PAH contain two-(naphthalene, acenaphthylene, and fluorene), or three-(phenanthrene and fluoranthene) aromatic rings. Larger, four-ring PAH like pyrene and chrysene are found in lower concentration, but at concentrations substantially higher than PAH with five or more aromatic rings [29,30].

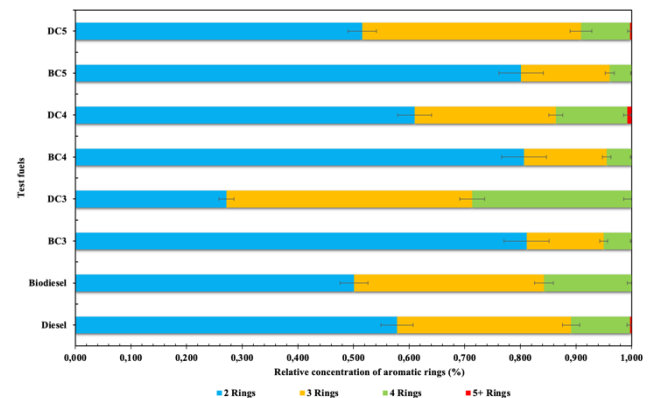


Figure 3. Relative Distribution of PAHs

As shown in Figure 3, PAHs from biodiesel, BC3, DC3, BC4, and BC5 were mostly composed of two, three and four aromatic rings. However, due to its diesel structure, it causes a 5-ring aromatic component, and DC4 and DC5 mixtures accompany the diesel with a very low 5-ring aromatic. The low molecular PAHs such as naphthalene, acenaphthylene, acenaphthene and fluorene and medium molecular weight PAHs such as phenanthrene and fluoranthene were the predominant compounds found in the exhaust for all test fuels. The formation of low PAHs is due to the pyrosynthesis of low molecular weight aromatic compounds into larger PAHs and their incorporation into the combustion processes of motor lubricant oil [31]. Therefore, the high levels of low PAHs indicate that this is due to the amount of test fuels pyrolyzed from incomplete combustion [23,24].

This inference indicates that large PAHs have higher boiling points and will therefore be more harmful than smaller compounds with lower boiling points [25,26]. When the aromatic ring distribution is considered, the addition of n-propanol to both biodiesel and diesel was detected less in high ring distribution than other alcohols. Also, when evaluated together with the total PAH emission, adding 7.5% (by vol.) C3, C4, and C5 to diesel and biodiesel reduced the PAH distribution, which could be harmful to both engine parts and human health.

3.3 Toxicity of PAH Emissions

The total carcinogenicity of collected PAHs is defined as toxic equivalent factor (TEFs) values [13,14]. BaP_{eq} is widely considered an important PAH marker for environmental assessments [25,32]. Therefore, the weighted benzo[a]pyrene equivalent (BaP_{eq}) of each PAH was calculated based on TEF. The toxicity distribution of PAH emissions is shown in Figure 4 and toxicity BaP_{eq} concentration in exhaust is given in Table 4.

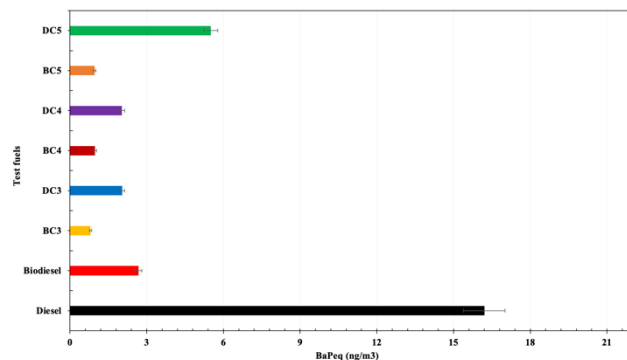


Figure 4. Toxicity of PAH emissions

Due to the chemical structure of diesel fuel, its aromatic content and incomplete combustion reaction caused toxicity. As can be observed in Figure 4 and Table 5, the highest total toxicity was detected in diesel, attributable to the five aromatic rings of Benzo[a]pyrene.

Table 5. Toxicity BaP_{eq} concentration in exhaust gas

PAH	Number of rings	Toxicity BaP _{eq} (ng/m³)							
		D100	B100	BC3	BC4	BC5	DC3	DC4	DC5
Acenaphthylene	2	0.211	0.246	0.226	0.521	0.51	0.011	0.262	0.666
Fluorene	2	0.593	0.223	0.269	0.148	0.12	0.128	0.295	1.188
Phenanthrene	3	1.194	0.66	0.178	0.187	0.22	0.251	0.282	1.511
Fluoranthene	3	0.288	0.18	0.049	0.063	0.06	0.345	0.106	0.329
Pyrene	4	0.403	0.305	0.069	0.052	0.04	0.348	0.147	0.337
Benzo[a]anthracene	4	0	0.919	0	0	0	0.861	0.853	1.244
Chrysene	4	0.094	0.065	0.01	0.01	0.01	0.021	0.032	0.032
Benzo[k]fluoranthene	4	0.046	0.077	0	0	0	0	0	0
Benzo[a]pyrene	5	13.378	0	0	0	0	0.072	0.051	0.201

Against a total value of 16.20 BaP_{eq} (ng/m³) for diesel, toxicity of 2.67, 0.80, 0.98, 0.96, 2.03, 2.02, and 5.50 BaP_{eq} (ng/m³), were found for biodiesel, BC3, BC4, BC5, DC3, DC4, and DC5, respectively. Compared to diesel, BC3, BC4, BC5, DC3, DC4, and DC5 reduced the total PAH emission by 95.05%, 93.94%, 94.07%, 87.43%, 87.48%, and 66.01%, respectively. BC3 showed the best reduction among the mixtures in total PAH emissions, similarly, it showed a greater decrease in toxicity compared to other mixtures. These reductions are due to the very low level of PAH and its chemical structure, which affects BaP_{eq} in these blends [27,32]. Acenaphthylene, fluorene, phenanthrene and fluoranthene are the four detected PAHs for all of the test fuels, and among these PAHs, BC3 has the minimum values of the BaP_{eq} (0.80 ng/m³). Thus, there is a clear reduction in the overall toxicity of the blended fuels used in this study, over biodiesel and diesel. Accordingly, n-propanol blends are indicated as the best option among the other blended fuels in terms of toxicity reduction.

4 CONCLUSIONS

Biodiesel and higher alcohols will be indispensable alternative fuel source for diesel engines in the near future. At this point, knowing the pollutants that will occur with the use of biodiesel and alcohol together in a diesel engine is very important for protecting human health and prolonging the working life of the engine. Although previous studies on biodiesel or diesel and higher alcohol blends have examined regulated emissions, there is a lack of scientific study on unregulated PAH emissions. To fill this gap, the PAH emissions produced by the addition of 7.5% (by volume) of n-propanol, n-butanol, and n-pentanol to diesel fuel and biodiesel in a diesel engine were investigated. Based on the results presented in this study, the following conclusions can be drawn:

- A significant improvement was observed in the cold flow parameters of the blends with the addition of alcohol to the biodiesel.
- Compared to diesel, BC3, BC4, BC5, DC3, DC4, and DC5 reduced the total PAH emission and toxicity. n-propanol blends performed best in reducing total PAH emissions and toxicity.

It is concluded that 7.5% higher alcohol addition to biodiesel or diesel decreased total PAHs, total BaP_{eq} and the amount of higher-ring PAHs in the exhaust. It has also been revealed that the combustion process affects the production of PAHs, even if the base fuel may be free of aromatic content in its chemical structure. Overall, the blends can be used as alternatives for reduction of carcinogenic pollutants and elimination of possible wet stacking in diesel engines operating at low load or cold operating conditions.

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OBSTACLES AND NEW TECHNOLOGIES RELATED TO HYDROGEN POWERED JET ENGINES

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Abstract

This paper summarizes the challenges and recent technologies associated with the development of hydrogen powered jet engines. To meet the 2015 Paris Agreement sustainability goals, the world must reduce CO₂ emissions to keep global temperatures below 2 °C from preindustrial revolution levels. One solution towards a greener aviation sector is replacing traditional aviation fuels such as Jet A with liquefied hydrogen (LH₂). The history of hydrogen as an aviation fuel was investigated from 1954 to 2024, as well as the various challenges such as nitrous oxides (NO_x) emissions, green hydrogen production, combustion, hydrogen storage and hydrogen embrittlement. A review of research relevant to the development of hydrogen powered jet engines was performed; advances in sustainable hydrogen production, infrastructure, hydrogen storage tanks and the improved ductility and strength of equiatomic alloys in hydrogen environments were investigated. Finally, recent developments in the areas of aircraft design and hybrid electric-hydrogen jet engines are discussed. This paper concludes that while hydrogen powered jet engines are a nascent technology, this is a promising fuel for the aircraft of the mid-21st Century.

Keywords: Hydrogen, Jet Engine, Sustainable Aviation

1 INTRODUCTION

In the 21st century the use of fossil fuels is no longer sustainable and within the next 200 years resources such as coal, oil and natural gas are expected to be depleted [1]. Hydrogen has been brought to the attention of both the industrial and scientific community as an alternative energy carrier. Hydrogen boasts a combustion energy of over 140 MJ/kg which is over three times the combustion energy of gasoline, this fuel has the potential to become the energy carrier of the future [2]. The commercial aviation industry has been a leader in reducing the greenhouse gas emissions and for several years has conducted research to maintain its leadership in sustainability. One of these research areas is in the technology of hydrogen powered jet engines. Aircraft powered by hydrogen would produce no CO₂ and reduced NO_x emissions [3]. Hydrogen has been investigated as a fuel source for decades with one of the earliest research projects being performed in 1954 under NACA, known today as NASA [4]. In the 1970s

Lockheed-Martin was tasked by NASA Langley Research Center to investigate the feasibility of a subsonic hydrogen fuelled commercial aircraft. By the end of the decade, Lockheed-Martin completed their study and found a short-range hydrogen powered aircraft was feasible. Between 2000 and 2002 the Cryo Plane concept from Airbus was investigated and found that hydrogen powered jet engines were just as safe as traditional aircraft, while reducing CO₂ and NO_x emissions [5-7]. Recently Airbus has been developing hydrogen combustion engines working in tandem with hydrogen fuel cells. Decades of investigations imply the promise of hydrogen fuelled aircraft.

2 HYDROGEN PRODUCTION

Sustainable production of hydrogen is critical for making these aircraft a reality. Currently, hydrogen production is color coded with grey, blue, green and purple as the main colors. Today the majority of the worlds hydrogen comes from grey hydrogen - fossil fuel-based hydrogen [8]. Most grey hydrogen is produced from coal

gasification and steam methane reforming. In coal gasification, coal is heated in a low oxygen environment producing hydrogen, carbon dioxide, carbon monoxide and other gases. In steam methane reforming, methane is chemically reacted with steam or cracked to form hydrogen, carbon dioxide and other gases. Fossil fuel-based methods that incorporate carbon sequestration technology to prevent greenhouse gas emissions are categorized as blue hydrogen [8]. Hydrogen made from nuclear power is classified as purple hydrogen. Either electrolysis or thermochemical reactions can be used in nuclear hydrogen production. In thermochemical reactions the heat from the nuclear reactor initiates a chemical reaction that splits water into hydrogen and oxygen [8]. It is suggested that during drops in nuclear energy demand power can be used to create hydrogen. This technology is limited by the corrosion and high temperature performance of nuclear materials [9]. Electrolysis utilizing the conventional steam turbine method of producing electricity can be applied to splitting water into hydrogen and oxygen through PEM (polymer electrolyte membrane) fuel cells [10]. Green hydrogen which is common in the literature uses renewable energy sources such as biomass, hydro, solar or wind energy to generate hydrogen [8-10]. Biomass uses a chemical reaction of heated biomaterials to produce hydrogen and other gases, this requires low water content and often has lower yields regardless of the source of biological materials used [8]. Hydro, solar and wind energy can be used to generate electricity for electrolysis using PEM methods [8-10]. Of these three methods, solar has more options for hydrogen production such as solar photovoltaic and solar thermal. In the short-term blue hydrogen utilizing mature technology will dominate but if solar, biomass and nuclear mature; green and purple hydrogen will gain more market share. Liquefaction of hydrogen requires a significant fraction of energy obtained

from combustion [11]. Establishment of an economical infrastructure within the supply chain and at airports is needed to realize a true hydrogen economy in aviation.

3 INFRACSTRUCTURE

To make hydrogen powered jet engines feasible the aviation fuel infrastructure will need major adjustments [12]. While there are a variety of ways to produce hydrogen it is necessary to reduce the cost of the transportation of hydrogen. Liquefied hydrogen can travel short distances via trucks [13-14]. There are limits to the volume of hydrogen that can be transported in this manner. To improve this, it is possible to transport hydrogen as metal hydrides. These metal hydrides can contain 1%-2% of their mass as hydrogen, resulting in increased amounts hydrogen that can be transported via trucks at the cost of a greater payload carried by the truck [12-14]. Releasing hydrogen from metal hydrides only requires heat. This gas would then need to be liquefied to be used as fuel. For larger distances it is possible to use pipelines to transport hydrogen in low concentrations with natural gas [12-14]. Also, hydrogen can be cracked from ammonia which is safer than liquid hydrogen and allows for overseas shipments. Due to the tendency for LH_2 to boil off onsite production will likely be needed. In 2002, D. Kramer mentioned that even smaller airports can produce at least 200kg of LH_2 per day [15]. Specialized equipment will be needed to ensure that hydrogen fuel is not leaked, and this fuel must maintain a specific temperature range [16]. LH_2 has a four-fold greater volume requirement than gasoline which would reduce space available at airports [17]. Some European airports are experimenting with the production of hydrogen on site, which may lead to more improvements in infrastructure [18].

4 LH₂ STORAGE

The storage of LH₂ within the aircraft is a challenge that must be overcome prior to the adoption of this technology [19]. In 1955 Silverstein and Hall proposed storing hydrogen within the wings of a bomber type military aircraft. The tanks would have been composed of stainless steel, foam and aluminum foil for reflecting thermal radiation. While this design showed promise for a 1950's military aircraft it is not conducive to commercial aircraft because of different requirements of civilian aviation [19]. In 2013, Verstraete suggested storing the high pressurized LH₂ fuel tanks within the front and rear ends of the fuselage [20]. By storing the fuel within the fuselage rather than the wings there is less exposure of the hydrogen fuel tanks to damage and the structural members of the aircraft will provide increased safety to the passengers [20]. One undesirable effect with fuel located in the rear and front of the cabin is that payload and passenger seating will be reduced. This significant change in fuel storage will require drastic modifications to the design of the aircraft. With the fuel no longer stored in the wings, as with traditional aircraft, the wing area for hydrogen powered jet engines could decrease having deleterious effects on the aerodynamic efficiency of the aircraft. The bulky storage tanks within the cabin will result in a similar weight as traditionally fueled aircraft, however due to the lower fuel weight nearly a 10% reduction in energy utilization can be expected which may offset the negative impact of this change [20].

5 COMBUSTION

As a fuel source LH₂ fuels produce water as a byproduct of combustion rather than CO₂ resulting in a greater specific thrust than traditional aviation fuels while reducing greenhouse gas emissions [19-20]. The hardware requirements of LH₂ jet engines are similar enough that hydrogen can be used as a fuel in the commercial

aircraft of the today with relatively minor modifications [21-25]. Water vapor from combustion at low altitudes will precipitate as rain, however, its effects at higher altitudes is less understood. When traditional fuel is burned in air various nitrous oxides will be produced in the combustion process, yet this is minimized with hydrogen combustion [21-22]. This is because hydrogen can burn at a lower temperature than Jet A so less of the nitrogen in the air is converted into NO_x. Hydrogen can also experience flameless combustion at high temperatures in low oxygen environments this can be achieved with the use of two combustion chambers [22]. Combustion in low oxygen environments also translates into fewer NO_x emissions when compared to traditional jet fuels, providing more design options for reducing emissions. Due to the cryogenic nature of LH₂ the fuel can be warmed through a cooling system to reach gaseous hydrogen temperatures prior to combustion while reducing engine temperature through heat exchangers. The development of fuel injectors for gaseous hydrogen into the combustion chamber would result in nearly uniform temperatures within the combustion chamber due to increased mixing again resulting in less NO_x emissions [23-25]. A systematic comparison of multiple heat exchangers for LH₂ engines is a current gap in the literature. While ground testing performance appears promising, the influence of altitudes is not well documented in the open literature.

6 HYDROGEN EMBRITTLEMENT

Inside the engine, temperatures in the range of 1000K to 2500K can be expected. A reaction between hydrogen gas and the alloys used in the hot section of the jet engine may compromise the mechanical properties through hydrogen embrittlement [23]. Hydrogen embrittlement was discovered by William H. Johnson in 1875 while investigating the effects of various

acids on iron and steel wires, he noted a reduction in the ductility and strength of these alloys [26]. While the mechanisms of hydrogen embrittlement are still debated and are driven by different phenomena, what is common is the deleterious influence of hydrogen within the metal matrix. The microstructural features such as grain boundaries, precipitates or carbides act as traps for hydrogen [26-29]. These traps impede the motion of hydrogen and reduce the material's ability to facilitate the motion of dislocations which reduces plasticity. As a result, the tensile and fatigue strength of an alloy can be drastically reduced. In 2015, Rezende and colleagues found that hydrogen travels with dislocations so excessive deformation can make an alloy more sensitive to hydrogen embrittlement. Alloys that are traditionally, used to transport hydrogen are typically low or medium alloy steels and austenitic stainless steels. For these alloys there are fewer microstructural features such as carbides to trap the hydrogen allowing improved plasticity and fatigue performance [30-31]. Temperature also influences hydrogen embrittlement, at high temperatures hydrogen can more easily diffuse into metals while at low temperatures this diffusion is significantly impeded. Since the motion of hydrogen atoms is slowed, they are less likely to penetrate beyond the surface and affect the bulk properties of the LH₂ fuel tanks [31]. It is noted that for various alloys such as steels temperatures between -70C and 30C are known to have increased susceptibility through an unexplained mechanism. To implement hydrogen powered jet engines into the aviation industry, the development hydrogen resistant alloys for the hot section of the engine that have good fatigue life and creep resistance is needed [32].

7 HYDROGEN ENGINE MATERIALS

Currently, nickel superalloys such as Inconel 625 are used for turbine disks and blades for commercial jet engines. At the

elevated temperatures experienced during combustion, the material for the turbine must possess mechanical properties that allow it to endure the stresses associated with rotating at over 10,000 rpm [23-26]. In 2021, Osigwe et al. compared the creep performance of an Inconel 625 in the conditions of burning Jet A and hydrogen. The results found that hydrogen reduced the oxygen required and temperature needed for combustion. This in addition to the reduced mass flow rate, associated with a lower LHV (Lower Heating Value) for hydrogen jet engines, showed improved thrust and better creep performance over their Jet A counterparts which require higher temperatures [25]. From a creep life perspective there is a potential for the reduction in maintenance downtime of jet engine components when hydrogen is used as the fuel. However, the effect of hydrogen embrittlement still needs to be investigated. Some of the mechanical properties that are important for turbine discs are tensile strength, creep and fatigue performance. In a 2015 publication, Rezende et al. presented that in Inconel 718, another nickel superalloy used in aviation, the δ , γ and γ' precipitates which are often added for enhanced strength act as traps for hydrogen. This means that if a hydrogen atom diffuses into the alloy these precipitates rather than adding strength drive hydrogen embrittlement. This problem is more prevalent at elevated temperatures [28]. Studies on the fatigue performance of gas turbine engines burning hydrogen is a challenge that needs to be addressed. Most alloys are susceptible to hydrogen embrittlement but at the elevated temperatures within a jet engine a greater propensity for this phenomenon can be expected. Thus, material selection for hydrogen jet engine components will be an important factor for the future of this technology. High entropy alloys (HEA) also known as equiatomic alloys such as Cantor's alloy have been shown to increase both strength and ductility for certain concentrations of

hydrogen at ambient temperatures. In a 2017 paper, Luo, H. et al found that Cantor's Alloy, a high entropy alloy, increased in strength by approximately 50 MPa and increased in ductility by approximately 2%-5% when charged with hydrogen during tensile testing [13]. This study indicates that for these FCC high entropy alloys hydrogen improves mechanical performance. In 2017, Zhao, Y. et al. described the performance of a CoCrFeMnNi alloy, another HEA, that experienced a negligible reduction in both strength and ductility when charged with hydrogen [33]. These findings are promising yet more research at elevated temperatures, cyclic loading and hydrogen atmospheres comparable to what would be within a hydrogen powered jet engine are needed. For these studies to drive change in the aviation standardized methods of testing alloys in a hydrogen environment need to be developed [30-33].

8 HYDROGEN-ELECTRIC ENGINES

Hybrid electric technology incorporated with LH₂ jet engines will result in the need for less fuel than hydrogen powered jet engines. The power requirements for an aircraft vary from take-off, cruise and landing [34]. Utilizing electric batteries or a PEM fuel cell has the advantage of some of the power needed to drive the turbofans being provided by electricity [34-35]. A PEM fuel cell can use heated LH₂ or gaseous hydrogen to charge the fuel cell [23]. Currently, hybrid jet engines are being developed and this technology is near term. It is well known that fuel tanks within a LH₂ jet will need greater volume than their fossil fuel counterparts. Utilizing PEM fuel cells with the jet engine will require less fuel thus saving space in the

aircraft for increased payload or passenger capacity. There is an added potential for decreasing the fuel infrastructure demands at airports that support hydrogen powered jet engines. A systematic review of the hybrid-hydrogen-electric jet engine concepts and their influence in airport infrastructure is needed in the open literature.

9 CONCLUSIONS

This article identified the rising challenges of infrastructure, storage, combustion, materials and aircraft design associated with hydrogen powered jet engines. The development of hybrid electric jet engines was found to be useful in creating technologies that would support this revolution in aviation fuel. Combustion at high altitudes was identified as a gap in the research, along with a lack of standards for mechanical testing materials for hydrogen environments and continued work in the redesign of aircraft for hydrogen fuel [30]. While the literature found current engine technology could potentially burn hydrogen insufficient studies of the fatigue performance at elevated temperatures in hydrogen environments were identified. High entropy alloys show the promise of good or improved performance in hydrogen environments, but they need to be tested at engine temperatures. As more technologies advance in the fields of hydrogen production, cryogenic storage, infrastructure, combustion, materials science and aircraft design the potential future of hydrogen powered jet engine in the mid-21st Century appears more feasible.

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ENERGY SOURCE OF THE NEAR FUTURE: GASHYDRATE RESEARCH

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Abstract

The cementing effect of gas hydrates in sedimentary pores renders them suitable as seal rocks, allowing methane to accumulate beneath them. The accumulation of free gas beneath numerous gas hydrate zones has been observed, with the gas column reaching a thickness of 200–300 m. Therefore, the formation of gas hydrates may be indicative of the presence of hydrocarbons at depth. The presence of substantial gas hydrate accumulations serves as a valuable indicator for deep hydrocarbon exploration. The oil industry and governments around the world have commenced the exploration of gas hydrates, ice-like energy minerals that contain hydrocarbon gases in cold, deep water and permafrost areas. In the current century, conventional oil and gas production will enter a continuous decline. Some energy companies, with long-term projects, have initiated research into alternative energy sources, with the aim of developing a sustainable energy future. A further advantage is that the gas hydrates increases energy security and strengthens Turkey's influence in the region. The strengthening of the natural gas industry is a consequence of the aforementioned factors. The existing infrastructure is developed by increasing the network capacity. Consequently, the utilisation of gas hydrates will have a profound impact on both the economy and the energy sector.

Keywords: Gas Hydrates, Energy, Oil Gas Industry, Geophysics

1 INTRODUCTION

The Black Sea is situated in close proximity to two of the world's oldest oil fields, namely the Indolo Kuban basin and the Moesian Platform. This geographical location has led to the Black Sea being identified as a potential candidate for becoming one of the most important hydrocarbon areas in the world, given the presence of methane and oil seeps. Furthermore, the Eastern Mediterranean and the Sea of Marmara also have this potential. Marine gas hydrate accumulations, both methane hydrate and methane gas with it, are found in very large areas. The majority of the world's hydrates are situated beneath the deep seabed, encompassing vast areas of thousands of square kilometers. The oil industry and governments around the world have commenced the exploration of gas hydrates, ice-like energy minerals that contain hydrocarbon gases in cold, deep water. In the current century, conventional oil and gas production will enter a continuous decline. It seems plausible to suggest that gas hydrates may become the world's future energy source as oil and natural gas reserves depleted. Methane gas has been identified as a promising starting point for the synthesis of complex molecular materials that can be utilized as liquid fuels. The United States government has increased

its investment in research and development of gas hydrates, as well as defining roadmaps for further investigation. A number of major oil companies have already initiated a series of measures in anticipation of the potential future scarcity of oil. Other countries, including the USA, Japan, Russia, China, France, South Korea, India, and Germany, are also becoming increasingly active in this field, with research being conducted at universities. A number of scientific projects, including LOTUS, OMEGA, GASHYDAT, HYDRATECH, MEGHA, SUGAR and others, have already commenced in various European countries, with ongoing research activities. Although there is considerable uncertainty regarding the global distribution of gas hydrate deposits, it is believed that the total volume of gas hydrate in the world is between 3700 trillion m³ and 10,000,000 trillion m³.

Methane hydrates are of significance in both Earth sciences and economics for three reasons. Firstly, the production and migration of methane in sediments can result in the formation of tsunamis. Secondly, methane seeps can serve as direct indicators of the presence of hydrocarbon reserves at depth and can also act as effective cover layers for hydrocarbons. Thirdly, methane hydrates themselves can be an important source of energy. Consequently, gas hydrates can be formed by

natural gas seams and other oil and gas outflows. In addition to its role as a source of energy, natural gas hydrate contains a high concentration of methane, which has the potential to significantly impact climate change on a global scale. This is due to the fact that methane is 20 times more effective than carbon dioxide in warming the atmosphere.

2 GASHYDRATE RESEARCH

It is of significant economic value to identify the leakage of gas and oil, which can serve as a primary indicator in the field of hydrocarbon exploration. Additionally, the identification of dense gas outflow channels on the seabed, which are the cause of such leakage, is of great importance. Such marine geophysical exploration researches are conducted with considerable financial resources on a global scale. The detection of the signature of gas hydrates on seismic sections represents the most significant indicator of the presence of oil and gas in the deep, with the image specific to gas hydrates. Prior to drilling, the presence of gas hydrates represents one of the most crucial parameters in the detection of hydrocarbons. The financial implications of a single offshore drilling operation are estimated to be in the region of 100 million dollars. At another crucial juncture, the presence of oil and gas in the Egyptian offshore field was identified through the discovering of structures such as mud volcanoes, gas and liquid deposits (pockmarks), which commenced with gas hydrate research.

The most important step for gas hydrate studies in our country is the establishment of the Seismic Laboratory (SeisLab), which includes a multi-channel seismic reflection system and a range of geophysical acoustic systems, on board the research vessel Koca Piri Reis. The objective of this initiative is to determine the existence and map the distribution of natural gas hydrate accumulations in all seas surrounding our country, with a particular focus on the eastern Black Sea. This endeavor will leverage the resources of SPO, TÜBİTAK, EU framework projects, BAP and other project resources. In order to advance the field of gas hydrate research, it is necessary to have access to multiple research vessels capable of operating in the oceans. Furthermore, the opening of polar regions to exploitation of living and non-living resources is imminent. It is therefore

evident that only those countries with research bases will be able to benefit from the exploitation of the vast methane deposits in the polar regions..

2.1 General Characteristics

Non-conventional energy sources include, but are not limited to, gas hydrates, shale gas, coal gas, geothermal energy, solar, and wind. In a scenario projected from the past to the future with a general overview in terms of resource and energy capacity, it can be observed that oil and coal begin to decline in terms of installed power capacity in 2025. Subsequently, the utilization of natural gas increases in a linear manner, with the prediction that it will retain its leading position in the 2040s. Gas hydrates are ice-like crystalline solids formed by the trapping of water molecules and low-molecular-weight gases in a lattice. They are formed under conditions of high pressure and low temperature, and typically contain methane gas, the principal component of natural gas. It can be defined as a distinct variant of the contemporary shale gas extraction process conducted on the seabed.

The general characteristics of gas hydrates can be divided into four basic elements, with secondary factors playing a role in the formation of gas hydrates. The essential conditions for the formation of gas hydrates are high pressure and low temperature, in addition to the presence of water and natural gas. The most notable characteristic of gas hydrates is that a cubic meter of hydrate contains approximately 164 cubic meters of natural gas, with the remaining volume comprising water. The most common hydrate-forming gases are methane, ethane, propane, nitrogen, and hydrogen. The water molecules are connected among themselves by hydrogen bonds, forming a cage-like structure with large cavities. The gas molecules (ethane, propane, butane, isobutane, nitrogen, carbon dioxide and hydrogen sulphide) settle in these cavities and connect with the cage they are in by van der Waals forces. A number of distinct hydrate crystal structures have been identified. The abundance of natural gas (methane) hydrates in the seas is such that they could meet the world's energy needs for centuries.

Distribution

Gas hydrates are distributed in a wide variety of locations, including passive and active continental margins, deep waters of marginal seas, polar areas and accretionary wedges of continental margins.

Gas hydrates are not commonly found in deep basins in ocean trenches, but do occur in inland and marginal seas, continental slopes and shelves. Shallow gas accumulations are frequently observed in association with pockmarks, gas seeps, mud volcanoes and gas hydrates, often accompanied by cold seep communities and methane-derived carbonate accumulations. The formation of gas hydrates in marine or onshore environments is contingent upon the presence of elevated methane gas production and favorable thermobaric conditions. It is anticipated that gas hydrates will become a significant source of energy in the future, given their substantial methane content. Due to their capacity to store vast quantities of gas in the solid phase, gas hydrates are regarded as a prospective energy source.

Greenhouse Effect

Furthermore, methane gas, which has a greenhouse effect, can play an important role in long-term global climate change when large amounts of methane gas stored in gas hydrates are suddenly discharged. This is because the sudden release of methane gas can create a large-scale greenhouse effect. Although hydrocarbon gases such as ethane, propane, butane or non-hydrocarbon gases such as CO₂, H₂S can be found in the composition of gas hydrates, methane is the most common hydrate-forming gas. Methane gas is stored in the intergranular spaces of sediments, which can be composed of a variety of host environments, including sand, clay, silt, etc. These sediments can then form a range of hydrate structures, including lumps, strips, layers, and massive structures, which can be up to several tens meters thick.

The seismic sections collected in the Black Sea reveal the presence of acoustic voids, acoustic turbidity, mud volcanoes, mud diapirs, gas pockets, gas chimneys, and other phenomena. These observations can be attributed to the free gas present below the BSR level in the gas hydrate areas, as well as the upward migration of these gases and liquids and leakage to the surface.

The cementing effect of gas hydrates in sedimentary pores renders them suitable as seal rocks, allowing methane to accumulate beneath them. The accumulation of free gas beneath numerous gas hydrate zones has been observed, with the gas column reaching a thickness of 200–300 m. Therefore, the formation of gas hydrates

may be indicative of the presence of hydrocarbons at depth. The thickness of the gas column beneath the hydrate zone may be contingent upon the current activity of the Deepwater petroleum system. Consequently, the presence of substantial gas hydrate accumulations serves as a valuable indicator for deep hydrocarbon exploration.

Upon dissociation of gas hydrates, the methane gas released into the water column reduces the density of the water. This results in a reduction in buoyancy, thereby impairing the ability of ships to maintain their position in the water. Furthermore, gas hydrates can decompose explosively when the pressure drops rapidly or the temperature rises rapidly. Furthermore, gas hydrates can impede the flow of natural gas through subsea pipelines and present a potential risk in offshore drilling operations. Furthermore, hydrates may be considered in the future as an alternative approach for transporting large quantities of gas over long distances from gas production fields to consumption areas.

Importance of Gas Hydrates

The importance of gas hydrates, both economically and geophysically, can be demonstrated by the following facts:

1. One square meter of gas hydrate contains 164 square meters of natural gas, which is regarded as an important energy source in the near future.
2. It is distinguished by its ability to accumulate oil and gas beneath it, acting as a reservoir layer.
3. The presence of gas hydrate is often sign of the presence of deeper gas and oil deposits.
4. The gas is released into the atmosphere 22 times more frequently than carbon dioxide when it transitions from a solid to a gaseous state. Therefore, the consumption or removal of this gas will have a significant impact on the climate.
5. The gas has a positive effect on ground hazards on structures such as pipelines, oil and natural gas platforms under the sea by preventing landslides by acting as a cement on the seabed. In geophysical seismic data, the BSR layer (Bottom Simulating Reflector), which resembles the seabed, is the signature in geophysical seismic data and indicates the bottom of the gas hydrate. Geophysical seismic data is the basis of all gas hydrate exploration and mapping studies conducted in marine environments worldwide.



Figure 1. The illustration depicts an example of a gas hydrate sampled from the seabed and designated as "burning ice," "zipped gas," or "flaming ice."

2.2 Geographical Regions

The species is distributed across a range of geographical regions, including both terrestrial and marine habitats. It is particularly prevalent in polar regions, although it can also be found in coastal and continental shelf waters. Furthermore, it is also prevalent in the Black Sea and the Mediterranean. It is estimated that the amount of technically producible gas hydrate in the Black Sea is 4.6 trillion m³, while in the Mediterranean Sea it is approximately 7.4 trillion m³. The Black Sea deposits are located in more challenging environments than those in the Mediterranean. Technical analyses and evaluations indicate that 12 billion m³ of gas can be produced annually from Black Sea hydrates, while 18 billion m³ of gas can be produced from Mediterranean hydrates. The potential of gas hydrates in the world is approximately twice that of total carbon deposits and approximately 50 times that of all oil and natural gas reserves. Gas hydrate is a natural gas that has been compressed 164 times into a different form. The objective set for today corresponds to the existence of vast reserves in accessible polar regions and the deep sea environment.

2.3 Recent Studies

The preceding overview of recent studies conducted globally on gas hydrates demonstrates their significance in the future of energy and climate change. A geographical analysis reveals that Messoyakha in Western Siberia is the location

where the initial production was initiated, the initial production trials were conducted in Alaska on land, and the Nankai trough continues to be a significant site for the first production in the sea. The Gulf of Mexico is the most renowned oil and gas-producing gulf, while the Gulf of Angola is the latest oil and gas-producing area.

In 2013, Japan initiated the first commercial production of gas hydrates from the marine area, achieving a successful outcome. In evaluating Japan's success in the production of methane hydrates and its implications for the global energy future, gas hydrates are discussed in conjunction with key terms such as electricity, energy security, and geopolitics. Following the successful production of gas hydrates in Japan, the country declared that it had finally obtained an indigenous energy source. The production of methane hydrates from the seabed represents a world first. The daily production has increased exponentially, from 20,000 cubic meters to hundreds of millions of cubic meters. Following the successful implementation of the seabed production technology in Japan, the US Department of Energy revised its 2006 roadmap in June 2013. The US Department of Energy provides an annual report to the Senate on the country's activities in the field of gas hydrates. The briefings include a roadmap for methane hydrate research beyond 2020, which presents research priorities and strategies to maintain the US as the unrivalled global leader in natural gas hydrates. Additionally, the briefings discuss priorities for the commercialization of gas hydrates, which is important for enhancing long-term national energy security.

The distribution of gas hydrates is relatively more evenly dispersed across the globe. In terms of global reserves, it is fortunate that this resource is found in three of our seas: the Mediterranean, the Black Sea and the Marmara Sea. These are located within our economic zones, in close proximity to our coastlines. The presence of gas hydrates in the Aegean Sea can be mapped through the use of geophysical seismic studies. When examining the discoveries and areas of gas hydrates and free gas in the Eastern Mediterranean, it is evident that gas hydrate areas were identified prior to the discovery of natural gas. There is a degree of overlap between the locations of gas and oil fields and those where gas hydrates have been observed and sampled. This includes areas such as mud

volcanoes and gas outflows, as well as structures and living organisms. In the eastern Mediterranean, the Zohar deposit in the Nile delta offshore Egypt represents the largest natural gas deposit, while oil has also been discovered in the south. In 1970, the accidental discovery of hydrate-supported gas production was made at Messoyakha in Western Siberia. In 1970, industry-based production tests were initiated. In 1998 and 2002, thermal formation and pressure production tests were conducted in Canada. In 2007 and 2008, BP and the Ministry of Energy conducted formation pressure production tests. In 2011-2012, Conoco Phillips conducted carbon dioxide and gas displacement tests on land, which were successful. In 2013, the Nankai trough offshore Japan was successfully tested, followed by a trial in the South China Sea in 2017, and a longer-term production trial in 2017. Between 2017 and 2019, Japan conducted further production trials with depressurization. India also undertook offshore gas production from gas hydrates with depressurization between 2018 and 2019. Additionally, geophysical integrated projects were conducted in five areas, drilling studies were carried out in two areas, and a scientific and operational plan was developed in the third area. Production plans are scheduled to commence after 2022. In 2022, the USA initiated a new drilling programme, in addition to a research, exploration and production technologies programme in deep waters in the Gulf of Mexico, commencing in April and May 2023.

To date, three methods of gas production from gas hydrates have been demonstrated to be successful: thermal induction, pressure reduction and chemical injection. The relative merits and drawbacks of gas hydrate production methods, such as chemical injection with heating and pressure reduction with heating of the well wall, vary according to the specific circumstances. In response to these variations, new methods, including the gas injection method, microbiology method, and ultrasonic wave stimulation method, have been introduced.

2.4 What were the origins of the research and pilot projects on the utilization of gas hydrates in Turkey?

Although some publications and studies have been made with the evaluation of collected seismic data, research within a programme was initiated at a later stage.

In August 1991, within the framework of the UNESCO-supported Training-through-Research Programme (TTR), Turkish scientists participated in this project with the research vessel *Gelincik* during the Black Sea cruises. The objective was to sample gas hydrates while discovering structures such as mud volcanoes erupting gas and liquid. Subsequently, the project focused on gas hydrate studies in international waters in 1995, 1996, 1998, 2000 and 2004. In order to navigate the new field, our country has taken steps to determine the reserve areas. In order to achieve this goal, two projects were initiated: firstly, a TUBITAK project and secondly, the "State Planning Organisation's (SPO) Advanced Research Project No. 2003K120360", which was planned and carried out by the author for the purpose of researching gas hydrates in all our seas. This infrastructure, which is unique in Turkey and ranks high in the world, has been implemented. In 2007, the "State Planning Organization (SPO) 2007K120740 numbered Çakabey Research Vessel Advanced Research Project" was accepted. The primary objective of this project is to conduct research on gas hydrates in both the Turkish and global seas.

In 2012, BSR structures, mud volcanoes, mud diapirs, gas seeps, and other phenomena associated with shallow gas reserves under gas hydrate were observed during TUBITAK-supported exploration offshore Trabzon. Furthermore, the existence of gas hydrate in the offshore TTR expedition between Turkey and Georgia was proven. The mud volcanoes that were identified for the first time in the area were named the Izmir and Pusan Mud Volcanoes. The feeding channel of the mud volcano is observed to exhibit acoustic masking, with the layers descending due to a decrease in velocity at the center and subsequent collapse following eruption. The high amplitude reflections observed at the peak are interpreted as BSR. Previous studies have commonly employed the sampling of gas hydrates in mud volcanoes.

In 2013, Germany concentrated its efforts on the development of "MeBo&Coil Tube drilling" technology for the production of gas hydrates, given the limited extent of its maritime economic zone. In the German SUGAR (Submarine Gas hydrate Reservoir) project for the exploration, production and transportation of marine gas hydrates, marine geophysical studies were

conducted on the Maria S Marian research vessel in the Danube delta offshore Romania and Bulgaria. The sampling and production systems developed were tested with the geophysical seismic data collected. The significance of this region is twofold. Firstly, this marks the inaugural instance of Turkish researchers conducting a PhD study on gas hydrates by collecting geophysical seismic data beyond the boundaries of Turkish territorial waters. Secondly, the area is situated in close proximity to the Danube 1 natural gas discovery zone.

The initial phase of the "National Gas Hydrate Project" was successfully concluded between 2014 and 2018 in a pilot area of Turkey. This was achieved following the author's involvement in numerous projects, including the TUBITAK-supported İğneada and Sakarya areas and the EU-supported Kızılırmak and Yeşilirmak areas.

Although marine gas hydrate deposits are not particularly prevalent in certain areas of the European Union's territorial waters, the European Cooperation in Science and Technology (COST) has supported the MIGRATE project, which aims to explore the potential of marine gas hydrates as a source of indigenous natural gas for Europe. The project "Marine gas hydrate-an indigenous resource of natural gas for Europe (MIGRATE)" was undertaken in collaboration with Turkish scientists.

Türkiye Petrolleri A.O. has engaged in collaborative research with Turkish scientists between 2004 and 2005 and between 2014 and 2019.

3 CONCLUSION

China has maintained a highly active programme, with the addition of four further fields to the original six. In this relatively nascent field, leading countries are investing significant financial resources in research.

A research institute specializing in energy has identified Asia as the region at the forefront of the emerging gas hydrate-to-gas frontier, with Japan and China playing a leading role in this regard. The report highlighted the key countries driving the development of gas hydrate technology. It was stated that China is the first country in terms of production technology and the most active country with its companies on the stock exchange in terms of patents, while Japan is successful in collaboration with China. In TRT 1's "Teşkilat" series, between the 19th and 31st chapters, the

subject of gas hydrate was covered in a realistic manner with the title "Cyber Attack on Gas Hydrate Project". The success and problems in this regard (efforts to prevent the project from inside and outside) were published.

Gas hydrates have established themselves as a key player in the field of unconventional hydrocarbon energy, and have now progressed to the next phase of their development. At the Houston Museum of Natural History, with the support of the ConocoPhillips oil company, Gas Hydrates has asserted its position as a key player in the field of unconventional hydrocarbon energy. The recent gains made in the field of unconventional hydrocarbon resources have made this a "game changer". Such a significant reserve discovery is situated in a geopolitically pivotal location that could potentially alter the trajectory of future generations. Even if the minimum quantity of gas is extracted from gas hydrates, this will ensure that Türkiye's gas consumption will be met for years to come. Gas hydrates, a novel energy source comparable to natural gas, hold immense economic and geopolitical significance for our country. It is therefore imperative that we prioritize comprehensive research in this area, encompassing the first, second, and third phases, as soon as possible.

The potential consequences of gas hydrate production in the Black Sea and other offshore regions on the energy sector are as follows:

Contribution to energy supply security: The contribution of gas hydrates to energy supply security is a significant factor to be considered. The availability of substantial gas hydrate reserves allows for a significant portion of the energy demand to be met from domestic resources, thereby reducing the country's reliance on imported energy sources.

Price stabilizing effect: The effect of increased supply on market prices is to exert a stabilizing influence, whereby lower prices are achieved, benefiting consumers and encouraging investors. The creation of new business areas and the generation of employment opportunities. The creation of new job opportunities is anticipated in the fields of production, transport and distribution. **Technological advancement:** It stimulates the development of new technologies that enhance the production process. An additional source of income is derived from exports. The export of a proportion of the gas produced provides a

significant foreign currency inflow. The production process is environmentally friendly. The utilization of methane as an alternative to fossil fuels has the effect of reducing emissions. A further advantage is that the project increases energy security and strengthens Turkey's influence in the region. The strengthening of the natural gas industry is a consequence of the aforementioned factors. The existing infrastructure is developed by increasing the network capacity. Consequently, the utilization of gas hydrates will have a profound impact on both the economy and the energy sector.

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POPULATION-BASED FORECAST MODEL FOR THE PRIMARY ENERGY CONSUMPTION OF ALGERIA

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Abstract

In this study, population-based forecasting model was established for Algeria's primary energy consumption (PEC). Once the forecasting model was established, the verification and forecasting accuracy of the established model were tested using several statistical indices such as determination coefficient (R^2), F – and – t tests, predicted vs actual values, relative root mean squarer error (RRMSE) and mean absolute percentage error (MAPE). Additionally, Algeria's PEC was forecasted by the proposed model for the foreseeable future. The modelling results showed that the proposed model is statistically valid and has good forecasting ability, leading to be able to employed successfully in order to forecast Algeria's PEC. Moreover, Algeria's PEC was projected to rise from 2.54 exajoule in 2023 to 2.84 exajoule in 2035, an increase of almost 13%.

Keywords: Total population, Primary energy consumption, Model, Forecast, Algeria

1 INTRODUCTION

Energy is one of the primary cornerstones of a nation's economic development. Any energy shortage has the potential to impede economic growth and development and even jeopardize national security [1]. Typically, energy can be derived from multiple sources and used in a variety of ways. These are known as the primary energy sources as they are either present in nature or have been stored there. On the other hand; energy sources that are commonly used, include coal, oil, natural gas (fossil fuels), nuclear, renewable, and hydropower, as depicted in Fig.1. These sources can be used as primary energy directly or transformed into secondary energy sources for industrial utilities. Fossil fuels (FFs), one of these energy sources, are responsible for a significant amount of the global energy supply. For instance, 81.5% of the world's primary energy consumption (PEC), amounted almost to 620 exajoule in 2023, was met by FFs, followed by renewables, hydropower and nuclear with 8.16%, 6.40% and 3.96% respectively. Among the FFs, the world largely depends on oil, a share of almost 32% and then, the coal and natural gas came behind

the oil with the rates of roughly 26.5% and 23% respectively in the same year [2]. On the other hand; numerous initiatives and regulations are recently being implemented to encourage the adoption of sustainable energy sources, although most of the world's energy needs are met by the FFs.

As the energy is crucial for economic growth, both at a global and at a national level, it has become a topic of great importance among all relevant parties such as academicians, policy makers, and energy investors. For proper investment planning of energy production, generation, and distribution, a robust forecasting technique is, therefore, necessary. With this approach, countries will be able to rigorously plan their energy projections. A variety of techniques have been employed by numerous scholars in the existing literature in recent decades for PEC prediction. Regression analysis [3-5], grey models (GM) [6-9], artificial neural network (ANN) [10-12], genetic algorithm-support vector regression (GA-SVR) [13-14], support vector machine (SVM) [15], adaptive neuro-fuzzy inference system (ANFIS) and its hybrid with particle swarm optimization

(ANFIS-PSO) [16], non-linear autoregressive distributed lag (NARDL) [17] and so on. However, these techniques have certain drawbacks such as black box in, when the

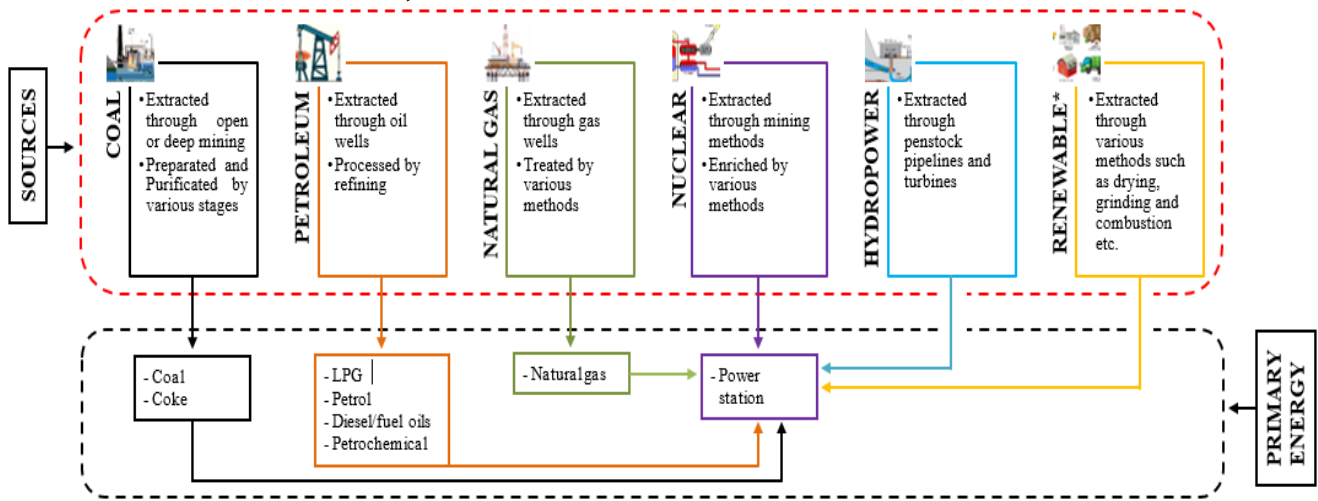


Figure 1. Classification of the energy resources

development of the models and applied in real-world scenarios due to their complex structures. Simpler and less accurate modeling strategies may be, therefore, more suitable to overcome the relevant challenges. Hence, this study develops, for the first time, population-based forecast models using trend analysis (TA) for Algeria's PEC. In the study, the total population (TP) and PEC were selected as independent and dependent variables respectively.

2 KEY INDICATORS OF ALGERIA

As the tenth largest country in the world and the largest country in Africa based on its land area, Algeria has over 45 million populations, constituting 0.57% of the world total. Additionally, its gross domestic products reached to 195 billion US dollars, with an annual growth rate of 3.2%, which was above the world's average annual growth rate of 3.09% in 2022 [18].

Algeria, which has the world's best irradiated zones known as the Sahara [19] hold 0.63% and 1.21% of the proven reserves of oil and natural gas in the world. The country has almost no coal reserves among the FFs. In addition to FFs, the country has small amount of renewable energy sources. It is evident from the reserve figures that Algeria is well-known for its natural gas and oil deposits. Its reserves of natural gas are eleventh in the globe, while its oil reserves rank

sixteenth globally and third in Africa. Additionally, in 2023, when the world's PEC reached 620 exajoule, it was 2.54 exajoule in Algeria. The FFs dominates the PEC of Algeria. That is, in 2023, only 0.27% of the PEC was met by hydropower and renewables while the FFs portion was 99.73% [2].

3 MODELLING STUDIES

3.1 Data

This study used the data for the PEC and TP from 1980 to 2023. The data was gathered from publicly accessible and officially recognized online sources [2,18]. The TP was chosen as the independent variable because of the strong association between it and energy needs, as well as the ease with which their time series can be found in numerous statistical databases. Table 1 presents the descriptive statistics for the variables which are PEC and TP. Additionally, Fig.2 illustrates the historical trends for the selected variables. As can be followed from Table 1, the PEC (exajoule) and TP (million) on average are 1.24 and 29.25 that are really substantial for Algeria. Moreover, the largest value for the PEC and TP are 2.22 and 39.54, while the minimum values are 0.64 and

Table 1. Descriptive statistics

	Min	Max	Mean	SD	Skew ¹ .	Kurto ² .
PEC	0.64	2.22	1.24	0.35	-0.09	-0.96

TP	18.74	39.54	29.25	5.89	1.16	1.11
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¹Skewness; ²Kurtosis and number of variables is 36.

18.74 respectively. On the other hand; for an observed series to be considered symmetric or normally distributed, the normal values for kurtosis and skewness must be zero (the ideal one). Nonetheless, some academics contend that the observed series is also comparable to a normal distribution if both values fall within ± 1.5 [20]. Based on the skewness and kurtosis in Table 1, the results suggest that every observed series has a normal distribution.

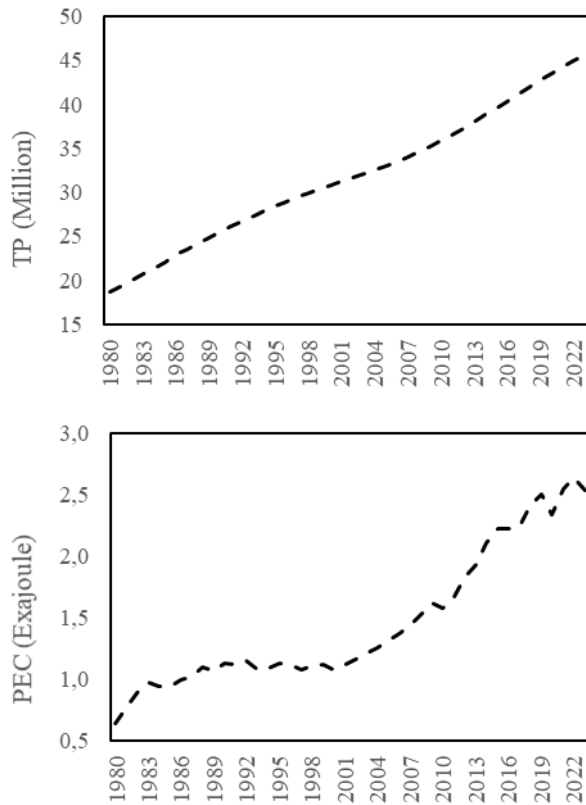


Figure 2. Historical trends of the PEC and TP of Algeria [2,18]

It is clearly indicated from the Fig.2 that the TP and PEC of Algeria have been trending increasing despite a small decrease in the PEC in 2019 due to the most probably coronavirus pandemic-COVID-19.

3.2 Methodology

Due to the main benefits such as easy to use and allowing the forecasts using any available data, the population-based forecast models were developed using the TA for the PEC of Algeria. The TA can develop models that forecast the

future values of the dependent variable by utilizing its historical trend. Therefore, it has been assumed throughout the analysis that the PEC will continue to follow their historical tendency. In the study, two datasets were created for annual variables. That is, the model was trained on around 82% of the whole data (from 1980 to 2015), and it was tested on 18% of the total data (from 2016 to 2023). Based on the functions whose equations are given in Table 2, all forecast models were derived by SPSS statistical software, providing a choice of regression.

Table 2. Mathematical expressions of the models developed through the TA

Model type	Equation
Linear	$y = a + b \cdot (t)$
Logarithmic	$y = (a) + \ln(t)$
Power	$y = (a) \cdot (t)^b$
Exponential	$y = (a) \cdot e^{b(t)}$
Inverse	$y = (a) + (b) \cdot \left(\frac{1}{t}\right)$
Growth	$y = e^{[(a)+(b) \cdot (t)]}$
S	$y = e^{[(a)+(b) \cdot \left(\frac{1}{t}\right)]}$

where; y is the PEC (Exajoule), a is the intercept or the constant, b is the slope, and t is the TP.

Once the models were developed, several statistical tests were applied for the models verification and performance accuracies. The coefficient of determination (R^2), the t-test, the F-test and the predicted versus the observed data were utilized for the verification, while the relative root mean square error (RRMSE) and mean absolute percentage error (MAPE) were employed to assess models forecasting accuracy. All these statistical tests were carried out at the 95% confidence level. The following formula belong to the performance metrics, which were used to gauge how accurate the models that were derived are (from Eqs. in Table 2).

$$RRMSE = \frac{RMSE}{\sigma} \cdot 100 \quad (1)$$

$$MAPE = \frac{1}{n} \sum_{i=1}^n \left(\frac{|x_i - y_i|}{y_i} \right) \cdot 100 \quad (2)$$

where; n is the total number of data points, X_i is the predicted PEC, Y_i is the actual PEC, $\bar{O}$ is the mean value of actual data.

4 RESULTS AND DISCUSSION

4.1 Model Development, Verification and Forecasting Accuracy

Models in all equation forms, presented in Table 2, were firstly developed and then, the best model was selected, based on its MAPE and RRMSE values. The best model to forecast the PEC of Algeria is explained by growth function whose equation is given below.

$$y = e^{[(-1.041) + (0.041).(TP)]} \quad (3)$$

where; y is the PEC (Exajoule) and TP is the total population (million).

The MAPE and RRMSE of the best model were determined as 14.98 and 9.88 respectively. Based on the classifications that are displayed in Table 3, it is evident that the model has good forecasting ability, while it gives excellent forecasting ability on the basis of MAPE and RRMSE respectively.

Table 3. Forecasting abilities of the MAPE and RRMSE [21,22]

MAPE (%)	RRMSE (%)	Forecasting ability
$MAPE \leq 10$	$RRMSE < 10$	Excellent
$11 \leq MAPE \leq 20$	$10 < RRMSE < 20$	Good
$21 \leq MAPE \leq 51$	$20 < RRMSE < 30$	Reasonable
$MAPE > 51$	$RRMSE \geq 30$	Poor

Based on the verification results in Table 4, it is seen that a strong degree of association between the TP and the PEC is indicated by the proposed model's R^2 value, which is 0.85. Additionally, Table 4 indicates that the calculated F – and – t values for the proposed model are substantially larger than the tabular F – and – t values. These results confirm that, at a 95% confidence level, the proposed model and individual variables involved in the developed model are statistically significant. Moreover, the predicted versus actual trends as indicated in Fig.3, have a strong correlation, demonstrating the ability of the developed model to provide accurate PEC

forecast for the study's conditions. Finally, it can be concluded that these results reveal the statistical significance of the proposed model.

Table 4. Statistical verification results of the proposed model

	$t_{calculated}$	t_{table}	$F_{calculated}$	F_{table}	R^2
Constant	11.924				
TP	14.319	1.690	205.051	4.125	0.85

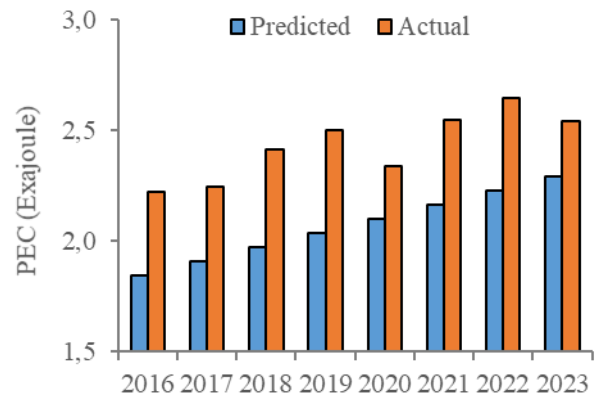


Figure 3. Actual vs Predicted PECs

4.2 Forecasting the PEC with the Proposed Model

In this section of the study, the proposed model projects the future PEC of Algeria for the years from 2025 to 2035. In this regard, the projected data of UN [23] on the TP was utilized and the forecasting results are depicted in Fig.4. One can infer from Fig.4 that Algeria's PEC will increase in the near future. In other words; total PEC of Algeria will amount to 2.87 exajoule in 2035 with an annual average and total increase 2% and almost 13%, as compared to 2023.

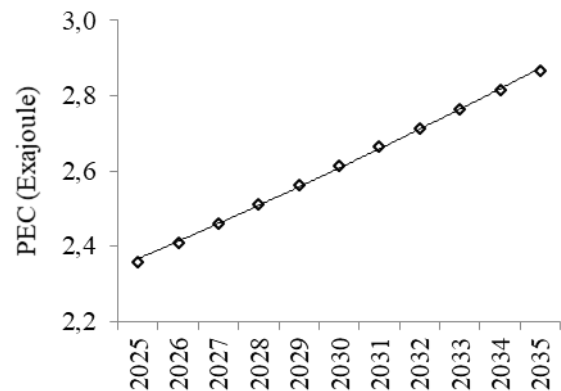


Figure 4. Forecasted results for the Algerian PEC

5 CONCLUSIONS

This paper intends to develop and propose population-based forecast model for projecting the PEC of Algeria. The main conclusions of the current investigation are as follows. It was seen that the proposed model successfully passed the statistical validation tests, revealing its usability in PEC forecasting. It was determined that the proposed model has at least good forecasting ability based on its error analysis or forecasting accuracy. In other words, it was reported that the proposed model can forecast the PEC of Algeria up to 85% accuracy rate. Additionally, the projected results demonstrated that the PEC of Algeria would increase to 2.84 exajoule with an increase almost 13%, when compared to the data in 2023.

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CISTUS SHELLS USED AS A SUSTAINABLE MATRIX FOR BIOENERGY PRODUCTION THROUGH SLOW PYROLYSIS PROCESS: KINETIC AND THERMODYNAMIC STUDY

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Abstract

Cistus shells have attracted considerable attention as a potential feedstock for second-generation biofuels, specifically through fixed-bed pyrolysis. Analyzing the composition of cistus shells exhibits a high proportion of volatile products (74.82%), carbon (69.02%), oxygen (26.48%), and notably, a high calorific value (23290 kJ kg⁻¹). Characterizing the bio-oil derived from cistus shells contains various compounds like fatty acids and alcohols that can be converted into fuels. The E_a values, determined using the FWO and KAS methods, were 179.773 kJ mol⁻¹ and 177.92 kJ mol⁻¹, respectively. The kinetics were described by the D₃, D₂, F₃, and P_{2/3} models, with corresponding energies of 87 kJ mol⁻¹, 78 kJ mol⁻¹, 56 kJ mol⁻¹, and 53 kJ mol⁻¹, respectively. Increasing the conversion rate from 35% to 55% results in an increase in ΔH and ΔG values for the FWO method from 148.11 kJ mol⁻¹ to 190.5 kJ mol⁻¹ and from 168 kJ mol⁻¹ to 202 kJ mol⁻¹, respectively. For the KAS method, the values increase from 146 kJ mol⁻¹ to 188 kJ mol⁻¹ and from 44.44 kJ mol⁻¹ to 85 kJ mol⁻¹. Notably, the entropy variation decreased as the conversion rates increased, indicating a stronger tendency to approach thermodynamic equilibrium during the pyrolysis process.

Keywords: Slow pyrolysis - Cistus shells - Bio-oil - Thermodynamic - Kinetics - Second-generation biofuels

ASSESSING THE POTENTIAL OF CONCENTRATED SOLAR POWER (CSP) TECHNOLOGY FOR ADDRESSING ENERGY CHALLENGES IN SYRIA: A SIMULATION STUDY USING GREENIUS SOFTWARE

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Abstract

This paper investigates the potential of (CSP) technology in addressing Syria's energy challenges amidst its ongoing crisis. Through simulation and modeling using GREENIUS software, the performance and financial viability of (CSP) facilities across two governorates (Homs, Reif Damascus) in Syria are evaluated. Factors, which include solar radiation, meteorological records, (LCOE), and plant configurations, are analyzed to optimize the power output and limit prices. Results indicate significant potential for (CSP) deployment, particularly in Reif Damascus. Despite higher initial costs, (CSP) offers advantages over (PV) systems, including higher energy generation capacity and dispatchable power. Moreover, (PV) technology necessitates only half the land area compared to (CSP) technology. However, (CSP) systems generate roughly two and a half-fold more electricity than (PV) systems. Integrating thermal energy storage (TES) enhances economic feasibility by mitigating intermittency issues. For Reif Damascus, the analysis shows a positive (CSP) deployment scenario, with a (LCOE) of 0.1434 €/kWh and a total net electricity production of 177,300 MWh/a. With its abundant sunshine and suitable geographic characteristics, Reif Damascus appears as an attractive location for (CSP) projects. Additionally, the study identifies optimization of solar field size as crucial for maximizing (CSP) plant efficiency and minimizing costs.

Keywords: CSP, TES, Greenius, Syria

INTRODUCTION

The global reliance on fossil fuels for energy production has raised concerns due to their substantial contribution to carbon dioxide emissions [1]. Recognizing the environmental drawbacks of fossil fuel-based power generation, there has been a global push toward renewable energy (RE) sources to mitigate these negative impacts [2]. Consequently, research and use of renewable energy have experienced significant growth in recent decades, spurred by concerns over fossil fuel scarcity and ecological impacts [3]. According to the British Petroleum Energy Perspective 2023 report, the finite nature of fossil fuel reserves underscores the urgency of transitioning towards (RE) [4]. This transition is not only seen as a substitution for conventional energy sources but also as a transformative force reshaping our relationship with the environment, economy, and societal values [5]. Alternative energy sources like hydropower, wind power, solar energy, and geothermal energy play critical roles in achieving

environmental sustainability [6]. Among these alternatives, solar energy has gained increasing popularity due to its versatility and wide-ranging applications, including electricity generation for residential and commercial purposes [7]. Solar power stands out as an abundant and technologically promising resource with a positive ecological impact and continuous advancements in technology, making it indispensable for decarbonization efforts [8]. Leading renewable energy technologies such as photovoltaics (PV), wind power harness solar, and wind energy to generate electricity for various applications, including residential use, agriculture, and water desalination. However, the intermittent nature of solar and wind energy poses challenges, leading researchers to explore energy storage solutions to mitigate fluctuations in power generation. In this context, (CSP) has emerged as a promising solution. Concentrating solar power (CSP) plants leverage thermal energy storage capabilities,

allowing them to store and dispatch large quantities of energy as needed, thus offering economic advantages over other renewable energy sources [9]. This ability to provide dispatchable power enhances the reliability and stability of (CSP) plants, contributing to their attractiveness in the renewable energy landscape.

1.1 CONCENTRATED SOLAR POWER (CSP) TECHNOLOGY

Concentrated solar power (CSP) is a possible method for producing power from solar radiation. Thermal energy storage (TES) assumes a vital role in (CSP) facilities by storing surplus heat from the solar field and deploying it as required, thus bolstering reliability and grid stability [9,10]. The four major components of solar thermal power generation are depicted in Fig 1: solar collector field, solar receiver, storage system, and energy conversion unit. The solar collection area is composed of an array of mirrors or reflectors that gather sunlight and direct it to a receiving tube. A receiver tube, equipped with a thermal energy carrier, receives heat from concentrated solar radiation and can create electricity either directly or through an auxiliary loop [11]. Concentrated solar power (CSP) plants are classified into four groups depending on the use of solar energy concentrator used to gather and concentrate solar energy as illustrated in Fig 2. Solar collectors, such as parabolic trough collectors (PTC) and linear Fresnel reflectors (LF), use an absorber tube to concentrate solar energy. Thus, they are referred to as linear concentrators. Point-focus concentrators, such as parabolic dishes (PD) and central receiver collectors (ST), direct solar energy to a specific receiver location [12]. The parabolic trough (PT) technique is the most advanced and commonly utilized among (CSP) technologies. This technique has proven reliable and long-lasting, as seen by multiple operational power plants globally. Scholars have investigated the possibilities of (CSP) technology for power generation globally. However, evaluating possible sites and the practicality of (CSP) technology is important, particularly in Middle Eastern countries [13].

1.2 CASE STUDY SITE

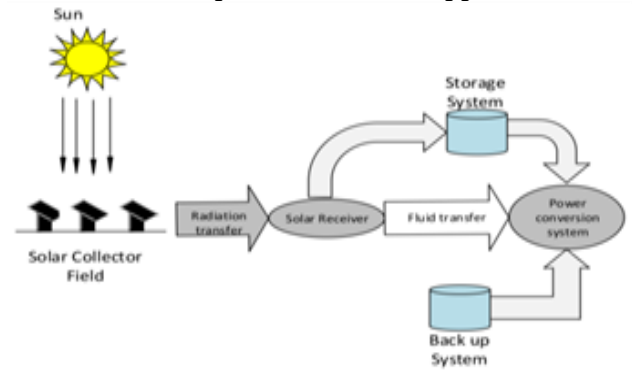


Figure 1. Basics concerning solar heat energy production [11]

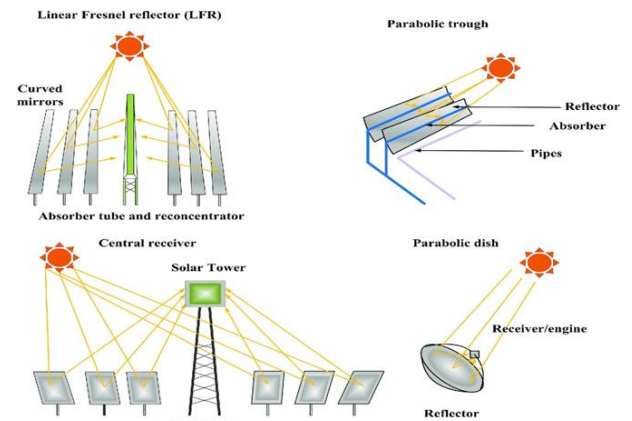


Figure 2. Classifications of concentrator solar power [23]

Syria, an Arab country in the Middle East, faces significant challenges in meeting its electrical generating demands due to excessive manufacturing and dispatch deficits. The lack of investment has led to frequent load shedding, particularly during the summer [14]. The country's state power usage per capita has increased by 15% since 2010, and in 2021, Aleppo experienced 10 hours of rationing for each hour, equivalent to half an hour of electricity. Damascus faced five "dead" hours for every hour of electricity, while provinces of Latakia, Tartous, and Homs experienced 30 minutes of electricity rationing, resulting in widespread blackouts lasting several days or even weeks. The Ministry of Electricity estimated that the rehabilitation of the sector's production and transmission would require approximately USD 2.4 billion in 2021[14]. To address these challenges, Syria can shift towards renewable energy sources, such as solar energy, which has the second-highest solar radiation among Arab countries due to its prolonged exposure to the sun [11]. Solar energy projects in Syria are economically feasible due to the country's 330 sunny days per year, which can be utilized for approximately 2829 to 3279 hours

annually despite 38 to 45 days of overcast weather [15]. The distribution of Direct Normal Irradiance (DNI) across Syria is illustrated in Fig 3. Sourced from Meteonorm 7.3 software, encompassing solar radiation, wind velocities, precipitation levels, sunshine durations, and daily temperatures. The annual average daily (DNI) for various governorates in Syria, measured in (kWh/m²/day) is highlighted in Fig 4.

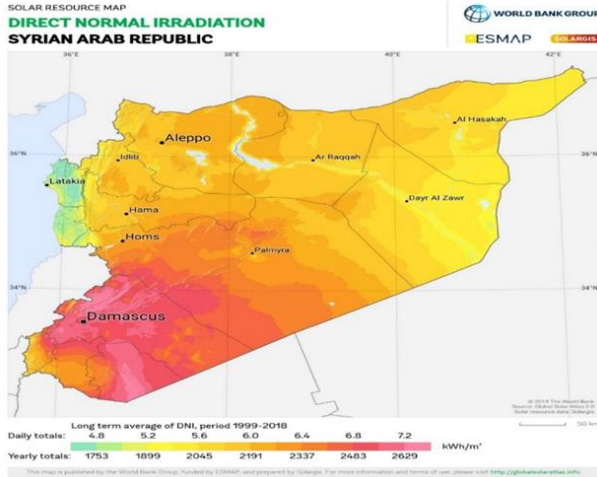


Figure 3. DNI distribution in Syria [24]

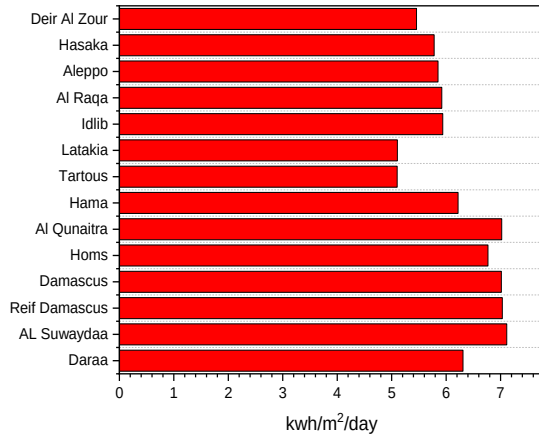


Figure 4. Annual average daily DNI for Syria's governorates

2. CALCULATION WITH GREENIUS

In this study, the evaluation of the (CSP) plant's performance through simulation and modeling was carried out using GREENIUS v4.5.0. This software provides a comprehensive blend of technical assessments and economic evaluations, essential for strategic planning and execution of renewable energy initiatives [16]. The Solar Research Institute of the German Aerospace Centre (DLR) developed

the Greenius simulation program, which is the largest German research centre in alternative energy using concentrated solar thermal power (CSTP). DLR is recognized as the largest German research centre in this field.

2.1 METEOROLOGICAL DATA

In addition to the technology's input settings, a weather data file for the specific place must be imported. In our investigation, meteorological data from METEONORM 7.3 program, a global meteorological database, was utilized [17]. This program encompasses various cities and allows the creation of custom sites or cities from scratch, as well as interpolating data from nearby cities. In this way, we can collect data for our website [18].

2.2 MATHEMATICAL DESCRIPTION

2.2.1 Parabolic trough power plant simulation

The equations used for this study are available in Ref [19, 20].

2.3 VALIDATION

The simulation model is identical to the one used at Andasol-1 capacity in Spain, which has been operational since 2008. The plant's entire parameters are provided in Fig. 5 and Table 1. The same model will be used to simulate our research locations and their meteorological data [18]. This part aims to validate the simulation's findings using real-world plants, demonstrating the reliability of simulations. Herrmann et al. provided the output data, which was then loaded into greenius for simulations [21]. The concentrating solar power (CSP) plant generates 50 MW of power, which has a (TES) capability of 3.5-7 hours; enabling the production of electricity throughout night-time. The thermal energy storage (TES) comprises of molten salt in two tanks and is utilized in various facilities worldwide. A big solar field is needed for charging thermal energy storage (TES) throughout daylight hours and provide additional heat for power block needs. A solar plant comprises 156 rows, each containing four sun collectors, with the tracking axis aligned south-north and the Sun tracking from east to west. The photovoltaic (PV) facility has a maximum capacity of 50 MW. The system consists of 177000 Yingli Panda YL280C modules coupled to 75 SMA Sunny Central 800CP inverters. We picked these components based on their technical specifications provided by Greenius [22].

Table 1. Reference plant design specifications [21]

Item	Value
Aperture width	5.77m
Collector length	148.5 m

Nominal capacity	50 MW
Focal length	1.71 m
Distance between rows	17.31 m
Field size	510 120 m ²
Net Capacity	97 000 kW _{hth}

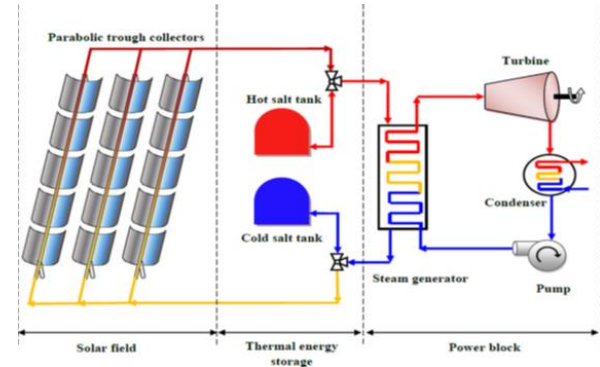


Figure 5. CSP plant system [25]

3. RESULTS and DISCUSSION

After defining all essential inputs, the simulation takes only 3-4 seconds on a contemporary personal computer. This time frame is sufficient for simulating a concentrating solar power (CSP) plant using hourly weather data. Simulating a photovoltaic (PV) plant is even faster when using simplified models [22]. The standard output of a (PV) plant is evaluated as its peak output under experimental conditions, specifically at 1000 W/m² irradiation and 25°C solar panel temperature [21]. The GREENIUS software simulates several solar energy technologies, allowing users to evaluate (CSP) and (PV) installations at the same location [21]. Table 2 displays the simulation outputs for each plant with hourly precision. These simulation results provide valuable insights into the potential of various governorates in Syria for (CSP) projects. Here is a summary of the key conclusions drawn from the analysis:

3.1 CONCENTRATING SOLAR POWER (CSP) PLANTS

- Reif Damascus: This governorate exhibit high potential for (CSP) projects, offering significant total net electrical output compared to others. Its favorable conditions make it a suitable location for efficient (CSP) technology implementation.

- Homs: Opportunities exist for optimizing (CSP) performance in this governorate, with potential cost reductions through suitable adjustments to plant configurations or operational strategies.

3.2 PHOTOVOLTAIC (PV) PLANTS

- Reif Damascus: With an (LCOE) of 0.0892 this governorate has one of the lowest costs for

electricity generation among the governorates. It also has a relatively high total net electrical output, indicating favourable conditions for (PV) plant implementation.

- Homs: This governorate shows varying levels of (LCOE) and total net electrical output, indicating differing degrees of economic viability and electricity generation capacity for (PV) plants.

- The comparative analysis of concentrating solar power (CSP) and photovoltaic (PV) plants across various Syrian cities reveals significant differences in their performance and cost-effectiveness. (CSP) plants generally exhibit higher net electrical outputs due to their ability to store thermal energy, which allows for continuous electricity generation even during non-sunny periods. However, this advantage comes with higher land requirements and higher Levelized Costs of Electricity (LCOE). For instance, the (CSP) plant in Damascus produces 168,650 MWh/a, with an (LCOE) of 0.1495 €/kWh, whereas the (PV) plant generates 85,488 MWh/a, with a significantly lower (LCOE) of 0.0909 €/kWh.

This trend is consistent across all analyzed cities, with (PV) plants consistently showing lower (LCOEs), thus making them a more economically viable option despite their lower energy output. The analysis underscores the importance of considering both the energy output and cost metrics when planning solar power projects. Additionally, the land footprint of (CSP) plants, which is almost double that of (PV) plants, must be considered, especially in regions with limited available land. These findings highlight the necessity for tailored, location-specific strategies to optimize the deployment of solar energy technologies in Syria.

- The performance of a 50-megawatt (MW) (using a trough power plant with storage 7 h) has been evaluated for proposed cities. The total annual output for the proposed power plants compared with Andasol-1 is demonstrated in Fig. 6 and we can find that some cities have higher total net electricity generation than reference one (Andasol-1) such as Reif Damascus and Damascus. The dynamics of power generation across governorates are elucidated in Fig. 7, displaying the shifting patterns between concentrating solar power (CSP) and photovoltaic (PV) plants. During summertime, the (CSP) plant emerges as a frontrunner in power generation, benefiting from prolonged sunlight hours, optimal sun angles, and higher direct normal irradiance (DNI). Conversely, in winter months, the (PV) plant exhibits greater efficacy in power

production. Interestingly, there are days when the (CSP) plant remains inactive while the (PV) facility continues to generate electricity, highlighting the flexibility and resilience of (PV) technology.

Table 2. Annual results of proposed cities

value	Reif Damascus		Homs	
Wnet MWh/a	CSP	PV	CSP	PV
	177300	87171	154993	80661
aperture area m ²	510120	289129	510120	289129
LCOE €/kwh	0.1434	0.0892	0.1631	0.0962

Moreover, on days characterized by significant cloud cover; although (DNI) may be limited, (GHI) remains accessible, enabling (PV) plants to continue functioning. Syria's geographical diversity presents a promising landscape for CSP-based power production, particularly in the southern regions. It's noteworthy that (PV) technology requires approximately half the land area compared to (CSP), albeit (CSP) systems tend to yield approximately two and a half times more electricity than (PV) systems. However, despite its higher efficiency, (CSP) plants entail an elevated (LCOE) compared to other power production methods. Nevertheless, they offer advantages such as portable electricity generation and the capacity to harness more solar energy. The levelized cost of energy (LCOE) figures provided for each plant serve illustrative purposes only and don't incorporate country-specific incentives [21].

3.3 OPTIMAL SOLAR FIELD SIZE

Simulation and optimization techniques may be used to increase the performance and efficiency of solar energy plants. Simulations may assist examine various situations and select the best setup for the project. Optimization algorithms can determine the optimal combination of aspects, including the size and features of the solar power system, to optimize energy output while minimizing expenditures. By running many

simulations, project developers may evaluate the influence of various elements and make educated decisions to maximize the project's performance. There are several possible solutions to finding optimal solar field size and these are the recommendations from (DLR) [16]:

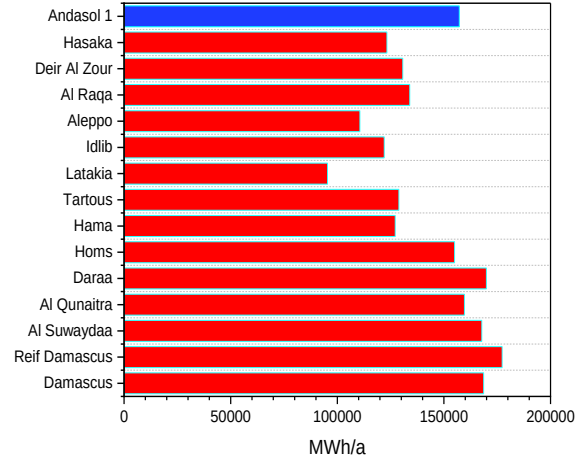


Figure 6. Total annual net electricity output for Andasol-1 and different governorates

- Fix the site and relevant Meteo file.
- Fix the power block size and specific cost parameters.
- Use reference DNI of 750 W/m² and find solar field size suitable for power block.
- Do several simulation runs varying the solar field size systematically around the value found above. Compare the (LCOE) results of those runs to find the cost-optimal solar field size. The optimal aperture area for the (CSP) power plant was evaluated in both scenarios without storage and with storage durations of 3.5 and 7 hours using (DLR) recommendations for proposed cities as illustrated in Fig 8.

with longer storage duration, as this configuration tends to yield lower (LCOE) values.

4. CONCLUSION

The feasibility of (CSP) technology in Syria has been investigated, based on the geographical advantages and energy needs. This study has been carried out by using GREENIUS software to estimate the electric power output, ideal solar field, and (LCOE) of a 50 MW (PTC) thermal power plant with and without (TES) in various governorates of Syria. The results of the study lead to the following findings:

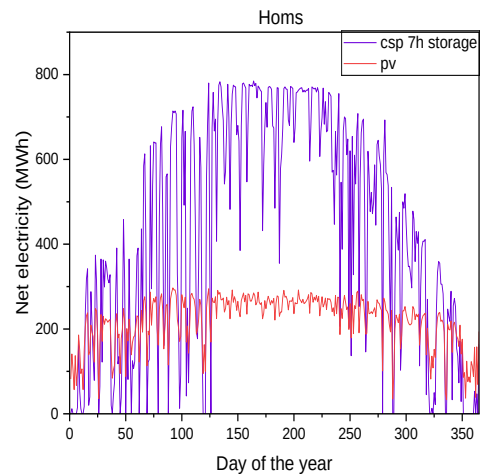
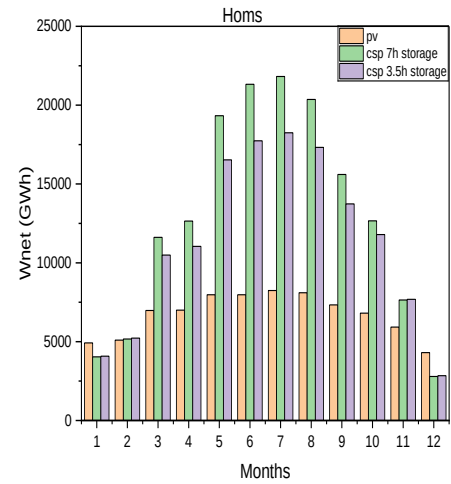
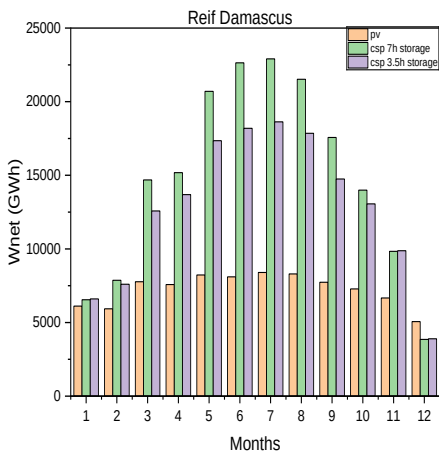
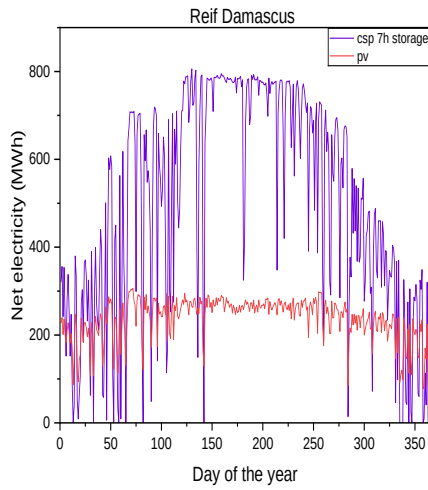


Figure 7. Monthly and daily electricity generation of PV and CSP for different cases

- Concentrated solar power (CSP) technology has significant potential to address Syria's energy challenges, especially in governorates like Reif Damascus. This region shows an average annual solar radiation (DNI) of approximately 6.0-7.5 kWh/m²/day, translating to a potential annual

We can find that plants without thermal energy storage (TES) have the highest (LCOE) and with an average area of roughly (550000m²) for all cities. The levelized cost of electricity (LCOE) decreases when (TES) is added to the plant. On the other hand, power plants with 7 h storage had a bigger solar field with the lowest (LCOE) for (Reif Damascus) city. For each aperture area, the (LCOE) tends to decrease as the storage duration increases. This is because longer storage durations allow for more flexibility in electricity generation and can help mitigate intermittency issues associated with solar power. Generally, larger aperture areas result in lower (LCOE) values across all storage durations. This is consistent with the concept of economies of scale, where larger solar plants benefit from lower per-unit costs. Comparing the levelized cost of electricity (LCOE) values for each aperture area and storage duration, we need to identify the combination that offers the lowest overall cost. Based on the data provided, the best technology for (CSP) power plant would be the configuration with the lowest (LCOE). This would likely be the combination of a larger aperture area

electricity generation exceeding 160,000 MWh/a per plant.

- Despite higher initial costs, (CSP) plants in Syria demonstrate competitive levelized costs of electricity (LCOE) ranging from 0.1434 to 0.1544 €/kWh, depending on location and plant configuration. This compares favourably with other renewable energy sources and underscores (CSP's) potential to offer stable, dispatchable power with a minimal carbon footprint.

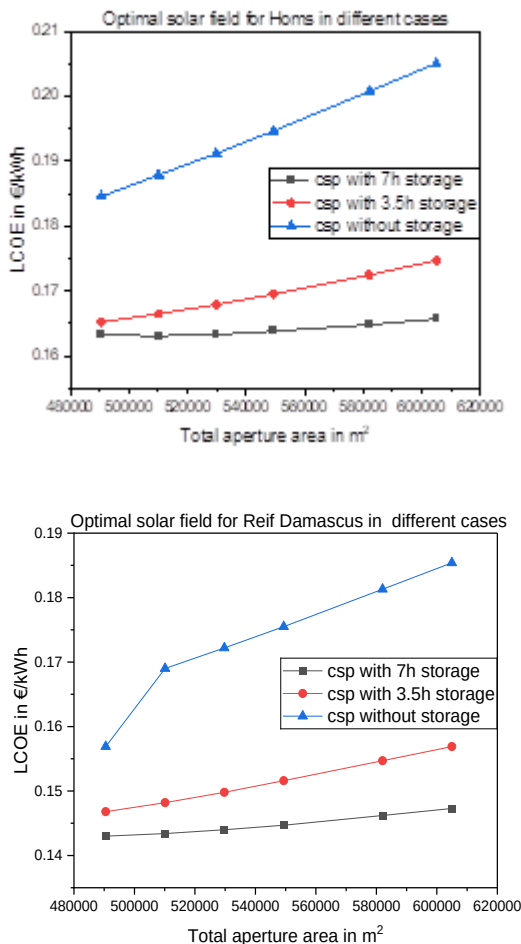


Figure 8. Optimal aperture area of governorates for different cases

- While (CSP) systems require larger land areas than photovoltaic (PV) installations, they yield approximately 2.5 times more electricity per unit of installed capacity. However, (PV) systems typically offer lower (LCOE) values (e.g., 0.0892 €/kWh in Reif Damascus) highlighting the need for strategic deployment based on local conditions and energy demands.

- Optimizing solar field sizes and integrating thermal energy storage (TES) is critical for improving (CSP) plant efficiency and economic feasibility. For instance, increasing storage duration from 3.5 to 7 hours can reduce (LCOE) by up to

15-20%, making (CSP) an attractive option for meeting Syria's growing energy demands sustainably.

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ANALISYS OF SECURITY SUPPLY WITH ENERGY RESOURCES OF EUROPEAN UNION TO ENSURE ITS ENERGY SECURITY

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Abstract

A strong and secure energy industry gives the European Union a solid and secure economy. In this way, the EU can become a good and strong strategic partner with powerful energy states. Thus, energy security becomes one of the most important pillars of European security. For a secure energy industry, the EU needs strategic energy resources and highly specialised human resources, and the EU has a key role to create stability and security factors for the supply of energy resources that are quantified by natural gas, oil, coal and uranium. The analisys of the security supply with energy resources to European Energy System, comes in the context in which the possibility of a black-out is very likely, and the lack of energy resources can cause major damage through enormous financial losses, which through the domino effect can spread economic and European insecurity. In this context, the analisys of the security supply with energy resources becomes an essential issue of European security and makes this paper of real interest. The authors consider that the security supply with energy resources of European Union is a strictly national for every country and European security issue because the lack of energy resources can cause enormous damage to the European industry and economy, which are almost entirely dependent on energy resources. European Union without energy resources cannot develop its defence industry which is becoming increasingly vulnerable. The European Union must be prepared in the event of a crisis indifferent to its nature and face all the challenges at any time.

Keywords: Security supply, Energy resources, Energy security

1 INTRODUCTION

In the new context of extended European security, energy resources plays among the most important roles in the position occupied by the European Union and its role in the system of international relations, in the context of ensuring European, and global energy security. Lack or precariousness of energy resources (natural gas, oil, coal and uranium) of less energy and economic developed countries, they have led to the amplification of games on their side and have allowed some energy dependencies in terms of energy security control. Under these conditions, energy security is no longer just an objective of foreign policy, but has become a solid and constant concern for the international energy community, in the context of ensuring european and global security. In order to prevent a collapse of the European Energy System, each

european state must have energy security strategies and secure its energy resources or critical power infrastructures that facilitate the population's access to energy resources, important factor in european security. These energy security strategies are developed only by preventive assessing the level of vulnerability of critical energy infrastructures and the security of energy resources supply, by identifying all risks, threats and vulnerabilities with energy insecurity effect. The EU has assessed the supply of energy resources, but the authors also come to the aid through a more intrinsic analysis, analyze all possible power supply routes and the effects that can be generated in the event of an energy collapse. [1]

2 VISIONS REGARDING ENERGY SECURITY

European vision

The European Union has a special interest in energy security and is one of the world's largest consumers of energy resources. On 8 March 2006, the EU adopted a new draft European Energy Strategy, namely the Strategy European Commission for Sustainable, Competitive and Secure Energy. The five directions of action targeted by the EU towards ensuring sustainability, competitiveness and security energy sources are: *ensuring the integrity of the internal market in natural gas and electricity, by adopting common standards and rules, but by building common energy networks or interconnecting existing ones; ensuring the security of energy flow and strengthening solidarity between Member States in this regard; diversification of energy sources; environmental protection and the promotion of energy and gas saving policies in a manner compatible with the Lisbon objectives; creating a strategic technology plan for electricity, gas and oil.*

The formulation of a common foreign policy for all EU countries must identify the EU's priorities for building a new energy protection infrastructure, adopting a European Energy Treaty, a new energy partnership with Russia and creating a crisis response mechanism. caused by short-circuiting of Europe's energy supply. [2,7,8]

International vision

Energy security is no longer just an economic issue, but has become a much deeper one, with politico-military implications. International acknowledged the need to put the issue of energy security. International strategic concept provides for the protection of vital electricity, natural gas and oil supply lines as one of the critical issues for the global security. In a statement at the Riga summit, the countries spoke in support of the coordinated efforts of the international community to assess the risks to energy infrastructure and to promote its security. The countries could play an important role in building international political solidarity in the event of a deliberate disruption to the supply of electricity, gas and oil and could also ensure the security of energy infrastructure in producing countries if necessary. [1,7]

International countries is engaged in the following areas: *merging and exchanging information; stability design; promoting international and*

regional cooperation; supporting consequence management; support for the protection of critical energy infrastructure.

The directions in which international countries could add value in the field of achieving energy security could be: *consultation, collaboration and cooperation between members and partners; dissemination of good practices, consequence management strategies , technology and information; critical infrastructure security; security of identified strategic points and other energy transit lines; the risk of undermining the supply of electricity, natural gas and oil caused by possible terrorist threats, natural or man-made disasters.*

3 SITUATION OF SECURITY SUPPLY WITH ENERGY RESOURCES IN EUROPEAN UNION

Energy security has become a political concern of the EU, especially in the last decade, after the "gas wars" between the Russian Federation and Ukraine, when in the winters of 2006 and 2009, temporary interruptions of natural gas transit from the Russian Federation through Ukraine to European markets they have caused serious supply crises in some Eastern European Member States. EU imports of energy products, 2019 - 2023 (monthly averages, € billion and million tonnes) (source: Eurostat database and estimates)

The EU is the world's largest energy importer at an annual cost of around € 400 billion.

In the European context, energy dependence creates vulnerability , especially with regard to natural gas:

- *6 EU Member States depend on Russia as the sole external supplier for all their natural gas imports;*
- *3 of these countries use natural gas to meet more than a quarter of their total energy needs.*

Priority actions proposed by the European Energy Security Strategy include:

- *strengthening mechanisms between states to increase the level of security, solidarity, trust, as well as the protection of strategic / critical infrastructure;*
- *moderating energy demand - "each additional 1% increase in energy savings reduces natural gas imports by 2.6%";*
- *building a fully integrated internal energy market;*
- *increasing energy production in the EU;*

- diversification of external sources of supply and related infrastructure;
- improving the coordination of national energy policies and conveying a unified message in foreign energy policy.

"EU Framework Strategy for a Resilient Energy Union with a Prospective Climate Change Policy", Communication COM (2015) 80, from February 2015, states that "The main determinants of energy security are the completion of the internal energy market and more efficient energy consumption, and these factors are related to the *internal dimension* of energy security." The Energy Union places energy security at the forefront of its priority objectives. [2]

The five interdependent dimensions of the Energy Union are the following:

- energy security, solidarity and trust;
- fully integrated European energy market;
- energy efficiency in support of demand moderation;
- decarbon (iz) of the economy (reduction of greenhouse gas emissions);
- research, innovation and competitiveness.

In 2021 in the EU, renewable energy was the leading source in electricity production (37%), ahead of fossil fuels (36.5%) and nuclear power plants (25%). Among renewable sources, the highest share of electricity came from wind turbines (13%), followed by hydropower plants (12%), solar power (6%) and biofuels (5%).

Gross available energy, EU, 1990-2021:

This article provides an overview of the energy economy in the European Union (EU) in 2021, based on annual data from each Member State. It provides trends for the main energy commodities for primary energy production, imports and exports, gross available energy and final energy consumption. Gross available energy in the European Union in 2021 increased compared with 2020 (+6.0 %). Oil (crude oil and petroleum products) continued to be the most significant energy source for the European economy, despite a long-term downward trend, while natural gas remained the second largest energy source. Both oil and natural gas increased by 5.3 % and 4.0 %, respectively in 2021 compared with 2020. This was mostly due to an increase of activities after the COVID-19 pandemic. The contribution of renewable energy sources continued to increase. Renewables already surpassed solid fossil fuels in

2018 and 2019, and gained further ground in 2020 and 2021. Solid fossil fuels increased by 15.7 % in 2021, partially recovering after the lowest value ever achieved in 2020. However, solid fossil fuels did not increase sufficiently to recover to 2019 levels.

Natural gas supply

The European Network of Transmission System Operators for Gas (ENTSO - G) represents 43 transmission system operators - TSOs, 1 associated partner and 9 observers members. (Figure 1.) [4]



Fig. 1. ENTSO-G states member

TSO members: Austria (2 company), Belgium (2 company), Bulgaria (2 company), Croatia, Czech Republic, Denmark, Estonia, Finland, France (2 company), Germany (12 company), Greece, Hungary, Ireland, Italy (3 company), Latvia, Lithuania, Luxembourg, Netherland (2 company), Poland, Portugal, Romania (Transgaz), Slovakia, Slovenia, Spain, Sweden. "The data are published by ENTSG (2024) "

Associated partner: Switzerland.

Observer members: Albania, Bosnia and Herzegovina, North Macedonia, Norway, Switzerland (4 company), Ukraine.

EU natural gas supply:

Russia:

PIPELINE - RUSSIA					
NAME	LINK		Length [km]	route	Capacity
	From	Up to			
NORTH STREAM 1 (Annex 2)	Vyborg (Russia)	Greifswald (Germany)	1224	Baltic Sea	55 trillion m ³ / year
YAMAL EUROPE (Annex 6)	Torzhok (Russia)	Frankfurt - Oder (Germany)	4196	Belarus Poland	33 trillion m ³ / year
TURK STREAM (Annex 3)	Russkaya (Russia)	Kyivkoy (Turkey)	2200	Black Sea	31.5 trillion m ³ / year
TRANSBALKAN PIPELINE (Annex 7)	(Russia)	(Turkey)	181 (territory Romanian)	Ukraine Romania Macedonia Greece	10 trillion m ³ / year
BLUE STREAM (Annex 4)	Beregovaya (Russia)	Samsun (Turkey)	1213	Black Sea	16 trillion m ³ / year

Norway:

PIPELINE - NORWAY					
NAME	LINK		Length [km]	route	Capacity
	From	Up to			
EUROPIPE	Draupner E (Norway)	Emden (Germany)	620	North Sea	18 trillion m ³ / year
EUROPIPE II	Karsto (Norway)	Dornum (Germany)	660	North Sea	24 trillion m ³ / year
NORPIPE	Ecofisk (Norway)	Emden (Germany)	443	North Sea	32 trillion m ³ / year
FRANPIPE	Draupner E (Norway)	Dunkerque (France)	840	North Sea	19 trillion m ³ / year
GJØA GAS PIPELINE	Gjøa (Norway)	Flaga (England)	131	North Sea	17 trillion m ³ / year
KNARR GAS PIPELINE	Knarr (Norway)	Flaga (England)	105	North Sea	17 trillion m ³ / year
LANGELED	Nyhavn (Norway)	Easington (England)	1166	North Sea	75 trillion m ³ / year
TAMPEN LINK	Statfjord (Norway)	Flaga (England)	24	North Sea	27 trillion m ³ / year
UTSIRA HIGH GAS PIPELINE	Edvard Grieg (Norway)	arrow (England)	94	North Sea	5 trillion m ³ / year
VESTERLED	Heimdal (Norway)	St. Fergus (England)	360	North Sea	39 trillion m ³ / year
ZEEPIPE I	Sleipner (Norway)	Zeebrugge (Belgium)	814	North Sea	42 trillion m ³ / year

Algeria:

PIPELINE - ALGERIA					
NAME	LINK		Length [km]	route	Capacity
	From	Up to			
MEDGAS	Hassi R'Mel (Algeria)	Almeria (Spain)	757	Mediterranean Sea	8 trillion m ³ / year
MAHREB EUROPE	Hassi R'Mel (Algeria)	Cordoba (Spain)	1620	Morocco Mediterranean Sea	12 trillion m ³ / year
TRANS MEDITERRANEAN PIPELINE	Hassi R'Mel (Algeria)	Minerbio (Italy)	2475	Tunisia Mediterranean Sea	30 trillion m ³ / year
Gals	Hassi R'Mel (Algeria)	TUSCAN (Italy)	1505	Mediterranean Sea Sardinia	10 trillion m ³ / year

Libya:

PIPELINE - LIBYA					
NAME	LINK		Length [km]	route	Capacity
	From	Up to			
GREEN STREAM	Wafa (Libya)	Gela (Italy)	757	Mediterranean Sea	11 trillion m ³ / year

Gas pipelines in the construction / project phase:

PIPELINE - CONSTRUCTION / PROJECT PHASE					
NAME	LINK		Length [km]	route	Capacity
	From	Up to			
NORTH STREAM 2	Ust-Luga (Russia)	Greifswald (Germany)	1200	Baltic Sea	55 trillion m ³ / year
SOUTH STREAM	(Russia)	(Italy)	900	Black Sea Bulgaria: a) Serbia: - Hungary - Austria b) Greece - Italy	31 - 63 billion m ³ / year
AGRI	Caspic Sea (Azerbaijan)	Constant (Romania)	-	Georgia Black Sea	8 billion m ³ / year
NABUCCO	Caspic Sea (Azerbaijan)	(Turkey)	3300	Georgia Black Sea	31 billion m ³ / year
	1: SCP - South Caucasus Pipeline (Azerbaijan - Georgia) <i>Natural gas source: Schah Deniz</i>				
	2: TANAP - Trans Anatolian Pipeline (Turkey)				
	3: TAP - Trans Adria Pipeline (Greece - Albania - Italy)				
	4: NABUCCO WEST (Bulgaria - Romania - Hungary - Austria)				

Important note:

- On 26 September 2022, a series of underwater explosions and consequent gas leaks occurred on the Nord Stream 1 (NS1) and Nord Stream 2 (NS2) natural gas pipelines, two of 23 gas pipelines between Europe and Russia. Both pipelines were built to transport natural gas from Russia to Germany through the Baltic Sea, and are majority owned by the Russian majority state-owned gas company, Gazprom. [5]
- South Stream is a canceled pipeline project to transport natural gas of the Russian Federation through the Black Sea to Bulgaria and through Serbia, Hungary and Slovenia further to Austria. It was never finished. The project was found in

non-compliance with the European Union's Third Energy Package legislation, which stipulates the separation of companies' generation and sale operations from their transmission networks. The Russian Government cancelled the project in 2014, seven years after the project was started. It was seen as rival to the Nabucco pipeline project, which was abandoned in favor of the Trans Adriatic Pipeline. Unlike South Stream, TAP is fully compliant with EU legislation by way of having obtained EU Third Party Access Exemption. Construction of the Russian onshore facilities for the South Stream pipeline started in December 2012. The project was cancelled by Russia in December 2014 following obstacles from the European Union, the 2014 Russian annexation of Crimea, and the resulting imposition of European sanctions on Russia. The project has been replaced by other proposed ones Tesla pipeline and Turkish Stream. The latter, renamed as TurkStream, was approved and later completed, sending gas supplies to Bulgaria on 1 January 2020. [5]

EU states will be better prepared to deal with potential disruptions to the gas supply due to a new solidarity mechanism that was voted in Parliament on 12 September 2017. Over the past two decades, natural gas has provided an increasing share of Europe's energy needs (unlike two other fossil fuels, oil and coal, whose importance has declined), now accounting for almost a quarter of domestic consumption. crude energy, especially for home heating and electricity generation, but this figure varies from country to country. Natural gas plays a much larger role in Germany, the Netherlands, Italy and England than in Sweden, Estonia and Finland, while Cyprus has only recently begun exploring gas.

The EU imports two-thirds of its natural gas through: *gas pipelines (large pipelines); LNG (liquefied natural gas) terminal*. More than a third of the imported gas comes from: *Russia; Norway; Algeria; Libya; Qatar*. Most EU countries are totally or almost entirely dependent on imports for their natural gas demand, and supply is almost dominated by a single supplier, Russia. Relying on a single source or route of transport can be a danger to supply, due to a *technical accident / incident* or *political / economic / military disputes*, such as those between Russia and Ukraine (a transit country for Russian gas). to the EU) in 2006 and 2009, disputes that affected natural gas supplies to several European countries. Following the crisis,

the EU strengthened its security of supply rules in 2010, forcing Member States to ensure that natural gas is supplied to households and other vulnerable customers, such as hospitals, even in difficult conditions, such as disruption. main gas infrastructure. In 2014, the European Commission carried out so-called *stress tests on* natural gas, which showed that Europe could only cope with gas supply disruptions if Member States cooperated more.

The European Union can cope with disruptions to the supply of natural gas, provided that the Member States cooperate very well with each other.

Use of natural gas in the EU: *heating and cooling: 46%; electricity produced with natural gas: 16.4%.* In 2019, the European Commission proposed updating the 2010 regulation by introducing a new solidarity (cooperation) mechanism to ensure that a Member State declaring a level of emergency could receive natural gas from neighboring countries. Rapporteur Jerzy Buzek (EPP, Poland) said that "*solidarity means that in difficult times we can send gas from one country to another to ensure the full supply of natural gas to households, to important social service providers, such as hospitals, and to gas-fired power plants, to avoid power outages.* "

Dependence on Russia:

The main supply routes for Russian gas are:

- route through Ukraine: (covering about 50% of total imports): *the Trans-Siberian route; trans-Balkan route.*
- Belarus route - *Yamal gas pipeline* (covering about 20% of total imports);
- Nord route - *Nord Stream gas pipeline 1* (covering about 30% of total imports);
- transport by *LNG liquefied natural gas* vessels (covering approximately 10% of total imports).

The main purpose of the Nord Stream 2 gas pipeline project is the EU's dependence on a single source (Russia), which is why it is criticized by the other energy actors involved.

Natural gas imports routes into the EU

The map displays the most relevant pipeline import routes into the EU and the location of LNG terminals. The largest share of gas used to be delivered from Russia via four distinct corridors Nord Stream, Yamal (via Poland), Ukraine, and Turkstream (via Turkey). These different Russian

gas routes are at the heart of current geopolitical tensions. [6]

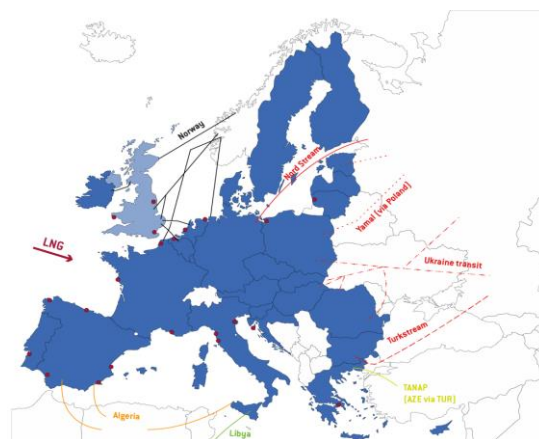


Fig. 2. Main EU Natural Gas Imports routes
(source: Bruegel)

Figure 3 depicts quarterly EU imports of natural gas since Q1 2021, providing an overview of the evolution in volumes from different suppliers over time.

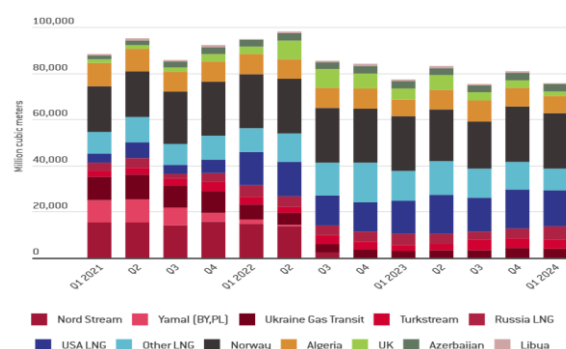


Fig. 3. EU quarterly imports by source

Figures 4 and 5 shows actual daily imports for the last 30 days. Imports are split by Russian routes, as well as shown for Norway, Algeria, LNG and the net imports from the UK. Russian exports via Ukraine Gas transit might contain flows from Ukrainian storages.

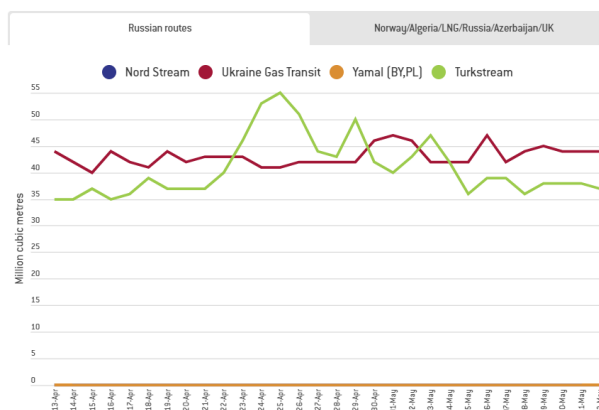


Fig. 4. Daily gas imports by Russian routes

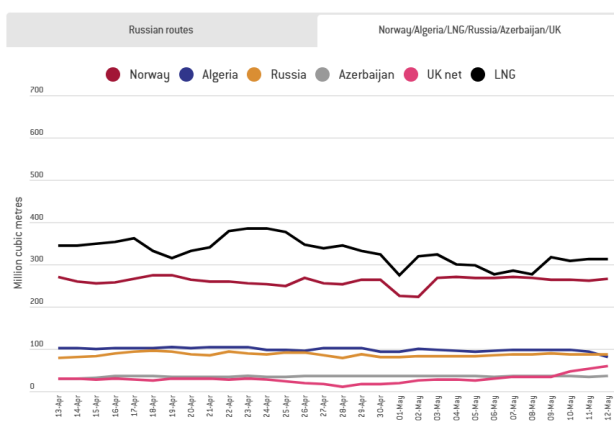


Fig. 5. Daily gas imports Norway, Algeria, UK and LNG (Sources: EntsoG,

Oil supply

Oil currently accounts for almost 37 percent of the European Union's gross energy consumption. Thus, oil is the most important source of primary energy, ahead of natural gas, solid fuels and nuclear energy. The European Commission starts from the premise that by 2030 oil consumption in the EU will continue to increase, even if only by 0.25 percent per year. However, oil will remain the EU's most important primary energy source by 2030, accounting for about 35 percent of crude energy consumption. While demand in the EU will grow slowly, much higher growth is expected worldwide. As oil is a non-renewable energy resource, it is not possible to predict exactly when this energy resource will be naturally depleted. [1,9]

Limitations on oil extraction consist of: *geological factors; technological factors.*

There are a lot of obstacles to increasing oil extraction around the world, namely: *political instability in some states; political, military or economic sanctions; insufficient legal protection; politically determined environmental protection measures; rational resource management - which limits the production potential.*

Oil reserves now stand at 1.2 trillion barrels, about double that of 1980. Demand increased over the same period from almost 62 million barrels per day to about 85 million barrels per day. In total, this results in a reserve *life* of 41.6 years, longer than in 1980.

The concept of oil reserve means: *the discovery of new deposits; exploitation of deposits; technological innovations; price.*

Total oil resources have been sufficient for centuries, but the volume of easily extractable oil has not increased as much as it has in recent years.

Another reality is the increasing concentration of easy-to-exploit reserves in several states of the "strategic ellipse", this is clear from the ratio of production to the size of reserves. New discoveries of deposits in other parts of the world, such as the Arctic region or the Greenland coast or technological advances leading to the economic exploitation of unconventional reserves, could change the ratio in favor of other regions, even if only to a limited extent. and at the same time, oil extraction from the EU is declining. Norway and the EU Member States currently cover about 30 percent of demand, but from the current perspective a substantial decrease in production is expected by 2030. The consequence of this situation is that the EU's dependence on imports will reach around 95% in the coming decades, according to the European Commission. There is a need for short-term response mechanisms that the EU has had since the late 1960s in the form of *strategic oil and oil reserves*. On the other hand, security of supply can only be guaranteed in the long run if proper planning is done. The time horizon for infrastructure investment is often 40 years or more. Thinking in such a large way is not an easy task, but such strategic planning must also take place at European level, where the main challenge is likely to be to increase supply, while at the same time significantly reducing consumption growth.

Increasing oil supply:

In the field of supply growth, three elements are of strategic importance:

- 1) *First, in the coming decades, according to the International Energy Agency (IEA), more than \$ 350 billion a year must be invested worldwide in the operation of new energy sources, as well as in the development of infrastructure (pipelines, ships, ports, refineries). etc.). This is only possible if companies are guaranteed security of investment inside and outside the EU. To this is added the possibility of obtaining an adequate profitability. The central instrument of supply security is the diversification of sources of procurement and in terms of security of supply, unconventional sources of oil, such as oil shale or oil sands and very heavy oil, offer great advantages as a result of their distribution in a large number of states;*
- 2) *secondly, research needs to be stepped up. The use of new materials can, for example, greatly reduce operating costs or provide drilling with*

lower environmental consequences. The new extraction techniques will lead, to an even greater extent than today, to an increase in reserves. About 80% of conventional resources are oil shale. These potentials need to be made usable in the future from an economic and ecological point of view. In other words, in the future, an important area will be the training of engineers and the promotion of cooperation between industry and research institutes;

- 3) thirdly, in the coming years, many conflicts in world politics have to be resolved. Iraq is slowly starting to extract more oil after the security situation stabilizes. Iran has huge reserves which, however, at present, for political reasons, can contribute very little to the expansion of international markets. The latest conflict between Georgia and Russia, as well as the intensification of pirate attacks on oil tanks in recent months, have made it very clear how vulnerable transport routes can be. Given the fact that terrorists may also be interested in attacking a VLCC (very large oil tanker), the urgency of a reaction from the international community becomes even clearer.

EU imports pf petroleum oil, Q2 2022 and Q2 2023 (montly averages in net mass – million tonnes)

Following a strong increase in energy imports in the EU between 2021 and 2022, the scenario is different in 2023, with imports dropping for the second quarter in a row when compared with the same period in the previous year. In the second quarter of 2023, compared with the same quarter of 2022, EU imports decreased by 39.4% in terms of value and 11.3% in terms of net mass (weight expressed in tonnes). These results follow declines of 26.5% and 6.1%, respectively, in the first quarter of this year. In terms of net mass, Russia's shares in the EU imports of petroleum oils and natural gas have been decreasing continuously over time since the second quarter of 2022. Petroleum oils imports from Russia fell from a monthly average of 8.7 million tonnes in the second quarter of 2022 to 1.6 million tonnes in the second quarter of this year (-82%), but, in contrast, the imports from the extra-EU partners except Russia increased by 5.8 million tonnes, from 31.5 million to 37.3 million tonnes. Russia's share in total EU imports of petroleum oils was 4.0% in the second quarter of 2023, a staggering difference from the 21.6% share recorded in the same quarter of last year.

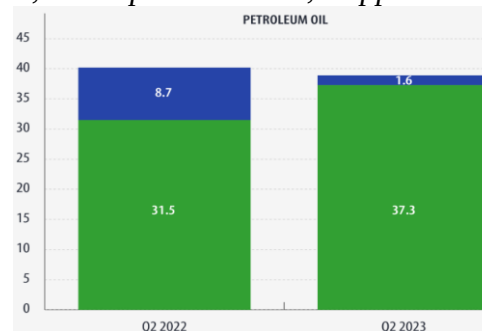


Fig. 6. EU imports pf petroleum oil, Q2 2022 and Q2 2023_(source: Eurostat)

Diversification of suppliers ongoing

Russia's war of aggression against Ukraine led the EU to implement several packages of sanctions, which directly and indirectly affected the trade of oils and natural gas. The impact is now visible in a growing diversification of energy suppliers. Regarding petroleum oil, the EU ban on seaborne imports of Russian crude oil entered into force on 5 December 2022, followed by the embargo on refined oil products as of 5 February 2023, which impacted results in the first and second quarters of 2023.

In the second quarter of 2022, Russia was the leading supplier of petroleum oils, with a share of 15.9% of total EU imports. In the second quarter of 2023, Russia ranked only 12th, with a share of 2.7%, down 13.2 percentage points (pp) compared with 2022. By contrast, Norway (+3.5 pp up to 13.7%), Kazakhstan (+3.2 pp up to 10.2%), the United States (+2.1 pp up to 13.6%) and Saudi Arabia (+2.3 pp up to 9.0%) saw their share increase over the same period, and Libya became an important partner, accounting for 8.1% of EU petroleum oil imports.

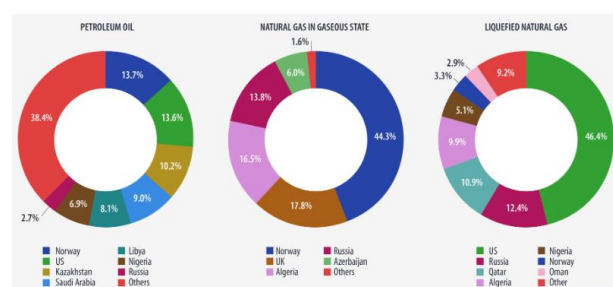


Fig. 7. EU imports by energy product and by partner, Q2 2023 (source: Eurostat)

The situation was similar for natural gas in a gaseous state, with Russia's share dropping by 14.5 pp to 13.8% of total EU imports, while the shares of Algeria (+9.3 pp) and Norway (+6.2 pp) increased significantly. In the second quarter of 2023, Norway was the EU's top supplier with a

share of 44.3% of total EU imports, followed by the United Kingdom (17.8%) and Algeria (16.5%). As far as liquefied natural gas is concerned, the United States remains by far the EU's leading supplier in the second quarter of 2023, with a share of 46.4% in total EU imports, followed by Russia (12.4%), Qatar (10.9%), Algeria (9.9%) and Nigeria (5.1%). Among these suppliers, only Algeria and Nigeria saw their share increase (+5.2 pp and +1.0 pp respectively) compared to the second quarter of 2022. By contrast, the respective shares of the United States, Russia and Qatar fell by -2.8 pp, -2.7 pp and -1.1 pp respectively. Norway and Oman became important suppliers, with shares of 3.3% and 2.9% respectively.

EU oil petroleum supply is next:

Russia:

OIL PIPELINE - RUSSIA					
NAME	LINK		Length [km]	route	Capacity
	From	Up to			
DRUZHBA I, II (Friendship)	(Russia)	(Belarus)	4000	Russia Europe	1.4 million barrels / day
	1 Belarus - Poland - Germany (I)				
	2 Belarus - Ukraine - Slovakia (II)				
	a) Slovakia - Czech Republic b) Slovakia - Hungary (south)				

Ukraine:

OIL PIPELINE - UKRAINE					
NAME	LINK		Length [km]	route	Capacity
	From	Up to			
SARMATIA	Odessa (Ukraine)	Brody (Poland)	674	Europe	5.3 million tons / year

Azerbaijan:

OIL PIPELINE - AZERBAIJAN					
NAME	LINK		Length [km]	route	Capacity
	From	Up to			
BTC Baku - Tbilisi - Ceyhan	Baku (Azerbaijan)	Ceyhan (Turkey)	1768	Tbilisi (Georgia) Caspian Sea Mediterranean Sea	1 million barrels / day

Norway:

OIL PIPELINE - NORWAY					
NAME	LINK		Length [km]	route	Capacity
	From	Up to			
NORPIPE OIL	Ecofisk (Norway)	Teesside (England)	354	North Sea	16 trillion m ³ / year

Nuclear power supply

In this context, the *Energy Union Strategy* and the *European Energy Security Strategy* emphasized the need for Member States to apply the highest standards in terms of: *nuclear security; nuclear safety; nuclear waste management; nuclear non-proliferation; diversification of nuclear fuel supply*, thus, contributing to meeting the 2030 climate and energy targets. The EU is currently one of the three major economies that generates more than half of its own electricity from low-carbon energy sources (around 58%). The Informative Nuclear Program - PINC provides a basis for examining how nuclear energy can contribute to the EU's energy goals. Given that nuclear safety remains the Commission's top priority, PINC specifically includes investments related to post-Fukushima. Nuclear safety

improvements, as well as those related to the long-term operation of existing nuclear power plants. In addition, PINC will contribute to the informed debate on issues such as investment needs and the management of responsibilities in the nuclear field, at a time when the EU nuclear industry is entering a new phase, characterized by an intensification of activities. from the final stage of the life cycle. PINC also addresses the need to invest in research reactors and the related fuel cycle, including the production of medical radioisotopes.

Recent developments in nuclear policy:

At present, 129 nuclear reactors are in operation in 14 Member States, with a total capacity of 120 GWe and an average age of almost 30 years. New construction projects are being considered in 10 Member States, with four reactors already under construction in Finland, France and Slovakia. Other projects in Finland, Hungary and the United Kingdom are in the process of being approved, while projects in other Member States (Bulgaria, the Czech Republic, Lithuania, Poland and Romania) are in a preparatory stage.

Many countries in Europe and the rest of the world will rely on nuclear power to generate some of their electricity needs in the coming decades. With regard to nuclear safety, the EU has the most advanced legally binding and enforceable regional framework in the world, and despite differing views from Member States on electricity from nuclear sources, there is a common recognition of the need to ensure the highest possible standards for the responsible and safe use of nuclear energy and to protect citizens from radiation. Since the previous PINC update in 2008, the EU's nuclear landscape has undergone significant changes, with the organization of comprehensive risk and safety assessments (stress tests) of EU nuclear reactors in response to the Fukushima Daiichi accident and the adoption of key pieces of legislation on nuclear safety, radioactive waste and spent fuel management and radiation protection. Strength tests have shown that the safety standards of nuclear power plants in the EU, Switzerland and Ukraine are high, but further improvements have been recommended. Nuclear operators implement these improvements in accordance with their national action plans. The Commission will continue to monitor the implementation of these plans through the European Nuclear Safety Regulatory Group. The amended Nuclear Safety Directive raises the level of nuclear safety standards. It sets an EU-wide

goal of reducing the risk of accidents and preventing the release of large amounts of radioactive effluents, and also introduces the requirement for a European *peer review system (scientific, academic evaluation). or professional of a person or a scientific paper before publication by other persons working in the same field*), which will allow to examine every six years specific aspects in the field of security. These requirements must be taken into account whenever investments are made in new nuclear installations and whenever reasonably possible when improvements are made to existing installations.

Investments in the nuclear field in the perspective of 2050:

Significant investments will be needed to support the transformation of the Energy System in line with the Energy Union Strategy. Between 2015 and 2050, between € 3.2 and € 4.2 trillion will need to be invested in the EU's energy supply. Investments in the nuclear sector are a small part of the overall effort and must be carried out within the framework established by EU law. In accordance with Article 41 of the Euratom Treaty, the Commission must be notified of new investment projects in the nuclear field. From 2008 to date, a total of 48 projects have been notified: *9 projects targeted installations intended for activities from the initial stage of the cycle; 20 projects focused on major modifications or improvements to nuclear power plants, related to long-term operations or post-Fukushima improvements; 7 projects related to new commercial or research reactors; 12 projects targeted installations from the final stage of the cycle.*

The Commission has issued non-binding opinions for all projects, providing Member States with comments and / or suggestions for improvements to be taken into account when authorizing projects. Particular attention was paid to issues related to: *nuclear safety; waste management; guarantees; security of supply.*

During 2017, the Commission proposed an update and better definition of the requirements for these notifications which, together with the recommendation on the application of Article 103 of the Euratom Treaty, will strengthen the Commission's ability to ensure that new bilateral energy investments and agreements agreements with third countries comply with the Euratom Treaty and reflect the latest security of supply considerations. The European nuclear fleet is aging

and significant investment is needed when Member States opt for an extension of the life of certain reactors (and related safety improvements), planned decommissioning activities and long-term storage of nuclear waste, in addition, investment is needed to replace existing nuclear power plants. Such investments could also be partly directed towards the construction of new nuclear power plants. It is expected that in the period 2015-2050, the total value of investments in the nuclear fuel cycle will be between 660 and 770 billion euros. Finally, the rapidly growing use of nuclear energy outside the EU (China, India, etc.) also means that the EU must maintain its global leadership and excellence in technology and security. This will require permanent investment in research and development.

Uranium producers globally

About two-thirds of the world's production of uranium from mines is from Kazakhstan, Canada and Australia. An increasing amount of uranium, now over 55%, is produced by in situ leaching. In 2022 Kazakhstan produced the largest share of uranium from mines (43% of world supply), followed by Canada (15%) and Namibia (11%). (<https://world-nuclear.org>)

Coal supply

The coal industry in Europe is one of the sectors hardest hit by the energy transition, and for hundreds of years coal has been at the heart of industrial and societal development in Europe and around the world. The European Union itself was set up by the act of political will to pool coal and steel production in the first six founding Member States. Current concerns about environmental protection, climate change and human health have given rise to a series of political and societal approaches that call into question the need to continue to use coal and other fossil fuels for electricity and heat production. With this new policy orientation, coal days seem to be numbered, despite the fact that more than a quarter of the EU's electricity is still generated by *280 coal-fired power plants* in *22 countries*. Six countries are completely independent of coal-fired electricity production: *Cyprus; Estonia; Latvia; Lithuania; Luxembourg; Malta*. While the idea of phasing out coal from the energy mix seems to be generally accepted in those Member States where no indigenous coal deposits are mined, the situation is very different in the EU regions where coal is mined. direct employment for 240,000 workers. If we take into account the jobs in

the mining equipment industry, the other jobs in the supply chain and the indirect jobs, the industry supports almost one million jobs, most of which are in regions in that there are few employment alternatives. 5 Member States exploit the upper coal (coal) for electricity production: *Czech Republic; Germany; Poland; Romania; Spain*. Ten Member States exploit lower coal (lignite) for electricity generation and these are: *Bulgaria; Czechia; Germany; Greece; Poland; Romania; Slovakia; Slovenia; Spain; Hungary*. In these countries, indigenous coal deposits play an important role in security of supply and thus contribute to the EU's energy security and reduction of import dependence, which is currently very high. In some EU Member States that exploit indigenous coal deposits on a large scale, for example in Germany and the Czech Republic, about 50% of electricity is generated in coal-fired power plants. In Poland, this percentage exceeds 80%.

In addition to its use for electricity production, coal has many other uses: *cement manufacturing; transformation into liquid fuels; filters or carbon fibers*.

Large coal users: *steel industry; aerospace industry (carbon filters / fibers); civil engineering sector; the military sector; paper producers; chemical industry (synthetic fuels, methanol, etc.); the pharmaceutical industry; food processing sector*.

Coal production and consumption up in 2022

In 2022, EU coal production and consumption continued to increase, reaching 349 million tonnes (+5% compared with the previous year) and 454 million tonnes (+2%), respectively. This rebound started in 2021 and was mainly driven by lignite, a solid fossil fuel with low energy content belonging to the bigger category of brown coal.

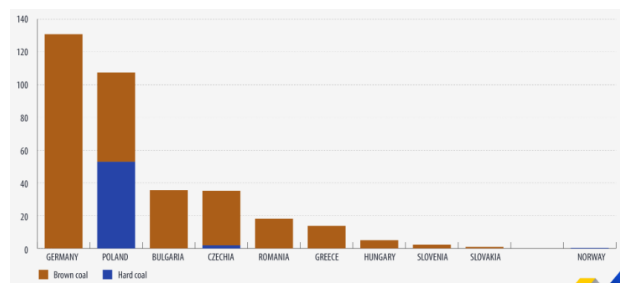


Fig. 8. Production of hard coal and brown coal, 2022 (million tonnes)

(source: Eurostat)

The EU produced 294 million tonnes of brown coal in 2022 (up 6% from 2021). Despite the recent

rebound, the production stayed below the pre-pandemic 2019 figures. Today, brown coal is produced by 9 EU members, with Germany taking the lead as the main producer. Last year, Germany (131 million tonnes) accounted for about 44% of the total EU brown coal production. The other Member States producing brown coal are Poland (19%), Bulgaria (12%), Czechia (11%), Romania, Greece, Hungary, Slovenia and Slovakia. Consumption figures for lignite and brown coal are very similar to production, as these coal types are usually not traded but are used domestically to produce electricity. While lignite is rarely the main fuel for electricity production in EU countries, it is in several Western Balkan countries. Nevertheless, in recent years, the share of lignite in electricity production decreased also in the Western Balkans with hydro and natural gas on the rise. For hard coal, a category of coal with higher energy content, production in the EU reached almost 55 million tonnes in 2022. At present, there are only two producers of hard coal remaining in the EU: Poland and Czechia. Consumption of hard coal in 2022 reached 160 million tonnes, 11% less than in 2019. Unlike brown coal, hard coal is used in other industries besides power production and is therefore traded and consumed by all EU countries except Malta. Poland (38%) and Germany (25%) accounted for almost two-thirds of the total hard coal consumption of the EU in 2022, followed by Italy, the Netherlands, France, Spain, and Czechia. [10,11]

4 CONCLUSIONS

Because energy resources (natural gas, oil, coal and uranium) are safety and security elements for those who own, control, exploit, distribute and/or use them, they can generate conflicts or energy wars, which is characterized by the use of energy instruments to compel the adversary to change his policy or behavior, or to undermine the capacity of that state to maintain normal relations with other states, in times of peace or war, which may be: *customs barriers, embargoes, boycotts, royalties, blockades, takeovers and mergers, espionage, naval piracy, economic-energy terrorism, etc*. Without energy resources (natural gas, oil, coal and uranium), the entire economy can collapse, because almost all industry and the European economy depend on these indispensable elements, and any short circuit on the European energy market, it is a danger to energy security and therefore energy

security is an important component of the European security and foreign policy strategy.

For this reason, energy resources (natural gas, oil, coal and uranium) are often used as instruments of political, economic and military pressure in order to gain some strategic advantages on the complex and dynamic stage of international relations, where some states or economic groups in power, use this energy weapon to set some strategic goals.

In this context, the analysis of the security supply with energy resources becomes an essential issue of European security and makes this paper of real interest. The authors consider that the security supply with energy resources of European Union is a strictly national for every country and European security issue because the lack of energy resources can cause enormous damage to the European industry and economy, which are almost entirely dependent on energy resources. Amid the war between Russia and Ukraine and Israel with Hamas and possibly Iran, a European Union without energy resources cannot develop its defence industry which is becoming increasingly vulnerable. The European Union must be prepared in the event of a crisis indifferent to its nature and face all the challenges at any time.

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MULTI-STAGE COMBUSTION KINETICS OF SOLID FUELS IN CHEMICAL LOOPING COMBUSTION: AN ADVANCED, CLEAN COMBUSTION TECHNOLOGY

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Abstract

This study presents a comprehensive analysis of the kinetics of Chemical Looping Combustion (CLC) using CuO and Co₃O₄ as oxygen carriers for low-volatile semi-anthracite coal, focusing on integrating CO₂ capture with the combustion process. CLC offers an advanced, eco-friendly method for converting solid fuels into energy, with inherent CO₂ capture, presenting a cost-efficient solution. However, the limited understanding of solid fuel CLC kinetics, crucial for reactor design, has hindered its application and optimisation. The research investigates the combustion kinetics of both volatiles and fixed carbon, bridging significant knowledge gaps and advancing the clean conversion of solid fuels. The study explores CLC using CuO and Co₃O₄ across varied temperature regimes (700-1000 °C) and oxygen carrier ratios ($\phi = 0.5, 1.0, 2.0$). The combustion process is characterised by distinct stages: the initial combustion of volatiles occurs with CuO at 450-580 °C and with Co₃O₄ at 460-650 °C, where the combustion efficiency ranges between 3-6 wt.%. This phase is followed by a complex interaction involving gas-phase volatiles and solid-phase oxygen carriers, transitioning to gas-phase oxygen and solid-phase fixed carbon under non-isothermal conditions. The combustion efficiency during this phase varies from 19-71 wt.% between 580°C and the isothermal temperatures of 750-1000°C. The activation energy for volatile combustion was determined to be 119 kJ/mol with CuO and 82 kJ/mol with Co₃O₄. For the initial combustion of fixed carbon in the non-isothermal stage, the activation energy ranged from 31-53 kJ/mol. In the final isothermal phase, the combustion of fixed carbon with gas-phase oxygen reaches a combustion efficiency of 77-96 wt.% at temperatures of 750-950°C with CuO and up to 1000°C with Co₃O₄. The activation energy for fixed carbon combustion in the isothermal stage was approximately 234 kJ/mol for both carriers, with reaction rate constants (k_0) of $7.84 \times 10^9 \text{ min}^{-1}$ for CuO and $3.7 \times 10^8 \text{ s}^{-1}$ for Co₃O₄. The kinetics transition from diffusion-controlled reactions at lower temperatures to first-order or phase-boundary controlled reactions and Avrami-Erofeev model kinetics at higher temperatures, influenced by the type of oxygen carrier and temperature. This pioneering study clarifies the multi-stage kinetics of solid fuel CLC using CuO and Co₃O₄, providing foundational insights for the enhanced design and efficiency of CLC systems, thereby supporting cleaner energy production and more efficient CO₂ capture.

Keywords: Chemical Looping Combustion, Advanced Combustion, Clean Energy production, CO₂ Capture

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EXPERIMENTAL INVESTIGATION OF THE IMPACT OF AQUEOUS AMMONIA, HYDROGEN AND DIESEL FUEL MIXTURES ON EXHAUST EMISSIONS AND ENGINE PERFORMANCE IN A COMPRESSION IGNITION ENGINE

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Abstract

In this study, experiments were carried out using aqueous ammonia, hydrogen and diesel fuels in a compression ignition engine. A heavy-duty diesel engine with a cylinder volume of 11 liters was used as the test engine. In the current study, 4 different torque values were used: 25, 50, 75 and 100% torque values. 300 Nm torque represents 100% torque value. All experiments were carried out at a constant engine speed of 660 rpm. Initially, Neat diesel was used in the experiments. Then, aqueous ammonia that is containing 25% ammonia was blended into the diesel fuel at the rates of 10% and 20%. In addition to the experiments conducted with neat diesel fuel and 10, 20% aqueous ammonia blended diesel fuels, experiments were continued using hydrogen fuel along with these mixtures. Hydrogen was delivered to the combustion chamber from the engine intake manifold at 1.5 bar pressure. Hydrogen was blown into the combustion chamber at a level corresponding to 10% of the energy value of each fuel mixture used in the experiments. As a result of the experiments, the addition of aqueous ammonia significantly increased the in-cylinder pressure compared to neat diesel fuel. Additionally, it has been observed that the addition of aqueous ammonia leads to an increase in thermal efficiency.

Keywords: Aqueous ammonia, Diesel, Hydrogen, Emissions, Performance

1. INTRODUCTION

In the 21st century, population growth and industrial development have led to unprecedented levels of energy demand. To meet this demand, the use of fossil fuels has become widespread, resulting in energy crises.[1] The intensive use of fossil fuels increases the risk of depleting energy resources and triggers global climate change due to the accumulation of greenhouse gases.[2]

Transportation vehicles and machinery equipped with internal combustion engine systems constitute a significant portion of fossil fuel consumption. These types of engines are widely used globally, significantly increasing the demand for fossil fuels. The number of such vehicles is expected to rise further in the future, putting considerable pressure on fossil fuel consumption.[3] Given the limited availability of fossil fuels, the widespread adoption of alternative fuels and renewable sources is

necessary. To produce alternative fuels for diesel engines, various chemical compounds have been blended with pure diesel in specific ratios to create alternative fuel mixtures. Wang et al. examined engine performance by mixing ammonia and hydrogen in certain proportions. They reported that the best results were achieved with a 30% hydrogen blend. This application resulted in increased in-cylinder pressure and power while reducing fuel consumption rates. However, an increase in NO_x emissions was observed due to the use of nitrogen.[4] Qian et al. investigated the effect of hydrogen in an ammonia-diesel dual-fuel mode, using a method where hydrogen was mixed at an energy ratio of 10% at each engine speed. The diesel energy was fixed at 45%. The addition of hydrogen increases the engine's heat release and pressure, reduces particulate emissions, but increases NO_x emissions. At low loads, the effect of hydrogen diminishes; however, with appropriate heating, ammonia emissions can be significantly reduced.[5] Bayramoglu K. investigated the effects of adding 5%, 10%, and 15% hydrogen and ammonia to diesel fuel on fuel consumption, energy efficiency, and carbon emissions. A 15% hydrogen blend reduced fuel consumption by 21%, while a 15% ammonia blend increased it. Hydrogen improved energy efficiency, whereas ammonia reduced it. Carbon emissions were reduced for both fuels, but the reduction was more significant with hydrogen.[6]

In this study, the aim was to reduce the impact of fossil fuels and increase thermal efficiency in diesel fuels. Ammonium hydroxide (25% NH₄OH) was added to pure diesel fuel, and various values were obtained with mixtures ranging from 0% to 20%. Additionally, hydrogen gas was added to the mixture through the intake manifold at an energy ratio of 10%, and the values were calculated. With these mixtures, engine performance and exhaust emissions were measured at torque values of 75 Nm, 150 Nm, 225 Nm, and 300 Nm, with 25% increments up to the engine's maximum torque value of 300 Nm, and at a constant engine speed of 660 RPM. The obtained data were compared with the results obtained using pure diesel fuel under the same experimental conditions.

2. MATERIAL AND METHODS

In this study, the experimental setup consists of a 6-cylinder compression ignition diesel engine, PCS performance measurement system, Bosch BEA60 emission analyzer, 200 bar pressure hydrogen cylinder, hydrogen pressure regulator, precision scale for measuring liquid fuel consumption and in-cylinder pressure measurement system. The test engine and its technical specifications are shown in Figure 1 and Table 1. Fuel specifications are presented in Table 2. Pure diesel, aqueous ammonia containing 25% ammonia and hydrogen were used as test fuels. The experiments conducted without using hydrogen fuel were named as D100, A10D90 and A20D80, respectively. Here, D100 represents pure diesel, A10D90 represents diesel with 10% aqueous ammonia and A20D80 represents diesel with 20% aqueous ammonia (aqueous ammonia added to diesel contains 25% NH₃). Later, hydrogen was added to the experiments conducted with these three fuels, corresponding to 10% of the energy consumption data. These fuels are coded as D100H10, A10D90H10 and A20D80H10, respectively.



Fig 1 Test Engine-HDV

Table 1 Test Engine-HDV Technical Specifications [1]

Test engine	NISSAN PE6H
Bore and Stroke.	133 mm , 140 mm
Displaced volume	11,670 cc
Max. Power and speed	234 Hp , 2300 rpm
Compression ratio	16.5
Injection timing	16 °BTDC

Table 2 Specifications of fuels

Specifications	Hydrogen	NH ₄ OH	Diesel
Density	0,09 kg/m ³ (gaseous)	880 kg/m ³ at 25 °C	820-845 kg/m ³
Stoichiometric ratio	34,48	3.83	14,92 (app.)
Flash point	-	-	55 °C
Auto ignition Temperature	858 °C	651 °C	186–230 °C
Low heat Value (LHV)	120 MJ/kg	4,65 MJ/kg (Aqueous ammonia containing 25% ammonia)	42.7 MJ/kg
Purity	99,999 %	-	-

A scale with a sensitivity of 0.5 g was used to measure liquid fuel consumption. Consumptions were recorded every 2 minutes. In experiments using hydrogen, the hydrogen was reduced from 200 bar to 1 bar via the regulator. The hydrogen adjusted to 1 bar was delivered to the combustion chamber from the intake manifold. In experiments using hydrogen, 10% of the liquid fuel consumption was replaced with hydrogen. The flow control of hydrogen was controlled with an ALICAT brand flow meter.

3. RESULTS, FIGURES AND TABLES

3.1 Engine Performance

Brake thermal efficiency is calculated by dividing the engine's brake power by the amount of fuel consumed and the fuel's lower heating value.[7]

$$\eta_{th} = \frac{P_b}{\dot{m}_f \times LHV} \quad (1)$$

P_b : braking power

$\dot{m}_f$: fuel mass flow rate

LHV : the lower heating value of the fuel

For the mixture, the LHV value is determined using Equation 2.

$$LHV_K = \frac{m_b \times LHV_b + m_m \times LHV_m}{m_b + m_m} \quad (2)$$

m_b : amount of first fuel

m_m : amount of second fuel

LHV_b : lower heat value of the first fuel

LHV_m : lower heat value of the second fuel

The graph shown in Fig 2 was created using the data obtained during the experiment and the equations provided above. In the graph, by following the Diesel and Diesel-H2 lines to

understand the effect of hydrogen, it is observed that using 10% hydrogen based on the energy ratio reduces the brake thermal efficiency (BTE) across all loads. To understand the effect of ammonium hydroxide, examining the Diesel-D90A10 and Diesel-D80A20 data shows that increasing the ammonium hydroxide ratio enhances brake thermal efficiency (BTE) at loads of 40% and above. Overall, the data indicate that the highest BTE is achieved with the D80A20 mixture. The D80A20 mixture is approximately 34.12% more efficient than Pure Diesel and about 14.35% more efficient than the D90A10 mixture.

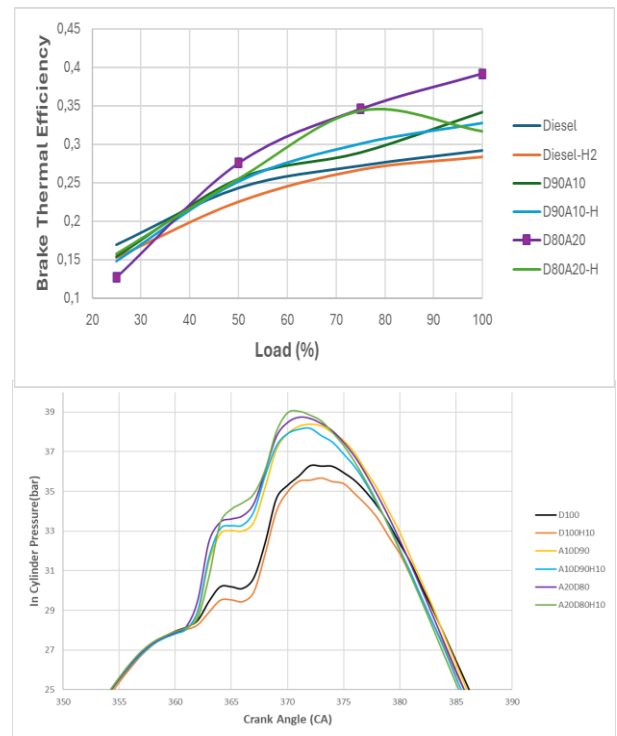


Fig 3 In Cylinder Pressure under 300 Nm Load

Figure 3 presents the cylinder pressure graph under a 300 Nm load. This graph can be evaluated from four different perspectives. Firstly, the addition of 10% hydrogen to the diesel fuel resulted in a 1.72% reduction in the maximum cylinder pressure. Additionally, it caused an approximate 1 CA ignition delay. The addition of hydrogen to diesel fuel can significantly reduce the overall fuel/air equivalence ratio, extend the ignition delay, and adversely affect combustion quality. This situation may lead to a decrease in the maximum cylinder pressure [8]. Secondly, under a constant hydrogen ratio of 10%, focusing on the cylinder pressures of different ammonia mixture ratios (0%, 10%, 20%) combined with diesel fuel shows that an increase in the ammonia ratio leads to higher in cylinder pressure. The reason for the highest cylinder pressure being observed with the A20D80H10 fuel mixture is that the combined use of hydrogen and ammonia provides a more effective auto-ignition temperature compared to direct hydrogen use in diesel engines. While the high flame speed of hydrogen increases the peak pressure, the low flame speed of ammonia balances this pressure. This mixture helps optimize the peak cylinder pressure throughout the engine cycle [9]. Thirdly, if the lines representing mixtures with ammonium hydroxide ratios increased from 0% to 20% are examined, the peak cylinder pressure rises as the ammonium hydroxide ratio increases. This is related to the fact that combustion occurs a few CA before the top dead center (TDC). [10] Fourthly, it is observed that adding hydrogen to the 20% ammonium hydroxide mixture and to the 10% ammonium hydroxide mixture requires a high proportion of ammonium hydroxide for effective hydrogen performance. Specifically, a higher ratio of ammonium hydroxide is necessary to increase in-cylinder pressure and prevent ignition delay.

3.2 Exhaust Temperatures and Emissions

3.2.1 Exhaust Temperatures

According to the data presented in Fig.4, as the amount of ammonia increases, the maximum exhaust temperatures decrease. When examining the effects of hydrogen and ammonia separately, it is observed that hydrogen addition raises the exhaust

temperatures, while ammonia addition lowers them. However, when using a ternary fuel mixture consisting of diesel, hydrogen, and ammonia, the lowest exhaust temperatures are achieved.

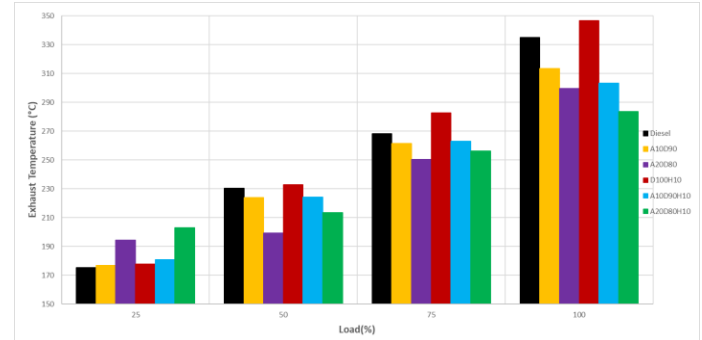


Fig 4 Exhaust Temperatures

3.2.2 Exhaust Emissions Nitrogen Oxides Emissions (NOx)

At low loads, increasing the proportion of ammonium hydroxide mixture results in higher nitrogen oxide (NOx) emissions. However, at medium and high loads, increasing the ammonia ratio reduces NOx emissions from the exhaust. In both the mixture created by adding hydrogen to pure diesel and the mixture created by adding hydrogen to ammonium hydroxide-enriched fuel, the presence of hydrogen reduces NOx emissions at low and medium loads. However, at high loads (>90%), adding hydrogen to a mixture with a low ammonia ratio will reduce the NOx levels.

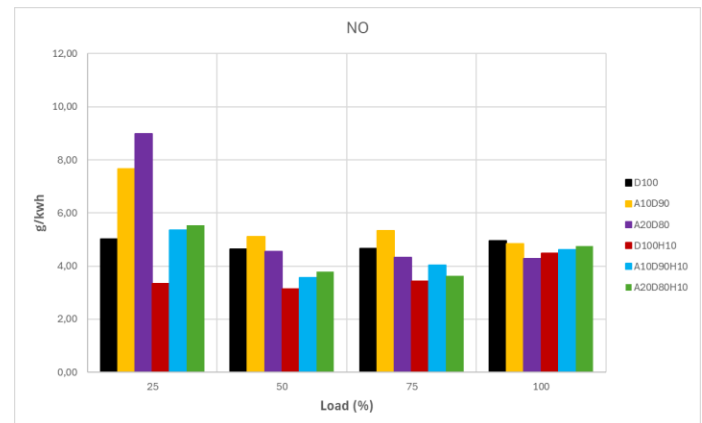


Fig 5 NOx Emissions

Unburned Hydrocarbon Emissions (HC)

At all loads, adding hydrogen to pure diesel increases HC (hydrocarbon) emissions. In contrast, it has been observed that HC emissions decrease as the amount of ammonium hydroxide increases. These findings indicate that hydrogen addition consistently increases

HC emissions, while the HC level is at its lowest in the ammonia hydroxide and diesel mixture. Additionally, it should be emphasized that HC emissions further decrease as the amount of ammonia hydroxide increases. This suggests that using ammonia hydroxide could be an effective method for reducing HC emissions.

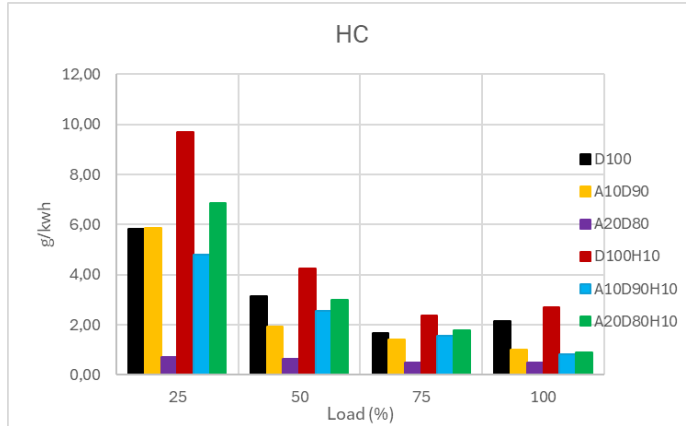


Fig 6 HC Emissions

CO₂ Emissions

In medium and high load conditions, the addition of ammonia to diesel fuel reduces CO₂ emissions as the amount of ammonia increases. Similarly, the addition of hydrogen to pure diesel also has a CO₂ reduction effect. However, adding hydrogen to an ammonia- diesel mixture results in increased CO₂ emissions. This indicates that the interactions between ammonia and hydrogen when used together complicate their effects on CO₂ emissions. Therefore, it can be concluded that careful balancing is necessary in emission control strategies for diesel engines.

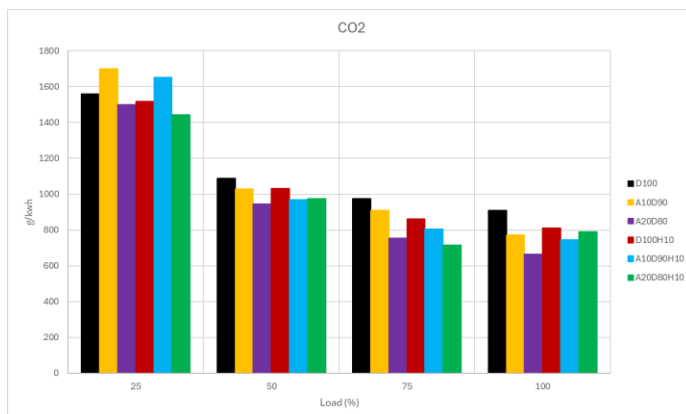


Fig 7 CO₂ Emissions

CO Emissions

At higher loads, CO emissions decrease, with the A10D90 mixture resulting in the

lowest CO emissions. Fuel mixtures with a high ammonia hydroxide content increase CO emissions at low loads but reduce them at high loads. The addition of hydrogen to pure diesel reduces CO emissions at medium and high loads. However, adding hydrogen to fuel mixtures with a high ammonia content increases CO emissions. These findings suggest that to keep CO emissions low, ammonia should be used at an optimal level, and specific fuel mixtures can achieve the lowest emission values.

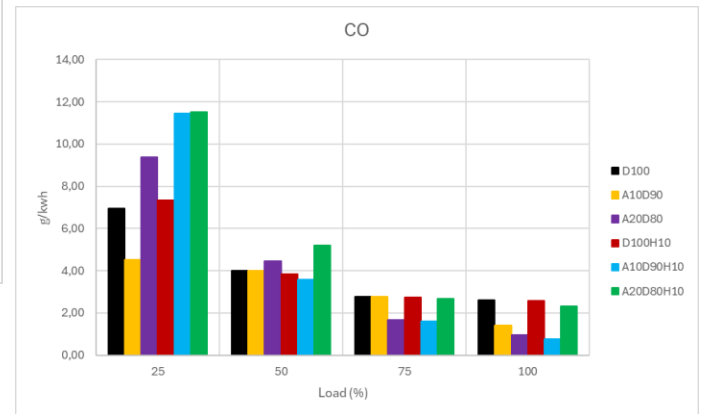


Fig 8 CO Emissions

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INVESTIGATION OF THE EFFECT OF AMMONIA ON HYDROGEN/KEROSENE MIXTURES

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Abstract

The civil aviation sector, a major source of pollutants like CO₂, NO_x, SO₂, water vapor, and soot from jet fuel combustion, faces growing pressure to reduce emissions. Technological advancements are vital for cutting greenhouse gases, with the International Air Transport Association (IATA) projecting that sustainable aviation fuel (SAF) will significantly contribute towards achieving net-zero CO₂ emissions by 2050. The research utilizes a GTM-120 gas turbine engine and applies Ansys Fluent for simulations. Compressibility effects and non-premixed combustion methods are incorporated, and the results are validated against experimental data. It is shown that hydrogen increases flame temperature, whereas ammonia reduces both flame temperature and NO_x emissions. A 10% ammonia addition is found to be more effective than 15% in reducing NO_x emissions. This is attributed to ammonia's lower heating value and its role in mitigating NO_x formation through nitrogen oxidation.

Keywords: Alternative fuels, Ammonia, Hydrogen, CFD, Gas Turbine Engine

1 INTRODUCTION

The rapidly developing civil aviation sector is increasingly recognized as a significant source of pollutant emissions, similar to many other industries. In addition to CO₂ emissions resulting from the combustion of carbon-based jet fuel in aircraft engines, NO_x, SO₂, water vapor, and soot are also generated. Technological advancements play the most significant role in reducing greenhouse gas emissions, alongside consumer behaviour, government policies, and sectoral measures. According to the International Air Transport Association (IATA), sustainable aviation fuel (SAF) will contribute 65%, offsets and carbon capture 19%, new technologies 13%, and infrastructure and operational efficiencies 3% towards achieving the net-zero CO₂ emissions target by 2050 [1]. Moreover, it is anticipated that the proportion of conventional fuels used will significantly decrease after 2045 [2].

The literature indicates that alternative fuels such as hydrogen, ammonia, and biogas are promising for use in gas turbine engines in aircraft [3]. It is known that the addition of hydrogen increases flame temperature and consequently NO_x emissions. Data from the literature suggest that the use of ammonia, another alternative fuel, is promising in mitigating this effect [4]. This study numerically

investigates the impact of adding hydrogen and ammonia to kerosene in a mini gas turbine engine [5], [6].

2 METHOD

2.1 Geometry

In this study, the GTM-120 engine, which has been experimentally and numerically tested in the literature, was utilized [7]. The engine features a single-stage centrifugal compressor, a reverse-flow combustion chamber, and a single-stage turbine. A 3D model of the engine, with sharp edges removed and impeller and turbine blades extracted for the simulation study, is presented in Figure 1.

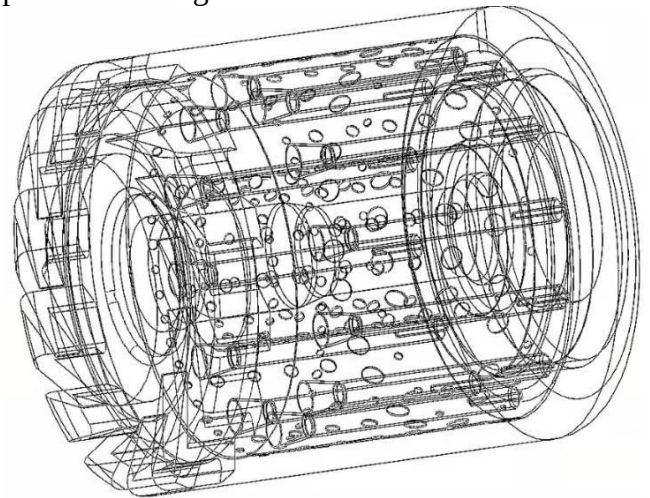


Figure 1. Simplified 3D Model of GTM - 120 [7]

Diffuser geometry was included in the simulations due to its effect on the direction of the air entering the combustion chamber. Since there are 13 diffuser pales against 12 fuel nozzles, a full body analysis was performed.

2.2 Numerical Setup

In the analyses conducted using Ansys Fluent, compressibility effects were activated, and the non-premixed combustion method was chosen. The simulations employed the k- ϵ with scalable wall function and discrete ordinates models. Given the presence of kerosene, hydrogen, and ammonia fuels, the NOx models activated were Thermal, Prompt, Fuel, and N2O Intermediate models. Kerosene fuel was injected through 12 nozzles using the discrete phase model. For model validation, the combustion chamber outlet temperature averages were compared with experimental results by varying the air/fuel flow rates, pressure, and temperature at three different engine speeds.

The results of the combustion chamber outlet temperatures obtained from simulations at three different engine speeds after 1600 iterations with the SIMPLE solution algorithm are shown in Figure 2. The results indicate a very low discrepancy compared to the experimental findings in the literature. The closest result was obtained at 100 K RPM, ensuring that grid independence analyses and alternative fuel studies were conducted with input data at this engine speed.

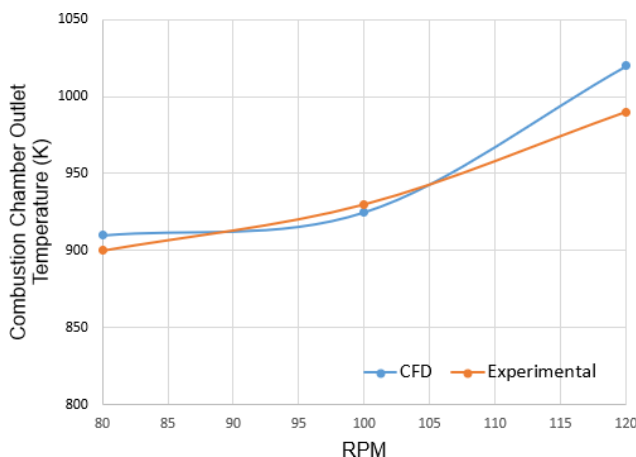


Figure 2. Validation of CFD Model [8]

2.3 Mesh Independence

In CFD studies, the mesh element structure, density, and pattern can significantly impact the results obtained from the simulations. To achieve the most accurate results, a mesh with a good pattern and as fine a grid as possible should be created. However, this can considerably increase computation time. Therefore, grid independence analyses are conducted to ensure that the most accurate results are obtained with an ideal mesh configuration. In this context, meshes with element sizes of 3.6 million and 5.1 million were created at 100 K RPM, and the combustion chamber outlet temperatures were compared with experimental results from the literature. It was observed that a significant increase in the number of elements did not positively contribute to the result provided in Table 1, but rather extended the computation time. Consequently, it was decided to continue the alternative fuel studies with the mesh having 3.6 million elements.

Table 1. Mesh Independence Analysis [8]

Element Number (m)	Temperature (K)	Difference %
Reference [8]	930	
3.6	925	0.541
5.1	944	-2.013

3 CONCLUSION

Alternative fuels were added to the mixture as a secondary stream, with increments of 10% up to 30%, while maintaining the thermal power constant at the level obtained with pure kerosene. Initially, 5% ammonia and 5% hydrogen were added to kerosene. Subsequently, the kerosene proportion was reduced by 10%, and the amounts of ammonia and hydrogen were increased by 5% each to obtain flame temperature and NOx emissions in the combustion chamber. Further, ammonia was added while keeping the total energy supplied by alternative fuels constant. The obtained results were compared with the kerosene/hydrogen mixture from the literature. Upon examining the flame temperatures for different mixtures shown in Figure 3, it was observed that the addition of hydrogen to jet fuel kerosene increased the flame temperature. However, when ammonia was added without changing the proportion of alternative fuels in

the mixture, the flame temperature decreased. This outcome is simply due to hydrogen having a higher lower heating value compared to kerosene, while ammonia has a lower lower heating value.

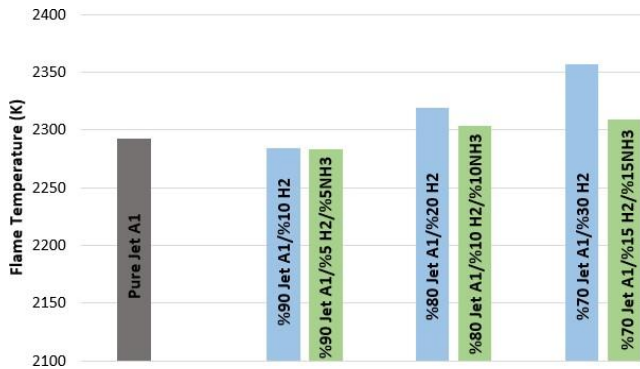


Figure 3. Effects of Ammonia Addition on Temperature in Kerosene-Hydrogen Mixture [8]

Upon examining Figure 4, which presents the NO_x emissions at the combustion chamber outlet, it can be observed that the addition of ammonia to the kerosene/hydrogen mixture reduces NO_x emissions. Considering that the flame temperature is above 2200 K in this gas turbine engine, it can be inferred that the most effective mechanism for NO_x formation is the Zeldovich Mechanism [9].

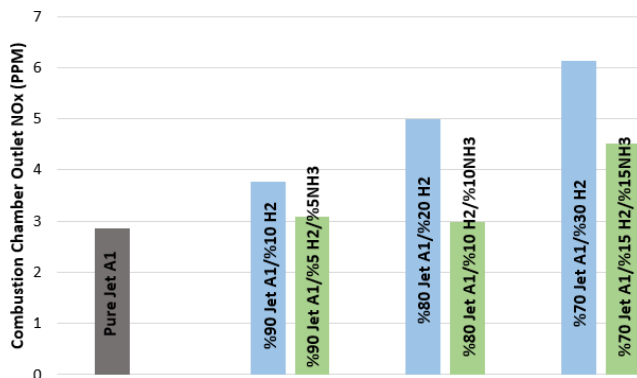


Figure 4. Effects of Ammonia Addition on NO_x in Kerosene-Hydrogen Mixture [8]

At this point, the reduction in flame temperature due to the addition of ammonia is considered the primary reason for the decrease in NO_x emissions. On the other hand, this reduction rate, consistent with the literature, is higher with a 10% ammonia addition and decreases with a 15% ammonia addition. This is because the nitrogen in ammonia contributes to the

formation of Fuel NO_x mechanisms through oxidation [10].

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INVESTIGATION OF COMBUSTION KINETICS OF RAW AND TORREFIED ROSE PULP, AND CHICKEN MANURE MIXTURES WITH LOCAL LIGNITE

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Abstract

In this study, 42 fuel blends were prepared by using raw and torrefied forms of chicken manure (CM), rose pulp (RP), local Kale lignite (L), and their blends in different ratios by weight (100%CM, 100%RP, 100%L, 40%CM + 40%RP + 20%L, 37%CM + 37%RP + 26%L, 33%CM + 33%RP + 34%L) to determine the activation energies of these fuel mixtures. Experiments were carried out using Polymer Laboratories Brand TG-1500 model TGA Device in the 25-950 °C temperature range, 40 ml/min dry air atmosphere, and four different heating rates (5°C/min; 10°C/min; 15°C/min; 20°C/min). The Flynn-Wall-Ozawa method was applied to the calculation of the activation energies of the prepared fuel mixtures. The calculated average activation energies of the raw fuel mixtures were 127.14 kJ/mol, 87.75 kJ/mol, 40.50 kJ/mol, 55.63 kJ/mol, 52.51 kJ/mol, and 52.11 kJ/mol for the 100%CM, 100%RP, 100%L, 40%CM + 40%RP + 20%L, 37%CM + 37%RP + 26%L, 33%CM + 33%RP + 34%L, respectively. The activation energies of the torrefied fuel mixtures were calculated as 69.61 kJ/mol, 67.55 kJ/mol, 53.85 kJ/mol, 51.60 kJ/mol, and 49.78 kJ/mol for the 100%TCM, 100%TRP, 40%TCM + 40%TRP + 20%L, 37%TCM + 37%TRP + 26%L, 33%TCM + 33%TRP + 34%L, respectively. Therefore, as the biomass content increased in raw and torrefied blends, the activation energies of the blends were also increased both in raw and torrefied fuel mixtures. Since biomass samples are more reactive than lignite, they burn more easily. Furthermore, the activation energies of the torrefied samples were found to be lower than their raw forms. Which indicates the carbonization of the biomass samples.

Keywords: Chicken manure, Rose pulp, Co-combustion, Activation energy, Flynn-Wall-Ozawa, TGA

1 INTRODUCTION

The energy needs of Türkiye are increasing due to the fast-growing population, economy, and high urbanization rate. The primary energy consumption of Türkiye was 147.2 Mtoe in 2020. Primary energy consumption, which increased by an annual average of 3.1% in the 2000–2020 period, will increase by 1.5% annually in the 2020–2053 period in Türkiye. The primary energy consumption per capita, 1.7 toes in 2020, will rise to 2.4 toes by 2053.

However, 76% of the primary energy demand is met by imports in our country. As a result, it is a fact that the energy needs of our country will

increase gradually, and meeting this energy need with our resources (non-renewable (lignite, coal natural gas) and renewable energy sources) is very important for the future of our developing economy.

Türkiye produces more than 65 % of the world's rose oil, concrete, and pulp. Furthermore, Türkiye ranks 10th in the world in chicken meat production with a share of 2%. The number of chickens raised in Türkiye in 2020 was 379,349,000 and it has been reported that approximately 5.5 million tons of chicken manure was generated annually as a result of this production. Therefore, an important amount of

waste biomass is produced in Türkiye. Co-combustion lignite and biomass are one of the preferred disposal options in terms of the evaluation of these types of bio-wastes. Furthermore, the co-combustion of lignite/biomass in thermochemical systems will also decrease the dependence on fossil fuels of the Türkiye.

In this study, 42 fuel mixtures were prepared by using raw and torrefied forms of chicken manure, rose pulp, local Kale lignite, and their blends in different ratios by weight (100%CM, 100%RP, 100%L, 40%CM + 40%RP + 20%L, 37%CM + 37%RP + 26%L, 33%CM + 33%RP + 34%L) to determine the activation energies of these fuel mixtures.

2 MATERIAL AND METHODS

In the study, rose pulps and chicken manure samples were taken from the enterprises located in Isparta Province. Local Turkish Lignite samples were purchased from the Kale/Denizli Province. Before the Thermogravimetric Analysis (TGA), samples were dried, crushed, and sieved to 300-800 µm.

The Flynn-Wall-Ozawa (FWO) Method was used to determine the thermal kinetics of the blends used in this study. Experiments were carried out using Polymer Laboratories Brand TG-1500 model TGA Device for four different heating rates(β); 5, 10, 15, and 20 °C/min dry air atmosphere, 25-950 °C temperature range, 40 ml/min dry air atmosphere and approximately 4 mg of sample and the conversion rates of the reactions were found for each heating rate using the FWO method and the average activation energies for each sample were calculated [1,2,3].

In this method developed by Wall and Ozawa, the calculation of non-isothermal data is used with the Doyle approach [4] (Equation 1). The temperature (T) values corresponding to different heating rates (β) were plotted against $\log \beta$ with a $1/T$ graph considering the constant mass conversion ratio (α) and the Activation energy (E_a) values were calculated using the slope of the line.

$$\log \beta = \log \left(\frac{AE_a}{Rg(\alpha)} \right) - 2,315 - 0,4567 \left(\frac{E_a}{RT} \right) \quad (1)$$

3 RESULTS AND DISCUSSION

The calculated average activation energies of both raw and torrefied fuel mixtures are given in Table 1.

Table 1. Calculated average activation energies of the fuel mixtures

Fuel mixtures	Activation energy (kJ/mol)
Raw mixtures	
CM	127.14
RP	87.75
L	40.50
40CM+40RP+20L	55.63
37CM+37RP+26L	52.51
33CM+33RP+34L	52.11
Torrefied mixtures	
TCM	69.61
TRP	67.55
40TCM+40TRP+20L	53.85
37TCM+37TRP+26L	51.60
33TCM+33TRP+44L	49.78

The average E_a of the fuel blends in the study was calculated for mass conversion ratios ranging from 10% to 90% and it was observed that the E_a values decreased as the amount of L in the fuel blends increased, similar to the literature [5]. Furthermore, the activation energies of the raw fuel mixtures were found to be higher than those of their torrefied forms. With the torrefaction of the fuel mixtures, the activation energies approached the activation energy values of the local lignite samples.

Conclusion

As the biomass content increased in raw and torrefied blends, the activation energies of the blends were increased both in raw and torrefied fuel mixtures. Furthermore, the activation energies of the torrefied samples were found to be lower than their raw forms.

ACKNOWLEDGEMENTS

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ELECTROLYSIS UNIT DESIGN TO IMPROVE THE COMBUSTION PROCESS IN A DIESEL ENGINE

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Abstract

The climate change problem our world has been facing in recent years and the measures being developed against this problem have attracted the attention of researchers. The most important cause of climate change is pollutant emissions resulting from combustion. Natural gas is largely used to reduce pollutant emissions resulting from home heating, and gasoline and diesel used in internal combustion engines are also classified as hydrocarbon fuels. The carbon atoms in these fuels react with oxygen and release CO₂ gas as a result of complete combustion. This emerges as the most important reason for the problem called greenhouse gas effect. Theoretically, just as CO₂ gas is released as a result of complete combustion, CO gas is also released as a result of incomplete combustion. This gas also has a negative impact on the environment. There are many studies on engine technologies, especially in the field of low- emission combustion. Due to the high flame temperatures that occur in these studies, the amount of NO_x gas from pollutant emissions increases. The aim of the study is to reduce emission values and increase performance by improving the combustion process of diesel engines. In order to improve the combustion processes in a diesel engine, the electrolysis unit is designed and the optimum HHO is achieved by changing the distance between the plates (2, 4, 6,...mm), number of plates (2,3,4,.....30) and applied voltage (12, 24V). gas production was calculated.

Keywords: Diesel engine, HHO, Emission, Alternative Fuels, Combustion Efficiency

SIMULATION AND ASSESSMENT OF EMISSIONS REDUCTION POTENTIAL OF AN ORC-BASED EXHAUST HEAT RECOVERY MODEL AUTOMOBILE APPLICATION

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Abstract

Context/Purpose: Exhaust heat recovery (EHR) has recently been considered a viable means of achieving sustainable use of fossil fuel resources in the transportation sector, meeting future CO₂ legislation, and improving thermal efficiency - the primary technological driver in internal combustion engine (ICE) research. The transportation industry accounts for a substantial share of global oil consumption, amounting to 64%, which translates to 16.2% of worldwide greenhouse gas (GHG) emissions. Among these emissions, on-road vehicles contribute 11.9%, with trucks alone responsible for 22% of the sector's total emissions. Unlike in developed nations, where dedicated environmental oversight entities monitor emissions from critical sectors, regions such as Nigeria and other developing countries lack adequate GHG monitoring systems, despite the profound impact of emissions on air quality and public health. Therefore, harnessing the exergy in these exhaust gases not only aids in emission reduction efforts but also enhances the efficiency of ICE technology. The study's objectives encompassed modeling the system coupled to a commercial truck engine, assessing its thermal efficiency, and quantifying its potential for emissions reduction.

Methods: The investigation employed three research methodologies, including model design and simulation employing GT-Suite software and evaluate emission reduction potential of the model.

Results: Employing R245fa as the working fluid and simulated in GT-Suite, the proposed model yielded notable results: a power output of 3.48 kW, thermal efficiency of 6.39%, and a 3.27% enhancement in specific fuel consumption (SFC) at a maximum truck speed of 119 km/h. Additionally, it achieved an annual reduction of up to 4,767 kgCO₂ emissions, marking a 4% decrease in typical commercial truck engine emissions. This research underscores the potential of integrating the proposed EHR system into automobiles to enhance ICE thermal efficiency while combating the global menace of greenhouse gas emissions from exhausts. Moreover, as a developing nation, Nigeria grapples with the adverse effects of global warming, including localized flooding and heightened temperatures due to increased fossil fuel combustion emissions. Hence, concerted efforts toward mitigation are imperative.

Conclusion: The research indicates that incorporating the proposed EHR system into trucks holds significant promise for improving the thermal efficiency of truck engines and simultaneously mitigating global threats posed by greenhouse gases generated from exhaust emissions.

Keywords: Exhaust heat recovery, CO₂ savings, Model Simulation, Organic Rankine Cycle, Quantifying Emission reduction Potentials.

WILL RENEWABLE ENERGY TRANSITION AND GREEN CREDIT SPEAK LOUDER TOWARDS ACHIEVING COP28 TARGETS ACROSS BRICS COUNTRIES: NOVEL EVIDENCE FROM REGRESSION DISCONTINUITY DESIGN

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Abstract

As the global focus on improving environmental conditions intensifies, identifying factors that can contribute to the establishment of environmental sustainability has become paramount. Renewable energy transition (RET) and green credit (GCR) are crucial for reducing carbon emissions, but little research has been done on them. Therefore, this study examines a sample of nine (old plus new) BRICS countries. Using yearly data from 2000 to 2020, this study also employed a Bayesian Neural Network (BNN) to estimate the interaction between RET, GCR, and CO₂ emissions. Using panel data, we also build a based-on Regression Discontinuity Design (RDD) that takes the implementation of RET and GCR as a quasi-natural experiment of Conference of the Parties (COP)17, which took place in South Africa in 2011 to limit the CO₂ emissions and, will energy transition and green credit will achieve the COP28 targets. The study's results affirm that the COP17 policy shock, has a measurable, significant impact on the carbon emissions of the BRICS nations. (a) the transition to renewable energy (RET) effectively reduces CO₂ emissions, and (b) green credits (GCR), natural resources (RNN), urban population (UP), and industrialization (IND) help increase carbon emission levels. The study provides valuable policy recommendations for keeping CO₂ emissions fair and sustainable in the BRICS countries.

Keywords: Carbon emissions, renewable energy transition, green credit, BRICS, BNN

THERMODYNAMIC ANALYSIS OF DESICCANT DEHUMIDIFICATION ASSISTED EVAPORATIVE COOLING SYSTEM FOR GREENHOUSE FARMING IN MULTAN (PAKISTAN)

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Abstract

This study thermodynamically investigates utilizing a desiccant dehumidification-based Maisotsenko cycle evaporative cooling (M-DAC) system for greenhouse air conditioning. Conventional cooling techniques, such as direct evaporative cooling, refrigeration systems, and passive/active ventilation, are commonly utilized in Pakistan. However, these methods are not feasible due to high energy costs or inefficiencies in creating an optimal microclimate based on different regions, growing seasons, and specific crops. For greenhouse crop production, the M-DAC system was suggested as an alternative for air conditioning to attain the ideal vapor pressure deficit (VPD) values. This study investigated the thermodynamic performance of temperature gradient, relative humidity level, and dehumidification gradient. The analysis result shows that the proposed system is best for May, June, July, August, and September for the climatic data of Multan, Pakistan.

Keywords: desiccant dehumidification, Maisotsenko cycle, greenhouse

INTRODUCTION

The production of crops and vegetables in greenhouses using different covering materials depends on the climate control system's efficiency. It must provide optimal growth conditions at a reasonable energy cost. The intense solar radiation during the daytime creates a greenhouse effect, leading to high air temperature and relative humidity levels that can exceed the ideal conditions. This can significantly decrease yield and fruit quality if proper ventilation and dehumidification systems are not in place. High relative humidity also makes plants and vegetables more susceptible to pests, fungal, and disease attacks, further impacting greenhouse production.

To mitigate the impact of suboptimal microclimate conditions, greenhouse growers in Pakistan conventionally utilize passive and active ventilation as well as direct evaporative cooling systems such as pad-and-fans or swamp coolers. However, these solutions do not offer control over the relative humidity level, leaving plants vulnerable to

pests, fungi, and diseases. Therefore, a cost-effective air-conditioning (AC) solution suitable for large-scale commercial production is needed. Desiccant dehumidification-based indirect evaporative cooling AC systems are gaining attention for their potential application in various closed-field plant production environments and need more evaluation.

The proposed study focuses on the city of Multan, Pakistan, situated in a warm desert climate where various cooling methods are used in agricultural greenhouses. The research proposes and evaluates a desiccant dehumidification-based Maisotsenko cycle evaporative cooling (MDAC) system as a solution to control humidity levels and achieve the optimum vapor pressure deficit (VPD). The study aims to thermodynamically analyze the proposed M-DAC system in terms of temperature gradient, relative humidity levels, optimum VPD, and dehumidification gradient. A review of relevant literature is summarized in Section 2 to identify recent achievements and gaps.

Section 3 covers the modeling of the M-DAC. Section 4 describes the thermodynamics analysis result.

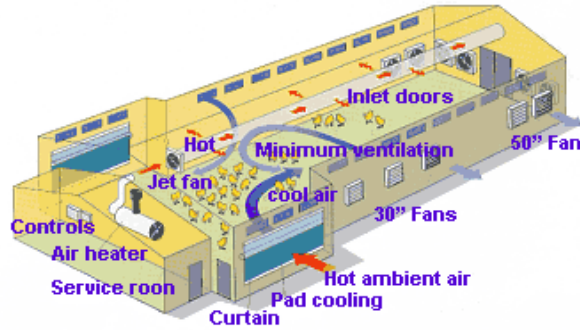


Figure 1 Evaporative cooling base greenhouse system Source: <https://artpictures.club/autumn-2023.html>

LITERATURE REVIEW

Evaporative cooling (EC) systems can be classified into three main types: direct evaporative (DEC), indirect evaporative (IEC), and Maisotsenko cycle evaporative (MEC) systems. The MEC system is extensively researched for heating, ventilation, and air-conditioning (HVAC) systems. A comparative study of eight independent M-cycle evaporative cooling setups was conducted by Pandelidis and Anisimov [1]. Energy and exergy evaluations of freestanding MEC systems for building air conditioning were investigated by Caliskan et al. [2] Zhan et al. [3] investigated cross-flow heat exchangers for indirect evaporative cooling and a counter-flow standalone MEC system for building air conditioning applications. Using energy and exergy calculations, Caliskan et al. [4] compared the MEC system with traditional vapor compression air conditioning systems. Chua et al. [5] examine new developments in cooling technology as well as approaches for use in buildings to bring down the average kW/R ton of cooling systems from 0.9 kW/R ton to 0.6 kW/R ton or less. The MEC system was numerically calculated by Pandelidis et al. [6] for a range of air conditioning applications. The MEC system for building air conditioning applications was confirmed experimentally and numerically by Rogdakis

et al. [7] for the climate conditions of Greece. The MEC system for precooling ambient air was investigated by Cui et al. [8] as an energy-saving method for hot and muggy climates. A numerical investigation of the MEC system under various inlet circumstances was conducted by Rianguvilaikul and Kumar [9]. Sultan [10] investigated the MEC system for ventilation and air conditioning in greenhouses. After analyzing the standalone MEC system for air conditioning both conceptually and empirically, Anisimov et al. [11] concluded that the MEC system was an effective indirect evaporative cooling method. Additionally, the study's findings indicated that the system's performance was impacted by the inlet air velocity. Through numerical investigation, Zhao et al. [12] determined the MEC system's performance for UK climate conditions, yielding a wet-bulb efficacy of 1.3. However experimental investigation of a commercial-type MEC air-conditioning system and evaluation of heat mass transit parameters inside a heat exchanger was conducted by Zube and Gillan [13]. Comparing commercially available standalone MEC systems to vapor compression air-conditioning (VCAC) systems, Weerts [14] reported on the possible electricity savings. The energy-saving potential of the standalone MEC system in comparison to the standalone VCAC system was previously noted by Maisotsenko and Treyger [15]. Comparably, [16] and [17] also conducted extensive research on the standalone MEC system and concluded that, in comparison to the VCAC system, the MEC system may be a more ecologically friendly air conditioning solution.

Numerous applications of the desiccant air-conditioning (DAC) system have been the subject of in-depth research in the literature. In general, areas with higher relative humidity in the surrounding air are more suited for the DAC system. The potential use of vehicle air conditioning with the DAC system was investigated [18]. To boost

system efficiency, the authors also employed a continuous input and output proportional-derivative (PD) controller. They concluded that the DAC system in conjunction with the PD controller was more energy-efficient than traditional AC systems [18]. Furthermore, a Hong Kong wet market saw the successful installation of the DAC system. Using Energy Plus for the meteorological conditions of Hong Kong, the authors statistically calculated the energy loads of a hypothetical wet market and compared the results with the real wet market [19]. The authors concluded that the DAC might be utilized in moist markets instead of traditional air conditioning systems. In Melbourne, Australia, an M-cycle, solar-assisted DAC system for grain storage was put through experimental testing [20]. The scientists concluded that a 5.85m³ solar collector surface may adequately cool up to 200 tons of grain. The coefficient of performance (COP) was a function of surrounding conditions and air mass flow rate. A maximum COP of 86.2 was observed under humid conditions for an air mass flow rate of 0.019 kg/s [20]. The standalone DAC system was investigated for a greenhouse air temperature and humidity management system [21]. Additionally, the scientists looked at the greenhouse's air conditioning system from the vapor pressure deficit (VPD) perspective. A stand-alone desiccant wheel system was investigated to recover residual heat waste in marine vessels [22]. The DAC system was found by the authors to be 33.4% more power-efficient than conventional maritime air conditioning systems. Two modes of an EC-coupled DAC system ventilation and recirculation were investigated by [23]

METHODOLOGY

A general working principle of the M-DAC system is shown in Figure 2, followed by the schematic representation in Figure 3 that demonstrates the application of the proposed system for greenhouse air conditioning for a possible higher yield. The model was used to

evaluate the performance of the silica gel-based desiccant wheel of the M-DAC system as described in the literature [25-26] for Multan (Pakistan) climatic conditions.

$$F_{1,ip} = \frac{\phi_1}{(T_{ip} + 273.15)^{1.49}} + \phi_2 \left(\frac{\omega_{ip}}{1000} \right)^{\phi_3} \quad (1)$$

$$F_{2,ip} = \frac{(T_{ip} + 273.15)^{1.49}}{\phi_4} - \phi_5 \left(\frac{\omega_{ip}}{1000} \right)^{\phi_6} \quad (2)$$

$$\eta_{F1} = \frac{F_{1,2} - F_{1,1}}{F_{1,8} - F_{1,1}} \quad (3)$$

$$\eta_{F2} = \frac{F_{2,2} - F_{2,1}}{F_{2,8} - F_{2,1}} \quad (4)$$

Where, $F_{1,ip}$, and $F_{2,ip}$ represent the combined potential as a function of the humidity ratio in kg/kg and temperature in °C of the solid desiccant-based air-conditioning system. η_{F1} and η_{F2} represent the efficiencies of the system correlating to the combined potentials. η_{F1} and η_{F2} have typical values of 0.05 and 0.95 for a high-efficiency silica gel-based solid desiccant wheel air-conditioning system. The values of coefficients ϕ_1 , ϕ_2 , ϕ_3 , ϕ_4 , ϕ_5 , and ϕ_6 are presented in Table 1

Table 1 Coefficients used in the Jurinak model (Equations (1) - (4)).[25]

Coefficient	Value
ϕ_1	-2865
ϕ_2	4.344
ϕ_3	0.8624
ϕ_4	6360
ϕ_5	1.127
ϕ_6	0.07969

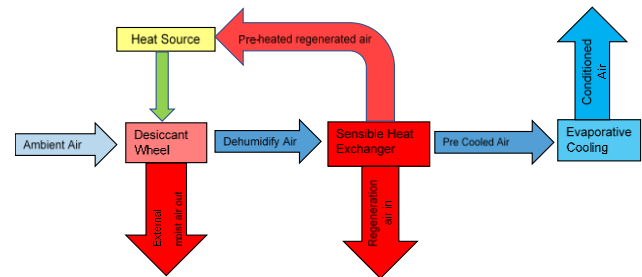


Figure 2 Working principle of a desiccant dehumidification-based evaporative cooling air-conditioning system

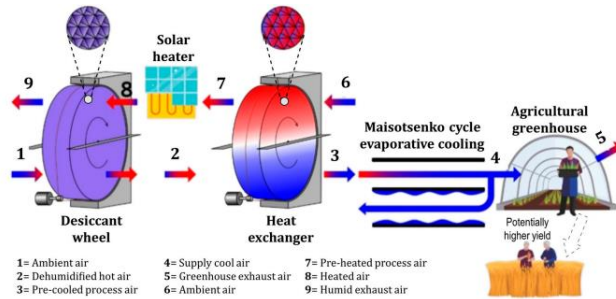


Figure 3 Schematic diagram and working principle of the proposed desiccant dehumidification Maisotsenko cycle evaporative cooling system [26]

The desiccant dehumidification-assisted evaporative cooling air-conditioning system consumes less energy than conventional vapor compression air-conditioning systems. This is because it does not require compressor work and can operate at lower regeneration temperatures (50–90°C), which can be easily achieved using solar thermal, biogas, and waste heat sources. In this study, the sensible heat exchanger (HX) was modeled using the heat exchanger standard Equation 5 provided in the literature by The American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE) [27]

$$T_3 = T_2 - \varepsilon_{HX}(T_2 - T_1) \quad (5)$$

Where T_3 represents the outlet temperature of the sensibly cooled process air resulting from the heat exchanger, T_2 represents the outlet temperature of heated and dehumidified air resulting from the desiccant air-conditioning system, ε_{HX} represents the sensible heat exchange efficiency of the heat exchanger (assumed as 0.9), and T_1 represents the dry bulb temperature of the ambient air inlet into the desiccant air-conditioning system. The Maisotsenko cycle evaporative cooling system was simulated using the model from

reference [28]. Equation (6) presents the performance model of the Maisotsenko cycle evaporative cooling system.

$$T_{out} = T_{3,db} - \varepsilon_{wb}(T_{3,db} - T_{1,wb}) \quad (6)$$

Figure 2 and Figure 3 illustrate the working principle and schematic of the sensible heat exchanger. Desiccant regeneration typically involves using regeneration air at a temperature higher than the ambient temperature. This air is heated by passing it through the heat exchanger, which sensibly heats the air to a certain limit. A heating unit or source is employed to heat the regeneration air further before it enters the desiccant. A heating source such as a heating electric coil, solar heater, or biogas-operated thermal heat source can be used. Waste heat from a condenser or any other industrial source can also be used to regenerate the desiccant material and absorb its moisture. In this study, a regeneration temperature of 50°C was utilized. This relatively lower temperature can be achieved through a solar thermal system, biogas-operated thermal heat source, or waste heat.

RESULT AND DISCUSSION

Figure 4 illustrates the yearly climatic ambient air conditions of Multan, Pakistan. The monthly variation in dry-bulb temperature indicates the necessity for cooling within the greenhouse environment. Conventional cooling techniques, such as direct evaporative cooling, refrigeration systems, and passive/active ventilation, are commonly utilized in Pakistan. However, these methods are not feasible due to high energy costs or inefficiencies in creating an optimal microclimate based on different regions, growing seasons, and specific crops. Therefore, the M-DAC system was suggested as an alternative for air conditioning to attain the ideal vapor pressure deficit (VPD) values for greenhouse crop production. Consequently, a desiccant dehumidification-based Maisotsenko cycle evaporative cooling

system was thermodynamically analyzed for the climatic conditions of Multan. The thermodynamics analysis result is shown in Figure 5

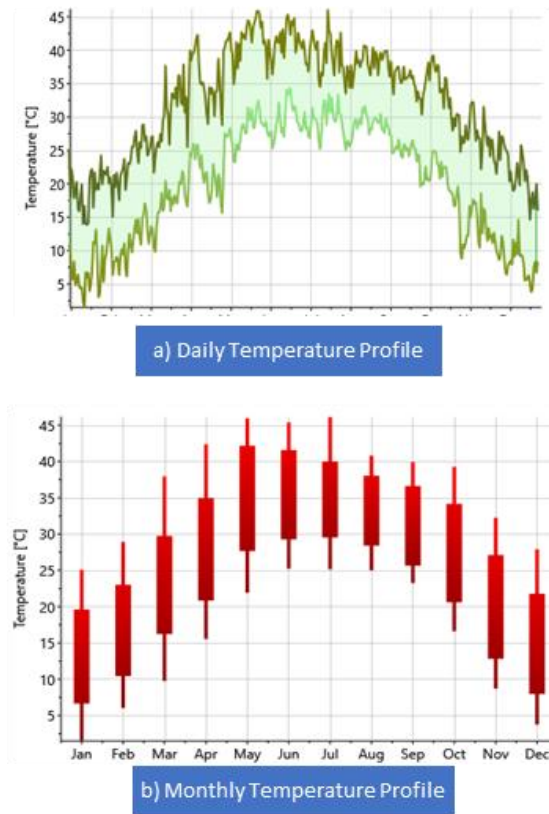


Figure 4 Profile of annual climatic ambient air conditions of Multan (Pakistan)

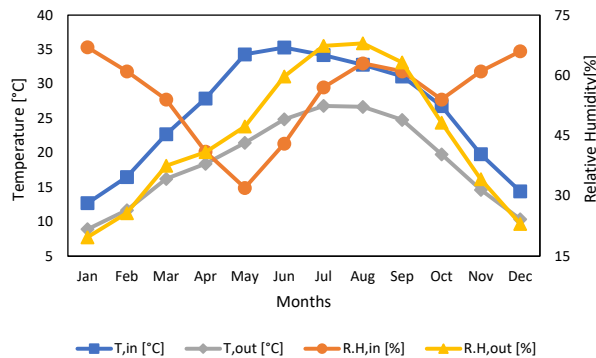


Figure 5 Thermodynamic Analysis of M-DAC System

Figure 6 illustrates the vapor pressure deficit (VPD) profile and growth stages of plants inside a greenhouse, where the temperature of the leaves is equal to the temperature of the

air inside the greenhouse environment. According to Figure 10, a VPD of 1.6 kPa is considered extremely dangerous for over/under transpiration. A VPD of 0.4–0.8 kPa is considered a slightly low transpiration zone, which is optimal for the propagation/early vegetative growth of the plants. The VPD of 0.8–1.2 kPa is considered a healthy transpiration zone, suitable for the late vegetation/early flowering stage of the plants. Lastly, a VPD of 1.2–1.6 kPa is considered a high transpiration zone, appropriate for the mid/late flowering stage of the plant.

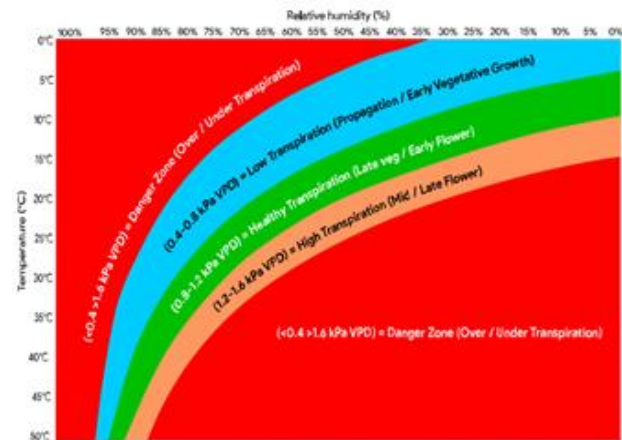


Figure 6 Vapor pressure deficit (VPD) profile and growth stages of plants inside a greenhouse [26]

CONCLUSION

The proposed study thermodynamically investigates the utilizing a desiccant dehumidification-based Maisotsenko cycle evaporative cooling (M-DAC) system for greenhouse air conditioning in Multan, Pakistan. Multan has a warm desert climate makes air-conditioning necessary in greenhouses to optimize temperature and humidity levels. Improving these conditions could enhance overall production. In this study, the Jurinak model was employed for desiccant dehumidification to conduct a thermodynamic analysis, while the wet bulb effectiveness equation was used for the MEC system. To potentially investigate the proposed system, a regeneration temperature

of 50°C was used for Multan climate conditions. The analysis results for Multan, Pakistan, and Nilai, Malaysia are presented in Figure 5. The analysis result shows that the proposed system is best for May, June, July, August, and September for the climatic data of Multan. Pakistan.

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TECHNO-ECONOMIC ANALYSIS OF WIND-POWERED GREEN HYDROGEN PRODUCTION BASED ON MODULAR PEM ELECTROLYZER: A CASE STUDY FOR İZMİR, TÜRKİYE

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Abstract

To achieve the net zero emission goal, many countries have prioritized the development of green hydrogen technologies to replace emission-causing fossil fuels. However, green hydrogen currently cannot compete with conventional methods (e.g., steam reforming of natural gas) mainly due to the high cost of electricity from renewables and equipment such as electrolyzers. There has been ongoing research to minimize the production cost of green hydrogen to make it commercially viable. In this study, a case study was performed for İzmir, Türkiye, which has a high wind energy capacity factor (40%-50%). A green hydrogen production system based on a wind-powered modular proton exchange membrane (PEM) electrolyzer system (nominal capacity of 10 MW) was economically assessed for several locations in İzmir. The results showed that the Çandarlı region yields the lowest levelized cost of hydrogen (LCOH), 4.56 \$/kg, and the highest net present value (NPV), 14.85 M\$. For Çandarlı, different scenarios were conducted such as getting electricity through a power purchasing agreement (PPA), investing in a power plant to create its own electricity, and modular designing of an electrolyzer system. Two different power allocation strategies for the modular electrolyzer system are compared. Operating the system with an average allocation strategy using 10 modules resulted in lower LCOH (4.51 \$/kg) and higher NPV (18.07 M\$) than the single module design.

Keywords: Green hydrogen, modular electrolyzer, power allocation, wind energy

1 INTRODUCTION

By 2050, the global warming must not exceed 1.5 °C under the optimal scenario. To ensure this condition, renewable energy must constitute 77% of the global primary energy supply in 2050 [1]. Until then, more green energy investments will be needed to reduce dependence on fossil fuels worldwide. Global renewable energy capacity has been increasing continuously. In 2023, this capacity increased to 507 GW, 50% higher than the 2022 value [2], and it is predicted that it will increase more in the coming years. Green electricity is needed for a cleaner future, and green hydrogen or its derivatives are also required as green fuels for the same purpose. Unfortunately, common and cheap hydrogen production methods currently release lots of GHG (greenhouse gases). To prevent that, green hydrogen production systems with renewable energy-powered water electrolysis have been developed, but there is a major challenge that

must be overcome. Currently, producing green hydrogen is not cost-competitive against the cheap, fossil-fuelled hydrogen production processes. Green hydrogen production costs must be minimized by performing techno-economic analyses that consider multiple scenarios to catch the hydrogen buyers' interest. A case study was performed for several locations in İzmir to find the region that yields the lowest LCOH, and the scenario that gives the most economical solution for that region, such as purchasing electricity or investing in a power plant to produce electricity and designing the electrolyzer system with multiple modules or designing it as a single module.

2 METHOD

A techno-economic analysis has been conducted using MATLAB to analyze the LCOH, cash flow, and net present value (NPV) of the green

hydrogen systems that can be proposed for the selected locations.

2.1 LCOH Calculation

The green hydrogen production system consists of a wind power plant and PEM electrolyzer modules. In analyses, grid connection is also considered for Power Purchasing Agreement (PPA) scenarios, which means purchasing electricity instead of making an investment in the power plant to produce electricity. Green hydrogen producers can invest in a renewable energy power plant to produce the electricity, but this will require high investment costs, including land procurement, equipment, and installation costs. Purchasing electricity from a renewable electricity producer can be a better option if electricity prices are low in the region where the system will be built because the grid usage charges must also be paid.

PEM electrolyzer was selected for the system because of its operational flexibility under dynamic loads, as the renewable energy input data mostly shows a fluctuating pattern [3]. An alkaline electrolyzer (AE) could also be an option, but a higher response time to fluctuations makes this technology less suitable. A single module system and a modular designed system are considered for this study. Daisy chain and average power allocation strategies are simulated for modular operation.

Reference capital and operation costs of the power plant and the electrolyzer system are taken from the data from the International Renewable Energy Agency (IRENA) [4,5]. Hourly wind energy operation data are taken from [6] based on the year 2019. Electricity prices are taken from “EPIAŞ (Energy Markets Business Incorporated Company) of Turkey” [7] for PPA scenarios.

LCOH is calculated by summing the components’ capital, operational, and maintenance costs and dividing them by the total hydrogen produced (Eq. (1)). In the denominator of this equation, a physical property of hydrogen is divided into a cost parameter. Mathematically, the equation is correct because the discount rate effect calculation reduces each other in the numerator and denominator sides.

$$LCOH = \frac{\sum_{i=1}^p \frac{CAPEX_i + OPEX_i}{(1+d)^i}}{\sum_{i=1}^p \frac{Hydrogen\ Production_i}{(1+d)^i}} \quad (1)$$

where p is the plant life, d is the discount rate, CAPEX is the capital expenditure, and OPEX is the operational expenditure.

2.2 Cash Flow Analysis

A cash flow analysis is performed to calculate the NPV. A sales margin is included in the cost of hydrogen, which is 2, meaning the hydrogen selling price is 2 \$/kg more than LCOH. Taxes for income, inflation rate, and interest rate for the loan were also considered. Inputs for the economic analysis can be found in Table 1. Some values are taken from the techno-economic study performed by Khan et al. [8].

Table 1. Input data for economic analysis

Parameter	Value
Discount Rate	10%
Tax Rate	20%
Inflation Rate	3%
Interest Rate	10%
Equity Share	70% of Total Investment [8]
Loan Share	30% of Total Investment [8]
Loan Term	10 years [8]
Salvage Cost	20% of Total Investment [8]
Decommissioning Cost	15% of Total Investment [8]
Sales Margin for H ₂	2 \$/kg [8]

In the study, equity share is preferred as 70% of the total investment required, meaning that a share of the investment would be paid from the H₂ producer’s equity. The remaining would be taken as a loan with an interest effect. The loan term was preferred to be 10 years, meaning 10 years of repayment would be made. Salvage and decommissioning costs are also considered for post-project outcomes.

Cash Flow

To calculate the net investment, total equipment, and land procurement costs are summed up, and then that value is multiplied by the equity share. To calculate annual cash flow, it is necessary to sum all annual operational expenses, electricity purchase costs and grid usage charges (if grid connection is in question), depreciation, loan payments, and tax then extract the total outcome from the sales.

$$CF_y = Sales_y - Expenses_y - Tax_y \quad (2)$$

where y represents the year, and CF represents cash flow.

Net Present Value

NPV presents the present value of the project to check whether the investment will be worth it after the system is decommissioned. It is calculated by dividing the cash flow by the discount of a period (Eq. (4)). For projects that have a long life, NPV is calculated according to (Eq. (5)).

$$NPV_y = \frac{CF_y}{(1+d)^y} \quad (4)$$

$$NPV = \frac{CF_y}{(1+d)^y} + NPV_{y-1} \quad (5)$$

3 RESULTS AND DISCUSSION

3.1 LCOH Calculations for Different Locations and Scenarios

Simulations are performed for the wind farm and the electrolyzer system, which have a nominal capacity of 10 MW. Four locations in İzmir are considered in this study: Aliğa, Çandarlı, Çeşme, and Karaburun. Çandarlı region provided the lowest LCOH, but as can be seen in Table 2, the values are close to each other since these locations are within the coastal regions of the Aegean Sea and thus close to each other.

Table 2. LCOH of selected locations for the 10 MW Wind Farm and the 10 MW PEM Electrolyzer (single stack)

Location	LCOH (\$/kg)
Aliğa	4.73
Çandarlı	4.56
Çeşme	4.57
Karaburun	4.59

For the Çandarlı region, the PPA scenario was also considered and simulated to see if it would give a more economical solution. The simulation resulted in an LCOH value of 7.5 \$/kg. This result showed that investing in the powerplant to produce electricity would be a cheaper option as electricity prices (15 \$/MWh PPA Price and 80 \$/MWh Grid Usage Charges [7]) are higher in Türkiye compared to the developed countries. Detailed cost assessments were performed to see which cost parameter affected the LCOH most

among the scenarios. According to Figs. 1 and 2, the capital costs of the power plant and electrolyzer are the most influential parameters if any grid connection is not in question. Within the PPA scenario, grid usage charges have the most effect, followed by the electrolyzer system's CAPEX.

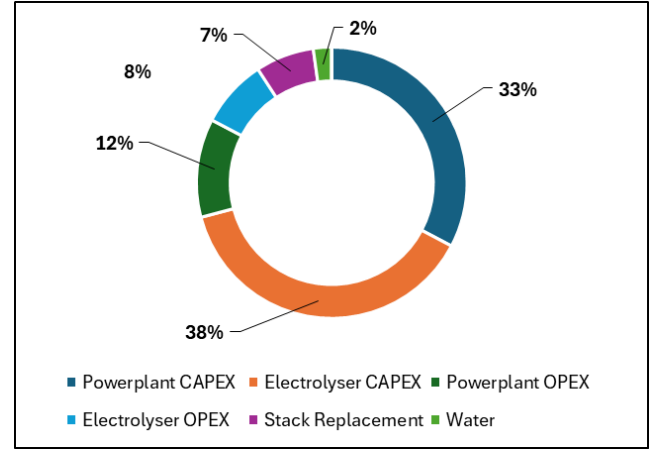


Figure 1. Cost shares for the power plant investment scenario

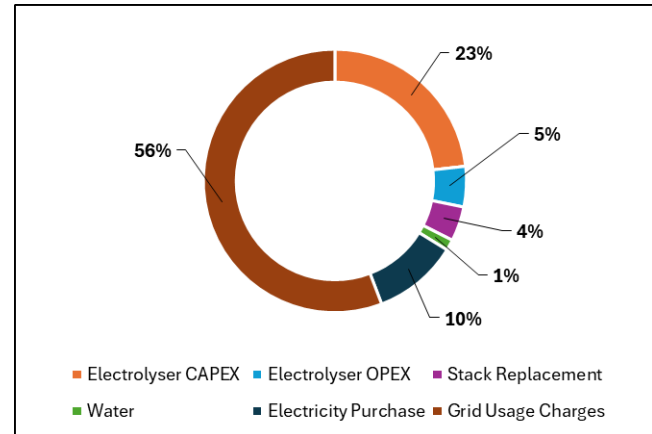


Figure 2. Cost shares for the PPA scenario

3.2 Effect of Using a Modular Electrolyzer System

Two values for the number of modules (4 and 10) and two strategies (power allocation and daisy chain allocation) are considered for the electrolyzer system. In the daisy chain allocation strategy algorithm, the first module starts to operate until it reaches its nominal power, and then the second module starts to operate with the same logic until the kth electrolyzer can not be loaded to its nominal power [9]. The average allocation algorithm has a simpler logic. All modules operate with the same power input. Electrolyzers have minimum and maximum operating limits for hydrogen production, in this study, these values are assumed as, 10% minimum load and 100% maximum load. This algorithm increases the hydrogen production

performance by decreasing the electrolyzer minimum operating limit with modules that have a smaller capacity than the single module scenarios. Simulation results are given in Table 3. Daisy chain allocation strategy resulted in less hydrogen production, and thus less LCOH is obtained, while average allocation reduced the LCOH and increased the NPV compared to the single module scenario. While the increase in module quantity does not affect the LCOH, NPV is affected more clearly.

Table 3. LCOH and NPV values of a single module and multi-module design scenarios

Strategy	LCOH (\$/kg)	NPV (M\$) (last year)
Single module	4.56	14.85
Daisy chain allocation		
4 Modules	4.67	14.45
10 Modules	4.73	14.35
Average allocation		
4 Modules	4.52	17.57
10 Modules	4.51	18.07

4 CONCLUSIONS

Power plant and electrolyzer CAPEX have the most effect on the LCOH for the year 2024. In the future, with the help of technological developments, these costs can be reduced further. In addition, grid electricity prices and PPA costs can be reduced with policy regulations created by governments to help reach the global net zero emission goal.

The average allocation strategy has resulted in being more efficient than the single module operation. The power is divided into the modules equally. The idea is to use numerous small-scaled electrolyzer modules to design a system that is capable of producing hydrogen continuously, even during periods of low renewable power supply. One of the reasons for the low difference in costs between the single-module scenario and the average allocation scenario is the extra stack replacement cost as the annual operating hours would increase with multiple modules. Higher operating hours would result in faster degradation. Therefore, a detailed calculation of the degradation is needed to get more accurate results.

Daisy chain allocation strategy resulted in an LCOH increase as the annual hydrogen production performance decreased. This is

because the relation between the specific energy consumption and the load of the module is non-linear. Therefore, annual hydrogen production performance can change for different scenarios. As the average allocation strategy does not have a significant effect on LCOH, different strategy algorithms can be simulated for further decrease. Oxygen and surplus electricity sales can be also taken into account.

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OVERVIEW OF EVAPORATIVE COOLING SYSTEMS FOR GREENHOUSE TEMPERATURE AND HUMIDITY CONTROL

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Abstract

In light of Pakistan's climate, this study explores the use of energy-efficient evaporative cooling methods to regulate humidity and temperature in greenhouses. Considering the difficulties caused by intense heat and humidity, managing the environment effectively is essential to raising agricultural output. The three main evaporative cooling methods under investigation are Maisotsenko Cycle Evaporative Cooling (MEC), Indirect Evaporative Cooling (IEC), and Direct Evaporative Cooling (DEC). To evaluate these systems' performance in the context of Multan, Pakistan, experimental setups were created. We gathered and examined data on energy efficiency, humidity control, and temperature reduction. The results show that although DEC can lower temperatures significantly, it can also result in high humidity, hence MEC and IEC are better options for preserving ideal greenhouse conditions. This study emphasizes how these cutting-edge cooling systems can enhance greenhouse management techniques, which would ultimately support Pakistan's food security and sustainable agriculture.

Keywords: Evaporative Cooling, Greenhouse climate Control, Temperature Reduction, Humidity Control

1 INTRODUCTION

Pakistan's harsh climate, with its high temperatures and humidity, presents serious difficulties for the country's agricultural industry. Because of the potential negative effects these variables may have on crop development, yield, and quality, efficient climate control in greenhouses is crucial to maximize agricultural output. Evaporative cooling, which uses the evaporation of water as a natural means of reducing temperature and raising humidity in greenhouse conditions, has become a popular and energy-efficient approach of controlling climate. This method decreases energy usage as well as dependence on traditional air conditioning systems, which is important in a nation where energy resources are frequently scarce. The potential of direct evaporative cooling (DEC), indirect

evaporative cooling (IEC), and Maisotsenko cycle evaporative cooling (MEC) to provide thermal comfort for livestock has been demonstrated through experiments on energy-efficient evaporative cooling systems for poultry farm applications in Multan, Pakistan. In order to control greenhouse temperature and humidity in Pakistan, this research will examine a variety of energy-efficient evaporative cooling methods.

It will evaluate these methods' efficacy, suitability for the region, and potential effects on crop performance. By concentrating on these creative fixes, we can support sustainable farming methods that improve food security and encourage environmental responsibility in the area.

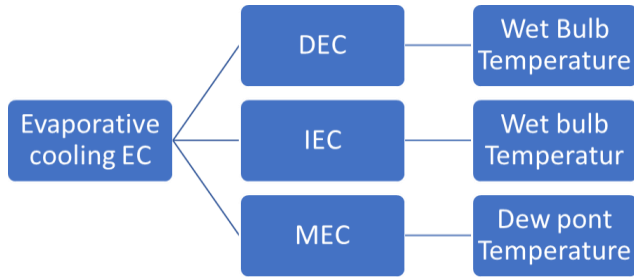


Figure 1. Classification of Evaporative Cooling (EC) (Raza et al. 2021)

2 MATERIAL AND METHOD

3 DIRECT EVAPORATIVE COOLING (DEC)

The basic idea behind ordinary evaporative cooling is called direct evaporative cooling (DEC), in which water vapors continuously evaporate into the air until air saturation occurs. Thus, the heat of the water has a cooling effect. Vaporization, as Figure 7(a) illustrates. -

$$(1) \quad \epsilon_{\omega b} = \frac{T_{in} - T_{out}}{T_{in} - T_{\omega b}}$$

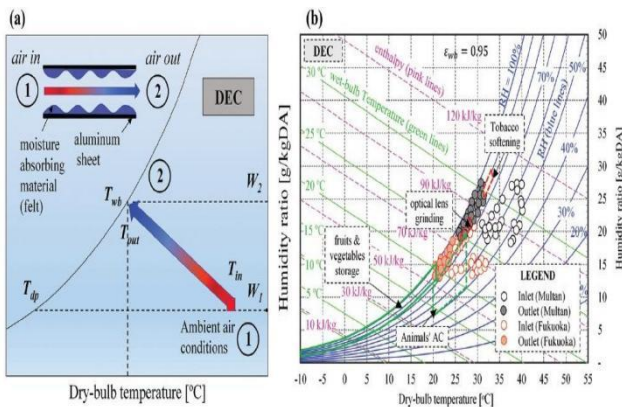


Figure 2. The DEC system, or direct evaporative cooling, is shown in (a) the following schematics:

(b) system performance for nonhuman AC applications for Multan and Fukuoka; each legend point indicates the hourly value (average) of a day (Sultan and Miyazaki 2017)

4 INDIRECT EVAPORATIVE COOLING (IEC)

The main drawback of a conventional DEC system is an increase in product air humidity; thus, indirect It is possible to use an evaporative cooling (IEC) system to maintain constant absolute humidity. IEC allows for hygienic air quality because it does not add moisture to the air. Figure 8(a) schematic diagram represents the IEC system's fundamentals and thermodynamic concept

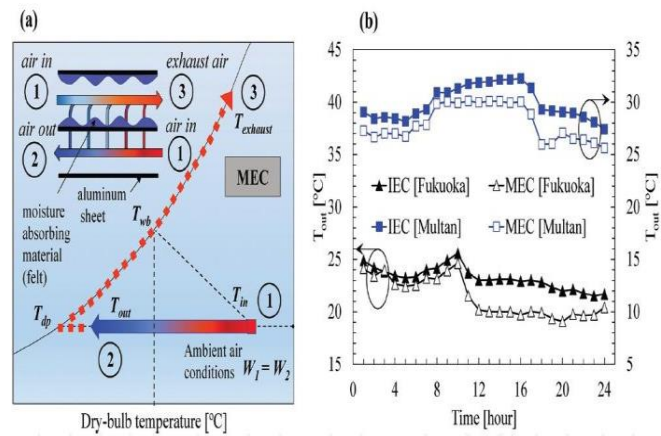


Figure 3 An illustration of the principles and thermodynamic concept for the indirect evaporative cooling (IEC) system is shown in (a); the system performance for nonhuman AC applications for Multan and Fukuoka is shown in (b); each legend point indicates the hourly value (average) for a given day (Sultan and Miyazaki 2017).

$$\epsilon_{\omega b} = \frac{T_{in} - T_{out}}{T_{in} - T_{\omega b}} \quad (2)$$

5 M-CYCLE EVAPORATIVE COOLING (MEC)

An advanced thermodynamic idea of IEC that allows the product air to be cooled to the ambient air dew-point temperature is the Maisotsenko cycle (M-Cycle) evaporative cooling (MEC) provides more specifics, Figure 9(a) presents the basic framework for MEC operation. The MEC system (dry and wet channels in Figure 4(a)) uses the latent heat of water vaporization to generate psychrometric renewable energy, which allows product air to be cooled to the dew-point of ambient air

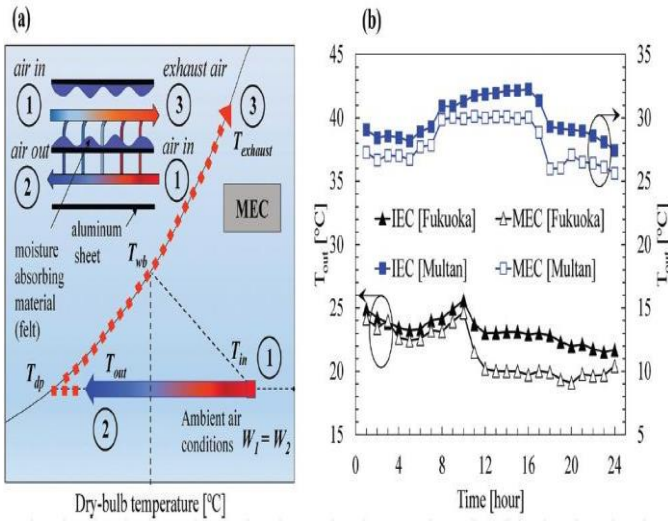


Figure 4. The Maisotsenko cycle evaporative cooling system is represented by the following schematic: (a) it shows the basic elements and the thermodynamic concept; (b) it compares the outlet air temperatures for Multan and Fukuoka with the DEC/IEC standard, with each point denoting the hourly value (average) of a day (Sultan and Miyazaki 2017).

result, the dew-bulb efficacy of MEC ϵ_{dp} [–] can be written like this:

$$\epsilon_{db} = \frac{T_{in} - T_{out}}{T_{in} - T_{db}} \quad (3)$$

6 RESULTS

For greenhouse air conditioning in areas where naturally ventilated screen buildings are not practical due to ambient circumstances, evaporative cooling may be an energy-efficient solution. examined the thermodynamic performance of Maisotsenko cycle, direct, and indirect evaporative cooling systems for greenhouse air conditioning in Multan, Pakistan. The ambient temperature, relative humidity, vapor pressure deficit, and the systems' efficacy with wet bulb and dewpoint were all considered by the writers. The research area's ambient circumstances were found to be unsuitable for greenhouse temperature and humidity requirements, leading the authors to conclude that the MEC system was the only way to attain the required levels of both.

Furthermore, the next-generation greenhouse's temperature and humidity requirements were only partially met by the DEC system. Nevertheless, the IEC system was unable to meet the necessary requirements. In addition, the authors observed that the MEC system was able to achieve a maximum dewpoint effectiveness of 0.5 to 0.6, while the DEC system was able to achieve a maximum wet bulb effectiveness of 0.9. Nevertheless, the high humidity ratio in the product air throughout the year made the DEC system impractical for greenhouse air cooling, suggesting that more workable and energy-efficient options should be investigated. The hourly variation in the ambient and product air temperatures and relative humidity for May 15 is displayed in Figure 4.1 below. The ambient air temperature has a direct impact on the outlet temperature of DEC, IEC, and MEC systems. The abrupt change in ambient air temperature is caused by a shift in the air's climatic conditions at that particular moment. It is seen that the ambient air trendline increases and the temperature reaches its peak between 2 and 4 p.m

The abrupt change in ambient air temperature is caused by a shift in the air's climatic conditions at that particular moment. It is seen that the ambient air trendline increases and the temperature reaches its peak between 2 and 4 p.m. It is evident from Figure that high temperatures and low humidity levels improve system performance.

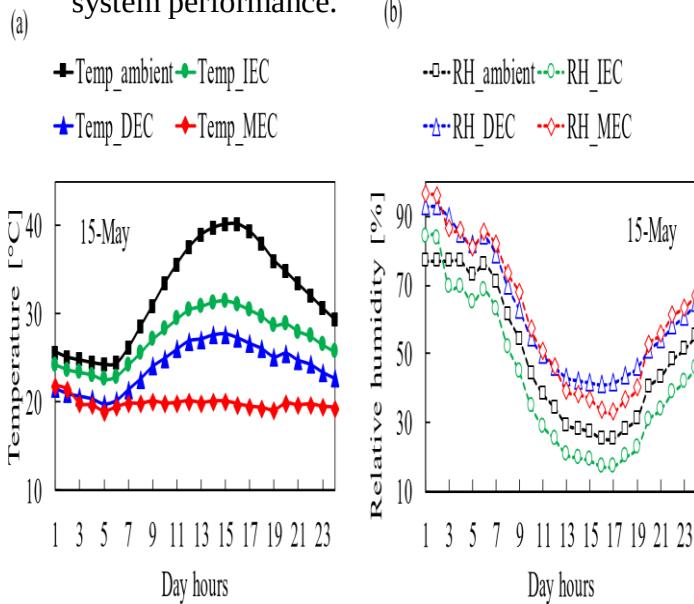


Figure 4. On an hourly basis, the DEC, IEC, and MEC systems' ambient and product air varied in two ways on May 15: (a) temperature and (b) relative humidity (Raza et al. 2021)

On an hourly basis, the DEC, IEC, and MEC systems' ambient and product air varied in two ways on May 15: (a) temperature and (b) relative humidity

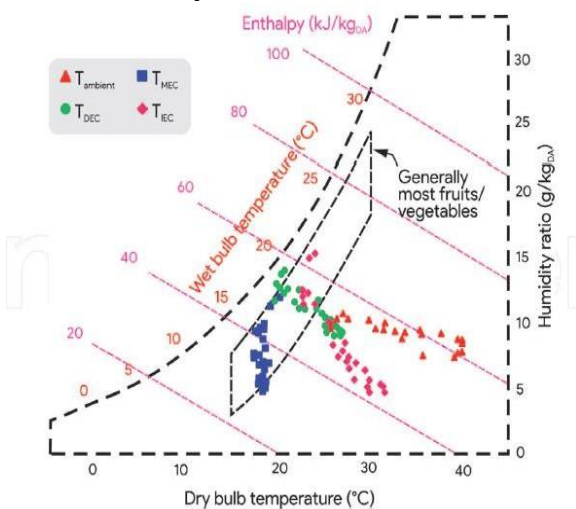


Figure 5. The psychrometric performance of evaporative cooling systems with direct (DEC), indirect (IEC), and Maisotsenko (MEC) cycles for greenhouse air conditioning in Multan, Pakistan, was

Energy Consumption(%) in Pakistan (1998 - 2021)

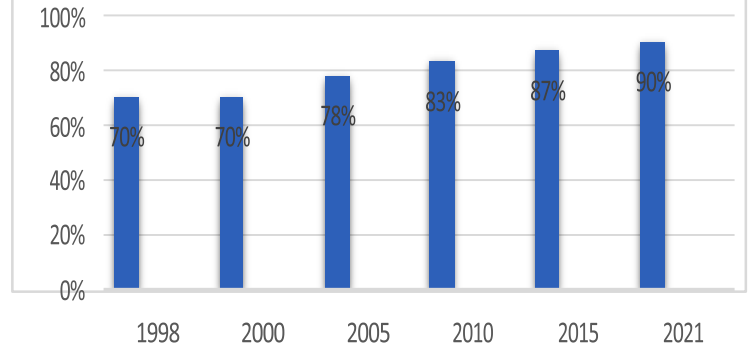


Figure 6. Energy Consumption (%) In Pakistan (Kaplan, Isloor, and Karinka 2023)

7 CONCLUSION

The substantial potential of energy-efficient evaporative cooling methods for improving humidity and temperature management in greenhouses throughout Pakistan is highlighted by this study. Depending on particular climatic circumstances and operational requirements, the evaluation of Direct Evaporative Cooling (DEC), Indirect Evaporative Cooling (IEC), and Maisotsenko Cycle Evaporative Cooling (MEC) systems demonstrates that each method has distinct advantages and disadvantages. DEC successfully lowers temperatures, but it may also raise humidity, which could be harmful to the health of crops. On the other hand, IEC and MEC offer a more balanced approach by obtaining significant cooling while preserving ideal humidity levels, which makes them more appropriate for Pakistan's varied climates

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DETERMINING THE EFFECT OF USER PROFILES ON ENERGY PEAK LOADS IN BUILDINGS FOR DIFFERENT CLIMATIC REGIONS

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Abstract

The literature shows a reduction in the maximum total energy consumption in simulations; however, it is not known how user profiles effect the maximum load of the building, which is necessary for the optimization of solar energy integration to the building. This study aims to investigate the effect of different user profiles on energy needs in the same building type for different climatic regions. TRNSYS simulations show the effect of one student or four people family using the same apartment building. The results show a 21.26% change of in the maximum heating load for the Mediterranean climate and a 3.49% for the cooling load. For the continental climate, the change is 6.21% for heating and 3.25% for cooling energy maximum loads.

Keywords: Energy performance in buildings, TRNSYS, schedule, climatic regions

1 INTRODUCTION

Today, major reasons such as population growth and global warming cause the use of fossil fuel resources and the need for energy to increase rapidly. Although almost every sector is dependent on energy, the building sector is one of the main areas in energy consumption with 41% according to IEA 2021 data [1] (González-Torres et al., 2022). In the construction sector, in many countries and especially EU member states, the building design and construction that meets user needs and meets comfort conditions has become mandatory within the framework of laws and regulations regarding the efficient use of energy. In this context, the Energy Performance in Buildings Directive (EPBD) was published in 2006, and recast in 2010 and last revised in 2018. EPBD lays down requirements for the member states to determine their own nearly zero energy building (nZEB) national plans (EPBD recast, 2018).

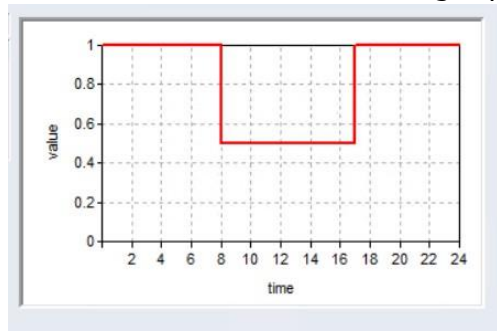
The latest Energy Performance Regulation in Buildings in Türkiye was published in 2013 [2]. It regulates the procedures and principles for the effective and efficient use of energy resources in buildings. According to this regulation, the heating energy need in buildings and the thermal conductivity values of building envelope elements must be lower than the limit values

specified in the TS-825 standard. Thermal conductivity of the building envelope, thermal bridge-free design and air infiltration are significant factors affecting the energy need in buildings.

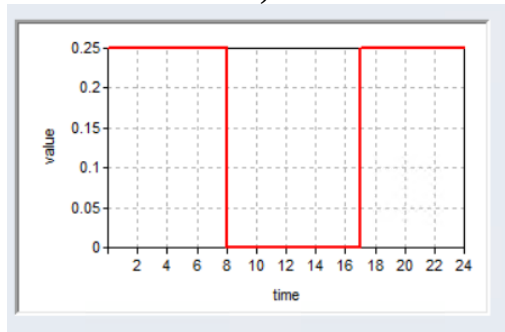
The user profiles and habits are another factor that determines the energy need in buildings. Sood et al. [3] provide an in-depth discussion on user effects on building energy simulation (BES). While O'Neill and Niu (2017) [4] found a 4% change HVAC peak demand, the IEA-EBC Annex 66 project had a focus on incorporation of occupancy into BES and their findings are also worth notice (<http://www.annex66.org/>). This study aims to determine the effect of different user profiles on energy needs in the same building type for different climatic regions.

2 METHODOLOGY

In order to determine the effect of user profiles on energy needs, different usage scenarios were created and energy needs were compared in an apartment located on the middle floor of a typical 3-story building in Türkiye. Occupant types are a) a family of four (with two adults and two children) and b) one student occupant. Schedules suitable for specified user types are defined in TRNSYS 18 as in Fig. 1.



a)



b)

Figure 1. Schedule for a) a family of four and b) a single student

TS-825 update (2013) defines five heating degree day regions. The reference building used in this study was modelled in the Sketch-Up program. Then the building envelope components and layers are defined with the TRNSYS software according to the U-value limits specified in TS-825. Izmir and Hakkari cities' climate data is also defined in TRNSYS. Izmir city has a Mediterranean climate and is in the 1st degree day zone according to TS-825. The Meanwhile, Hakkari with its continental climate is in the 5th degree day zone.

Heating system of the apartment building is natural gas combi boiler, cooling system is electric split air conditioners. It uses natural gas for hot water, and electrical energy for other equipment and lighting. In the final stage of the work, in order to eliminate the need for fossil fuel consumption, reduce the carbon footprint and turn it into an nZEB, the energy demand results were calculated and the required number of PV panels was determined. The energy needs for different user profiles were determined in a one-year cycle. The preliminary results are from the TRNSYS model in Fig. 2.

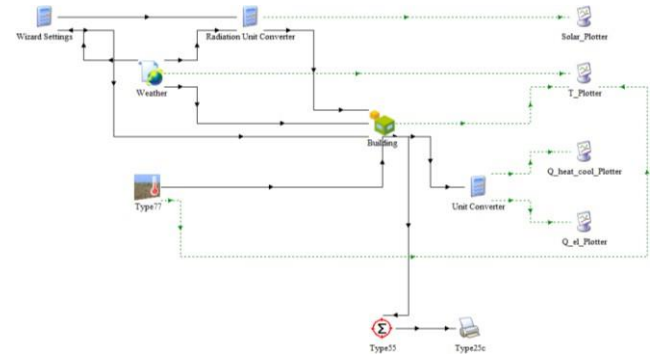
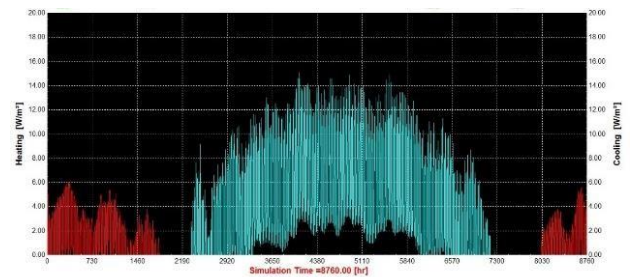


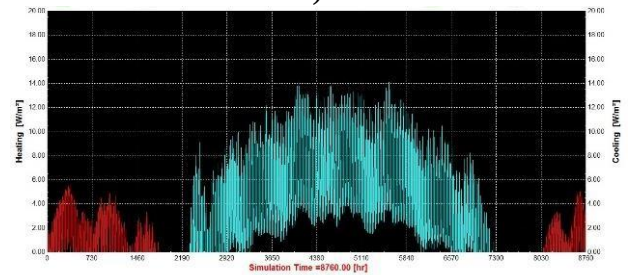
Figure 2. TRNSYS model

3 RESULTS AND DISCUSSION

Figure 3 shows the yearly heating and cooling energy requirement (W/m²) for Izmir in the 1st climate zone for a family of four and a single student, respectively. Fig. 4 shows the same results for Hakkari city in the 5th climate zone.

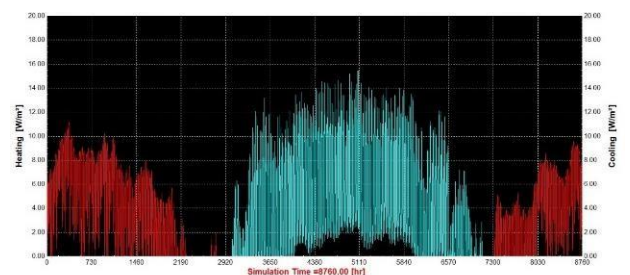


a)



b)

Figure 3. Heating (red) and cooling (blue) demand for: a) a family of four and b) a single student in Izmir.



a)

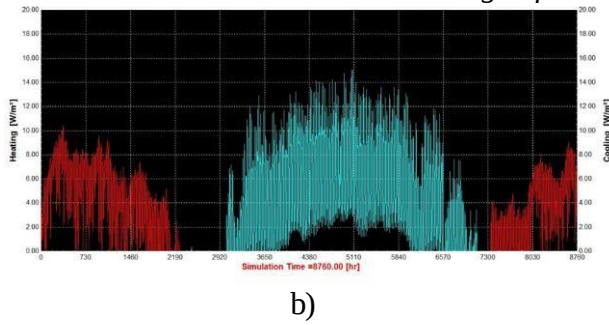


Figure 3. Heating (red) and cooling (blue) demand for: a) a family of four and b) a single student in Hakkari.

Table 1 shows the difference in maximum energy demand for the four scenarios. The results show a 21.26% change of in the maximum heating load for the Mediterranean climate in January and a 3.49% for the cooling load in June. For the continental climate, the change is 6.21% for cooling in January and 3.25% for cooling energy maximum load in July.

Tab. 1: Maximum energy demand changes for twelve months in percentages (%)

Months	İzmir	Hakkari
1	21.26	6.21
2	15.28	4.71
3	46.41	7.97
4	13.16	83.83
5	5.47	10.35
6	3.49	4.35
7	3.14	3.25
8	3.43	3.52
9	5.10	4.96
10	7.2	9.44
11	-	20.19
12	29.28	4.09

4 CONCLUSION

The assumptions in design to reach energy efficient and nearly zero buildings show a general guideline for design. However, the findings show that the user numbers, lifestyles and preferences have a significant effect on the maximum heating and cooling loads of the building; thus, the required renewable energy generation to offset this consumption. Therefore, future research will focus on optimizing the number of photovoltaic panels in terms of efficiency and cost.

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HEAT TRANSFER PERFORMANCE OF AL₂O₃/CU-H₂O NANOFLUIDS

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ABSTRACT

In this study, the heat transfer performance of Al₂O₃/Cu-H₂O nanofluid in natural convection in an enclosure with partially active thermal side walls and an additional active hot sources placed in the bottom and in the top walls is investigated numerically by using Lattice Boltzmann Method (LBM). The statistics focused specially on the effects of different key parameters like as volume fraction of nanoparticles from 0 to 4% and Rayleigh number (Ra=103- 105), and position (xH) and height (LH) of hot source. The principal goal of this current work is studying the impact of pertinent parameters on the flow and heat transfer enhancement of nanofluid. The results showed that the streamlines, isotherms lines, velocity maps and average Nusselt numbers had different patterns at different volume fraction, Rayleigh number Ra, and the position/ height of heating source. The natural convection increases as the nanoparticles volume fraction and Rayleigh number Ra. Also, the findings reveal that the Nusselt number Nu increases with the increase of Ra, so, the heat transfer performance enhances. At the same time, an increase of the height of heated source reflects the enhance of heat transfer. The obtained numerical results agree well with previous results

Keywords: Nanofluid, Heat Transfer, Natural Convection, LBM, Rayleigh number

NUMERICAL INVESTIGATION OF HEAT TRANSFER IMPROVEMENT OF RING TURBULATORS PLACED IN A PIPE

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Abstract

In this study, the effect of ring turbulators placed in an empty circular-section pipe on heat transfer was investigated numerically. The internal design of the ring turbulators placed in the pipe has a wire cage appearance designed in three different densities, and the ring turbulators are placed in the pipe with a pitch ratio (p/d) of 1 and 2.

Pipe models with empty pipe and ring turbulators were numerically modeled in the Ansys Fluent program using turbulent air flow. The velocity values used in the CFD analyzes performed by giving 2500 w/m² heat flux from the outer surface of the pipe were determined according to Reynolds numbers in the range of 5000-30000. The results were processed with the help of graphics and the result was reached.

Keywords: Ring Turbulators, Pipe, Air Flow

DETERMINATION OF BUBBLE BEHAVIOR AND GAS-SOLID DISTRIBUTION CHARACTERIZATION IN A FLUIDIZED BED SYSTEM

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Abstract

Fluidized bed systems have a wide range of usage in energy production facilities and many chemical and metallurgical industries due to their advantages such as high heat and mass transfer. Fluidized bed boilers are based on the principle of burning solid fuel particles brought to a certain grain size in the main column, in a bed fluidized by bed material consisting of non-burning particles such as sand and/or ash and compressed air blown at a certain speed from the bottom. In the stage after the minimum fluidization point, as the fluid velocity increases, the physical phenomena observed in the bed constitute the fluidization stages. These phenomena differ from each other in different fluid speed ranges and exhibit characteristic features. As the speed increases, air bubbles appear in the bed and the bubbles appear similar to water boiling and leave the bed. In this study, a model and simulation were developed to analyze fluidized bed hydrodynamics and bubble behavior. Ansys Fluent program, based on computational fluid dynamics, was used in modeling studies. In the hydrodynamic model study, the effect of different bed gas velocities on bubble formation and gas-solid homogeneity was investigated and in this context, an optimal fluidization rate was determined. In addition, within the scope of model studies, flow analyzes were carried out for bed hydrodynamics, pressure losses between the reactor inlet and outlet, and temperature changes within the reactor.

Keywords: Fluidized bed, Flow Characterization, Hydrodynamic Model.

1. INTRODUCTION

With the increasing global population and industrial development, energy demand is rising worldwide and in our country as well. As a result, reducing energy costs and minimizing negative environmental impacts have become crucial, necessitating the development of new energy systems and sources [1,2]. Energy needs directly affect national economies and indirectly

impact social life. Fluidized bed combustion (FBC) enables efficient burning of such fuels under appropriate combustion conditions, with inherent emission control for clean burning, including SO₂ capture and suppression of CO and NO_x formation, without requiring additional investments [3,4]. Unlike other countries where well-designed and developed fluidized beds efficiently burn coal, it is challenging to achieve efficient combustion of

our lignite with different characteristics in existing fluidized beds. Therefore, fluidized bed designs must be tailored to the specific properties of the coal, including coal feeding, ash discharge, and heat extraction zones, to optimize combustion efficiency based on operational conditions and coal characteristics. Heat transfer simulations were performed using a circulating fluidized bed model capable of simultaneously predicting hydrodynamics and combustion [8,9,10]. The agreement between the simulation results and experimental data at different temperature values, which represent the heat transfer coefficient as a function of bed bulk density, indicates that the simulation is valid for both cold and hot fluidized beds. [11,12]

Heat transfer and hydrodynamics in bubbly fluidized beds were investigated using the computational fluid dynamics (CFD) program. Observations have revealed that the gas-solid entrainment function has a significant effect on the solid volumetric fraction, bubble size and shape. Additionally, using the rebound and kinetic theory model, it was determined that the viscosity and granular temperature of the solid phase changed and the distribution of the solid volumetric fraction was limited.

2. MATERIALS AND METHODS

In fluidized beds, combustion and emission behavior are primarily determined by bed hydrodynamics, which explain the gas-solid two-phase flow model and interactions. This study investigates the hydrodynamics of two-phase flow within a fluidized bed using the FLUENT computational fluid dynamics package. Visualizations of the gas-solid flow cycle, pressure contours, gas velocity distributions within the column, solid velocity distributions, and profiles of inlet velocity and

pressure at the system entry were created to examine flow characteristics. Initially, the analysis was conducted in two dimensions. Analyses in two dimensions can be thought of as a cross-section of a three-dimensional design. Figure 1. shows the CAD drawing of the designed circulating fluidized bed system model.

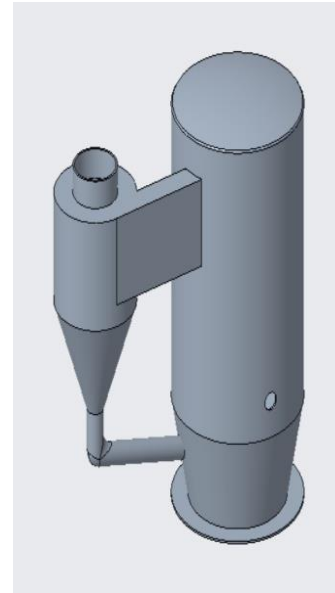


Figure 1. Fluidized Bed System CAD Model

The density of solids in a circulating fluidized bed fluctuates significantly as you move up from the gas distributor. As a result, a circulating fluidized bed is usually split into different sections along its length, each with its own solids concentrations and flow patterns. In particular, the bed is often categorized into a dense bottom region and a lighter upper region. One crucial factor affecting the reactions in a circulating fluidized bed is how well the solids mix in the bottom zone. For instance, in combustion processes, uneven distribution of char particles can result from where the coal is fed into the bed. Solid carbon dioxide experiments revealed good vertical mixing but limited horizontal mixing in the lower zone of a circulating fluidized bed. As a result, the lower zone is modeled based on specific assumptions

[5]. The concentration of the solid tracer in a specific volume can be defined as:

$$\rho_T = \frac{m_{T,i}}{V_i} \quad (1)$$

The equation for convection-dispersion is typically expressed as:

$$\frac{\partial \rho_T}{\partial t} - D \frac{\partial^2 \rho_T}{\partial x^2} + \frac{\partial (v_x \rho_T)}{\partial x} = S \quad (2)$$

When using solid carbon dioxide as tracer particles, the source term can be calculated from:

$$S = \frac{\partial m_{T,i}}{V_i \partial t} \quad (3)$$

The mass of the tracer in the volume element can be found by multiplying the number of particles by the average particle mass. This relationship can be derived from Eq [5].

$$S = - \frac{N}{V_i} \frac{\pi x^2}{k} \frac{\psi}{\psi} \quad (4)$$

Please remember this: "The size 'd' represents the effective particle size inside the riser (i.e., the diameter of the volume equivalent sphere). The 's' value is a shape factor that describes how different the particle shape is from a sphere. The number 'n' of particles in the volume can be calculated using the solid tracer mass concentration, 'C', in tracer per bed volume, and the size of the tracer particles." [5]

$$\frac{N}{V_i} = \frac{m_{T,i}}{V_i \rho_{CO_2, solid} \frac{\pi x^3}{6}} = \frac{6 \rho_T}{\rho_{CO_2, solid}} \frac{\pi x^3}{6} \quad (5)$$

The sublimation source term can be calculated by multiplying a constant factor with the tracer mass concentration in the volume element. Additionally, the feed of tracer particles causes an extra source of tracer in the feed volume element [5].

$$S_{feed} = \frac{\partial \rho_{feed}}{\partial t} = \frac{\dot{m}_{feed}}{V} = \frac{\dot{m}_{feed}}{H_b B \Delta x} \quad (6)$$

3. MODEL FOR BUBBLE BEHAVIOR AND GAS-SOLID DISTRIBUTION CHARACTERIZATION

Investigating the behavior of bubbles and the

characterization of gas-solid distribution in a fluidized bed system are critical components for understanding the complex dynamics of this specific system [6,7]. This research involves a comprehensive study of the intricate interplay between gas and solid materials in the fluidized bed, examining factors such as bubble size,

distribution patterns, gas velocities, and solid particulate movements. Understanding these aspects will provide valuable insights for optimizing the performance and efficiency of fluidized bed systems across various industrial applications. We examined the analysis in a fluid bed of our own design. Many parameters

such as the combustion chamber area where combustion takes place, cyclone size, and the amount of sand inside are our own design and dimensioning.

As the number of nodes increases, accuracy will increase, but analysis speed will decrease. There are 38169 nodes and 156584 elements. Therefore, the optimal number of nodes must be found. Figure 2. shows the mesh sizing of the analyzed circulating fluidized bed.

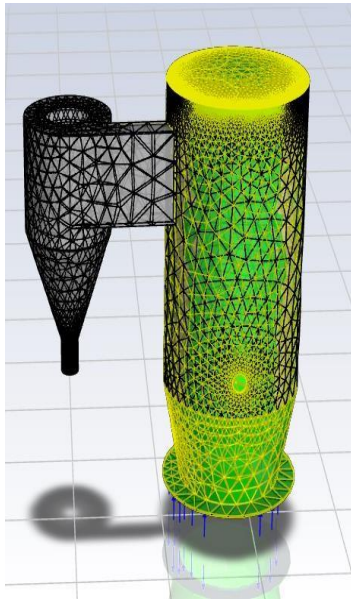


Figure 2. Mesh Sizing of Fluidized Bed Model

In this study, the Eulerian model in which the conservation equations of both phases are solved separately is used. (two fluid model) was used. In this model, each phase has its own characteristics within the flow field. But has common pressure in the flow field. Mass and momentum to be used in the solution. The conservation equations are given in their most general form. Based on operating cold bed conditions. Since it is realized, the energy equation is closed.

The conservation of mass equation for steady flow is,

$$\frac{\partial(\rho u)}{\partial x} + \frac{\partial(\rho v)}{\partial y} + \frac{\partial(\rho w)}{\partial z} = 0 \quad (6)$$

4. CONCLUSION

Fluidized bed systems create a type of fluidized bed in which solid particles are contained in a fluid and this fluid interacts with the particles. In fluidized bed systems, bubbles may form as a result of interactions between gas and solid particles. Bubbles are generally associated with the distribution and movement of gas within the fluidized bed. The formation, size, distribution and movement of these bubbles have a significant impact on the performance of the

system. Characterization of bubbles is critical information for the design, optimization and determination of operating conditions of the system. Homogeneous distribution of gas and solid particles is important in fluidized bed systems. The homogeneity of this distribution can have a direct impact on the efficiency, stability and operating costs of the system. Various methods are used to characterize the distribution between gas and solid particles. For example, techniques such as particle size distribution analyses, density profiling, thermal and fluid dynamics simulations can be applied. Determining bubble behavior and gas-solid distribution in fluidized bed systems enables a better understanding and optimization of these systems. These optimizations can save energy and costs in industrial processes, improve product quality and reduce environmental impacts.

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NUMERICAL ANALYSIS OF THE INFLUENCE OF THE GEOMETRICAL PARAMETER ON THE KENICS STATIC MIXER EFFICIENCY

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Abstract

The influence of the geometrical parameters of a KENICS static mixer was studied by exploitation of the drop pressure and therefore the combining potency of a flow of a Newtonian fluid with a variation in the Reynolds number ($Re=0.1-100$). The results of this numerical simulation were dispensed to match the efficiency of changing styles of static mixers with the initial case. The simulations were performed with the commercial code ANSYS cfx18.2 for streamline flow of The numerical modeling began within the RANS modelIn this work.

1. INTRODUCTION

Many mixers of static varieties are extensively employed in numerous homogenisation processes in industrial operations as an instance cosmetics, food processing, compound blending, heat transfer, chemical reaction, pharmaceuticals, and conjointly in waste material treatment. they're largely used in disposable applications, like in situ mixings of 2 parts epoxy adhesive and sealants [1-3]

The static mixer thought of within the study is that the Kenics for in-line mixing of liquids beneath streamline flow conditions. The Kenics is comprised of a series of

blending components aligned at 90° . The coiled mixing component directs the flow of fabric radially toward the pipe walls and back to the center. further rate reversal and flow division result from combining the alternating elements. The complicated fluid flow in the mixer has propelled many studies on its pressure drop, mixing performance [4-7]

study the symmetrical structure of the Kenics static mixer itself from the perspective of its influence on the fluid flow, we have a tendency to introduced the eccentricity issue g, that changes the middle position of parts at a twist ANgle 90° . This paper set heat transfer studies because the

background and selected thermal-hydraulic

performance factor h as an examination between the warmth transfer performance and also the pressure drop of various structures. applied mathematics correlations between the relative Nusselt variety and the relative friction factor were planned with the eccentricity factor, side ratio, and painter number[8-10]

2. PRESENTATION OF CASE STUDIED

The current case study involves a cylindrical pipe with a length of L and 6 mounted whorled elements, the length of that is remarked as step P . The angle of contact between 2 fixed items will vary from zero to ninety degrees.

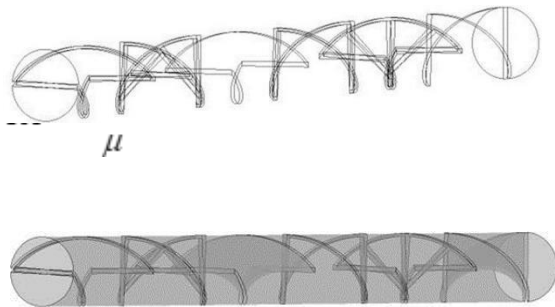


Figure. 1 – Geometry modified

3. MATHEMATICAL MODEL

The governing equations about the equations of mass conversation, momentum conversation and energy conversation deduced from the N-S

And the governing equations are expressed as :

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{v}) = 0 \quad (1)$$

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{v}) = -\nabla p + \nabla \cdot (\vec{\tau}) \quad (2)$$

$$\frac{\partial (\rho E)}{\partial t} + \nabla \cdot (\rho E \vec{v} + p \vec{v}) = -\nabla \cdot (k \nabla T + \nabla \cdot (\vec{\tau} I)) \quad (3)$$

function were solved by the CFX software codes. Where is the symbol of gradient operator, ρ is the density of the helium gas, $\vec{v}$ is the velocity in vector form, t is the time, p is the static pressure, I is the stress tensor, k is the thermal conductivity.

4. EFFECT OF REYNOLDS NUMBER

to test the result of Reynolds range on the motion intensity of fluid particles, the Tangential speed profiles inside the center of the static mixer are shown in Fig. two ,3 and four .the most price is obtained within the middle of the mixer wherever the friction is negligible, this peak weakens even a lot of with the increase in Reynolds number

Friction factor can be written as:

$$f = 2D_h \Delta P / L \rho u^2 \quad (5)$$

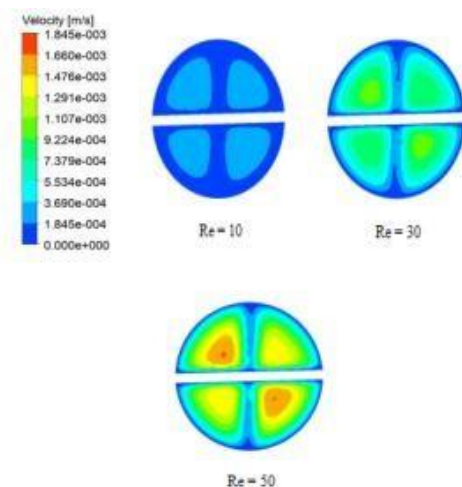


Figure 2– Velocity fields for geometry

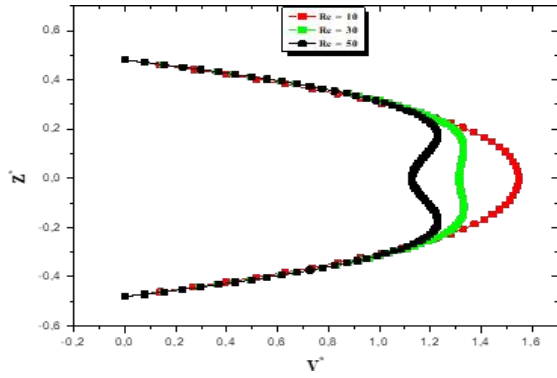


Figure 3– Tangential velocity for modified geometry

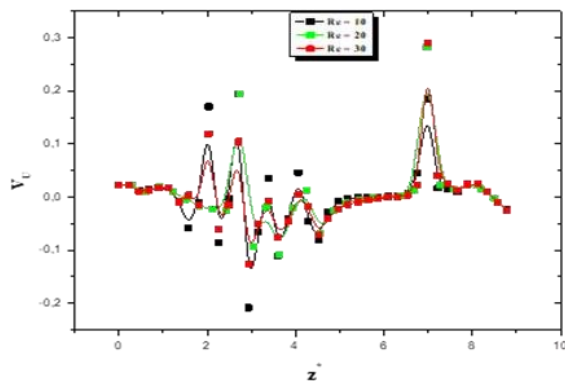


Figure – Axial velocity for modified geometry

Pressure drop

The energy dissipated at intervals the spiral mixer is obtained by deciding the pressure drop between the outlet and water sections of the mixer.

The pressure drop across the mixer resolve as a operate of Sir Joshua Reynolds vary variation (from 0.1 to 100).

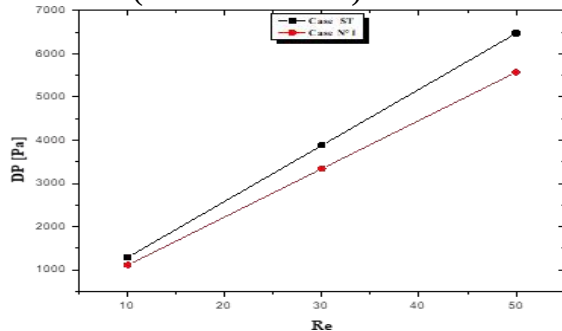


Figure 5 – Pressure drop versus Reynoldsnumber

5. HEAT TRANSFER ANALYSIS METHOD

The heat flux q' through the wall was obtained by the output writing of Total Surface Heat Flux within the CFX, and the wall temperature T_w is the temperature of the solid wall facing the chemical element gas, and also the gas bulk temperature T_b is the temperature of the across the sectional gas flow, Thus, the warmth transfer constant is calculated by,

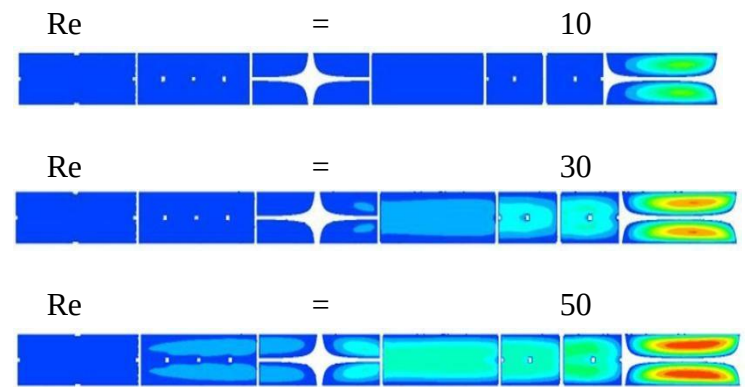


Figure. 6 – Temperature fields for different Reynolds numbers

$$h = \frac{q}{A(T_w - T_b)}$$

(6)

The Nusselt number is calculated

$$Nu = \frac{hD}{k}$$

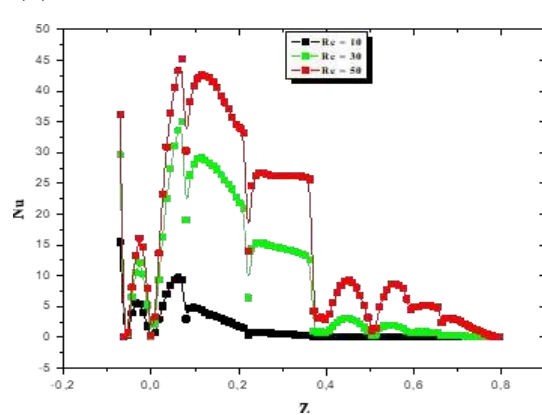


Figure 7- Nusselt number for modified geometry.

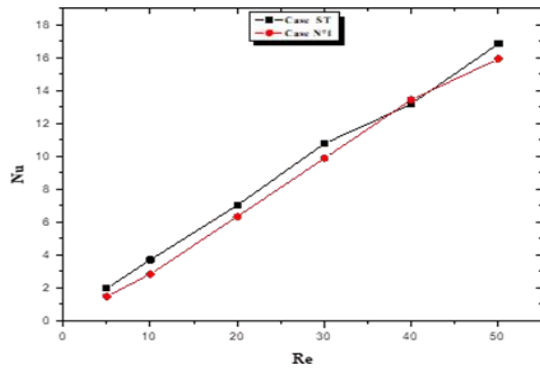


Figure 8 – Nusselt number versus Reynoldsnumber

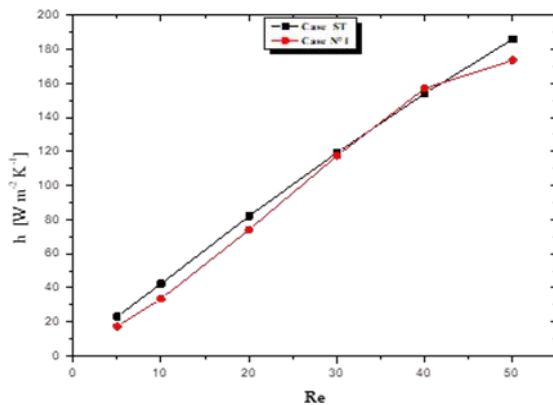


Figure 9 – heat transfer coefficient for differentReynolds number.

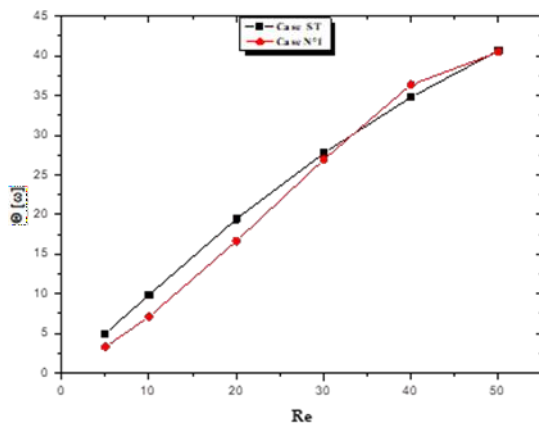


Figure10 – flux thermique for differentReynolds number.

CONCLUSION

Investigating the thermal and hydraulic performance show that pressure drop is larger within the mixers with higher

effectiveness in rising of the warmth transfer rate.

a new correlation for pressure drop has been derived for a Kenics static mixer. due to CFD calculations, comprehensive pressure drop knowledge can be obtained over a good vary of method parameters. From the appliance of dimensional analysis, it's found that the pressure drop correlation can be delineated in terms of 3 dimensionless groups, C_f , Re , ϕ .

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IMPACT OF SHADING ON COOLING LOADS: A CASE STUDY OF A BUILDING

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Abstract

This study investigates the cooling loads requirements of a primary school building which exposed to shading from adjacent (surrounding high-rise buildings) and local shadings (its own architectural features). Cooling loads were calculated with using the ASHRAE Heat Balance method by IESVE software. The impact of shading on the total cooling load of building and the behavior of cooling loads on spaces exposed to shading were numerically analyzed. Total cooling load requirement was calculated for no shading and shading effect as 409.3 and 389.8 kW, respectively that was 4.8% reduction on cooling load because of the shading. Furthermore, when examined in detail the impact of shading on cooling loads, it was found that shading from local shading had the most significant effect. Cooling load of spaces which exposed to local shading 19% decreased and all this change almost related to reduced solar radiation effects.

Keywords: cooling load, shading effect, IESVE

1 INTRODUCTION

Between 1991 and 2010, there was an increase in global surface temperatures by up to 0.30°C. Since temperature records have been kept since the 1800s, the year 2022 ranks among the top 10 hottest years [1]. Therefore, the cooling of buildings is becoming more important day by day. Moreover, today, the energy used for cooling buildings and spaces constitutes 20% of total electricity consumption [2] and it will increase 37% until 2050 [3]. Using improvements in cooling processes such as passive cooling techniques can reduce cooling loads by more than 25% against this increase [4].

Cooling load is the amount of heat that needs to be removed (cooled) to maintain required temperature and humidity conditions inside a space. It accounts for heat gains from various processes including building envelope, internal sources, and system components. Components affecting cooling load include external heat gains (walls, roofs, windows, skylights, doors, ceilings, and floors), internal heat gains (lighting, occupants, equipment, appliances, and others), ventilation and infiltration heat gains (air leakage and moisture), and system heat gains (duct leakage, reheat or cooling, fan-pump energy, and energy recovery) [5]. There have been many studies for the optimization of the cooling load. One of them is the shading effect on cooling loads [6].

2 MATERIALS, METHOD AND MODELING

IESVE software was used in this study, and it's a Building Energy Modeling (BEM) software and calculates heating and cooling loads according to industry standard methods such as ASHRAE Heat Balance Method or CIBSE Admittance Method [7].

A primary school building with U-shaped architecture and spaces providing different services was modeled on the IESVE software, including nearby high-rise buildings, balconies, entrance areas, and sunshades that contribute to shading effects. The photographs of the building and the building modeled on IESVE (the pinks represent high-rise buildings which caused adjacent shading, the greens represent balconies, entrance areas, and [porches](#) which caused local shadings) are shown in Figure 1. In addition, spaces with local shading effects are illustrated in Figure 2.



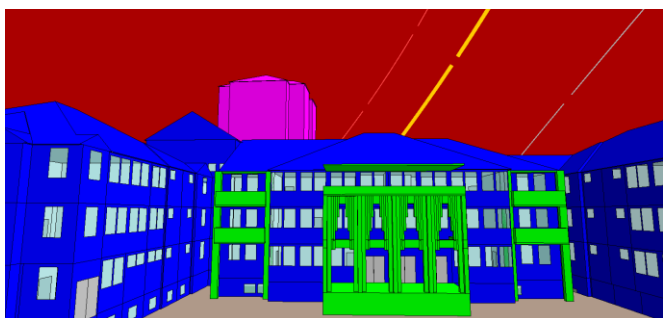
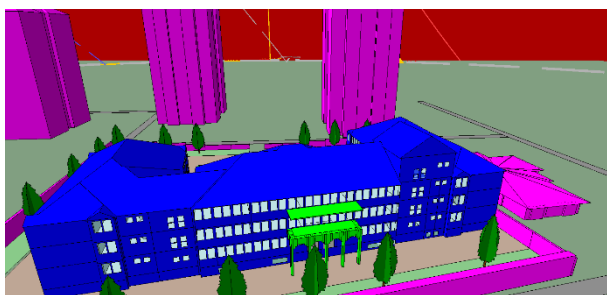
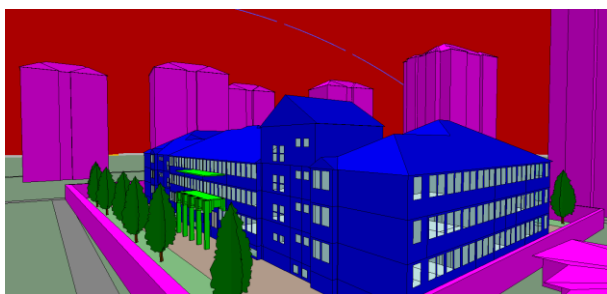


Figure 1. The photographs of the building and the building modeled on IESVE

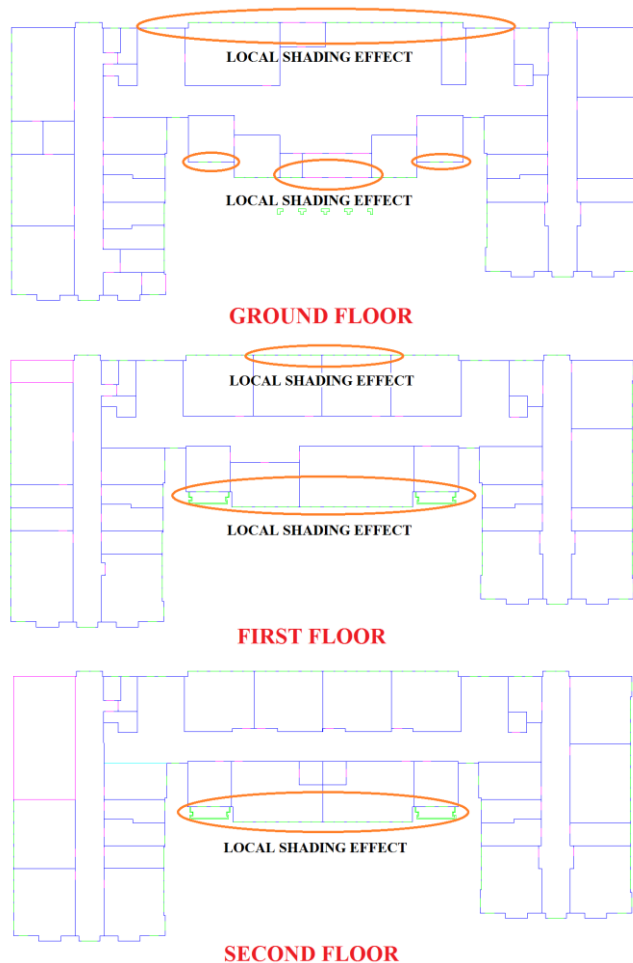


Figure 2. Spaces with local shading effects

3 RESULTS

This model was created in the Model-IT section of IESVE, IESVE's ApacheSim module was used for calculating cooling load requirements and suncast module in IESVE's which the durations and areas of solar energy for building was calculated. The resulting file from these calculations was used in the IESVE ApacheSim cooling load calculation module, allowing the effects of shading to be included in the load calculations.

After entering the necessary data inputs (such as U-values, SHGC, building properties, number of occupants, lighting, equipment, and ventilation), calculations were performed separately for scenarios where there was no shading, only adjacent shading, only local shading, and all shadings. The results obtained were as follows: 409.3 kW, 403 kW, 393.3 kW, and 389.8 kW, respectively. According to the results, the differences were calculated as 1.5%, 4%, and 4.8%, respectively. These differences are more clearly in Figure 3.

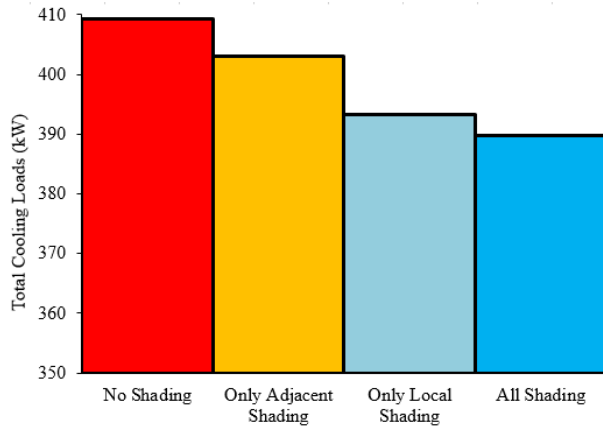


Figure 3. Cooling load change calculated depending on shading effect

When the impact of shading on cooling load was examined in detail, it was found that the shading from local shading had the numerically largest effect. For the selected spaces exposed to local shading shown on Figure 2, the total cooling load value was calculated as 82.8 kW without shading and 69.6 kW with shading, indicating a decrease on cooling load of 13.2 kW or 19%. Additionally, the effect of radiation through windows on the total cooling load was calculated as 28.5 kW without shading and 16.5 kW with shading, indicating a decrease in cooling load of 12.0 kW or 73%. Thus, it was caused that 91% of the total decrease on cooling load due to shading on the selected spaces was from radiation heat transfer.

According to the obtained data, it was demonstrated that the primary reason for the decrease on total cooling load on spaces exposed to shading was due to radiation effects, as illustrated in Figure 4. On the graph, while the cooling load requirement from solar radiation through windows decreases, cooling loads requirement from walls, doors, conduction through windows, and others unchange with shading. This evidence indicates that the reduction on total cooling load is entirely due to shading effects, specifically solar radiation effects.

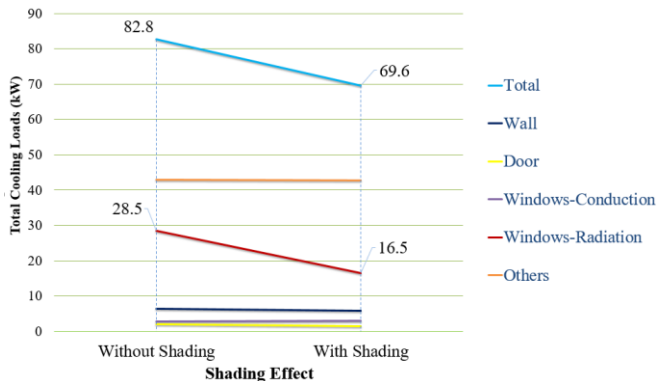


Figure 4. Cooling load analysis of spaces exposed to local shading

4 VALIDATION

Using REVIT which is Building Information Modeling software to verify our study. The cooling load calculations were performed using the Radiant Time Series method in REVIT, and the same building was modeled and analyzed.

In the first scenario, shading effects were neglected in both IESVE and REVIT, and a comparison was made between software using Heat Balance and Radiant Time Series methods. The result of this comparison showed a difference of 0.6% in the total cooling load of the building between IESVE (Heat Balance Method) and REVIT (Radiant Time Series Method) [8].

In the second scenario, with the shading effect, the cooling load requirements for the Computer Classrooms on the 2nd floor of the school, which are dark shaded, were calculated in both software tools. The result showed 4% difference between IESVE and REVIT.

5 CONCLUSION

The shading affecting the building and the building's orientation relative to the sun are important factors in terms of their impact on cooling load. For buildings exposed to shading, calculating cooling loads while including the shading effect ensure accurate calculations and lead to reducing the capacity and size requirements of selected equipment. This result should be considered, impacting aspects from initial investment costs to operational savings. However, increasing shading, while it reduces cooling loads, also arises a situation where it prevents people indoor environment from benefiting from natural sunlight. Increasing shading also means reducing the amount of lighting indoor environment. This situation leads to the use of lighting fixtures for lighting, thereby increasing energy consumption within the building. To address spaces with shading, solutions such as light shelves that transmit natural light into spaces can be implemented. This approach allows occupants to benefit from natural sunlight while optimizing the design for shading effects [9].

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MULTIWALLED-CARBON-NANOTUBE-MODIFIED $\text{Li}_2\text{ZnTi}_3\text{O}_8$ AS ANODE WITH IMPROVED CYCLING STABILITY AND RATE CAPABILITY FOR LITHIUM-ION BATTERIES

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Abstract

$\text{Li}_2\text{ZnTi}_3\text{O}_8$ (LZTO) modified with multiwalled carbon nanotubes (MWCNTs) offers promising potential as a Li-ion battery anode due to improved conductivity and higher lithium storage. Using a ball-mill-aided solid-state method, LZTO@MWCNTs is synthesized, and its electrochemical performance is tested through cyclic voltammetry (CV), galvanostatic charge-discharge, and electrochemical impedance spectroscopy (EIS). CV results show that the LZTO@MWCNT electrode has a smaller anodic-cathodic peak potential difference (0.184 V) compared to LZTO (0.211 V), indicating better electrochemical reversibility after five cycles. LZTO@MWCNTs also outperforms LZTO in charge-discharge capacity at 0.1–5 C rates. After 100 cycles, the LZTO@MWCNT electrode retains initial discharge capacities of 227 and 142 mAh g^{-1} at 1C and 5C, respectively, while LZTO achieves only 144 and 28 mAh g^{-1} . EIS analysis shows LZTO's charge transfer resistance is 19.31 ohms, and SEI resistance is 62.74 ohms after 30 cycles, whereas LZTO@MWCNTs exhibits much lower values, with charge transfer resistance at 7.93 ohms and SEI resistance at 12.06 ohms, highlighting its enhanced electrochemical properties.

Keywords: $\text{Li}_2\text{ZnTi}_3\text{O}_8$, Anode material, Lithium-ion batteries, Multi-walled carbon nanotubes, Specific capacity

1 INTRODUCTION

Rechargeable lithium-ion batteries (LIBs) are widely used, but graphite's poor performance and lithium dendrite formation pose safety risks. Therefore, new, safe, and high-capacity anode materials are needed [1]. Lithium zinc titanate ($\text{Li}_2\text{ZnTi}_3\text{O}_8$, LZTO) has attracted attention for its eco-friendliness, decent theoretical capacity (227 mAh g^{-1}), and strong cycling stability [2]. However, LZTO suffers from low electronic conductivity and slow ion diffusion. To address this, methods such as carbon coating, particle size reduction, and doping have been explored [3]. Among these, conductive carbon modification has been effective in enhancing cycling performance, rate capability, and capacity retention [4]. Carbon nanotubes (CNTs) have shown better specific capacity than graphite due to their unique structure [5]. Single-walled (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) can achieve high conductivities of up to $10^6 \text{ S}\cdot\text{m}^{-1}$ and $10^7 \text{ S}\cdot\text{m}^{-1}$, respectively [6]. CNTs can also minimize electrode expansion during lithium intercalation and offer excellent

conductivity [7]. In this study, MWCNT-modified LZTO anodes were synthesized using a ball-milling technique. Functionalizing MWCNTs with oxygen improved their distribution, enhancing interfacial adhesion and electrochemical performance [8].

2 EXPERIMENTAL

Chemical Oxidation of MWCNTs—Multi-walled carbon nanotubes (MWCNTs) from Bayer Chemicals (BAYTUBES® C 150 P) had inner and outer diameters of $\sim 4 \text{ nm}$ and $\sim 13 \text{ nm}$, respectively. The oxidation procedure is described in the previous manuscript [9]. LZTO and MWCNT-modified LZTO were synthesized using a ball mill-assisted solid-state method. MWCNTs were added at a 10% weight ratio, based on previous LZTO@RGO research [10].

Assembly of Li-Ion Cells—LZTO and LZTO@MWCNTs were tested as working electrodes in half-cells with lithium foil as the counter electrode and Whatman GF/D as the separator. Cell assembly was done in an argon-filled glove box, with O_2 and H_2O levels kept

below 0.5 ppm. The active materials were mixed with Super P (10%) and PVDF (10%) in NMP, applied to a copper foil by doctor blade, and vacuum dried at 120°C. The final anode material was about 5 mg cm⁻². The electrolyte used was 1 M LiPF₆ in a 1:1 mixture of ethylene carbonate and dimethyl carbonate.

Electrochemical Testing—Half-cells were charged and discharged at various current densities (1 C = 227 mA g⁻¹) between 0.02–3.0 V. The MWCNT content in LZTO was determined by DTA/TG, and electrochemical performance was measured using an MTI battery analyzer. CV and EIS measurements were performed with a VersaSTAT MC electrochemical workstation, with CV scans from 0.02 to 3.0 V at 0.1 mV s⁻¹, and EIS measurements at 0.6 V with frequencies from 100 kHz to 10 mHz.

3 RESULTS AND DISCUSSION

XRD Analysis of Materials—Figure 1a shows the XRD patterns of pristine and MWCNT-modified LZTO anodes. Both matches well with standard LZTO peaks (JCPDS#01–083–8262), though the pristine sample shows TiO₂ impurities (JCPDS#01–084–1284). MWCNT modification supports pure LZTO formation by preventing raw material segregation and aiding heat transfer during synthesis [10]. The MWCNT graphite peak (002) is visible at 25.4° in Fig. 1b.

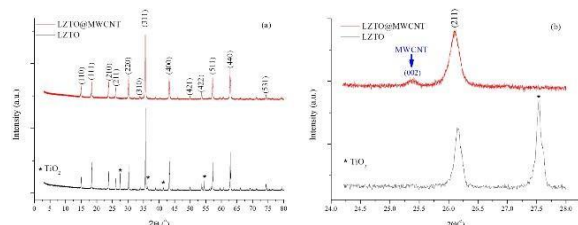


Figure 1. (a) the XRD Patterns of LZTO and LZTO@MWCNT. (b) the Magnified (211) Diffraction Peaks of LZTO and LZTO@MWCNT.

Panalytical X'Pert HighScore refinement software was used to calculate lattice parameters, and the results, including Rietveld refinement indexes.

As shown in Table 1, the composite material has a particle size 15 times smaller than the pristine material, which can improve lithium diffusion by shortening diffusion pathways [11]. Table 1 also presents the pore size and volume, both of which are higher for LZTO@MWCNT, enhancing

wettability and mitigating volume changes during electrochemical cycling [11].

Table 1. Some Physicochemical Parameters of the Anode Active Materials.

Synthesized sample	Crystal size (nm)	Average particle size (nm)	BET Surface area (m ² g ⁻¹)	Pore Volume* (cm ³ g ⁻¹)	Pore Size** (Å)	Conductivity (S.cm ⁻¹)
LZTO	80	666	2.053	0.00818	276.982	8.0x10 ⁻⁵
LZTO@MWCNT	80	45	33.617	0.18009	320.491	2.7x10 ⁻⁴

As shown in Table 1, LZTO@MWCNT conductivity is 10 times higher than that of LZTO, improving contact between the active material and current collector, and reducing kinetic limitations.

FESEM images of the anode materials (Fig. 2) show approximately 100 nm interconnected particles. Figures 2b–2d reveal that MWCNTs are evenly distributed between LZTO particles, which is achieved through MWCNT use and ball milling. The red areas in Fig. 2c highlight the MWCNTs. This uniform distribution may enhance the anode performance of LZTO.

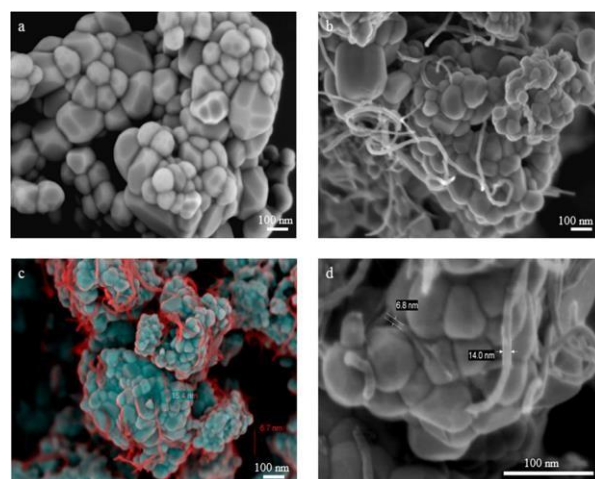


Figure 2. High Resolution FESEM Micrographs of (a) Pristine LZTO and (b)-(d) LZTO@MWCNT.

TEM imaging (Figs. 3a–3c) shows LZTO particles averaging 100–200 nm in size. Figures 3b and 3c reveal tube-like MWCNT networks uniformly mixed with LZTO particles, consistent with the FESEM results.

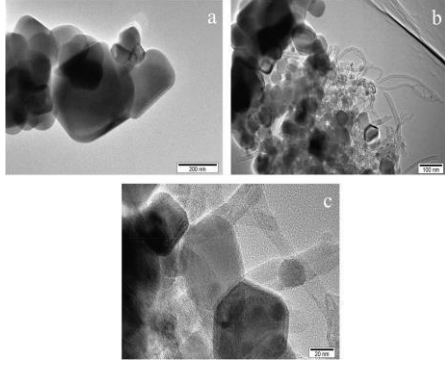


Figure 3. TEM Images of (a) Pristine LZTO (b), (c) LZTO@MWCNTs.

The CV profiles of anodes (Figs. 4a and 4b) show a sharp anodic peak at 1.6 V and a weak cathodic peak at 1.3 V, corresponding to the Ti^{4+}/Ti^{3+} redox reaction, with a reduction peak at 0.6 V related to the restoration of Ti^{4+} ions in LZTO and LZTO@MWCNT anodes [13]. MWCNTs increase the sharpness and current density of the peaks, enhancing electrochemical reversibility after five cycles.

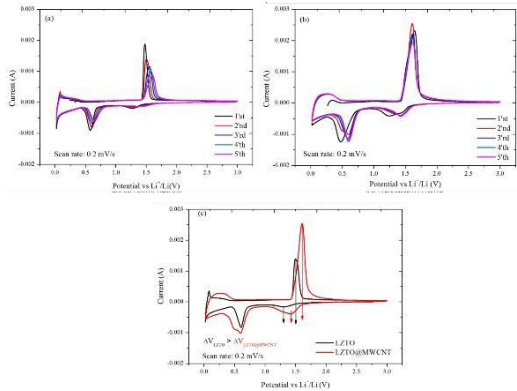


Figure 4. CV of (a) LZTO, (b) LZTO@MWCNTs Anodes and (c) the Comparison of the Redox Potential Differences of the Anode Electrodes.

Table 2 and Fig. 4c reveal that the LZTO@MWCNT electrode, with a lower $\Delta\phi$ (0.184 V), shows reduced polarization compared to LZTO (0.211 V). The improved conductivity from MWCNTs mitigates polarization. The lithium diffusion coefficient (D_{Li^+}) was calculated from CV experiments at different sweep rates (Fig. 5), and Table 2 shows that the MWCNT-modified anode supports better charge/discharge performance due to higher lithium diffusion.

Table 2. Anodic (ϕ_p) and Cathodic (ϕ_c) Peak Potentials and $\Delta\phi$ for LZTO and LZTO@MWCNT in the 2nd Charge-Discharge Cycle

Sample	ϕ_p (V)	ϕ_c (V)	$\Delta\phi$ (V)
LZTO	1.508	1.297	0.211
LZTO@MWCNT	1.609	1.425	0.184

The charge-discharge profiles of pristine and MWCNT-modified anodes are shown in Fig. 6. The pristine anode shows charge-discharge plateaus at 1.40 V and 0.60 V, while the MWCNT-modified electrode's profile is nearly identical, indicating no significant change in electrochemical reactions after modification [14].

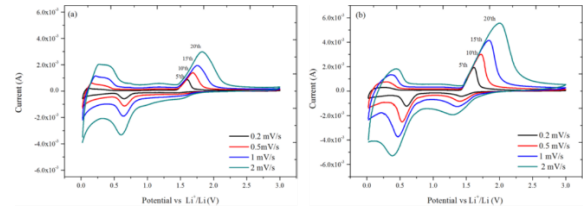
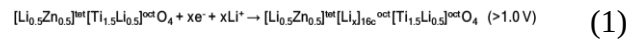


Figure 5. CV Curves of (a) LZTO, (b) LZTO@MWCNTs Electrodes at the Different Sweep Rates.

SEI formation consumes Li^+ , resulting in a higher first discharge capacity for LZTO and LZTO@MWCNT compared to the theoretical capacity of pristine LZTO (227 mAh g⁻¹) [15].



The electrochemical discharge reactions (1) are as listed [16].

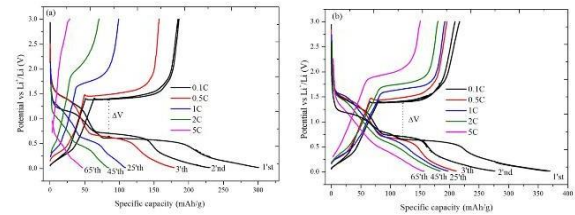


Figure 6. The Charge-Discharge Profiles of (a) LZTO and (b) LZTO@MWCNTs at Different C Rates from 0.1 C to 5 C (1 C = 227 mAh g⁻¹).

Fig. 6 shows that LZTO@MWCNT has better charge-discharge capacity at all C rates, with ideal coulombic efficiencies at 0.5 C, 1 C, 2 C, and 5 C, though lower efficiency at 0.1 C due to

SEI layer formation. The improved performance is attributed to the conductive CNT network enhancing Li^+ storage [17]. The ΔV values of LZTO@MWCNT are smaller than LZTO, and ΔV increases sharply with higher current density for LZTO, indicating greater polarization. These results align with the CV data. Figure 7 shows the cycling performance of all anodes in the 0.02–3.0 V range. A rate capability test at 0.1 C, 1 C, and 5 C was conducted, followed by cycling back to 0.1 C. As seen in Fig. 8, LZTO@MWCNTs anode has higher discharge capacities than LZTO, with better cycling stability and performance at high current densities. At 1 C (3rd cycle), LZTO@MWCNTs delivered 227 mAh g^{-1} , while LZTO had 144 mAh g^{-1} . At 5 C (105th cycle), LZTO@MWCNTs reached 142 mAh g^{-1} , while LZTO only achieved 28 mAh g^{-1} . The significant capacity fade at 5 C for LZTO is due to low electronic conductivity and limited active surface area. Discharge capacity retention was 97% for LZTO@MWCNTs and 80% for LZTO.

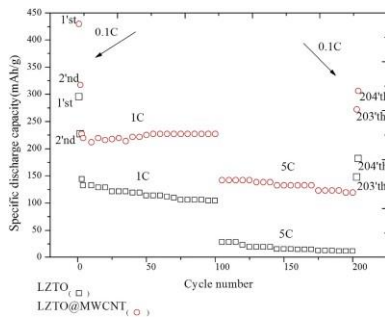


Figure 7. Cycling performances of LZTO and LZTO@MWCNTs anode at different current rates.

Fig. 7 shows LZTO suffered a 20% irreversible capacity fade after 204 cycles, while LZTO@MWCNTs had just 3%. MWCNTs improve electronic conductivity, prevent particle agglomeration, and enhance lithium-ion access to active sites, leading to superior rate capability and cycling performance [18]. EIS experiments were used to evaluate the electrochemical kinetic properties of the anodes. Measurements were taken from the fresh cell and after the 30th cycle at 1 C (Fig. 8a). The Nyquist plots show a small high-frequency intercept, two semicircles in the high-to-medium frequency range, and a straight tail at low frequencies. The spectra were analysed using the equivalent circuit shown in Fig. 8b. Here, R_e represents the electrolyte and cell component impedance, C_{sei} and R_{sei} correspond

to the SEI layer capacitance and resistance, and C_{dl} and R_{ct} represent the double-layer capacitance and charge transfer resistance. The low-frequency tail is related to lithium-ion diffusion in the LZTO electrode, consistent with findings from other studies [19].

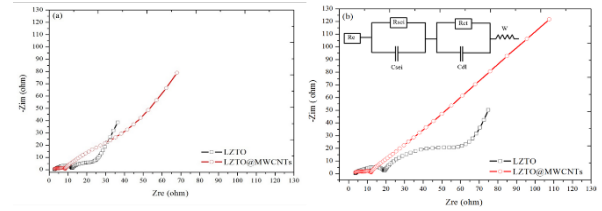


Figure 8. EIS patterns of electrodes (a) before cycling, (b) after the 30th cycling at 1 C rate.

As seen in Fig.8, R_{sei} and R_{ct} for LZTO@MWCNTs are lower than for LZTO. After 30 cycles, R_{sei} and R_{ct} for LZTO@MWCNTs were measured at 7.93 and 12.06 Ω , respectively. These results indicate that MWCNT modification reduces SEI and charge transfer resistance in the LZTO anode.

4. CONCLUSIONS

In conclusion, the solid-state ball milling technique successfully produced LZTO@MWCNTs anode material. TEM and FESEM images confirmed a uniform blend of MWCNTs with LZTO particles. CV measurements showed that the LZTO@MWCNTs electrode has higher redox peak intensity and electrochemical reversibility compared to LZTO. The D_{Li^+} for LZTO@MWCNTs was calculated as $2.43 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$, significantly higher than LZTO's $6.79 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$. Charge-discharge tests revealed that LZTO@MWCNTs has greater specific capacity and better capacity retention (100% at 1 C and 83% at 5 C), compared to LZTO's 72% and 39%. EIS measurements showed lower SEI resistance (R_{sei}) and charge transfer resistance (R_{ct}) for LZTO@MWCNTs. The improved electrochemical performance of LZTO@MWCNTs, including better specific capacity, cycling stability, and rate capability, is attributed to enhanced electronic and ionic conductivity, making it suitable for long-life LIBs at high C-rates.

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EFFECT OF FIN STRUCTURES, PCM, AND POROUS MEDIA ON LATENT HEAT THERMAL ENERGY STORAGE PERFORMANCE

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Abstract

This study examines the effect of triangle fin geometries, inclination angles, and porous media on the melting performance and energy storage capability of Latent Heat Thermal Energy Storage (LHTES). Two scenarios were considered: one with only phase change material (PCM) and one with PCM embedded in porous media. The Brinkman-Darcy-Forchheimer model was used to solve the governing equation, assuming the local thermal equilibrium hypothesis. The enthalpy-porosity method was applied to solve the melting process. Results were analyzed for liquid fraction, melting time, and energy storage. The findings indicate that porous media significantly influence liquid fraction, melting time, and enthalpy, providing more homogeneous changes than those without porous media. The fastest melting occurred at 120° without porous media and at R-60° with porous media. It was observed that the porous media increased the melting time by 87.5 times and the triangular fins opposite to the melting direction extended the melting time. Additionally, the case with porous media stored more energy than without, with the highest storage at R-60°.

Keywords: Porous media, Phase change material, Thermal energy storage, Rectangular cavity, Latent heat, Triangle fin structure

1 INTRODUCTION

It is known as a phenomenon that increases global temperature and climate crisis. To cope with this problem, 175 countries have signed the Paris Agreement and agreed to reduce their emissions by 45.0% by 2030 and net zero by 2050. Judging by today's energy sources, we still consume 80.0% of the energy generated by non-renewable sources according to the International Energy Agency 2023 report. Evidently, the existing actions do not fulfill the energy requirements and the investigation and investment in renewable energy should be raised. However, the main restriction in solar, wind, etc. energy sources is that the continuum and capacity of these sources are significantly affected by weather conditions, seasons, and time. To prevent this restriction, energy storage systems such as batteries, thermal energy storage (TES), pumped hydro storage (PHS), flywheel energy storage (FES), compressed air energy storage (CAES), hydrogen energy storage (HES), supercapacitors are developed in today, and investigations on their technology shows a remarkable improvement.

In these systems, TES is essential for separating

the supply and demand of energy. Effective TESmissions are important for optimizing intermittent energy sources, such as solar thermal devices. Among the various types of TES, LHTES systems present an alternative to conventional sensible TES solutions because of their higher energy density capability. Solid- liquid PCMs are generally utilized in LHTES, and they release or absorb the energy at constant temperature (latent heat). These materials have unique properties such as a small temperature range, cost-effective, reusing, and easy integration into the thermal systems. It's also become prominent with high energy storage density compared to sensible heat storage fluids such as oil, air, water, etc. The biggest limitation of PCMs is low thermal conductivity, which considerably affects system performance [1]. Because of this difficulty, it has to be enhanced with the help of some applications.

Based on the low thermal conductivity of PCM, Choure et al. [2] have grouped the techniques under four subsections to enhance the heat transfer: a) using high heat conductive material, b) modifying the geometry, c) use of multiple phase change materials, and d) using fins of different shapes. Among these applications, the

porous media application, which is included in the using high heat conductive material group, is the technique that has the most intensive use in PCM applications due to its high thermal conductivity, high heat transfer surface area, and low thermal resistance. In this scope, Moaveni et al. [3] carried out a thermal management study on the working of lithium-ion batteries under maximum performance and safety. The results revealed that taking advantage of nanoparticles with $\phi=9.0\%$ and 4 fins decreased the peak temperature at the value of 5.18K and 10.36K for 4C discharge rate, respectively. Furthermore, utilizing copper porous media with $\varepsilon=0.90$ cooled the battery system at the value of 12.57K for a 3C discharge rate. Liu et al. [4] both experimentally and numerically tested the effect of non-uniform porous media embedded in a PCM to reduce the negative effect of solar systems and increase the employability of solar energy. When investigating the relationship between phase interface, temperature field, and velocity field, natural convection accelerated the PCM melting contrary to solidification. It is considered that while $\varepsilon=0.94$, optimum conditions are acquired as 0.84-0.92-0.99 for the melting process and 0.87-0.94-0.97 for the solidification process compared to uniform porous media arrangement. Also, a reduction of 9.7% and 6.2% are observed in the consumption time of both the melting and solidification process.

The above literature shows that many studies have investigated the heat transfer characteristics of LTES systems supported by porous media under different conditions and natural convection. However, there needs to be a detailed investigation of the triangle fin structure and its various angles within the scope of PCM and porous media compound methods. It is seen that these systems can easily find applications in LTES systems such as solar systems [5], microelectronic devices [6], or buildings [7]. Taking advantage of the gap in the literature, heat transfer, heat storage, and melting performance of triangle-finned rectangular cavities filled with PCM embedded with porous media have been investigated in detail. In the numerical study, the effect of triangle fin inclination angles for different tending and aluminium porous media has been researched for a laminar flow regime at the natural convention.

2 MATERIAL AND METHODS

A two-dimensional schematic view of the computational domain is presented in Figure 1. It represents a rectangular cavity with a height (H) of 30 mm and a width (W) of 10 mm. Besides, the domain is filled with PCM and PCM+porous media, separately, to comparison for cases with and without porous media. The left side of the domain is considered to have a constant wall temperature of 335.15 K and the other walls have been considered as an adiabatic and no-slip condition. The initial temperature of cases is adjusted as 298.15 K. The top wall of the domain has a triangular shape, and the angles are adjusted to vary from left to right. The aim here is to reveal the performance of the heat moving through the PCM when it encounters any obstacles as the melting begins. As PCM, RT58 paraffin wax from Rubitherm was considered and this PCM is a material in the organic group. It was considered that the porous media was made of aluminum material and its porosity and pore density were considered as $\varepsilon=0.9$ and $\omega=20$ PPI.

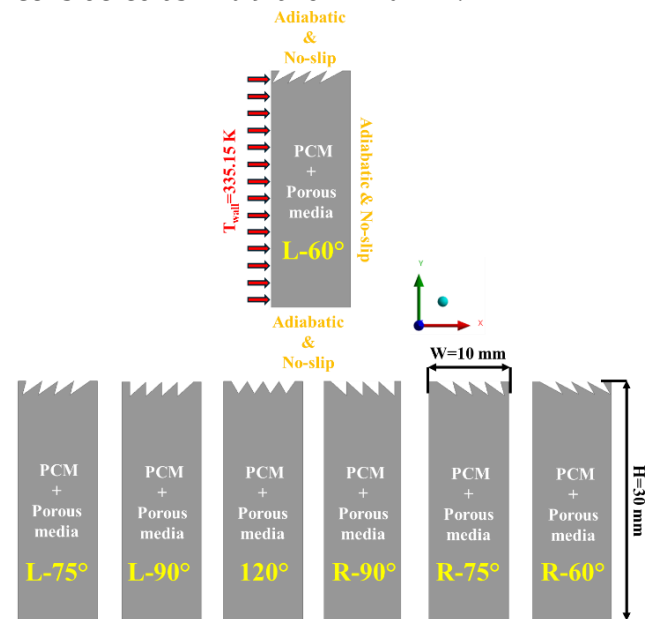


Figure 1. Schematic View of The Computational Domains

2.1 Assumptions

The Forchheimer-extended Darcy model has been used to model the heat transfer between PCM and porous media by considering the local thermal equilibrium (LTE) hypothesis. This hypothesis assumes that the internal averages of the time-averaged temperatures of the fluid and solid phases are equal, and there are studies in the literature on its usability in aluminium foams with

$\omega=20$ PPI [8,9]. Furthermore, the following assumptions have been considered in this study:

- The liquid phase of PCM is Newtonian and incompressible.
- Except for the density of PCM, the other thermophysical properties of the PCM and porous media are not changed according to the phase.
- The Boussinesq approximation is employed to calculate density, which is considered for the buoyancy effect in the momentum equation, due to the low-temperature difference.
- The structure of the porous media is homogenous and isotropic for each direction.
- During melting, there is no change in domain volume.

2.2 Governing Equations, Data Reductions, and Solution Methods

The governing equations for PCM and porous media combinations are presented below based on the given assumptions and accepted hypotheses. Besides, the enthalpy-porosity method is employed to solve the melting process. In this method, the melt interface is not explicitly tracked. Instead, each cell in the domain is assigned a value called the liquid fraction, which represents the portion of the cell volume that is in liquid form. The liquid fraction is calculated at each iteration based on an enthalpy balance [10]. According to this, the continuity equation is given in Equation 1 [11].

$$\nabla \cdot V = 0 \quad (1)$$

where V describes the velocity in the computational domain. The momentum equation is represented in Equation 2 [12].

$$\begin{aligned} \frac{\rho_p}{\varepsilon} \frac{\partial V}{\partial t} + \frac{\rho_p}{\varepsilon^2} V \cdot \nabla V \\ = -\nabla P + \frac{\mu_p}{\varepsilon} \nabla^2 V \\ - \frac{(1-\beta)^2}{(\beta^3 + 0.001)} A_{mush} V \\ - \left(\frac{\mu_p}{K} V + \frac{C_F}{\sqrt{K}} \rho V|V| \right) \\ + \rho_p g \gamma \Delta T_0 \end{aligned} \quad (2)$$

where ρ , μ , and γ specify the density, dynamic viscosity, and thermal expansion coefficient of PCM, respectively, while ε , β , A_{mush} , C_F , g , ΔT_0 , K , and P show the porosity of porous media, liquid fraction, mushy constant (set to 10^5

$\text{kg/m}^3\text{s}$), Forchheimer drag coefficient, gravity (equal to 9.81 m/s^2), the temperature difference in buoyancy effect based on the Boussinesq approximation, permeability, and pressure. Since a calculation is conducted for the LTE hypothesis, the energy equation is given in Equation 3 [11].

$$\begin{aligned} (\rho c)_{eff} \left(\frac{\partial T}{\partial t} + V \cdot \nabla T \right) \\ = k_{eff} \nabla^2 T - \varepsilon \rho_p H \frac{\partial \beta}{\partial t} \end{aligned} \quad (3)$$

where k_{eff} , also given in Equation 4, identifies the volume averaged effective thermal conductivity between fluid and porous zone while H_L represents the latent heat of PCM [10].

$$k_{eff} = \varepsilon k_{pcm} + (1 - \varepsilon) k_{porous \ medium} \quad (4)$$

The terms in the momentum equation with regard to porous media have to be defined with the help of some validated equations. For this purpose, the permeability of porous media is calculated with Equation 5 [13].

$$K = \frac{k}{36 (\delta^2 - \delta)} \quad (5)$$

where d_k and δ specify the characteristics length and tortuosity coefficient of porous media and these parameters can be expressed by Equation 6 and 7, respectively [13].

$$d_k = \frac{\delta}{3 - \delta} d_p \quad (6)$$

$$\delta = 2 + 2 \cos \left[\frac{4\pi}{3} + \frac{1}{3} \cos^{-1}(2\varepsilon - 1) \right] \quad (7)$$

Forchheimer's drag coefficient (inertial) coefficient can be found in Equation 8 [13].

$$C_F = 0.00212(1 - \varepsilon)^{-0.132} \left(\frac{d_f}{d_p} \right)^{-1.63} \quad (8)$$

where d_f and d_p symbolize the fiber and pore diameter of porous media and these parameters can be calculated with Equation 9 and 10, respectively [13].

$$d_f = 1.18 \sqrt{\frac{1 - \varepsilon}{3\pi}} \left(\frac{1}{1 - e^{(-0.04)}} \right) \quad (9)$$

$$d_p = \frac{0.0254}{\omega} \quad (10)$$

where ω identifies the pore density determined as 20 PPI. One of the most important parameters in solidification and melting phenomena is the determination of liquid fraction (β). This parameter is included in the momentum equation (Equation 2) and shows a variation between $0 \leq \beta \leq 1$ according to solidus and liquidus

temperatures. As a result, the equation defined the variation of β is given in Equation 11 [13].

$$\beta = \frac{\Delta H}{H_L} = \begin{cases} 0 & \text{if } T < T_s \\ \frac{T - T_s}{T_L - T_s} & \text{if } T_s < T < T_L \\ 1 & \text{if } T > T_L \end{cases} \quad (11)$$

where T_s , T_L , and T identify the solid phase, liquid phase, and local temperature, respectively. Besides, β relies on the local temperature (T), and when it exceeds the T_s , PCM begins to melt. The enthalpy variation indicates the stored energy can be calculated with Equation 12-16.

$$\Delta H = \Delta H_{PCM} + \Delta H_{MF}$$

$$= \varepsilon \int (\rho \Delta h)_{PCM} dV + (1 - \varepsilon) \int (\rho \Delta h)_{porous media} dV \quad (12)$$

$$(\rho \Delta h)_{porous media} = c_{p_{porous media}} (T_{porous media} - T_{in}) \quad (13)$$

$$(\rho \Delta h)_{PCM} = (\rho c_p)_{PCM,S} (T_{PCM} - T_{in}) \text{ if } T_{PCM} < T_s \quad (14)$$

$$(\rho \Delta h)_{PCM} = (\rho c_p)_{PCM,S} (T_s - T_{in}) + \rho_{PCM} H_L \beta \text{ if } T_s < T_{PCM} < T_L \quad (15)$$

$$(\rho \Delta h)_{PCM} = (\rho c_p)_{PCM,S} (T_s - T_{in}) + (\rho c_p)_{PCM,L} (T_{PCM} - T_L) \text{ if } T_L < T_{PCM} \quad (16)$$

where ΔH_{PCM} and ΔH_{MF} show the enthalpy variation of the PCM and porous media while the total of these two terms presents the total enthalpy variation of the TES. Besides, h , V , and T_{in} symbolize the specific enthalpy, volume, and initial temperature of the TES, respectively. In the analyses, RT58 (Rubitherm) and porous media have been analyzed as PCM and porous media, respectively, and the thermophysical properties of these materials are given in Table 1.

After the information, which has a critical statement for a description of the tackled problem, has been given, it has to be defined as the solution method of the numerical analysis. ANSYS Fluent 2024 R1 software, which carried out the calculations according to the finite volume method, has been used to conduct the analyses. The pressure-velocity coupling is addressed using the SIMPLE algorithm, while the pressure calculation is handled with the PRESTO

algorithm. Under-relaxation factors of pressure, density, momentum, liquid fraction, and energy are set to 0.3, 1.0, 0.7, 0.9, and 1.0, respectively. Furthermore, convergence limit values are considered as $1e^{-06}$, $1e^{-05}$, and $1e^{-06}$ for continuity, momentum, and energy, respectively.

Table 1. Thermophysical Properties of PCM and Porous Media [11].

Properties	RT58	Aluminium
Density, ρ [kg/m ³]	825	2719
Specific heat, c_p [J/kgK]	2000	871
Thermal conductivity, k [W/mK]	0.2	202.4
Dynamic viscosity, μ [kg/ms]	0.0269	
Thermal exp. coeff., γ [1/K]	0.00011	
Latent heat, H_L [J/kg]	160000	
Solidus temperature, T_s [K]	326	
Liquidus temperature, T_L [K]	332	

2.3 Mesh Convergence, Time-Step Sensitivity, and Validation

To determine the effect of mesh number and time step value, a convergence and sensitivity analysis have been carried out in the case of 120° for porous media included state. The fluid domain divided small volume cells with the help of some local mesh settings independently of mesh quality metrics and mesh convergence analysis has been conducted for three different mesh numbers. The quality metrics for the minimum orthogonal quality and the maximum skewness values are kept approximately constant at 0.730 and 0.528, respectively. As can be seen in Figure 2(a), liquid fraction does not change with vary of mesh numbers, and the maximum error rate is acquired as 0.2% compared to the case of 19400 mesh numbers. Based on these results, it can be mentioned that the mesh number does not affect the result. Thanks to this, the mesh setting given 7500 mesh numbers has been selected for further analysis and the schematic view of the mesh structure is presented in Figure 3. Furthermore, the time step sensitivity analysis is carried out for $t=0.1$, 0.5, and 1.0s, respectively, at 7500 mesh

numbers. According to Figure 2(b), the trends show the same inclination with each other as time increments. The maximum error rate in liquid fraction results between the $t=0.1s-0.5s$ and $t=0.1s-1.0s$ is obtained as 3.23% and 7.08%, respectively, and $t=0.5s$ is selected as the time step value for further analyses.

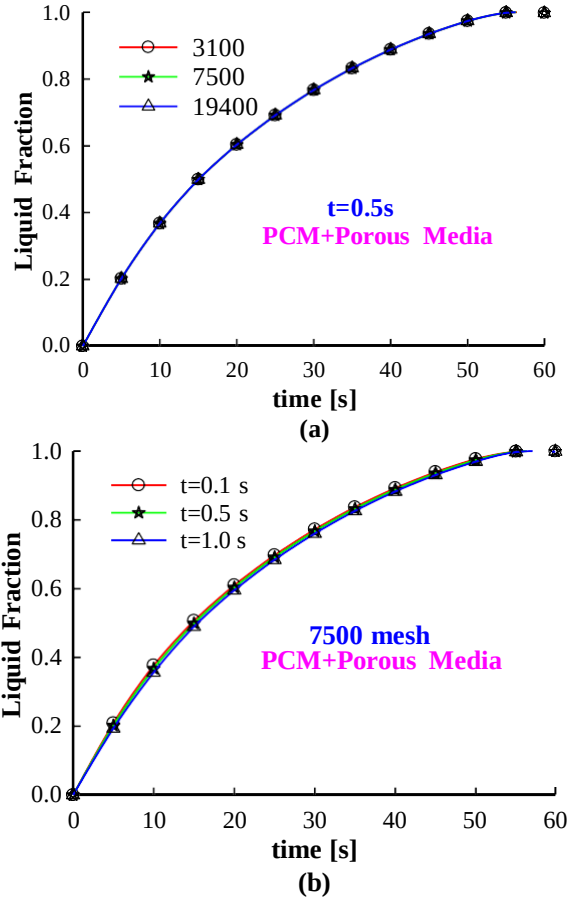


Figure 2. The Result of; (a) Mesh Convergence Analysis at $t=0.5s$ and (b) Time Step Sensitivity Analysis for 7500 Mesh Number

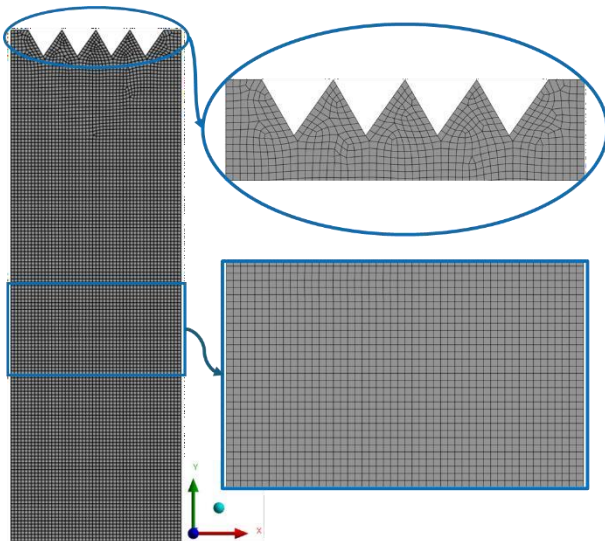


Figure 3. The Mesh Structure Schematic View of The Selected Fluid Domain (7500 Mesh Numbers)

To ensure the accuracy of the solution, and methods implemented in the numerical study, a validation study was carried out with the literature. The comparative analysis was conducted by Huang et al. [13], and the comparisons were carried out for the fluid domain that does not have a fin structure over the liquid fraction. The obtained results have been compared in Table 2, and it was determined that the contours exhibited a high level of similarity.

Table 2. Validation of The Numerical Methods by Comparing Liquid Fractions

Time, t [s]	Huang et al. [13]	Present study
60		
180		
360		
540		
720		
900		

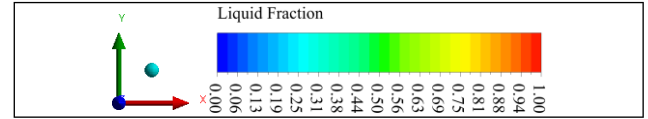
3 RESULTS AND DISCUSSION

In Table 3, the effect of porous media and the inclination angle of triangle fins are presented. According to the results, it was firstly observed that the cases including porous media greatly decreased the melting time approximately 87.5 times. The reason for this decrease can be

explained by the increasing effective thermal conductivity of the system. As a result of this, heat is more easily conducted in the domain, and thermal diffusion increases. Besides, it has been concluded that porous media affected the system characterization. Namely, the case of 120° performed the highest melting in the absence of porous media. However, the case of R-60° presented the highest melting presence of porous media. Besides, it has been concluded that the liquid fraction of the PCM embedded in porous media is more homogeneous than that of the PCM without porous media.

Table 3. Comparison of Liquid Fraction Contours of 120° and R-60° at Some Melting Times

Case	Time, t [s]	120°	R-60°
without Porous Media	875		
	2187.5		
	3500		
	4812.5		
with Porous Media	10		
	25		
	40		
	55		



The melting performance of the cases has been tackled in Figure 4 to detail the investigation. As can be seen in Figure 4(a), the shortest melting time belongs to the case of 120°. However, this behavior is changed with using of porous media and the earliest melting is realized in the case of R-60° in Figure 4(b). The underlying reason for fast melting in PCM with porous media can be explained by increasing of effective thermal conductivity of the system along with using the porous media. The combined influence of heat conduction and heat convection led to a faster melting rate of the PCM when porous media was present.

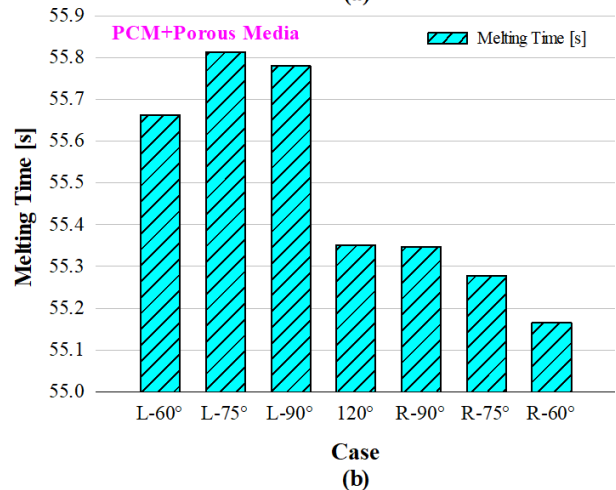
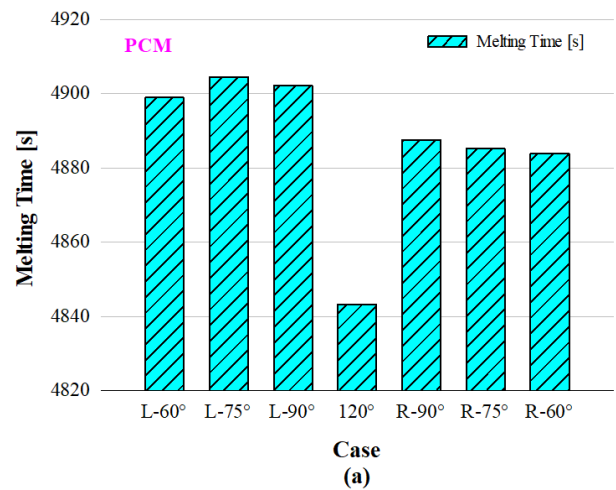


Figure 4. Comparison of The Melting Time of The Cases with; (a) only PCM and (b) PCM+Porous Media

Figure 5 compares the energy storage performances of cases with and without porous media over time. The analysis of the results from both scenarios reveals that the energy storage

trends are similar regardless of the time frame. However, the stored energies correlate closely with the average temperature changes in the system. Additionally, the cases with porous media demonstrate higher energy storage compared to those without. This is primarily because porous media conduct heats more effectively, allowing for better accumulation throughout the PCM volume. Similar to the results for liquid fraction and average temperature, the energy storage process in cases with porous media is more homogeneous, with the highest storage occurring at R-60°.

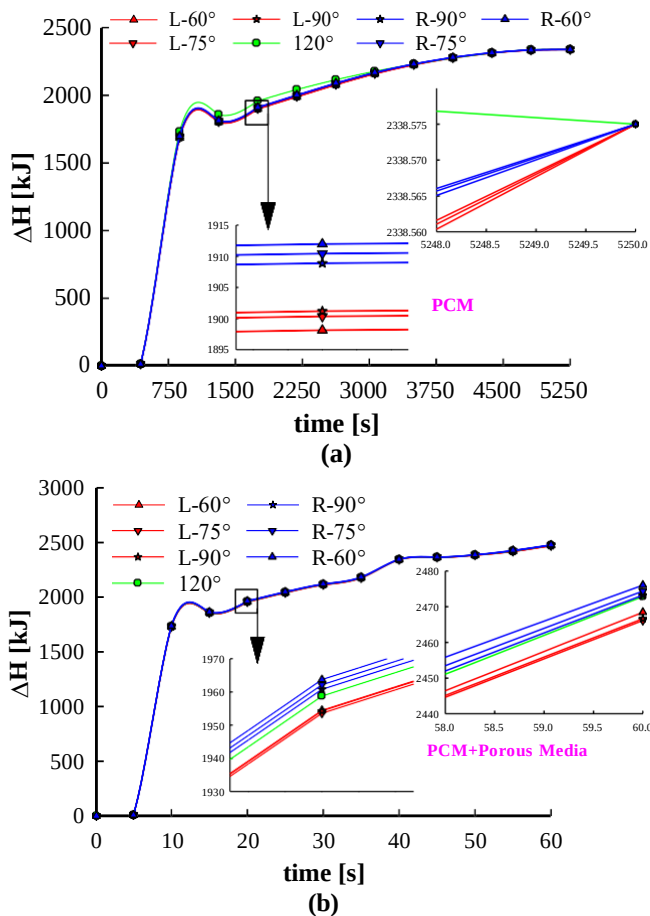


Figure 5. Variation of The Stored Energy as A Time Function for Cases Including; (a) only PCM and (b) PCM+Porous Media

4 CONCLUSION

This study examines the performance of LHTES by focusing on the different inclined triangle fins and porous media effects. Liquid fraction, melting time, and energy storage parameters have been taken into account for evaluation. RT58 (Rubitherm) PCM and aluminum porous media with $\varepsilon=0.9$ and $\omega=20$ PPI have been used in the systems. In all simulations, the Brinkman-Darcy-

Forchheimer model and enthalpy-porosity method have been considered for solving governing equations and melting processes by assuming the local thermal equilibrium hypothesis. According to the results, the key findings are as follows:

- Porous media greatly decreased the melting time by approximately 87.5 times due to it enhances the effective thermal conductivity of the system. Thanks to this, heat is easily conducted in the cavity, and thermal diffusion increases.
- Whereas the case of 120° performed the highest melting in the absence of porous media, the case of R-60° presented the highest melting presence of porous media.
- The liquid fraction of the PCM embedded in porous media is more homogeneous compared to the PCM without porous media.
- Considering the melting time, the shortest melting time occurs at 120° for a non-porous medium, while the early melting in cases containing porous media occurs at R-60° due to the combined effect of heat conduction and heat convection.
- The cases with porous media exhibit higher energy storage than the absence of porous media, primarily because the porous media conducts heat more effectively, enabling better accumulation throughout the PCM volume.
- The findings for liquid fraction and average temperature, the energy storage process in cases with porous media is more homogeneous, with the highest storage occurring at R-60°.

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SITUATION OF ROMANIAN ENERGY RESOURCES FOR STABILITY AND ENSURE ENERGY SECURITY

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Abstract

At present situation, the geostrategic and geopolitical positioning of Romania, regardless of its membership and role in various economic-military unions or blocs, is no longer based solely on its military power, but rather on its energy, economic, information and especially technological domination. The emergence and increasing development of energy disputes and conflicts with possible military escalation and the strong desire of the major world economic powers states, to have control and world power, makes energy resource (coal, uranium, oil and natural gas) to be used by their holders as instrument for pressure. Lack of energy resources can cause energy instability that automatically leads to national insecurity and with possible European or global repercussions, by the fact that all sectors of an economy depend on energy resources, which generate energy security and welfare for that state. Paper contain essential informations regarding natural resources, situation of primary energy resources (reserves) and situation of energy security in Romania. The aim of the paper is to demonstrate that energy in all its forms can be a reason for cooperation and confrontation with connotations often military, generating wars that seriously damage all social environments and thus global welfare. The authors propose to suggest some actions for Romanian decision-makers of need to create energy stability factors in order to combat energy poverty, vulnerable consumers and ensure energy security.

Keywords: Energy resources, Energy security

1 INTRODUCTION

The lack, reduction or depletion of energy resources (coal, uranium, oil and natural gas) in some states that are automatically becoming energy dependent on other energy-rich and energy-secure states makes the issue of great importance and topicality, as the great powers world energy companies want to control and monopolize energy in order to use energy resources as a instrument of political pressure in the context of profitability and blackmail in pursuit of their own interests. Lack of energy resources (coal, uranium, oil and natural gas) leads to regional and / or global crises that cause imbalances leading to extreme damage to regional or global security, as all sectors of a state economy depend on energy resources

which are subsequently converted into other forms of energy. as well as electricity. [1]

2 GENERAL INFORMATIONS REGARDING NATURAL RESOURCES

The United Nation 21 Agenda 1992 stated that “energy is indispensable for societal development and the improvement of livind conditions of life” The all organization’s Member countries reaffirm “the critical role that energy (in all its forms) plays in the development process, given that access to modern and sustainable energy services contributes to the eradication of poverty, saving lives, improving health and supporting the provision of basic needs of the individual”. Natural resources, especially energy (hydrocarbons, uranium, coal, etc.) and

electricity, have influenced the evolution and development of human society since ancient times, and the modern economic development of a state is dependent on energy resources, where the volume of energy (in all its forms) consumed per capita has become a significant indicator of the progress and modernization of a state. The national power of a state is the possession, control and rationalization of energy resources in order to maintain its energy independence and eliminate dependence on other states. For this reason, energy resources (coal, uranium, oil and natural gas) become strategic because they ensure economic development and security of a state and are influenced by the political element in the context of military development. To these can be added coal, non-ferrous metals (aluminum, tin, etc.), uranium ores and precious ores (gold). [2]

Resources – necessity elements that provide certain human needs for the purpose of societal development. [1,4]

Natural resources - the totality of minerals, agricultural lands, forests and hydrographic network without human intervention: air, water, soil, mineral substances, plants, animals, solar, wind, tides, etc. Natural resources are natural components and factors of production available to mankind to meet its economic and social needs and/or quantities of naturally formed substances, organisms and energy, available to mankind, necessary for its survival and evolution, which can be used in the present and/or future.

Energy resources – an important part of natural resources, are found in the earth's crust with a thickness of 40 kilometers (basalt layers, granite and sediments): coal, shale and tar sands, oil, natural gas and uranium. [3]

Strategic resources – available, real, tangible and potential resources that have the role of ensuring, growing and achieving the strategic objectives of a state. They are generating stability and economic, societal, educational, energy and military development and resilience in the event of crisis, conflict or war. Among the most important strategic resources that a state should have in order to sustain its national power, one can include: economic resources (GDP value, GDP share in the world, etc.); human capital (aging rate, school rate, etc.); natural resources (electricity production, share of energy used for commercial purposes, arable

land, freshwater stretches, etc.); capital resources (gross domestic investments, capital market value, net foreign direct investment rate, etc.); knowledge and technological resources (number of computers, patents, articles in technical and scientific journals, internet hosts, research and development expenses, etc.); government resources (share of government expenditure in GDP, etc.); military resources (armed forces, military expenditures, etc.); international resources (exports and services, imports and services, royalties, etc.). [1,4]

Classification of natural resources:

a) By the place where they are located: [4,7]

- Terrestrial resources: atmospheric; hydrospherical; biospheric; terrestrial crust.
- Sun resources: solar energy.

b) After the possibility of regeneration:

- Renewable resources: plants; animals; solar energy; some mineral substances.
- Non-renewable resources: other mineral substances.

c) After obtaining energy from them:

- Energy resources: air; water; solar radiation.
- Non-energy resources: soil; some mineral substances.

d) According to the specific nature of the substance:

- Organic resources: plants; animals; fossil energy fuels
- Inorganic resources: some mineral substances.

e) After the possibility of burning:

- Combustible resources: some woody plants; fossil fuels;
- Non-combustible resources: soil; animals; some grassy plants; some mineral substances.

f) After the possibility of using as food:

- Food resources: vegetables; animals; some mineral substances.
- Non-food resources: some plants; some animals; some mineral substances.

3 HISTORY OF ENERGY RESOURCES

History of oil, is presented in Table 1. [4]

Table 1. History of oil

THE YEAR	THE EVENT
1440 1442	In the 15th century, the oil pits from Lucăcești (Moinești - Bacău) are mentioned.
1646	The inhabitants of the villages of Mosoare, Poieni, Dofteana and Păcuri used crude oil extracted from wells. Dimitrie Cantemir mentions in Descriptio Moldaviae the existence and exploitation of oil in this region.
Oil extraction has been known in Moldova region for over 5 centuries, through primitive exploitation, then starting with the second half of the 19th century through mechanical probes of small and great depth (150 - 1000 m). The beginnings of the oil industry in Romania take place in the Trotuș River basin, respectively Tazlăului Valley and in the Dărmănești Depression.	
1837 1840	The appearance of the first industrial oil distilleries in the world, in Lucăcești - Bacău.
1844	The appearance of the distillery from Moinești.
1856	Bucharest, the first city in the world illuminated with lampante oil.
1857	The appearance of the Ploiești Refinery - Marin Mehedințeanu's Gas Factory (the first in the world), which meant a big step towards civilization.
1861	The first mechanical drilling rig in Romania was manufactured and used in Poieni (Târgu Ocna - Bacău) and consisted of a percussion screed with wooden rods.
1900	Romania, the first country in the world to export gasoline.
1914	In Romania, in Cămpina, was founded the first school in the world for master drillers.
1970 1977	Historical maximum of oil production - 14 650 000 tons.
1989	Establishment of the Autonomous Petroleum Authority - Petrom RA, which took over all the activities of exploitation of crude oil resources.
1996	Establishment of the Romanian Petroleum Company as a joint stock company, constituted by the reorganization of Rafirom, Peco and Petrotrans. The Romanian Petroleum Company owns: - 10 refineries; - extraction fields; - deposits; - gas stations.
1997	The Romanian Petroleum Company was divided, 8 refineries operating on its own, the rest of the assets becoming the property of the National Petroleum Company - SNP Petrom, which inherited: - Arpechim Pitești refinery; - Petrobrazii Ploiești refinery; - PECO distribution network; - Petrotrans pipeline system; - the exclusive right to extract crude oil from oil fields in Romania.
2000	The Romanian state sells the company Prospeccțiuni SA to the businessman Ovidiu Tender, the only company in the country that provides geological surveys for drilling.
2001	Listing on the Stock Exchange of the National Petroleum Company - Petrom SA
2002	Starting the privatization process of SNP Petrom SA
2002	Establishment of Petromservice by divesting Petroserv from Petrom.
2004	Privatization of SNP Petrom SA through the acquisition by OMV (Austrian company) of 51.01% of the shares of SNP Petrom SA, bearing the name of OMV Petrom.

History of natural gas, is presented in *Table 2*. [4]

Table 2. History of natural gas

THE YEAR	THE EVENT
1909	The first natural gas emissions discovered in Sărmășel, Mureș County. Probe 2 Sărmășel, originally intended for the extraction of potassium salts, accessed one of the richest natural gas fields in the world at that time.
1910	Europe's first intention to transport gas.
1912	The discovery of the largest natural gas field in Romania, located in Deleni (between Băgaciu commune and Mureș county) with proven reserves of 85 billion cubic meters.

1914	The first natural gas transmission pipeline in Europe, from Sărmășel to Turda over a distance of 55 km.
1915	Establishment of the first company in Europe, <i>Ungarische Erdgas Gesellschaft – UEG</i> , having as its object of activity exclusively: <i>exploration, drilling, exploitation, transport and distribution of natural gas</i> in the Transylvanian basin.
1917	The city of Turda becomes the first city in Europe lit with natural gas.
1925	The founding of the National Methane Gas Company - Sonametan, which takes over the assets of UEG in the following years.
1928	For the first time in Europe, the installation of the natural gas compression station in Sărmășel is completed, equipped with 3 Ingersol Rand horizontal motor compressors.
1933	The first gravimetric survey in Romania on a natural gas structure is being carried out in Sărmășel.
1958	The first natural gas storage depot in Romania, Ilimbav, Sibiu County.
1959	Romania becomes the first exporter of natural gas in Europe, exporting to Hungary.
1965	Romania becomes the first country in Europe to build a natural gas compression station on the route of a main pipeline.
1974	The natural gas pipeline that transits the Romanian territory for the transport of natural gas to Bulgaria is put into operation.
1978	Romania begins importing natural gas from the USSR
1986	Peak natural gas production - 36.2 billion m ³ .
1991	The National Methane Gas Authority - ROMGAZ RA is established
1996	The signing of the Convention between Romania and the Russian Federation, for the development of new import points, the increase of the quantity of imported natural gas and of the gas transit capacity on the Romanian territory, for Turkey, Greece and other Balkan countries.
1998	The National Natural Gas Company is established - ROMGAZ SA Mediaș
2009	100 years of natural gas exploitation in Romania

History of uranium, is presented in *Table 3*. [4]

Table 3. History of uranium

THE YEAR	THE EVENT
1950 1957	Carrying out an intensive geological research program for the identification of radioactive mineralizations in the Banat and Bihor regions, completed with the opening and exploitation of the Natra, Dobrei and Ciudanovița deposits in Banat and the Băița Plai deposit in Bihor
1952	The start of the exploitation of uranium ores from the Băița Plai Quarry
1954	The Romanian-Soviet joint venture SOV - ROM QUARTZIT is set up to support the Soviet military nuclear program.
1956	Establishment of the Institute of Atomic Physics from Măgurele
1960	The start of the exploitation of uranium ores from Avram Iancu from Bihor
1961	The uranium mining activity is subordinated to the General Directorate of Rare Metals within the Ministry of Mines. The Rare Metals Trust operates in parallel
1963	The activity of SOV - ROM QUARTZIT is taken over by the Geological Expedition Organization
1966	Romanian authorities announced that Romania had sent preliminary offers for the delivery of nuclear power plants and heavy water plants to the USSR, France, Sweden, Great Britain, Germany and Canada
1963 1968	Identification and contouring of uranium deposits from Crucea, Botușana and Grințes in Suceava and Piatra Neamț counties
1970	The Olt Nuclear Power Plant and the Hârșova Nuclear Power Company are established It is decided that based on the studies carried out, the first nuclear power plant equipped with CANDU (Canadian Deuterium Uranium) 600 reactors with natural uranium fuel and heavy water will be in the Hârșova area, the source of cooling water will be the Danube.
1976	Completion of the CANDU study in Romania. It was chosen not to use Soviet or American technology, because the Cernavoda Power Plant would operate with naturally enriched uranium.

1978	Commissioning of the Feldioara Uranium Hydrometallurgical Concentration Plant Signing of contracts between Romenergo (state-owned company with a foreign trade profile) and AECL for taking over the CANDU license
1981	Signing of contracts with General Electric and Ansaldo (Italy) for the classic part of Unit 1
1982	The first concrete is poured at Cernavoda
1985	Installation of the Calandria vessel at the first reactor Olt Nuclear Power Plant changed its name to Cernavoda Nuclear Power Plant
1983 1985	Commissioning of the Crucea field (Suceava county)
1986	Commissioning of the Uranium Concentrates Processing Plant on the Feldioara platform
1990	First PRE - OSART mission at the Cernavoda NPP of the International Atomic Energy Agency - IAEA Vienna
1996	The Cernavoda reactor is supplied for the first time with fuel made from Romanian UO_2
	The first connection to SEN of Unit 1 Cernavoda NPP
	Entering into commercial operation of Unit 1 Cernavoda NPP
1997	The National Uranium Company is established, subordinated to the Ministry of Economy and Trade
1997	Cessation of the mining activity at the mines of the Banat Branch
1998	Cessation of the exploitation activity at the Avram Iancu mine - Bihor Branch
	Establishment of SN Nuclearelectrica SA through the reorganization of RENEL
2007	Commercial operation of Unit 2 of the Cernavoda Nuclear Power Plant and connection to the National Energy System
2009	Complete cessation of mining activity at the Bihor Branch
2010	Commissioning of the UO_2 sintering plant at the Feldioara Plant to perform the Canadian product quality control test
2015	Initiation of the Memorandum of Understanding on the development, construction, operation and decommissioning of Units 3 and 4 of the Cernavoda Nuclear Power Plant, between SN Nuclearelectrica SA and China General Power Corporation

History of coal, is presented in Table 4. [4]

Table 4. History of coal in the Jiu Valley

THE YEAR	THE EVENT
century XIX	Coal, through its importance and the multitude of its uses, transforms the quiet Jiu Valley into the main source of raw materials, so necessary for the development of railway and naval transport - on the Danube, the energy and steel industry. The development of the coal deposits discovered here marks the beginning of the industrial and technical revolution, which is rapidly penetrating the young mining industry, which is becoming more and more pronounced in the coal basin on the two Jiuri. The Hungarian underground, as well as some large companies financed by the Hungarian bank capital, which is under the control of the German, French, Belgian and English banks, have focused on the great underground wealth.
1840	Baron Victor Maderspach, the heir to large estates in the Jiu Valley, discovers the outcrops of coal on the bottom of the valleys in his estate. Urged by the economic capitalization of his discoveries, he used the services of brothers Karol and Rafael Hoffman, mine owners at Rusca Montană and mining specialists, who come to the Jiu Valley to study geologically the existence and possibility of exploiting the discovered coal deposits. Against the protectionist background created by the Austro-Hungarian state, the brothers Hoffmann and Karol Maderspach started the surface exploitation of the coal deposit from Vulcan, Petroșani and Petrila.
1854	The initiators of the Jiu Valley Mining have joined the "Transylvania-West Mining Company"
1857	The mines of this company were bought by the "Brasov Mining and Furnace Joint-Stock Company", which, being financially supported by Wiener Bankverein, the Commercial Bank of Pest, Deutsche Bank and Banque de Paris et Pays-Bas, became the fourth largest producer of cast iron. EMPIRE

1865	The first acquisitions of mining perimeters in the Jiu Valley of the Austrian state. The company from Brașov expanded its possessions, buying coal and iron deposits and forests in addition to mine, also building smelters and the railway Simeria - Petroșani (1867 - 1870), extended in 1867 to Petrila
1879	The state mines, no longer able to compete, were leased for 27 years by the "Brașov Mining and Furnace Corporation"
1885	The Germans Iosif Ritter and G. Gerbert founded the "Coal Mine Company of the Upper Jiu Valley", based in Vulcan and with some possessions in the northern part of the basin, in Dâlja, Iscroni and Vulcan and others in the western part in Uricani and Neag's field. The company will operated until 1930 when it was absorbed by the "Petroșani Society"
1890	The "Jiu - Uricani Coal Mining Joint Stock Company" with Hungarian private capital was established, which undertook the construction of the Petroșani - Lupeni railway and leased the mining perimeters located along the railway under construction.
1891	By associating with a series of French capitalists, supported by the bank "Credit Lyonnais", the company changed its name becoming "The joint-stock company of mines and coals from Uricani-Valea Jiului", based in Lupeni
1899	Together with the German company "OberschlesischeKokswerke", was founded the "Cricket Company of Uricani-Jiu Valley", which built in 1900 the first coke shop in the area, which supplied the kilns in Călan
1894	"Salgotarjan Coal Mining Joint Stock Company", financially supported by Wiener Bankverein, bought all the mines and leasing rights of the Brașov Mining and Furnace Joint Stock Company
1920	The Romanian joint-stock company "Petroșani" was set up, consisting of two large groups of shareholders: the group formed by the former joint-stock company "Salgotarjan" together with Banque Comerciale Hongroise and a group of 19 large banks
1924	A group of 12 Romanian banks, together with the company "Uricani-Valea Jiului" formed the Romanian Joint Stock Company "Lupeni"
1926	The "Lonea Coal Company" was founded, owned by the Romanian state
1928	Due to the economic crisis, the closure of some mines began: Lonea I (1928), Lonea II (1931), Dâlja and Vulcan (1931)
1931	On May 29, the "Petroșani" and "Lupeni" companies merged under the name "Petroșani" Mining Company. At Petrila, a modern preparation was built, with a capacity of 270 tons / hour, which was considered one of the largest in the world.
1949	On August 20, by the Decree Law published in the Official Gazette no. 54, the ROMANIAN - SOVIET SOCIETY ON SHARES "SOVROMCĂRBUNE" was established with its headquarters in Bucharest, the General Directorate of Sovromcărbune moves its headquarters to Petroșani, based on order no. 8477
1952	Several trusts are set up: 1. The Petroșani Coal Trust (to which the Petrila mine also belonged); 2. Lupeni Mining Trust; 3. Petroșani Mining and Construction Constructions Trust; 4. Anina Coal Trust; 5. Câmpulung-Muscel Coal Trust; 6. Petroșani Mining Equipment Repair Plant (URUMP); 7. Petroșani Geological Research Division; 8. Vulcan Power Plant
1953	The company SOVROMCĂRBUNE is liquidated, and the Romanian part, on April 1, 1954, took over the management of the subordinated enterprises, the final liquidation being made on June 1, 1954
1956	On September 14, by Order of the Ministry of Mines, the Valea Jiului Coal Plant was established, which operated from October 1, 1956 to April 1, 1969.
1969	On April 1, the Valea Jiului Coal Plant becomes "Petroșani Coal Plant", and from August 1977 "Valea Jiului Mining Plant"
1991	Following the abolition of the CMVJ, the Romanian Autonomous Coal Authority is established and an extensive restructuring / reorganization process begins.
1994	Lonea Pilier Mining ceases operations
1998	On November 20, Regia was transformed into the "National Coal Company SA - Petroșani", on which occasion the mining operations in Banat were detached and the Petroșani Electronic Computing Center.
1999	Câmpu lui Neag and Petrila Sud Mining Operations ceased their activity

2003	Dâlja Mining is ceased its activity
2004	Valea de Brazi Mining Exploitation ceased its activity
2006	Aninoasa Mining ceased its activity
2012	On November 26, the National Mine Closure Company Valea Jiului SA was established - Romanian legal entity with full state capital, sole shareholder of the Romanian state through the Ministry of Economy, having the legal form of a joint stock company and operating in accordance with Romanian laws

History of electricity, is presented in *Table 5*. [4]

Table 5. History of electricity

THE YEAR	THE EVENT
1882	The first two power plants in Bucharest are put into operation, which provided the necessary for the Cotroceni Palace and the Royal Palace on Calea Victoriei. The lighting of the palace on Calea Victoriei is ensured by a 2 kV direct current power line.
1884	The first electric street lighting in Europe is put into operation in Timișoara
1896	The Sadu Hydroelectric Power Plant is put into use
1898	The first hydropower plant - Sinaia I
1902	The Grozăvești hydroelectric power plant, on the Dâmbovița River, is put into operation, according to the plans of the engineer Elie Radu
1907	Sadu II Hydropower Plant is put into operation
1910	Through the effort of the mayor Carol Telbisz, the Hydroelectric Power Plant from Timișoara is put into use
1913	The first electrified railway on the current territory of Romania, on the route Arad-Ghiocor-Pâncota and Ghiocor - Radna
1930	The first electrical distribution network on reinforced concrete poles in the country is put into operation in Bucharest
1931	
1938	Installed power (in the interwar reference year): 501 MW
1939	Electricity all over the country
1955	Establishment of the National Energy Dispatcher
1959	On January 24, the 100th anniversary of the Union of the Romanian Principalities, the "attachment" to the national energy system of the Moldova area takes place
1958	Development of the electric transmission network
1965	The first modern section of electrified railway in the country: Brașov - Predeal
1996	Entering into commercial operation of Unit 1 of the Cernavoda Nuclear Power Plant
1990	This year, the production, transmission and distribution of electricity was owned by the state company RENEL, but following the massive restructuring, until 2000, the company was divided into: Nuclearelectrica, Termoelectrica, Hidroelectrica, Transelectrica, Electrica (8 branches)
1998	The CONEL company is established
2000	The Transelectrica company is established

4 DESCRIPTION OF PRIMARY ENERGY RESOURCES (RESERVES)

The main primary energy resources were, in 2017, 34 291 tons, of which (*table 6.*): [5]

- 21303 tons from domestic production;
- 12987 tons from import.

Table 6. The main primary energy resources for 2017

Resources of primary energy	TOTAL Tons of oil equivalent	From which:		Mix [%]
		output intern	Import	
Coal	5164	4654	510	15
Crude oil (oil)	11175	3421	7754	32
Natural gases	9282	8337	944	27
Energy: - hydroelectric; - nuclear power; - solar;	5203	4889	314	15

- imported electricity.				
Petroleum products (import)	-	-	2985	8
TOTAL	34291	21303	12987	-

Source: National Institute of Statistics (www.insse, 2024)

Romania has a balanced and diversified energy mix, according to *table 7*. [5,6]

Table 7. Situation of national primary energy resources

Primary energy carrier	Resources		Reservs		Estimated annual production		Insurance period with resources and reserves	
	million tonne ¹⁾	million met	million tonne ¹⁾	million met	million tonne ¹⁾	million met	Resources years	reserves years
Lignite	690	124	290	52	25	4.5	28	12
Coal	232	85	83	30	0.8	0.3	290	104
Crude oil (oil)	229.2	-	52.6	-	3.4	-	67.4	15.5
Natural gases	726.8	-	153	-	10.5	-	69.2	14.6
Uranium ²⁾	-	-	-	-	-	-	-	-

¹⁾ - exclusively natural gas expressed in billions m³; ²⁾ - data (classified). (source: National Agency for Mineral Resources) (www.insse, 2024)

Coal

Coal is the primary energy resource in the energy mix, being a strategic fuel in support of national and regional energy security. In extreme weather conditions, coal is the basis for the resilience of the energy supply and the proper functioning of the National Energy System, covering one third of the electricity needs. Lignite resources in Romania are estimated at 690 million tons [124 million toe], of which 290 million tons [52 million toe] can be exploited in concessioned perimeters. At an average resource consumption of 4.5 million toe / year, the degree of insurance with lignite resources is 28 years, provided that in the next 25 years the consumption will remain constant and no other deposits will be valued. of lignite. The average calorific value of lignite mined in Romania is 1800 kcal / kg. As the lignite deposit in Oltenia consists of 1-8 layers of exploitable coal, their superior recovery requires the urgent adoption of regulations that guarantee the rational exploitation in conditions of safety and efficiency, with minimal losses. The known coal resources in Romania are 232 million tons [85 million toe], of which 83 million tons [30 million toe] can be exploited in concessioned perimeters. At an average consumption of reserves of 0.3 million toe / year, the degree of insurance with coal resources is 104 years, but the exploitation of this primary energy resource is conditioned by the economic feasibility of the

exploitations. The average calorific value of coal mined in Romania is 3650 kcal / kg.

Oil and natural gas

Currently, in Romania, approx. 400 crude oil and natural gas deposits, as follow:

- *OMV Petrom operates more than 200 commercial crude oil and natural gas fields in Black Sea platforms;*
- *Romgaz carries out its activity, as the only holder of an oil agreement, on 8 perimeters of exploration, development, exploitation.*

For other 39 deposits, oil development-exploitation and oil exploitation agreements were concluded, with various companies as owners. Most of these deposits are mature, with a lifespan of over 25-30 years. In the short and medium term, safe reserves of crude oil and natural gas can be increased by implementing new technologies that lead to increased recovery in deposits and by implementing projects for deep exploration and offshore areas of the Black Sea continental shelf. [4]

Crude oil (oil)

In 2017, *domestic crude oil production covered almost 32% of demand.* The decline in average annual production has been 2% in the last five years, being limited by investments in drilling new wells, re-production, secondary recovery, etc. Romania's proven crude oil reserves will be depleted in about 16 years at a consumption of 3.4 million t / year. [4]

Natural gases

Natural gas accounts for about 30% of domestic primary energy consumption. Their significant share is explained by the relatively high availability of domestic resources, the low impact on the environment and the ability to balance the electricity produced from intermittent RES. Infrastructure The existing mining, transportation, underground storage and distribution facility is expanding throughout the country. The natural gas market benefits from Romania's favorable position in terms of transport capacity in the region and the possibility of interconnecting the National Transport System with European central transport systems and gas resources in the Caspian Basin, the eastern Mediterranean and

the Middle East, through The Southern Corridor. In 2017, the total consumption of natural gas was 129.7 TWh, of which domestic production covered 89.4% and imports 10.6%. Consumption structure was: [5]

- *household consumption - about 33.4 TWh (25.73%);*
- *producers of electricity and heat - approx. 35.4TWh (27.27%);*
- *chemical industry - approx. 12.9 TWh (9.93%);*
- *commercial sector - approx. 8.5 TWh (6.59%).*

Uranium

Romania has a complete open cycle of nuclear fuel, developed on the basis of Canadian CANDU technology. Uranium dioxide (UO_2), used to make the nuclear fuel needed for Cernavoda reactors 1 and 2, is the product of processing and refining uranium extracted from indigenous production. The National Uranium Company has entered a restructuring process, and in parallel with the process of closing the Crucea mine (Suceava County), it will exploit new deposits in conditions of efficiency. Until the opening and exploitation of new indigenous uranium deposits, the operator of the Cernavoda nuclear power plant, Nuclearelectrica SA, purchases the raw material both on the internal market and on the external market in order to manufacture nuclear fuel. Existing and exploitable ore reserves provide the demand for natural uranium for the operation of two nuclear power units throughout its operation. [4,5]

Renewable energy sources – RES

Romania has rich and varied renewable energy resources: *hydropower; wind power; solar energy; biomass, bioliquids, biogas, waste and fermentation gases from waste and sludge; geothermal energy* . They are distributed throughout the country and will be able to be exploited on a larger scale as the performance-price ratio of the technologies will improve, by maturing the new generations of equipment and related installations. The potential of hydropower is used to a large extent, although there is a possibility to continue the hydropower management of the main watercourses, while respecting good practices for the protection of biodiversity and ecosystems. In the last six years, Romania has advanced in the use of an

important part of the wind and solar energy potential. [4,5]

Hydropower

Romania benefits from a high potential of hydropower resources. Out of a total of the theoretical potential of approximately 70 TWh / year, the theoretical potential of inland watercourses is approximately 51,6 TWh / year, and that of the Danube (only the Romanian part) is estimated at approx. 18,4 TWh / year. The schemes for the complex arrangement of the inland rivers and the Danube have been developed since 1918-1939 and were largely completed by 1990. These have been designed to allow complex uses: [4,5]

- *hydropower;*
- *navigation;*
- *multiannual or seasonal regularization of water stocks to allow water supply or irrigation;*
- *industry and population*
- *flood mitigation and safe transit of riverbeds.*

Wind energy

Due to its geographical position, Romania is at the eastern border of the atmospheric circulation generated in the North Atlantic basin, which is manifested with a sufficiently high intensity to allow energy recovery only at high altitudes on the Carpathian ridges. The atmospheric circulation generated in the area of the Black Sea and the Russian Plain, in conjunction with the North Atlantic, offers possibilities for energy recovery in the area of Dobrogea, Bărăgan and Moldova. Also, on restricted areas there are local atmospheric circulations that allow the economic capitalization through projects of small wind farms. [4,5]

Solar energy

Solar energy can be used in the form of heat, which can be used for domestic hot water preparation and heating of buildings, or for the production of electricity in photovoltaic systems. The distribution of solar energy on the national territory is relatively uniform with values between 1100 and 1450 kWh / m² sqm / year. The minimum values are registered in the depression areas, and the maximum values in Dobrogea, the east of Bărăgan and the south of Oltenia. Correlated with the development of

houses or other buildings inside the localities, according to the ICEMENERG 2006 study (www.icemenerg, 2024), solar collectors with an area of 34,000 sqm could be used to produce an energy of 61200 TJ / year. [4,5]

Biomass, bioliquids, biogas, waste and fermentation gases from waste and sludge

The energy potential of biomass is estimated at a total of 318000 TJ / year, with an equivalent of 7.6 million toe. Data on solid biomass production show a high degree of uncertainty (about 20%), the central estimate being 42 TWh in 2015. The main form of energy biomass produced in Romania is firewood, burned in stoves with low efficiency. The consumption of firewood used in households is estimated at 36 TWh / year. In 2015, the production of biofuels was about 1.5 TWh and that of biogas 0.45 TWh. In 2015, only 0.7 TWh of electricity produced nationally came from biomass, bioliquids, biogas, waste and waste fermentation gases and sludge, with capacities totaling 126 MW of installed capacity. (www.insse.ro). [4,5]

Geothermal energy

Several areas have been identified in Romania where the geothermal potential is estimated to allow economic applications, over a large area in western Transylvania and on smaller areas in northern Bucharest, north of Ramnicu. Vâlcea and around Tândărei. Research prior to 1990 revealed that the potential of known geothermal resources in Romania amounts to approximately 7 PJ / year (approx. 1.67 million Gcal / year). (www.insse.ro). [4,5]

5 SITUATION OF ENERGY SECURITY

Energy security is one of the fundamental objectives of Romania's energy strategy, along with the economic competitiveness of the energy sector, the protection of the environment.

Energy security of Romania takes into account the following aspects: *the existence, accessibility and (re) supply of finite (re)sources of raw materials (oil, natural gas, coal, hydrocarbons, uranium, etc.) and renewable, sufficient and available; clear and stable international / European trade agreements on access to these finite (re)sources of imported raw materials; price stability of these finite (re)sources of raw materials; control of transmission and distribution routes and alternatives to finite (re) sources of raw materials; the safety and security*

of the transformation of these finite (re)sources of raw materials into electricity; clear and stable trade agreements on trade in electricity with neighboring or European Union countries; electricity price stability; control of electricity transmission and distribution routes; secure critical energy infrastructures; accessibility of each consumer (domestic / industrial) to electricity; ensuring professional, well-trained and transparent human resources; jobs and workers in a secure work environment and the mitigation of climate change. [8,9,10]

Energy security is a major concern of the countries of Southeast Europe (EEA), of which Romania is a part, given the quasi-monopolistic nature of the natural gas market in this region. The concept of *energy security* must be distinguished from that of *energy independence*, with which it is often confused. In an age of globalized energy markets and interconnections between electricity and natural gas networks, energy security is advanced through international trade, competitive market mechanisms and energy diplomacy. These instruments are particularly valid in the European Union, whose energy policies aim to integrate energy markets across the continent into a single market.

Energy independence represents self-sufficiency and national energy insularity, is a politically counterproductive and economically inefficient aspiration. It is also important to distinguish between *the external dimension* and *the internal dimension* of energy security. The external capacity of a state to secure its energy imports (or, as the case may be, its exports to secure markets) must be achieved under conditions of political autonomy and economic sustainability. To this end, countries' external energy policy must be geared towards reducing the risk of dependence on a single external supplier and / or a single transit territory, by diversifying energy sources and transport routes. Internally, energy security depends on the quality of infrastructure, energy governance and energy policies.

Romania's short-term energy security - concerns the State's ability to manage short-term energy supply crises caused by natural disasters, physical or cyber attacks on critical infrastructure, or the deliberate action of an energy supplier or transit State.

Romania's long-term energy security - depends on the systemic capacity of the state to

continuously ensure its energy needs, in conditions of political and economic autonomy. Short and long term energy security requires different planning and is achieved through separate instruments: *strategic stocks; back-up systems and regional cooperation arrangements; diversification of energy sources; infrastructure and institution development; competitiveness and liquidity of energy markets*. [8,9,11,12]

6 CONCLUSIONS

To ensure energy security, romanian decision-makers need to create energy stability factors in order to combat energy poverty, vulnerable consumers and ensure energy security through the following actions: reducing energy dependence by ensuring the minimum need for energy raw materials for underdeveloped or developing countries; protection of national and international critical infrastructure for the transport of energy raw materials to ensure continuity of supply and prevent energy collapse; exploring new onshore and offshore energy sources; new critical energy infrastructures; development of renewable energy sources; introduction of clear and transparent energy efficiency measures; rationalization of energy use: electricity; natural gas; oil; fuel, etc. stopping the exodus abroad by energy specialists (ultra-qualified human resource); place major investments in the energy research and development segment; development of specialization courses for energy sector personnel; increase the salaries for the human resources in energy sector; improving working conditions.

All these actions must be carried out by the state through its mechanisms for ensuring a strong energy security, and in this context, national energy security is in fact European and regional security.

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OUTLIER DETECTION IN ENERGY CONSUMPTION OF COURIER MOTORCYCLES USING ACCELERATION PATTERNS FROM GPS DATA

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Abstract

This study investigates the acceleration and deceleration patterns of motorcycle couriers using GPS data to identify regional driving behaviors and outlier thresholds. By examining data without regional outlier analysis, we observed distinct driving patterns across different areas, highlighting regions with aggressive acceleration and smoother driving behaviors. Outlier thresholds, ranging from -4 to +4 km/h/sec, were identified, with the majority of data falling between -1 and +1 km/h/sec. However, using a singular approach risks overlooking intra-regional driving variances. To address this, we employed hexagonal grouping and outlier thresholds to capture the unique driving characteristics within each region, revealing thresholds ranging from 3.9 to 10.8 km/h/sec in 250-meter clusters and 5.4 to 9.1 km/h/sec in 500-meter clusters. Comparative analysis of hex groups showed higher limits in areas with arterial roads versus residential zones. These findings suggest that hex grouping and outlier detection can effectively identify regions with poor driving patterns and high energy consumption, providing insights for targeted interventions to improve road safety and efficiency. This approach underscores the importance of considering regional characteristics in driving behavior analysis for urban planning and traffic management.

Keywords: Acceleration, Energy Consumption, GPS, Motorcycle

1 INTRODUCTION

The rapid growth of urbanization and the increasing demand for delivery services have led to a significant rise in the number of motorcycle couriers on the roads. These couriers play a crucial role in the logistics and delivery sector, especially in densely populated urban areas where quick and efficient transportation is essential. However, the driving behaviors of motorcycle couriers, particularly their acceleration and deceleration patterns, have important implications for road safety, traffic flow, and energy consumption.

Acceleration and deceleration behaviors are key indicators of driving dynamics and can reveal much about a driver's style and the conditions of the driving environment. Aggressive driving behaviors, characterized by rapid acceleration and harsh braking, are not only hazardous but also lead to higher fuel consumption and increased emissions. Conversely, smoother driving patterns are generally associated with safer and more fuel-efficient driving. Understanding these patterns is therefore essential for developing strategies to improve

urban mobility and reduce the environmental impact of transportation.

Previous studies have primarily focused on analyzing driving behaviors on a broad scale, often overlooking the regional variations that exist within urban environments. This study aims to address this gap by examining the acceleration and deceleration patterns of motorcycle couriers in different regions, using GPS data. By identifying outlier thresholds for these patterns, we can gain a deeper understanding of the driving behaviors prevalent in specific areas and how they vary within and across regions.

One of the main challenges in analyzing regional driving behaviors is the potential for overlooking intra-regional variations. A region might display an overall trend in driving behavior, but significant deviations can occur within that region due to various factors such as road type, traffic conditions, and local driving habits. To capture these nuances, we propose using hexagonal grouping and outlier detection methods. Hexagonal grouping allows for a more granular analysis by dividing the study area into smaller, manageable units, while outlier

detection helps identify driving behaviors that deviate from the norm within each hex group.

This study employs a data-driven approach to map and analyze acceleration and deceleration patterns across different regions. By calculating outlier thresholds for each hex group, we aim to identify areas with unusual driving behaviors and higher energy consumption. This information can be instrumental in developing targeted interventions to improve road safety and traffic efficiency. Moreover, understanding the regional characteristics of driving behaviors can inform urban planning and policy-making, contributing to the creation of safer and more sustainable urban environments.

A region called Beşiktaş is selected as the study area, which is located between two freeways that are followed by two bridges on the Bosphorus Strait in Istanbul, Türkiye. The street comprises road segments containing different traffic features such as roundabouts, traffic lights, bus stops, and freeway connections. This region includes a university and schools, hospitals, and commercial and restaurant districts with high valet traffic and multiple traffic lights. There is traffic congestion even outside of peak hours. This also leads to a major uncertainty in terms of traffic, which makes testing this methodology here is therefore appropriate.

In summary, this paper explores the acceleration and deceleration patterns of motorcycle couriers using GPS data, highlighting the importance of regional analysis in understanding driving behaviors. By employing hexagonal grouping and outlier detection, we aim to provide a detailed and nuanced view of how these patterns vary within and across regions. The findings of this study have significant implications for road safety, traffic management, and energy consumption, offering valuable insights for urban planners and policymakers.

2 LITERATURE REVIEW

The rapid growth of e-commerce has led to a significant increase in the use of motorcycles for courier services. This mode of transportation offers flexibility and speed in congested urban areas but also presents unique challenges related to driving behaviors and energy consumption. Efficient and safe operations are crucial for sustainability and operational success in this sector.

This literature review aims to explore the utilization of GPS data in transportation

research, the factors contributing to aggressive driving behaviors among motorcyclists, and the patterns of energy consumption in motorcycle couriers. By examining these themes, this review provides a comprehensive understanding of current research and identifies areas requiring further investigation.

2.1 GPS Data Utilization in Transportation Research

GPS technology has transformed transportation research by providing accurate and detailed data on vehicle movements. This section examines the methodologies and applications of GPS data in studying driving behaviors and energy consumption in the transportation sector.

Numerous studies have demonstrated the effectiveness of GPS data in analyzing driving patterns [1, 2]. Fafoutellis *et al.* utilized GPS data to evaluate the impact of eco-driving programs on fuel consumption, finding significant reductions in fuel use [3]. Zhang *et al.* leveraged GPS data to study the spatial-temporal dynamics of urban traffic, and their impact on fuel efficiency [4].

While GPS data offers valuable insights, challenges such as data privacy and the need for advanced analytical tools persist. Azadani *et al.* emphasize the importance of integrating GPS data with other data sources to enhance the accuracy of transportation models [5]. This integration can provide a more comprehensive understanding of driving behaviors and their impact on energy consumption, highlighting areas for improvement and innovation.

2.2 Aggressive Driving Behavior in Motorcyclists

Aggressive driving is a significant concern in motorcycle courier services, impacting both safety and fuel efficiency. This section reviews studies on the factors contributing to aggressive driving behaviors among motorcyclists.

Research by Senderal *et al.* identifies key factors such as time pressure, road rage, and risky driving habits as various contributors to aggressive driving [6]. Joewono *et al.* found that younger motorcyclists are more prone to aggressive behaviors, which correlates with higher accident rates and increased fuel consumption [7]. These studies highlight the need for targeted interventions to address aggressive driving.

While these studies provide valuable insights, there is a need for more research on interventions to mitigate aggressive driving. Zhang suggests that targeted training programs can significantly reduce aggressive driving behaviors [8]. Additionally, integrating psychological assessments into these programs can help tailor interventions more effectively, promoting safer and more efficient driving practices.

2.3 Energy Consumption Patterns in Motorcycle Couriers

Energy consumption in motorcycle couriers is influenced by various factors, including driving behaviors, route choices, and vehicle maintenance. This section reviews research on the patterns and determinants of energy consumption in this sector.

Koossalapeerom *et al.* conducted a comprehensive study on the fuel consumption patterns of motorcycle driver, highlighting the significant impact of driving style on energy efficiency [9]. More recent studies by Duc *et al.* used GPS data to model fuel consumption, identifying key behaviors such as frequent acceleration and deceleration as major energy drains [10]. These findings underscore the importance of efficient driving practices for energy savings.

While these studies underscore the importance of driving behavior, there is a gap in research on the effectiveness of fuel-saving technologies and policies. Vagg *et al.* suggest that real-time feedback systems can help drivers adopt more efficient driving habits [11]. Moreover, comparative analyses of different fuel technologies could provide insights into more sustainable options for the industry, promoting long-term energy efficiency.

This literature review has examined the use of GPS data in transportation research, the factors contributing to aggressive driving behaviors among motorcyclists, and the patterns of energy consumption in motorcycle couriers. Significant progress has been made in these areas, demonstrating the potential of GPS data to enhance our understanding of driving behaviors and energy consumption.

However, gaps remain, particularly in the integration of GPS data with other data sources, the development of effective interventions for aggressive driving, and the exploration of new fuel technologies. Addressing these gaps through

future research can contribute to safer, more efficient, and environmentally sustainable motorcycle courier services, supporting the growing demand for rapid and reliable delivery solutions.

3 METHODOLOGY

3.1 GPS to Acceleration Calculation

The primary data source for this study consists of GPS records, which include timestamp, latitude, and longitude. From these GPS records, speed and acceleration can be calculated. To calculate speed, we first determine the distance between consecutive GPS points.

The Haversine formula is used to calculate the great-circle distance between two points on the Earth's surface, given their latitude and longitude. This formula accounts for the Earth's curvature, providing an accurate measure of distance.

$$d = 2r \cdot \arcsin \left(\sqrt{\sin^2 \left(\frac{\Delta\phi}{2} \right) + \cos(\phi_1) \cdot \cos(\phi_2) \cdot \sin^2 \left(\frac{\Delta\lambda}{2} \right)} \right) \quad (1)$$

where r is the Earth's radius, $\Delta\phi$ is the difference in latitude, and $\Delta\lambda$ is the difference in longitude. Speed is then calculated by dividing the distance by the time interval between the two GPS points. Once the speed between consecutive GPS points is determined, acceleration can be calculated by finding the change in speed over the time interval between these points, as

$$\text{Speed} = d / \Delta t \quad (2)$$

$$\text{Acceleration} = \Delta \text{Speed} / \Delta t \quad (3)$$

where d is the distance, Δt is the time difference. This calculation provides the rate of change of speed, indicating how quickly the vehicle is accelerating or decelerating.

3.2 Locational grouping

To analyze regional variations in driving behavior, GPS records are grouped into hexagonal grids. This approach allows for a detailed spatial analysis by dividing the study area into smaller, uniform units.

The study area is overlaid with a hexagonal grid, where each hexagon has a side length of 250 meters or 500 meters, depending on the scale of analysis. The side length can be adjusted to suit the needs of the analysis.

Each GPS record is assigned to a hexagon based on its latitude and longitude. This is done using a spatial indexing algorithm, which determines the hexagon that contains each GPS point.

Once the GPS records are grouped into hexagons, indices are set for the records within each hexagon. This indexing facilitates the calculation of location-based statistics, such as average speed and acceleration, for each hexagonal group.

3.3 Outlier calculation

Outliers in acceleration data are identified using the Interquartile Range (IQR) method, which is robust against the influence of extreme values.

For each hexagonal group, the acceleration data is sorted, and the first (Q1) and third quartiles (Q3) are calculated. Q1 is the median of the lower half of the data, and Q3 is the median of the upper half.

The IQR is calculated as the difference between Q3 and Q1:

$$IQR = Q3 - Q1 \quad (4)$$

Outliers are defined as values that fall below Q1 minus 3 times IQR or above Q3 plus 3 times IQR. These thresholds help identify acceleration values that are significantly different from the typical range within each hexagonal group.

$$\text{Lower Threshold} = Q1 - 3 \times IQR \quad (5)$$

$$\text{Upper Threshold} = Q3 + 3 \times IQR \quad (6)$$

By applying these methods, we can effectively analyze and identify regional variations in driving behaviors, providing insights into the acceleration and deceleration patterns of motorcycle couriers across different urban areas.

4 RESULTS

In examining acceleration and deceleration patterns without conducting a regional outlier analysis, certain areas exhibit more aggressive acceleration patterns, while others show a predominance of smoother driving behaviors. This observation suggests that different regions have distinct driving characteristics, which can be influenced by a variety of factors such as road type, traffic conditions, and the driving habits of the local population. By identifying these patterns, we can gain insights into the driving behaviors prevalent in specific areas, which can be crucial for urban planning and traffic management.

This study identifies outlier thresholds ranging from -4 to +4 km/h/sec, with the majority of the data falling between -1 and +1 km/h/sec (Figure 1). These thresholds are significant because they help in distinguishing normal driving behaviors from those that are more extreme. Understanding the range of acceleration and deceleration that is

considered typical can assist in setting benchmarks for safe driving. However, it is important to note that simply identifying these thresholds may not be sufficient for a comprehensive analysis, as it does not account for the variability within each region.

This approach highlights the natural characteristics of a region but may overlook driving behaviors that deviate within the same area. To address this limitation, it is essential to consider the unique driving patterns within each region and use outlier thresholds to identify behaviors that fall outside these patterns. By doing so, we can better understand the driving dynamics in different areas and develop targeted interventions to improve road safety and efficiency. For instance, regions with higher instances of aggressive driving could benefit from increased enforcement of traffic laws or public awareness campaigns on safe driving practices.

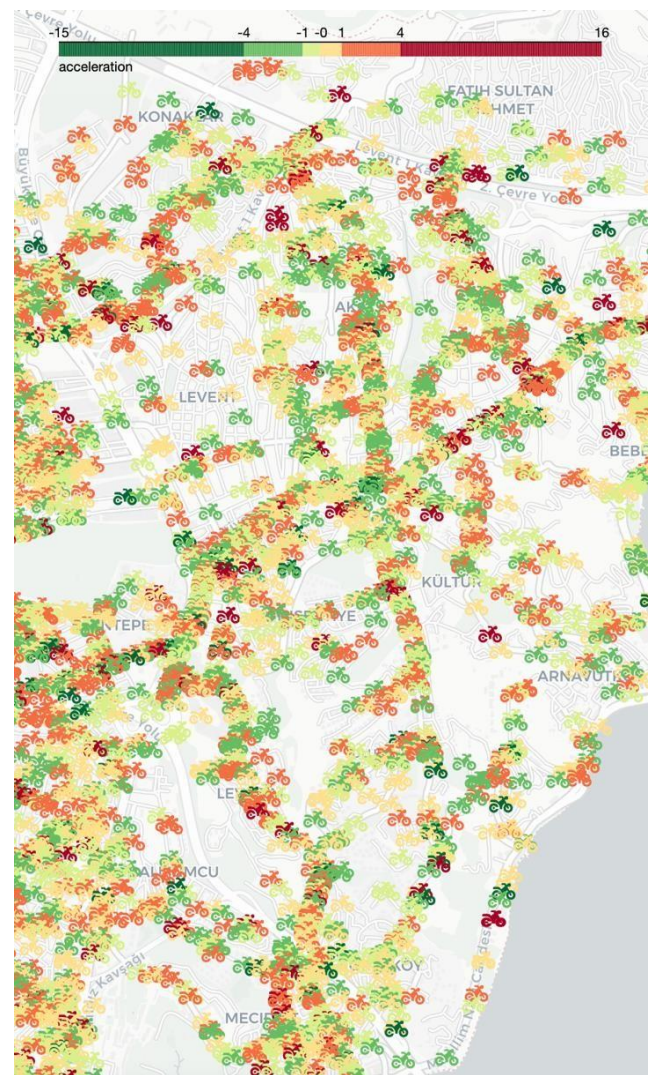


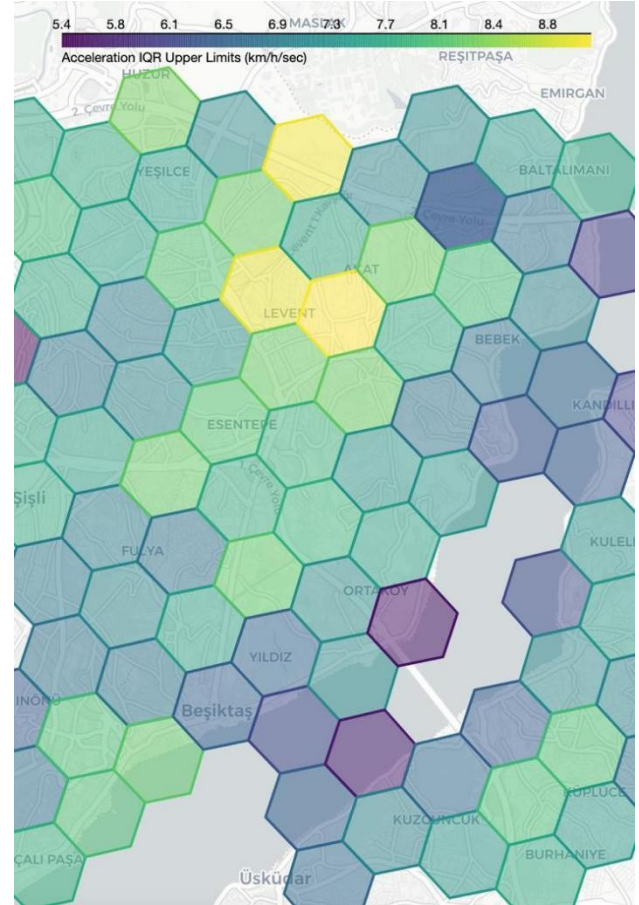
Figure 1. Subset of calculated acceleration & deceleration patterns using GPS records

To further illustrate the variability within regions, the distribution of these thresholds on a map reveals significant differences in driving behaviors. For example, in 250-meter clusters, the thresholds range from 3.9 to 10.8 km/h/sec, while in 500-meter clusters, they range from 5.4 to 9.1 km/h/sec (Figure 2). This variability indicates that even within relatively small geographic areas, there can be substantial differences in driving behaviors. Mapping these thresholds can provide a visual representation of where more extreme driving patterns occur, which can be valuable for urban planners and traffic authorities in identifying hotspots for intervention.

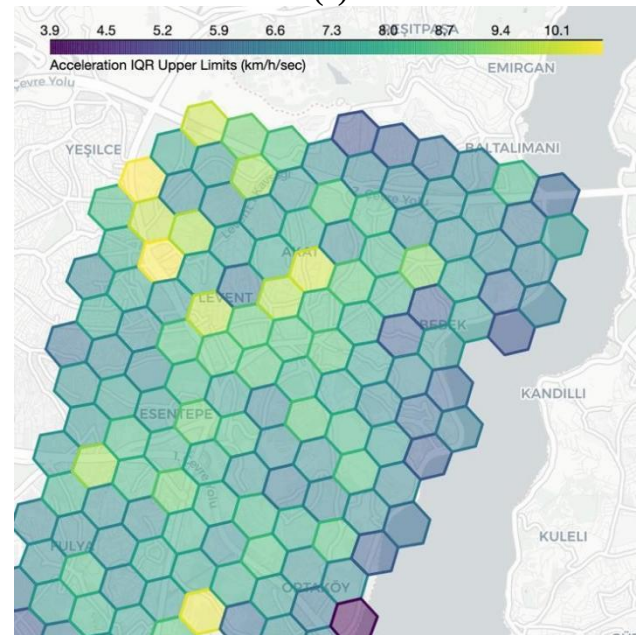
Some hex groups exhibit higher limits, such as Hex 1 (Table 1). The average speeds in this group are higher compared to Hex 2. Hex 1 includes an arterial road, whereas Hex 2 is situated in a more residential area. This difference in road type likely contributes to the observed variations in driving behaviors. Arterial roads typically experience higher traffic volumes and speeds, which can lead to more aggressive driving patterns. In contrast, residential areas are usually characterized by lower speeds and less aggressive driving. By comparing different hex groups, we can gain a better understanding of how road type and environment influence driving behaviors.

Table 1. Hex group-based speed and acceleration statistics

		Hex 1	Hex 2
Speed (km/h)	Mean	27.375	16.645
	Median	26.183	14.654
	25 th Percentile	15.640	9.384
	75 th Percentile	37.555	21.761
Acceleration (km/h/sec)	Mean	-0.063	-0.021
	Median	-0.213	-0.152
	25 th Percentile	-1.343	-1.001
	75 th Percentile	1.049	0.884
	IQR Lower	-8.520	-6.656
	IQR Upper	8.225	6.539



(a)



(b)

Figure 2. Upper limits of acceleration outlier thresholds using the IQR method in (a) 250 and (b) 500-meter hex groups

In conclusion, hex grouping can be utilized to identify poorly executed trips based on regional energy consumption. This method allows for a more nuanced analysis of driving behaviors, taking into account the specific characteristics of each region. These findings can also be used to warn drivers who exhibit dangerous driving behaviors, thereby enhancing road safety. Furthermore, the insights gained from this analysis can inform the development of targeted interventions to improve traffic flow and reduce accidents. Overall, understanding the regional variations in driving behaviors is crucial for creating safer and more efficient transportation systems.

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ENERGY AND EXERGY ASSESSMENT OF GEOTHERMAL ENERGY-BASED TRIGENERATION PLANT

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Abstract

Geothermal energy is gaining popularity due to its advantages, such as being a renewable, sustainable, environmentally friendly, and stable energy source. Hence, geothermal energy should be used effectively in cogeneration or trigeneration plants. This study targets power, heating and freshwater production using geothermal energy as a primary source. Therefore, a double flash geothermal plant (DFP) is used to harness geothermal heat energy for power production; a condenser is integrated into a double flash plant to generate a heating effect and a freshwater production plant (FWPP) is used to produce fresh water from seawater. Energy and exergy analyses are performed in the designed trigeneration plant (TP) evaluation part. Parametric analyses were done to see the effects of the reference temperature, geothermal fluid temperature, and mass flow rate. According to the results, energy and exergy efficiencies of the designed trigeneration plant are found to be 38.16% and 41.27%. In addition, the system performance improves as the reference temperature, geothermal fluid temperature, and the geothermal mass flow rate increase.

Keywords: Geothermal energy, double flash geothermal power plant, freshwater production, trigeneration plant, thermodynamic assessment

1 INTRODUCTION

Geothermal energy has emerged as a promising renewable resource, offering a sustainable and environmentally friendly alternative to conventional fossil fuels [1]. As the global energy demand continues to rise, the need for efficient and reliable energy sources becomes increasingly critical. Geothermal energy, characterized by its stability and low greenhouse gas emissions, presents a viable solution for meeting these demands [2]. This study focuses on developing and assessing a geothermal energy-based trigeneration plant (TP), which aims to simultaneously produce electricity, heating, and freshwater, thereby maximizing the utilization of geothermal resources [3].

The trigeneration approach uses the inherent thermal energy of geothermal fluids, typically extracted from deep underground reservoirs. The TP enhances overall energy efficiency and resource management by integrating power generation, heating, and freshwater production into a single system [4]. The double-flash geothermal power plant (DFP) serves as the system's core component, utilizing advanced

thermodynamic processes to convert geothermal heat into mechanical energy [5]. Additionally, incorporating a freshwater production plant (FWPP) allows for seawater desalination, addressing the growing concerns of water scarcity in many regions [6].

This study conducts a comprehensive thermodynamic analysis of the TP, focusing on key performance indicators such as energy and exergy efficiencies. By examining the effects of operational parameters, including reference temperature, geothermal fluid temperature and mass flow rate, the research aims to identify optimal conditions for maximizing the plant's output. The findings of this study not only contribute to the understanding of geothermal trigeneration systems and provide valuable insights for the design and implementation of sustainable energy solutions in the context of global energy challenges.

2 SYSTEM DESCRIPTION

The geothermal energy-based trigeneration plant (TP) is a unique energy solution that harnesses geothermal resources to simultaneously produce electricity, heating, and freshwater, as

demonstrated in Figure 1. Table 1 presents the thermodynamic design parameters of the trigeneration plant. The system primarily utilizes a double-flash geothermal power plant (DFP) to extract thermal energy from geothermal fluids. The process begins with heated geothermal fluid to approximately 190°C and is directed from the geothermal well to the DFP. Upon entering the plant, the fluid passes through a series of valves and turbines, where it undergoes a pressure reduction process that allows for steam generation. This steam drives high-pressure and low-pressure turbines, converting thermal energy into mechanical energy, which is then transformed into electrical energy.

In addition to power generation, the system incorporates a condenser that captures waste heat from the turbines, facilitating the production of heating energy for various applications. The integration of a fresh water production plant (FWPP) further enhances the system's capabilities by utilizing the residual thermal energy to desalinate seawater, thereby producing fresh water. The TP operates under a closed-loop system, where geothermal fluid is reinjected back into the geothermal reservoir after passing through the turbines and heat exchangers, ensuring sustainability and minimizing environmental impact. The overall design, with its emphasis on efficiency and sustainability, is a testament to our commitment to responsible energy solutions. The trigeneration plant's efficiency is a result of meticulous design and engineering, ensuring optimal performance. Energy and exergy analyses are conducted to further optimize performance and assess the effects of operational parameters such as reference temperature, geothermal fluid temperature, and mass flow rate on the system's output.

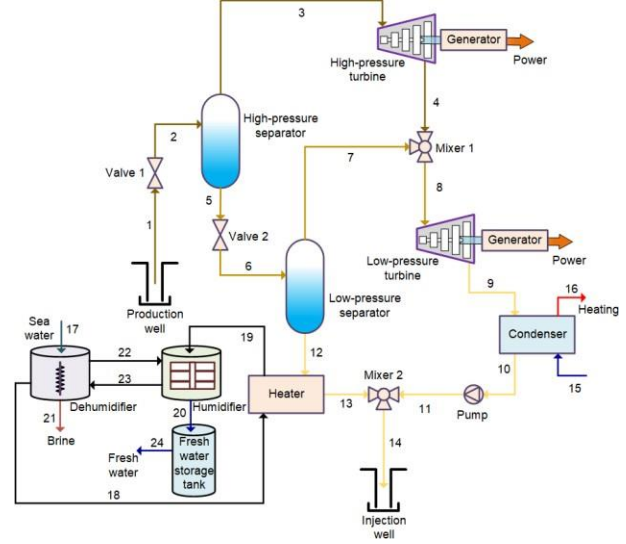


Figure 1. The schematic diagram of the geothermal energy-based trigeneration plant

Table 1. Thermodynamic design parameters

Indicator	Value
Reference temperature, T_o	25 °C
Reference pressure, P_o	101.3 kPa
Geothermal fluid production temperature, T_1	190 °C
Geothermal fluid production pressure, P_1	1400 kPa
High pressure turbine inlet temperature, T_3	187 °C
High pressure turbine inlet pressure, P_3	1200 kPa
Low pressure turbine inlet temperature, T_8	142 °C
Low pressure turbine inlet pressure, P_8	385 kPa
Geothermal fluid injection temperature, T_{14}	84 °C
Geothermal fluid injection pressure, P_{14}	385 kPa
Isentropic performance of high-pressure turbine, η_{HPT}	0.85
Isentropic performance of low-pressure turbine, η_{LPT}	0.85

3 THERMODYNAMIC ANALYSIS

To make a thermodynamic analysis, the mass, energy, entropy, and exergy balance equations can be defined as follows [7]:

$$\sum \dot{m}_i - \sum \dot{m}_e = 0 \quad (1)$$

$$\sum \dot{m}_i h_i + \sum \dot{Q}_i + \sum \dot{W}_i - \sum \dot{m}_e h_e - \sum \dot{Q}_e - \sum \dot{W}_e = 0 \quad (2)$$

$$\sum \dot{m}_i s_i + \sum \left(\frac{\dot{Q}_i}{T_{gen}} \right) + \dot{S} - \sum \dot{m}_e s_e = 0 \quad (3)$$

$$\sum \dot{m}_i ex_i + E_i^Q + E_i^W - \sum \dot{m}_e ex_e - E_e^Q - E_e^W = 0 \quad (4)$$

The sub-expressions i and e are the inlet and outlet conditions. Also, $\dot{m}$, W and Q are the rates of mass flow, work, and heat transfer, respectively. h and s are the specific enthalpy and entropy. $E x^Q$ and $E x^W$ are the heat transfer and work exergy rates as given below:

$$E x^Q = (1 - \frac{T_o}{T}) Q \quad (5)$$

$$E x^W = W \quad (6)$$

The flow exergy ex_{ph} can be defined as:

$$ex_{ph} = (h - h_o) - T_o(s - s_o) \quad (7)$$

Moreover, the exergy destruction rate is:

$$E x_d = T_o S_{gen} \quad (8)$$

The energy and exergy efficiency assessment are utilized to investigate the effectiveness of the geothermal energy-based trigeneration plant. Therefore, the energy and exergy efficiency equations are written as:

$$\eta = \frac{\text{Useful energy output in product}}{\text{Energy input}} \quad (9)$$

$$\psi = \frac{\text{Exergy output in product}}{\text{Exergy input}} \quad (10)$$

4 RESULTS AND DISCUSSION

In this part of the study, thermodynamic analyses are performed to show energy efficiencies, exergy efficiencies, and exergy destruction rates of sub-plants and the whole plant. Analysis results reveal that the total power production rate of the trigeneration plant is 13461 kW, as seen in Table 1. Moreover, the heating and freshwater production rates are 7436 kW and 13.78 kg/s, respectively. Table 3 shows energy and exergy efficiencies with exergy destruction rates of sub-plants and the trigeneration plant. The exergy efficiency of the FWPP is about 60%, which shows that it is highly efficient in producing fresh water. Also, the energy and exergy efficiencies of the TP are 38.16% and 41.27%, a high-performance converting plant using geothermal energy to produce power, heating and fresh water.

Table 2. The useful outputs of the trigeneration system

Outputs	Value
High pressure turbine power production rate, $\dot{W}_{HPT}$	3583 kW
Low pressure turbine power production rate, $\dot{W}_{LPT}$	9878 kW
Total power production rate, $\dot{W}_{Total}$	13461 kW
Heating production rate, $\dot{Q}_{Heating}$	7436 kW
Fresh water production rate, $\dot{m}_{FW}$	13.78 kg/s

Table 3. Thermodynamic analysis results

Integrated plant and its sub-plants	Energy efficiency	Exergy efficiency	Exergy destruction rate (kW)
Double flash plant	0.2774	0.3658	18046
Fresh water production plant	0.6593	0.6084	3925
Integrated plant	0.3816	0.4127	21971

4.1 Parametric analyses

In this part of the study, three parameters which are the reference temperature, the geothermal fluid temperature, and the geothermal fluid mass flow rate are evaluated to see their effects on the system performance.

The effect of the reference temperature

Figure 3 demonstrates the effect of the reference temperature on energy and exergy efficiencies. As seen from the figure, all energy and exergy efficiency values increase with increasing reference temperature. As the reference temperature varies from 0 °C to 40 °C, the exergy efficiency of the FWPP increases from 63.35% to 67.53% and the exergy efficiency of the TP reaches to 43.16% from 38.31%.

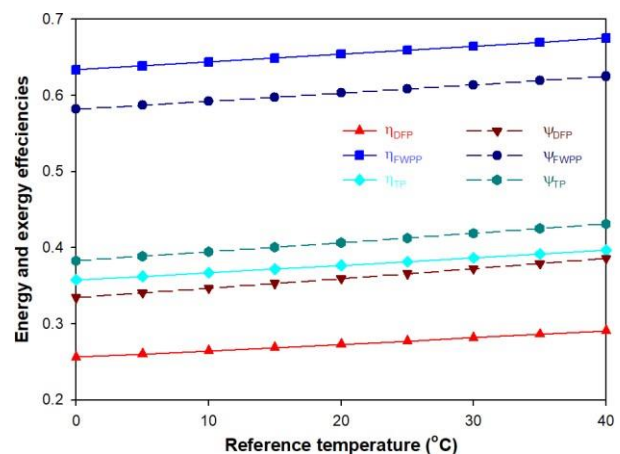


Figure 2. The effects of the reference temperature on energy and exergy efficiencies

The variation of production rates of the TP with respect to increasing reference temperature is given in Figure 3. As shown in the figure, total power production rate increases from 11279 kW to 14968 kW, heating production rate improves

from 5996 kW to 8461 kW and the fresh water production rate rises from 12.29 kg/s to 14.75 kg/s.

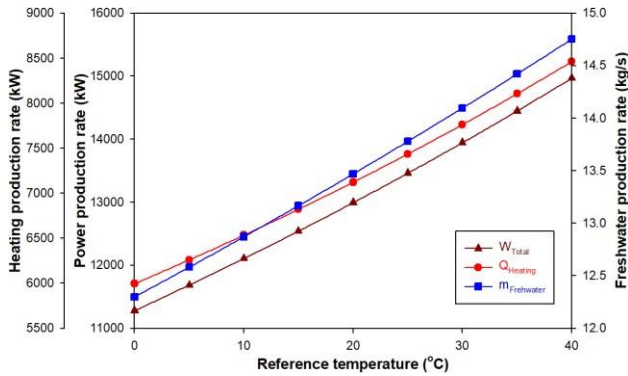


Figure 3. The effects of the reference temperature on production rates

The effect of the geothermal fluid temperature

The effect of geothermal fluid temperature on energy and exergy efficiencies is significant, as higher temperatures generally improve the performance of the trigeneration plant.

As the geothermal fluid temperature rises, the system's energy efficiency tends to increase, as seen in Figure 4. This is because higher-temperature fluids can produce more steam, enhancing the turbines' power output. The study indicates that as the geothermal fluid temperature increases, the energy efficiency of the trigeneration plant improves, allowing for a more effective conversion of thermal energy into electrical energy and proper heat. Similarly, the exergy efficiency, which measures the quality of energy and the potential to do work, also improves with higher geothermal fluid temperatures. The exergy efficiency reflects how well the system converts the available energy into practical work. As the temperature of the geothermal fluid increases, the exergy associated with the thermal energy also increases, leading to higher exergy efficiencies in both the power production and heating processes.

The analysis shows that as the geothermal fluid temperature increases, the exergy efficiency of the freshwater production plant (FWPP) and the trigeneration plant (TP) also rises. For instance, the FWPP's exergy efficiency can increase from 57.78% to 62.43% with rising temperatures, while the TP's exergy efficiency can reach up to 42.69% from lower values.

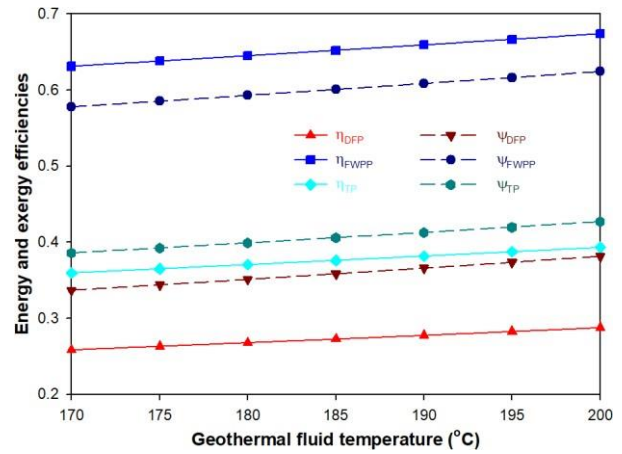


Figure 4. The effects of the geothermal fluid temperature on energy and exergy efficiencies

As the geothermal fluid temperature increases, the total power production rate of the TP also rises. Higher temperature fluids can generate more steam, which drives the turbines more effectively. For example, the total power production rate can increase from 11595 kW to 14503 kW as the geothermal fluid temperature rises. The heating production rate can improve significantly, from 6212 kW to an impressive 8136 kW with increasing geothermal fluid temperature, demonstrating a significant enhancement in the heating output. As the temperature increases, the efficiency of the freshwater production process improves, leading to higher output rates. The freshwater production rate can rise from 12.34 kg/s to 14.56 kg/s as the geothermal fluid temperature increases.

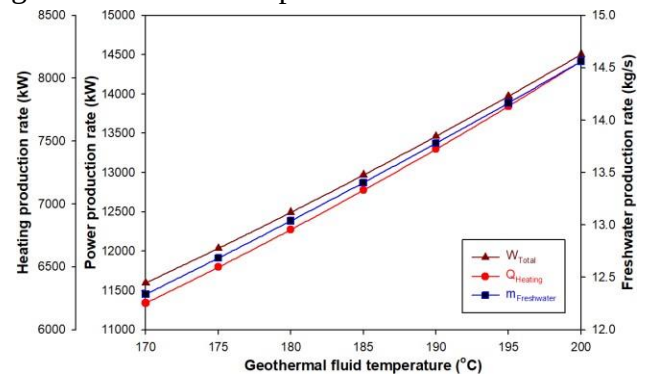


Figure 5. The effects of the geothermal fluid temperature on production rates

The effect of the geothermal fluid mass flow rate

Increasing the geothermal fluid mass flow rate generally leads to higher energy efficiency in the system. A higher mass flow rate means more geothermal fluid is available to extract thermal energy, which can be converted into steam for

power generation. Like energy efficiency, exergy efficiency also tends to improve with increased geothermal fluid mass flow rate. A higher mass flow rate enhances the potential for work extraction from the thermal energy, as more fluid can be processed through the turbines. As seen in Figure 6, the exergy efficiency of the TP improves from 37.75% to 43.54%.

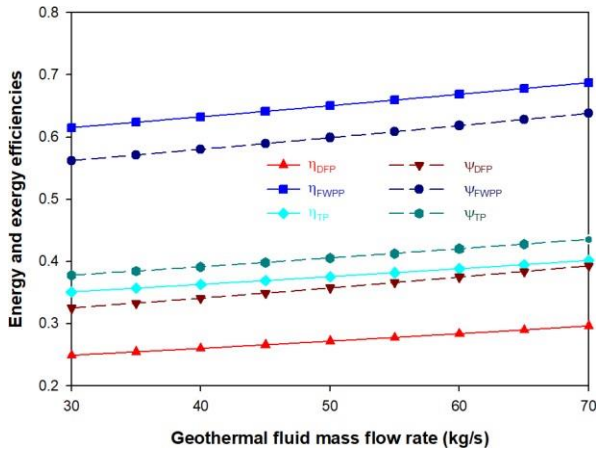


Figure 6. The effects of the geothermal fluid mass flow rate on energy and exergy efficiencies

An increase in the geothermal fluid mass flow rate typically leads to a higher total power production rate, as seen in Figure 7. This is because a greater mass flow of geothermal fluid allows for more steam generation, which drives the turbines more effectively. Total power production rates reach up to 15229 kW at 70 kg/s of geothermal fluid mass flow rate. Also, heating and freshwater production rates increase from 5882 kW and 11.72 kg/s to 8559 kW and 15.19 kg/s.

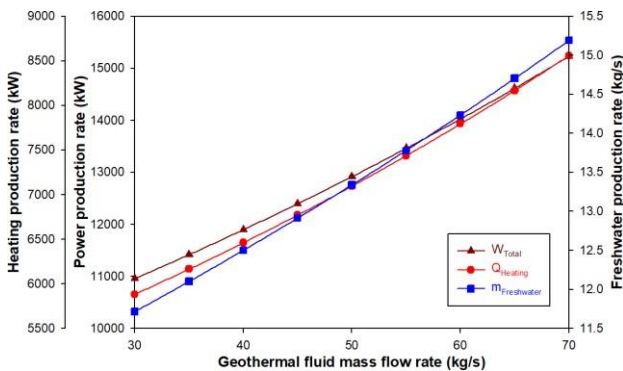


Figure 7. The effects of the geothermal fluid mass flow rate on production rates

5 CONCLUSION

In conclusion, the thermodynamic analysis of the geothermal energy-based trigeneration plant

demonstrates the significant potential of utilizing geothermal resources for simultaneous power, heating, and freshwater production. The study reveals that energy and exergy efficiencies are positively influenced by critical parameters such as geothermal fluid temperature and mass flow rate, leading to enhanced performance metrics across the system. Specifically, higher geothermal fluid temperatures and mass flow rates result in increased electricity, heating, and freshwater production rates, underscoring the trigeneration approach's effectiveness. The findings highlight the importance of optimizing operational parameters to maximize the efficiency and output of geothermal systems, thereby contributing to sustainable energy solutions and resource management. Overall, this research provides valuable insights for designing and implementing efficient geothermal trigeneration plants, promoting the use of renewable energy sources in meeting global energy demands.

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GLOBAL TRENDS OF THE SIGNIFICANT WAVE HEIGHT UNTIL 2100 AROUND OFFSHORE WIND FARMS: IMPLICATIONS FOR OPERATION AND MAINTENANCE

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Abstract

The sixth Assessment Report of the International Panel for Climate Change was released in August 2021. This report was based upon the climate projections until 2100 obtained with the CMIP6 climatological models run by many institutions worldwide. Then, these projections have been nested into the WaveWatch III model to obtain the significant wave height (swh) outputs.

Two climate-change driven boundary scenarios of CMIP6 estimations have been analyzed into the present work: SSP585 and SSP126. Starting from 3-hourly estimations corresponding to the 2015-2100 period, global trends of swh have been calculated in percentage terms with respect to current-day values.

Apart from the wind resource itself an important aspect that may compromise the development of the offshore wind industry is the sea-conditions for operational installation and maintenance. More specifically, the wave height is the key element involved in making more difficult the regular access and service to offshore facilities that may be dozens of kilometers away from the coast.

The results indicate that in Northern Atlantic areas, as well as in the Sea of China and Western Australia which are the zones with the highest concentration of offshore wind facilities, the significant wave height can be expected to decrease by 1%-2% per decade until 2100.

Paradoxically is under the least environmentally friendly scenario (SSP585) where this swh reductions are more relevant, while almost a static picture with respect to current-day situation emerges for the SSP126 scenario

This is good news for the development of offshore wind farms that are expected to increase their numbers in the generally-speaking the same zones. Along with the decreasing costs of installation, these results can also mean a future reduction in maintenance and operation costs, thus contributing to the development of a clean source of energy in the framework of general costs reduction for the industry.

Keywords: CMIP6, offshore wind energy, climate change

1 INTRODUCTION

Climate change is a subject of major concern worldwide and in the last years and as a consequence, renewable energies have experienced an important increase during the last years worldwide.[1][2][3][4]

If more efforts are to be made to meet the greenhouse gases objectives so that the maximum 1.5°C temperature threshold target is met [5], it is important to know how climate change will also impact on the electricity generation from renewables.

This is important because if climatic oscillations lead in the forthcoming years to a reduction of electricity generated by water, winds, waves and sun, this may shortcut any effort to reduce greenhouse emissions that among other things, heavily depend on precisely the development of clean energies.

Most studies focus on different scenarios [6] regarding the future evolution of greenhouse gases (GHG) emissions. Two boundary scenarios are usually considered: SSP126 (“green” scenario) and SSP585 (no significant reduction of GHG emissions until 2100)

In a recent paper authors [7] after analyzing the most recent CMIP6 projections until 2100 [8] have concluded that in the case of the offshore wind energy almost a static picture emerges for the two boundary emission scenarios. Nevertheless, in the case of SSP585 scenario existing changes concentrate in a few areas. Besides, as important as the resource itself, having an idea on how sea conditions near those wind farms, may impact on the operation and maintenance (O&M) activities around these facilities is an important issue. the wave height (SWH) is the key element involved in making more difficult the regular access and service to offshore facilities that may be dozens of kilometers away from the coast. In this paper, three areas with a high density of operational and/or projected wind farms have been analyzed.

1. **Sea of China.** Delimiting boundaries [114° E, , 26° N], [130°E, 31° N] (Fig. 1)

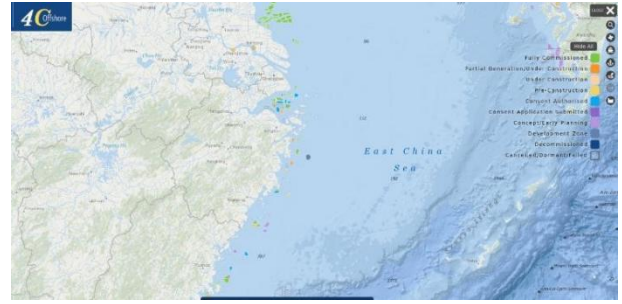


Fig. 1. Offshore wind farms in the Sea of China at different stages of development. Image retrieved from <https://www.4coffshore.com/windfarms/>

2. **Western Australia.** Delimiting boundaries [98° E, -39° N], [160°E, -9° N] (Fig. 2)

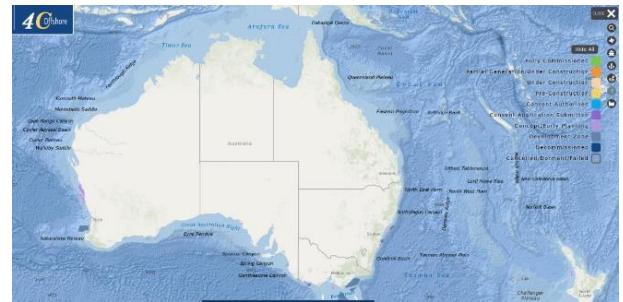


Fig. 2. Offshore wind farms in Western Australia at different stages of development. Image retrieved from <https://www.4coffshore.com/windfarms/>

3. **Northern Europe.** Delimiting boundaries [12° E, , 48° N], [27.5°E, 59.2° N] (Fig. 3)

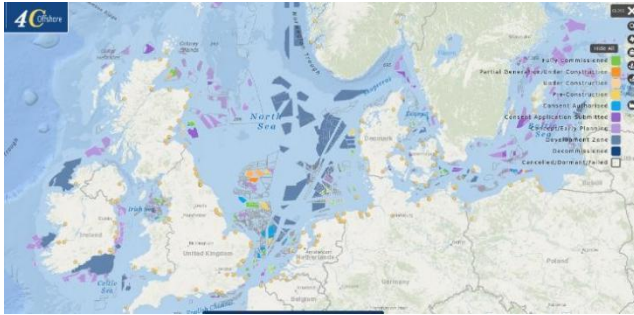


Fig. 3. Offshore wind farms in Northern Europe at different stages of development. Image retrieved from <https://www.4coffshore.com/windfarms/>

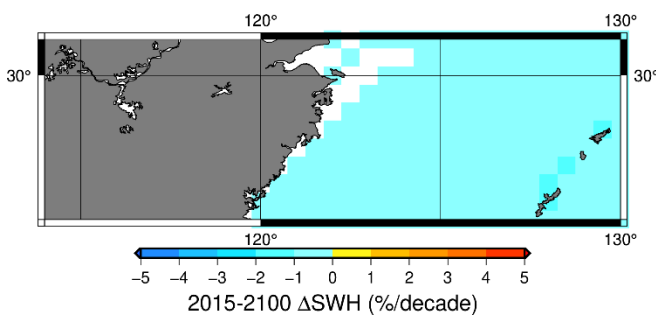
The key indicator has been the Significant Wave Height (SWH) and trends until 2100 have been calculated around these areas. Increases in SWH around offshore wind facilities may make more difficult the navigation with narrower windows of opportunity to carry out the regular maintenance activities. Reversely, more calmed sea-states will certainly reduce risks and can contribute to a better planning and reduction of O&M costs.

2 DATA AND METHODOLOGY

Data for this study has been retrieved from the CSIRO repository, where WaveWATCHIII outputs derived from the CMIP6 models, for the two scenarios (SSP126 and SSP585) are freely available [8][9][10]. This includes SWH and then, robust Theil-Sen trends [11][12] corresponding to the 2015-2100 period have been calculated for the areas analyzed and expressed in percentage terms with respect to current day values. To define the former, the SWH averages corresponding to the 1984-2015 period have been computed.

3 RESULTS

The results of the SWH trends in the selected areas exhibit differences depending on the scenario. While for the SSP126 scenario, no significant trends of SWH for these areas appear, in the case of SSP585 scenario (the less



environmentally friendly) negative trends of SWH are predicted by the models. This can be seen in Fig.4-6.

Fig.4. CMIP6 projected significant wave height trends for the Sea of China. 2015-2100. SSP585 scenario

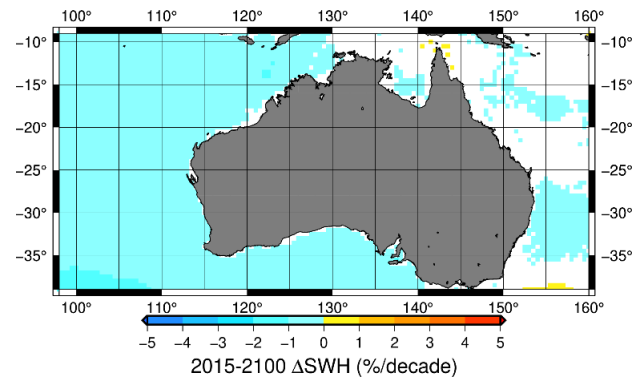


Fig.5. CMIP6 projected significant wave height trends for Australia. 2015-2100. SSP585 scenario

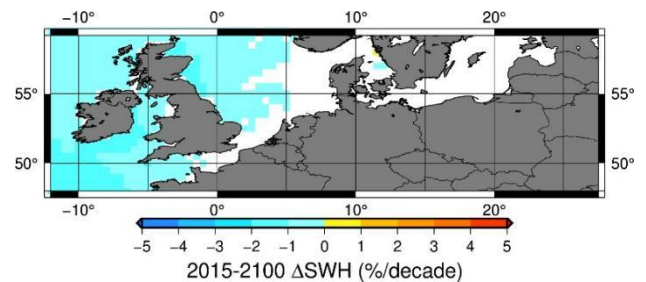


Fig.6. CMIP6 projected significant wave height trends for Northern Europe. 2015-2100. SSP585 scenario.

4 DISCUSSION, CONCLUSIONS AND FUTURE OUTLOOK

The results indicate that in Northern Atlantic areas, as well as in the Sea of China and Western Australia which are the zones with the highest concentration of offshore wind facilities, the significant wave height can be expected either to remain constant or to decrease by 1%-2% per decade until 2100 under the SSP585 scenario. In the case of the SSP126 scenario a similar behavior as current-day situation can be expected.

So, paradoxically is under the least environmentally friendly scenario (SSP585) where this SWH reductions are more relevant, while almost a static picture with respect to current-day situation emerges for the SSP126 scenario.

This is good news for the development of offshore wind farms that are expected to increase their numbers in the generally-speaking the same zones. Along with the decreasing costs of installation, these results can also mean a future reduction in maintenance and operation costs, thus contributing to the development of a clean source of energy in the framework of general costs reduction for the offshore industry.

This implies a reliable situation for the offshore wind industry at least regarding O&M operational protocols and costs related to reaching the wind farms in a regular basis. This means that there is no need for further future investments beyond the initial and current estimations and protocols of operational wind farms for this aspect of the general O&M . As 3mentioned above, this, in general terms, contributes to defining a more reliable and constant horizon for any operational or future wind farm, at least in the three areas analyzed in this study, with an important density of facilities.

Additionally, a secondary advantage is that mechanical efforts from waves impacting on the wave turbine pillars can be expected to reduce in the long-term thus reducing also the O&M costs and increasing the life of wind farms. The results indicate that in Northern Atlantic areas, as well as in the Sea of China and Western Australia which are the zones with the highest concentration of offshore wind facilities, the significant wave height can be expected either to remain constant or to decrease by 1%-2% per decade until 2100 under the SSP585 scenario. In the case of the SSP126 scenario a similar behavior as current-day situation can be expected.

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PERFORMANCE ENHANCEMENT OF LI-ION BATTERIES BY ELECTROSPRAYING-ASSISTED COATING OF BORON NITRIDE NANOTUBES ON SEPARATORS

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Abstract

In this research, electrospaying process is employed to coat boron nitride nanotubes (BNNT) on polyethylene (PE) Lithium-ion battery separators. It was observed that BNNT are uniformly dispersed and distributed on PE surface through the effect of applied electric field in the electrospaying system. Well-dispersed BNNT is highly contributed to the enhancement of ionic conductivity by acting as a Li-ion conductor. As a result, optimized concentration of BNNT on PE surface showed 1.09 mS/cm ionic conductivity, while it was 0.97 mS/cm for Neat PE at room temperature. Furthermore, thermal properties of PE is also highly enhanced by heat dissipating due to very high thermal conduction ability of BNNT. It was observed that BNNT coated separator can resist up to 150 °C, while neat PE separator totally melts out at the same temperature.

Keywords: BNNT, Li-ion batteries, battery separator, ionic conductivity, electrospaying

1 INTRODUCTION

Lithium-ion battery separators, which are employed in between the anode and cathode play an important role at battery systems by keeping short circuits from happening while yet enabling lithium ions to flow. Microporous polymer membranes, such polyethylene or polypropylene, are frequently employed for manufacturing these separators owing to their thin yet robust structure. They provide electrolyte retention and mechanical stability, which are essential for battery safety, durability, and performance. Nanomaterial with superior properties would further enhance the performances of these separators as a coating or blending material [1, 2]. Therefore, in this research, BNNT are utilized to further enhance the properties of battery separator by coating them on PE separators. While fabricating these BNNT-coated separators, novel technology: electrospaying is applied for the coating on the battery separator surface.

2 METHODS AND MATERIALS

After dispersing 0.1%, 0.5% and 1% BNNT in IPA solvent, they are placed in syringes and placed in a lab-scale electrospaying system. Then, 1 ml, 1.5 ml and 2 ml BNNT/IPA suspensions are coated on PE separators under various electrical conditions where IPA totally

evaporated and BNNT remains on PE surface (Figure 1). The ionic conductivity of the separators are measured with an Electrochemical Impedance Spectrum (EIS) after placing them in between two stainless steel (SS) electrodes. Thermal stability of the samples are measured by placing them for 30 minutes in a pre-heated oven at 150 °C.

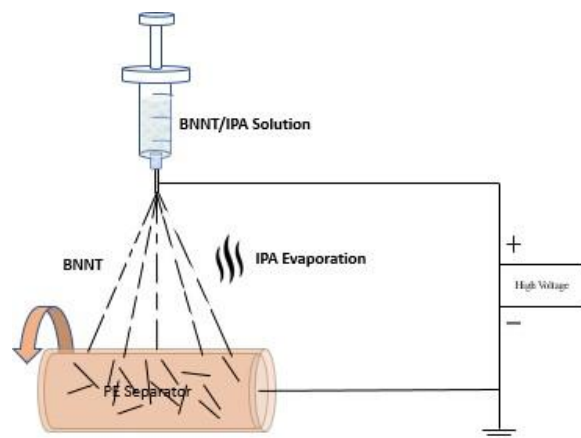


Figure 1: BNNT/IPA coating on PE separators

3 RESULTS AND DISCUSSION

After the preliminary experiments 0.5% BNNT/IPA is selected as the optimal ratio for both dispersing BNNT in IPA and for uniform process to coat BNNT on PE. 1 ml, 1.5 ml and 2ml BNNT/IPA coated PE separators all showed

uniformly dispersed and distributed BNNT on the surface (Figure 2)

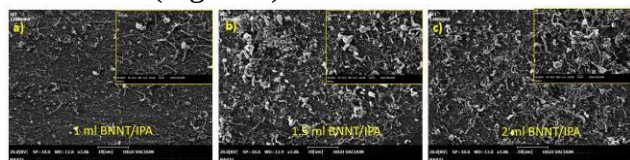


Figure 2: BNNT coated separators: a) 1 ml BNNT/IPA, b) 1.5 ml BNNT/IPA c) 2 ml BNNT/IPA

Among the three samples in comparison with a neat PE separators (0.97 W/mK), 1 ml BNNT/IPA coating showed the highest performance with 1.09 mS/cm ionic conductivity while 1.5 ml and 2 ml coated samples showed 1.04 mS/cm and 1.03 mS/cm ionic conductivities, respectively. Optimal sample which is coated with 1 ml BNNT/IPA suspension is also tested for thermal stability at 150 °C. It was observed that while Neat PE loses its shape, BNNT coated PE can still keeps its circular shape even at such high temperature (Figure 3).

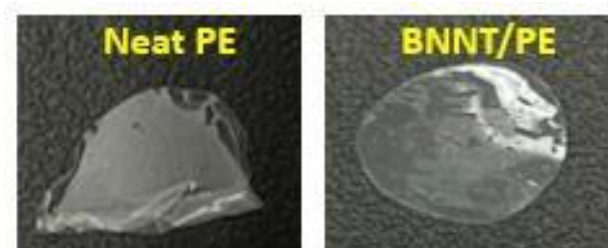


Figure 3: Neat PE and BNNT coated PE after 150 °C heat exposure in a oven

4 CONCLUSION

In this research, BNNT are coated on PE separators through electrospraying method, and obtained as high as ~12% enhanced ionic conductivity at room temperature compared to a neat PE separators. Such novel coating also enhanced thermal stability of the PE separator by the effect of high thermal dissipating property of BNNT.

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ESTIMATION OF GREENHOUSE DEHUMIDIFICATION REQUIREMENTS FOR TOMATO AND CUCUMBER CROPS

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Abstract

Greenhouses typically have high humidity levels due to plant transpiration and evaporation from the soil surface or growth media. To prevent fungal attacks and diseases, greenhouses require dehumidification to achieve the optimal level of relative humidity (RH). This study aims to predict the dehumidification load for tomato and cucumber crops in hot regions inside greenhouses. Additionally, a control strategy is developed to optimize the RH taking into consideration, the condensation and ventilation for the greenhouse located in Multan, Pakistan. In Multan's winter season (November and December), dehumidification will primarily occur during the condensation process because the outdoor temperature is lower than the indoor temperature. Dehumidifiers powered by heat or solar energy might provide a cost-effective option. The model's shortcoming lies in its lack of suitability for a range of crops, as it solely takes into account one variable for plant properties. The energy-efficient and cost-effective control strategies for dehumidification need to be studied in the future.

Keywords: Greenhouse, relative humidity, dehumidification, control strategy, modelling

1 INTRODUCTION

Greenhouse crop production (controlled environment agriculture) is one of the best ways to meet the food demand worldwide. Greenhouse production yields 15 times more per acre than field conditions [1], [2]. The greenhouse is a controlled environment that allows crop production in climates and seasons which would otherwise not be suitable for growing or prolonging the cultivation periods of seasonal crops and allows them to be grown near locations of consumption. Greenhouse (CEA) also helps to reduce water, land, and pesticide consumption [3]. However, greenhouses are energy-intensive compared to the rest of the agricultural industry as they consume up to 25% of the operating costs of large vertical farms in the U.S. [4]. An increase in crop yield in the energy-efficient greenhouse has been identified as a sustainable development goal (SDG) for food production [4].

Plant transpiration and evaporation from plant growth media are the main humidity sources in the greenhouse. High humidity in terms of vapor pressure deficit (VPD) can be the cause of fungal attacks and plant diseases. It can be optimized somehow in the climates having less outside humidity using ventilation. But the ventilation also be a moisture source when the outside air is more humid [5]. Therefore,

dehumidifiers become necessary for moisture removal. The dehumidifier of an exact capacity would not only save cost but would be environmentally friendly as well.

The manuscript first includes the vapor pressure deficit (VPD) analysis for tomato and cucumber crops to know the optimal ranges. Second, the dehumidification requirement modeling is conducted to predict the dehumidification load in the greenhouse located in Multan, Pakistan.

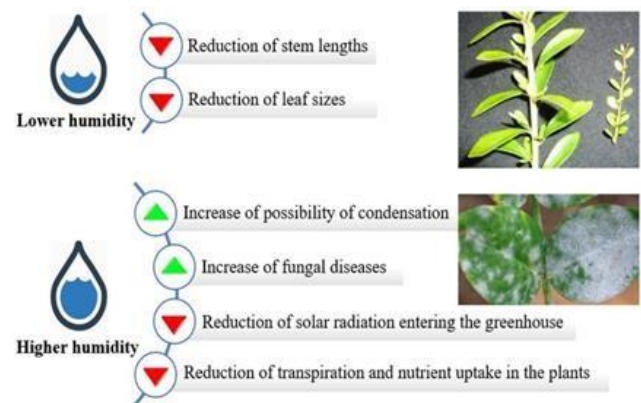


Figure 1. Effects of lower and higher humidity levels in greenhouses.[6]

2 MATERIALS AND METHOD

2.1 Vapor pressure deficit (VPD) estimation

Temperature and humidity are functions of VPD. It also requires the leaf temperature that varies for different stages of plant growth and is

also dependent on seasons and regions of the plant. Most fruits and vegetable plants require 15 to 30°C temperature with 50 to 90% relative humidity for optimum growth inside an agricultural greenhouse [7]. Fig. 3 is showing optimum temperature and humidity conditions for various fruits/vegetables inside an agricultural greenhouse.

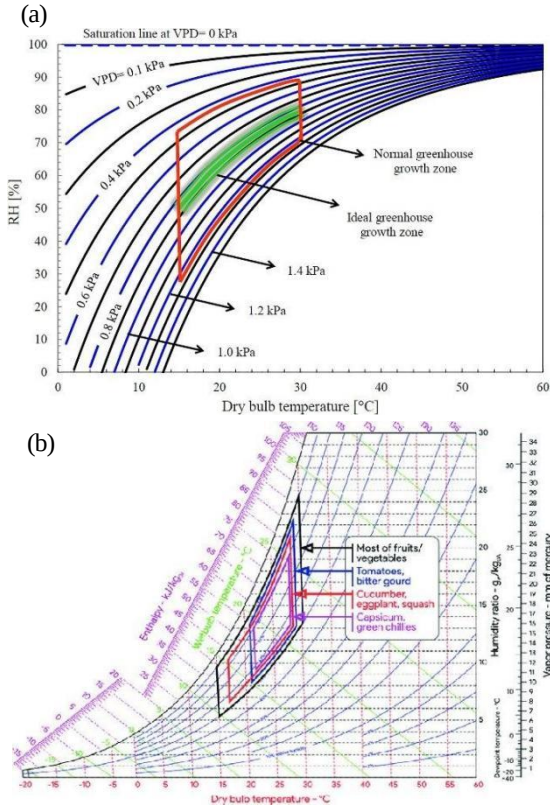


Figure 2. (a). Identifying the normal and ideal greenhouse growth zones for agricultural products based on water vapor pressure deficit [6]. (b) Optimum temperature/ humidity conditions for various fruits and vegetables inside an agricultural greenhouse [7].

VPD is the difference between the plant's saturated vapor pressure (which can find with the help of leaf temperature) and the vapor pressure (with the help of temperature and humidity) of the air. Mathematically it is explained in equations 1,2 and 3.

$$VP_{sat} = \frac{c_g 10^{(7.5T)/(237.3+T)}}{1000} \quad (1)$$

$$VP_{air} = \frac{c_g 10^{(7.5T)/(237.3+T)}}{1000} \frac{RH}{100} \quad (2)$$

$$VPD = VP_{sat} - VP_{air} \quad (3)$$

where, VP_{sat} represents the vapor pressure of the saturated environment (i.e. leaf of the plant)

in kPa, VP_{air} represents the vapor pressure of the air inside the greenhouse in kPa, c_g denotes a coefficient (i.e. 610.7), and T represents the surface temperature of the leaf [8].

2.2 Dehumidification requirement modelling

In greenhouses, the primary source of moisture is plant transpiration. Additional moisture comes from evaporation from the growth media and soil or floor surfaces, but this is minor compared to plant transpiration [8], [9][10]. These two sources together are referred to as evapotranspiration. Moisture removal happens through ventilation and condensation, as well as any dehumidification measures. Ventilation can also introduce moisture if the outside air humidity is higher than that inside the greenhouse. Condensation occurs on the inner cover surface when the ambient temperature is low, which removes moisture from the air and releases latent heat[11].

$$E_{dhrs}q(t) = E_p(t) - E_c(t) - E_v(t) \quad (4)$$

Where, $E_{dhrs}q(t)$ represent the dehumidification demand at time t in $\text{kg hr}^{-1}\text{m}^{-2}$, i.e. the amount of moisture that needs to be removed by the dehumidifier; $E_p(t)$, in $\text{kg hr}^{-1}\text{m}^{-2}$ is the moisture added to the greenhouse by evapotranspiration at time t ; $E_c(t)$, $\text{kg hr}^{-1}\text{m}^{-2}$ is the moisture added or removed to the air by condensation process at time t , $E_v(t)$, $\text{kg hr}^{-1}\text{m}^{-2}$ is the moisture removal or gain due to air exchange at time t .

3 RESULT AND DISCUSSION

3.1 VPD analysis

The analysis are conducted for the tomato and cucumber crop according to their temperature and humidity ranges. Multan, Pakistan is a hot region lying between 30.2°N and 71.45°E.

Table 1. Temperature and RH ranges of tomato and cucumber

Tomato	$T_{\text{Day}} = 23\text{-}27^\circ\text{C}$ $T_{\text{Night}} = 13\text{-}16^\circ\text{C}$ $\text{RH} = 50\text{-}80\%$ References: [12]–[14]
Cucumber	$T_{\text{Day}} = 25\text{-}30^\circ\text{C}$

$T_{\text{Night}} = 16-18^{\circ}\text{C}$
 $\text{RH} = 70-90\%$
 References: [13], [15], [16]

The figure illustrates the analysis of tomato crop performance under various temperature circumstances (both during the day and at night) at varied levels of relative humidity (RH). The VPD at different temperatures is represented by separate lines, which include daytime temperatures ranging from 23°C to 27°C and nighttime temperatures ranging from 13°C to 16°C .

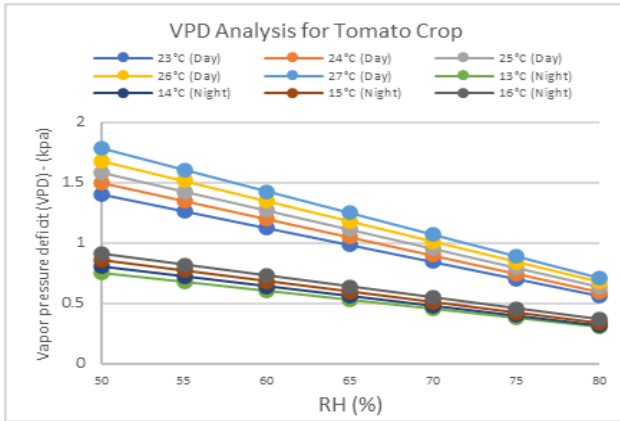


Figure 3 VPD analysis for tomato crop

The vapor pressure deficit (VPD) has an inverse relationship with relative humidity (RH) across all temperature conditions. Higher daytime temperatures result in higher VPD readings compared to midnight temperatures. The data indicates that as relative humidity decreases, the vapor pressure deficit (VPD) increases dramatically, suggesting a greater difference in water vapor pressure between the inside and outside of plant leaves.

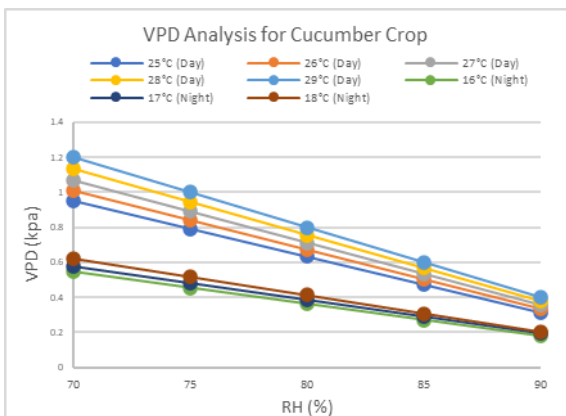


Figure 4 VPD analysis for cucumber crop

The trend for both the crops is same. For tomato, VPD range lies between 0.3-1.8kpa for day, and for the night it is 0.2-0.95kpa.

3.2 Dehumidification requirement prediction

This graph shows the dehumidification load for a tomato greenhouse in Multan during the winter months (November and December) at different times of the day. The temperature ranges between $23-27^{\circ}\text{C}$, and the relative humidity (RH) ranges from 50-80%. The dehumidification load is measured in $\text{kg}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ and is displayed for both maximum and minimum daily values. The peak load is between 0.25-0.3 $\text{kg}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$. The greenhouse area is 21m^2 , so the dehumidifier's peak capacity for November should be 6.3 kg h^{-1} .

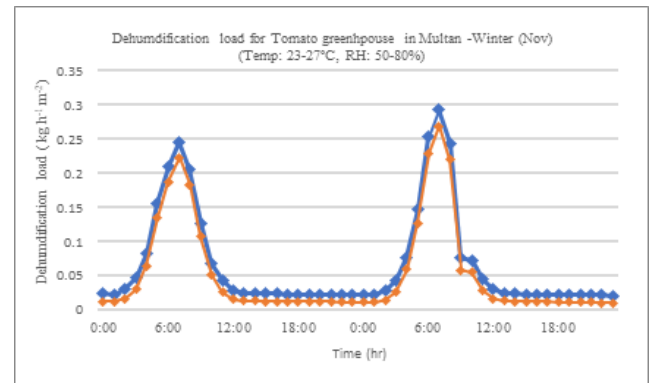


Figure 5 Dehumidification load profile for Multan (Nov)

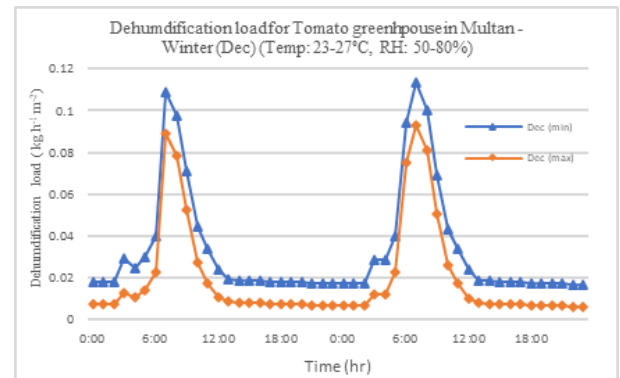


Figure 6 Dehumidification load profile for Multan (Dec)

4 CONCLUSION

Greenhouses typically have high humidity levels due to plant transpiration and evaporation from the soil surface or growth media. To prevent fungal attacks and diseases, greenhouses require dehumidification to achieve the optimal level of relative humidity (RH). This study aims to predict the dehumidification load for tomato and cucumber crops in hot regions inside greenhouses. Additionally, a control strategy is developed to optimize the RH taking into consideration, the condensation and ventilation

for the greenhouse located in Multan, Pakistan. The profile follows the same trend, and the December load is approximately up to 0.12 kg h⁻¹m⁻². The dehumidifier should have a capacity of 2.52 kg h⁻¹. In Multan's winter season (November and December), dehumidification will primarily occur during the condensation process because the outdoor temperature is lower than the indoor temperature. Additionally, a dehumidifier powered by renewable energy sources will be needed for the greenhouse. The ventilation process will act as a source of moisture and will also release heat from inside the greenhouse.

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COMPREHENSIVE CHARACTERIZATION OF ACTIVATED CARBON FUNCTIONALIZED WITH Fe_3O_4 AND L-ARGININE

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Abstract

Activated carbon (AC) is considered to be one of the most popular and widely used adsorbents in water and wastewater treatment worldwide. Physical, chemical, biological modification methods are used to increase the adsorption capacity of activated carbon. In this study, the effects of chemical modification using nitric acid and Fe_3O_4 -L-arginine on the structural and chemical properties of activated carbon were investigated. Characterization analysis of AC modified with nitric acid and Fe_3O_4 -L-arginine was determined by scanning electron microscope (SEM), Brunauer–Emmett–Teller (BET), Fourier transform infrared spectrophotometer (FTIR) analysis. From the BET data, it is understood that the specific surface area of the prepared Fe_3O_4 -L-arginine@AC is $249.83 \text{ m}^2/\text{g}$ and pore volume is $0.30 \text{ cm}^3/\text{g}$.

Keywords: Activated carbon, characterization, Fe_3O_4 -L-arginine, modification, nanomaterial.

1 INTRODUCTION

Pesticides are chemicals used in various agricultural applications to control harmful pests, weeds and diseases in plants [1, 2]. Pesticides can generally be classified according to the living class they affect and their chemical structure. According to the living group they affect, pesticides are classified as herbicides, insecticides, fungicides, rodenticides and other components. According to 2020 data, nearly 4.3 million tons of pesticides were used worldwide [3]. According to nationwide studies in the USA, 11 herbicides, 4 insecticides and 1 fungicide were found in 39 major rivers at

concentrations higher than the chronic reference limit for aquatic life [4,5]. In monitoring studies conducted in 38 rivers in the United States, 8 of the 10 most detected organic chemicals belonged to pesticides containing metolachlor [6]. Although the use of pesticides is important for agricultural productivity, excessive and uncontrolled use of these drugs can be harmful to nature and the ecosystem. Acetochlor has B2 carcinogenic and thyroid disrupting effects [7], while metolachlor has toxic effects on the kidneys, liver, cardiovascular and nervous systems [8, 9]. According to the Environmental

Protection Agency (USEPA), metolachlor is classified as a probable human carcinogen, however, liver damage has been observed in female mice exposed to high doses of metolachlor [10]. In an ecological study conducted in Maryland, it was observed that the risk of childhood bone cancer was significantly increased in areas with detectable amounts of metolachlor in groundwater sources [11]. Metolachlor, a type of herbicide, must be removed from water sources due to its harmful side effects on the ecosystem and humans. Activated carbon (AC) is considered one of the most popular and widely used adsorbents in water and wastewater treatment worldwide. Physical, chemical and biological modification methods are used to increase the adsorption capacity of activated carbon [12]. Activated carbon can be modified chemically with acid, base and various metals, physically with heat, and biologically with bacteria [13]. Studies in the literature have proven that acid-modified activated carbon provides better pollutant removal efficiency than powdered activated carbon [14, 15, 16, 17]. At the same time, studies have proven that Fe_3O_4 -modified activated carbon provides better pollutant removal efficiency than powdered activated carbon [16, 18, 19, 20]. The purpose of modifying activated carbon with nitric acid is to increase its surface volume and pollutant retention capacity [13]. Fe_3O_4 @L-arginine can be used to add sustainable renewable properties to activated carbon [18]. AC can be modified with L-arginine to increase the iron retention

capacity of activated carbon [21]. AC modified with Fe_3O_4 -L-arginine is advantageous in terms of effective treatment capacity, economic, sustainable and renewable. This study aimed to investigate the modification and characterization of activated carbon (AC) by nitric acid, followed by functionalization with Fe_3O_4 and L-arginine for water treatment. AC Puriss, a commercial activated carbon, was selected for this study. The original AC-N and functionalized AC samples were characterized in terms of morphological properties, pore size distributions, and structural properties using techniques such as scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET) analysis, Fourier transform infrared spectroscopy (FTIR), dynamic light scattering (DLS), and point of zero charge (pHpzc). The characterization results can serve as a reference for AC activation and functionalization in research investigating the potential application in specific pollutant adsorption for water and wastewater treatment.

2 MATERIALS AND METHODS

The procedure outlined by Pormazar et al. [21] with minor modifications was followed for the preparation of Fe_3O_4 -L-arginine@AC nanoparticles. Initially, 6 g of $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ and 11.7 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved in 300 mL of water, then added 5 grams of nitric acid functionalized activated carbon (AC-N). The sample was mixed in a three-necked flask at 70 °C for 30 minutes under N_2 gas. Subsequently, 15 grams of L-arginine were dissolved in 100

mL of deionized water and slowly added to the solution, followed by gentle stirring for 1 hour. Then, 100 mL of NH_4OH was added dropwise to the solution and stirred for 1.5 hours. Finally, the precipitated black nanoparticle mass was collected using a magnet or filter paper, washed with deionized water, and dried in an oven at 50 °C for 12 hours. The physicochemical characterizations of original AC-N and functionalized AC were conducted by assessing specific surface area, point of zero charge (pHpzc), SEM, and FTIR analyses. The pHpzc values of the adsorbents were determined using a pH equilibration method, where a 0.1 M NaCl solution was adjusted to pH values ranging from 2 to 12 with 0.5 M HCl or 0.5 M NaOH. Samples containing 100 mg of adsorbent were mixed in this solution for 48 hours at 100 rpm and 20 ± 5 °C, followed by a 1-hour settling period to measure the pH. The pHpzc value was defined as the pH that remained constant after the 48-hour contact time. This process was applied to both original AC-N and modified activated carbon to assess the effect of acid modification on the adsorbents' net surface charge. The surface morphology of the adsorbents was examined using a Zeiss Evo LS10 scanning electron microscope (SEM). The specific

surface area of the samples was determined using a Micromeritics Gemini V analyzer with nitrogen adsorption at 77 K. The surface areas were calculated from nitrogen adsorption isotherms using the Brunauer–Emmett–Teller (BET) equation. FTIR analyses were performed using a Perkin Elmer 400 FT-IR/FT-FIR spectrometer in the wavelength range of 400-4000 cm^{-1} . Dynamic light scattering (DLS) measurements were conducted at room temperature with a Malvern NanoZS90 instrument equipped with a 633 nm laser, collecting data at a scattering angle of 173°.

3 RESULTS AND DISCUSSION

The FTIR analysis was used to determine the functional groups of Fe_3O_4 -L-arginine@AC magnetic nanoparticles. For iron oxide (Fe_3O_4) nanoparticle, the FTIR spectra demonstrate that the Fe-O adsorption peak at 609 cm^{-1} is a characteristic feature of iron oxides. The literature indicates that this peak is observed at 440 cm^{-1} - 620 cm^{-1} [22,23]. The bands at 1554 cm^{-1} and 2324 cm^{-1} are attributed to the stretching vibration of C=O (amide) and C-H bonds, respectively [21]. The band at 898 cm^{-1} assigned to C- O-C stretching.

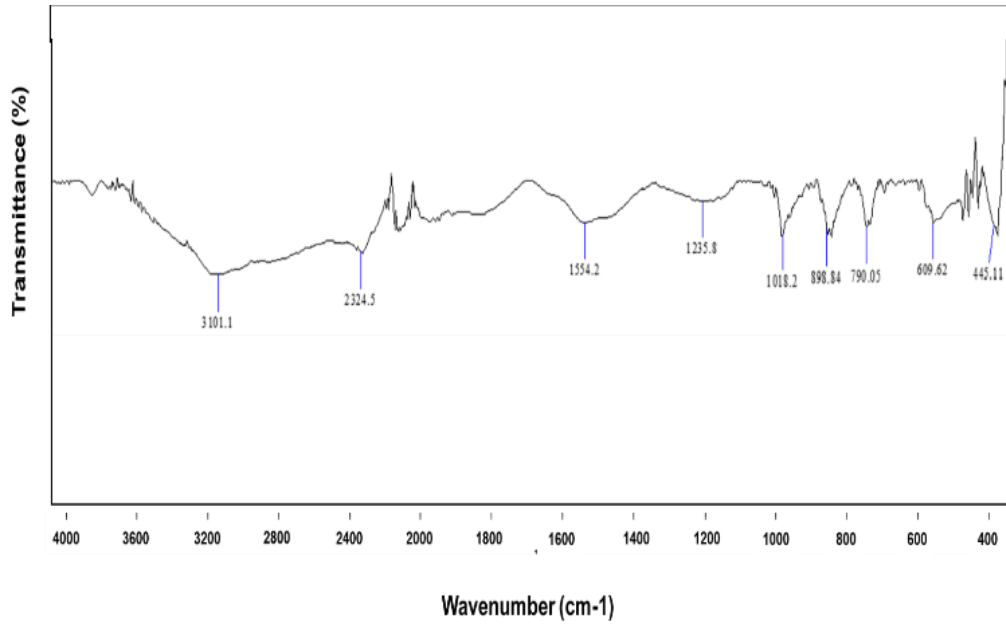


Figure 1. FT-IR spectra of Fe₃O₄-L-arginine@AC.

The surface morphology of Fe₃O₄-L-arginine@AC particles was analyzed via SEM and is presented in Fig. 2. The SEM images demonstrate that the Fe₃O₄ particles are nearly spherical and have an average surface size of

less than 40 nm. The addition of L-arginine resulted in the formation of a rose-like form of nano-flower morphology with nanometer-sized leaves. This result indicates that L-arginine was successfully grafted onto the Fe₃O₄ surface.

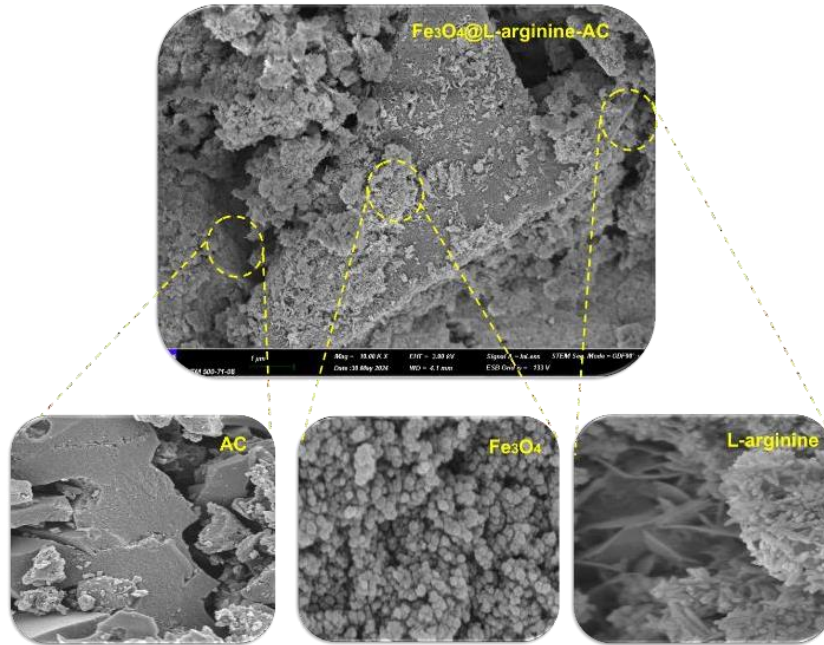


Figure 2. SEM images of Fe₃O₄-L-arginine@AC.

BET analysis was performed to determine the surface area, porosity, and bulk density of the produced $\text{Fe}_3\text{O}_4\text{-L-arginine@AC}$ (Fig.3). The

BET results were given in Table 1. The BET surface area and pore volume of nanomaterial were $249.83 \text{ m}^2/\text{g}$ and $0.30 \text{ cm}^3/\text{g}$

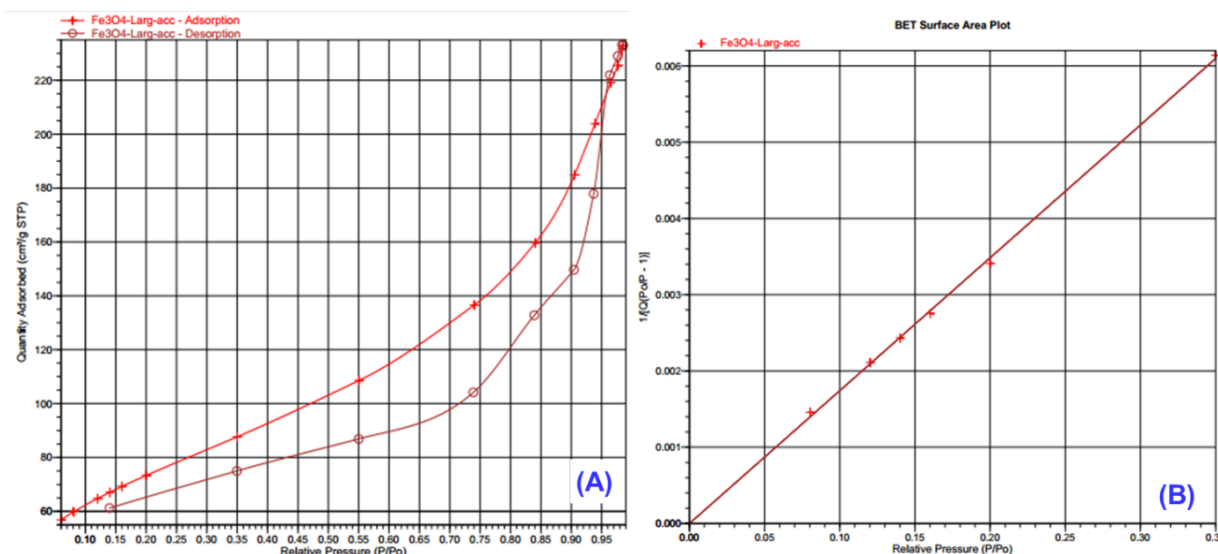


Figure 3. (a) BET analysis of nitrogen adsorption/desorption isotherms and BET surface area of $\text{Fe}_3\text{O}_4\text{-L-arginine@AC}$.

Table 1. Basic BET properties of $\text{Fe}_3\text{O}_4\text{-L-arginine@AC}$.

Adsorbent	BET surface area (m^2/g)	Pore volume (cm^3/g)	Bulk density (g/cm^3)
$\text{Fe}_3\text{O}_4\text{-L-arginine@AC}$	249.83	0.30	1.00
AC-N	821.27	0.54	1.00

*AC-N: Nitric acid modified activated carbon.

The addition of Fe_3O_4 and L-arginine to the AC-N can lead to changes in both the structure and particle size. L-arginine can create interactions between transition metal cations and anion groups within the Fe_3O_4 structures, which may alter the structure and subsequently affect the particle size. The particle size of the nanomaterial was found to range between 27.45

and 105.10 nm, with an average particle size of 42.6 nm. On the other hand, the zeta potential of the nanomaterial was measured as -39.52 mV.

4 CONCLUSION

It has been understood that the flower-like structure detected in the $\text{Fe}_3\text{O}_4\text{-L-arginine@AC}$ SEM photograph represents a specific type of nanostructured material consisting of AC-N

coated with the Fe₃O₄ nanoparticles and L-arginine, a type of amino acid. Appearing new peaks on the FTIR spectrum indicated that the Fe₃O₄ and L-arginine are successfully coated on the AC-N surface. According to the results of BET analysis, the surface area and pore volume of Fe₃O₄-L-arginine@AC was determined as 249.83 m²/g and 0.30 cm³/g, respectively. Consequently, the new adsorbent Fe₃O₄-L-arginine@AC was successfully synthesized.

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ASSESSING THE ENVIRONMENTAL IMPACTS OF INTERNATIONAL FINANCIAL INFLOWS IN CLEAN ENERGY R&D AND PRODUCTION IN ASIAN COUNTRIES

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This study uses FGLS and system GMM methods to explore the impact of international financial inflows on clean energy research and development (R&D), production, and other critical economic variables on greenhouse gas (GHG) emissions in 22 Asian countries. The analysis shows a significant negative association between international financial inflows and GHG emissions, highlighting the critical role of these investments in reducing emissions. In addition, renewable energy consumption shows a significant negative impact on emissions, highlighting the effectiveness of switching to renewable energy in reducing environmental degradation. The study also finds that foreign direct investment (FDI) helps reduce emissions, which may be due to the introduction of advanced technologies and stricter environmental standards. In addition, the dynamic analysis confirms the existence of an environmental Kuznets curve effect (EKC), whereby emissions initially increase with economic growth but decrease after reaching a certain income level, reflecting a shift towards more sustainable economic practices. The total rent of natural resources also contributes to reducing emissions, suggesting that proper management can support environmental sustainability. The results indicate that international financial flows, the use of renewable energy, and responsible resource management are essential strategies for reducing GHG emissions and achieving long-term environmental sustainability in the region.

Keywords: Clean Energy R&D, Clean Energy Consumption & Production, Economic Growth, FDI, EKC, Asia.

RECENT DEVELOPMENTS ON BATTERY THERMAL MANAGEMENT SYSTEMS BY COOLING WITH MINICHANNEL

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Abstract

Li-ion batteries (LiBs) generate heat during charging and discharging which can cause to thermal runaway. The thermal runaway of LiBs quickly triggers a chain reaction because of series/parallel characteristics of battery pack. Therefore, a battery thermal management system (BTMS) is required to ensure they safety, efficiency and cycle life of LiBs. The temperature of LiBs should be kept between 15°C -35°C and temperature difference on a LiB should not be exceed 5°C. BTMSs are divided into main two groups active and passive which require and does not require extra energy consumption, respectively. Forced air cooling, liquid cooling and thermoelectric cooling can be sampled as active BTMS, while passive BTMSs consist of heat pipe and PCM. Since these systems have advantageous and disadvantageous, researchers have tried to find an optimum system. This review study presents recent improvements on BTMS for electrical vehicles especially minichannels. It is concluded from the extensive literature review that water flowing in a minichannel can be a good choice for BTMS for extreme operating conditions.

Keywords: Electric Vehicles, Battery Thermal Management Systems, Minichannels

1 INTRODUCTION

The world's population is increasing and people prefer city centers as their living space. It is predicted that the world population will be 9.1 billion in 2050 and 80% of the world's population will live in cities. Such large populations living together causes some problems and affects the quality of life. Some of these problems are noise and environmental pollution. Exhaust emissions from transportation vehicles are increasing and triggering environmental pollution. In the next stage, it becomes one of the causes of global warming and climate change. [1,2]

As a solution to the environmental problems caused by automobiles, internal combustion vehicle emissions had to be gradually reduced and reduced to zero. In order to combat climate change, the European Union (EU) made it mandatory for new cars and light commercial vehicles to be zero-emission after 2035. [3] Electric vehicles (EVs) and hybrid electric vehicles (HEVs) are two methods we encounter to achieve zero-emission targets. Electric vehicles operate by transferring energy from the battery pack to the wheels via an electric motor. In this way, they do not emit emissions and operate without noise. However, long charging times and short ranges are the biggest obstacles to electric

vehicles. For this reason, hybrid electric vehicles (HEVs) are offered as an intermediate product in the transition period to electric vehicles. The concept of hybrid refers to the use of 2 or more energy sources together.

The most common HEVs are a combination of an electric motor and an internal combustion engine (ICE). The ICE powers the vehicle when needed, while the electric motor alone powers the vehicle when not needed. This makes them more economical and cleaner than internal combustion engine vehicles. HEVs are a good alternative to EVs because they do not require long charging times and do not have a range limitation. However, it should be noted that HEVs cannot provide zero-emission values. [4]

Li-ion batteries are used as a power source in electric vehicles. Compared to other energy storage systems, LiBs is superior to others due to its higher power and energy density, light weight and rechargeability. LiBs comes in 3 different forms: pouch, prismatic and cylindrical. While cylindrical and prismatic batteries are generally preferred in electric vehicles, pouch batteries are also used. They have superior aspects compared to each other. When comparing prismatic and cylindrical battery packs, prismatic batteries of the same volume have higher energy density, while they are relatively expensive and short-

lived. Cylindrical batteries, on the other hand, are long-lived, cost-effective and impact resistant, while they have low energy density and thermal management is more difficult.

In LiBs, heat is generated due to internal electrochemical reactions during charging and discharging. Heat generation will increase the battery temperature. The increased temperature should be kept within certain levels (15°C -35°C) and the temperature difference across the LiB should not exceed 5°C. When these limits are exceeded, a phenomenon called thermal runaway occurs in the battery. Thermal runaway can cause the temperature to increase suddenly, the battery to burn or even explode. To prevent this, battery thermal management (BTMS) is essential.

Cooling in batteries is done as active, passive and hybrid. In the active cooling method, which requires additional energy to operate, the coolant provides heat removal from the batteries with a pump or fan. Cooling with phase change material (PCM), heat pipe (HP) and thermoelectric cooler (TEC) is defined as passive cooling because it does not require an energy source. In hybrid cooling, active and passive cooling are combined. [5]

In this study, the latest developments related to BTMS using mini channels, which is one of the active cooling methods in thermal management of cylindrical and prismatic li-ion batteries used in electric vehicles, were examined. The results showed that the use of mini channels gave very good results in controlling the temperature.

2 BATTERY HEAT GENERATION MECHANISM

LiBs store energy with electrons. When desired, the movement of these electrons allows the stored energy to be used in the desired place. The movement of electrons occurs due to the potential difference between the negative and positive regions. When examined in their internal structure, a LiB consists of 3 main parts: anode (negative electrode), cathode (positive electrode) and separator. In the resting state, lithium and electron remain together in the anode region. Electron and lithium movement begins during battery discharge. While electrons pass through a circuit from the negative current collector to the positive current collector and reach the anode region, lithium ions pass through the separator and reach the anode region. The separator does not allow electron passage, otherwise a short circuit occurs. However, lithium can pass through

the separator. In addition, lithium is provided with a movement environment with the electrolyte material added to the battery. During charging, lithium in the cathode region passes through the separator and recombines with electrons in the anode region. If all of the lithium in the cathode region passes to the anode region, it means that the battery is fully charged. Thanks to this movement of lithium, LiBs gain rechargeable properties.

During these processes, heat is generated within the battery, causing the battery temperature to increase. If the generated heat cannot be removed from the battery, a phenomenon called thermal runaway occurs due to uncontrolled lithium and electron movement. As a result of this event, the battery temperature suddenly increases 6-7 times, causing smoke and flame formation, and eventually the battery may explode. Therefore, battery thermal management is essential to prevent negative situations from occurring. [6,7]

3 BATTERY THERMAL MANAGEMENT WITH MINI CHANNELS

As mentioned above in chapter 2, thermal management of batteries is essential. For this reason, many active, passive and hybrid BTMS designs have been made by researchers. In this article, recent studies on the use of mini channels in cylindrical and prismatic battery thermal management has been reviewed.

3.1 Cylindrical Battery Thermal Managements

Heat transfer between the fluid and the solid surface is calculated from Newton's Law of Cooling, which is formulated as,

$$Q=h \times A \times dT \quad (1)$$

As can be seen from this expression, increasing the surface area, convection coefficient and temperature gradient, while other variables are constant, will improve the heat transfer. Studies on mini channel and cylindrical batteries have focused on increasing the contact area between mini channel and batteries. Studies on serpentine channel and cold plate-heat conducting member-are compiled in this section.

Wiriyasart et al. [8] numerically investigated the pressure drop and temperature distribution of a pack containing 444 cylindrical 18650 Li-ion batteries under different cooling conditions. The cases where nanofluid was used and not used at three different mass flow rates and 3 different flow directions were investigated. It was assumed

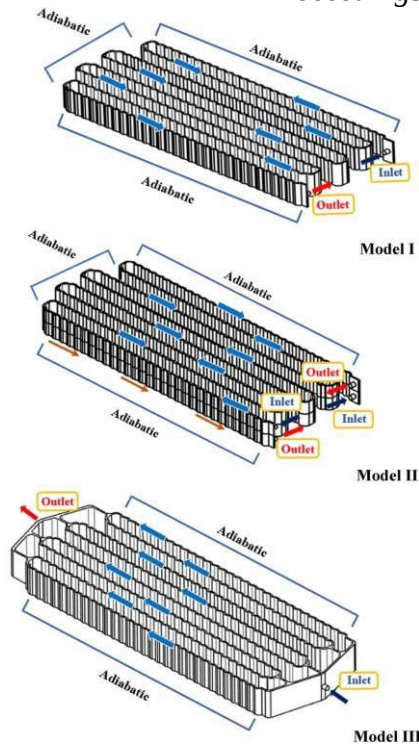


Figure 1 Serpentine Mini Channel for 444 Cylindrical LiBs [8]

that there was a constant heat flux value of 3330 W/m^2 from the contact surface between the battery and the mini channel. The average battery temperature remained below 35°C in the case of underflow and overflow in different directions. The results showed that the battery surface temperature decreased as the coolant mass flow rate increased. However, there was a limit to this temperature drop and the pressure drop increased with the increasing mass flow rate. In the study, TiO_2 nanoparticles were added at 0.25% and 0.5% by volume and it was observed that the battery temperature decreased. It was suggested that the battery surface temperature could be reduced by further increasing the nanoparticle ratio.

Xu et al. [9] conducted thermal analysis of 32 18650 LiB modules. Since the coolant temperature increases in the flow direction, the heat rejection rate of the package decreases. In order to prevent this, they aimed for a lightweight and uniform battery pack temperature with a wrench-shaped cold plate with a min-channel inside. The ambient temperature and fluid (water) inlet temperature were selected as 25°C . Analyses were performed for a discharge rate of 3C when water entered the channel at 0.1 m/s. As a result of the numerical analysis, it was seen that the wrench-shaped cold plate among 4 different designs provided the desired battery temperature

values, with a maximum battery temperature of 30.32°C and a maximum temperature difference of 3.83°C . It was also noted that the weight was reduced by 19.68% in the wrench-shaped cold plate design. In addition, the pressure drop in this design was at the lowest level with 43.64 Pa compared to the others. The effect of the starting point of the bifurcation on the temperature for the wrench-shaped design was also examined. The results showed that starting the bifurcation after the 4th cell (8 cells in total) provided the most effective cooling. While starting the bifurcation early reduced the pressure drop, it will increase the weight.

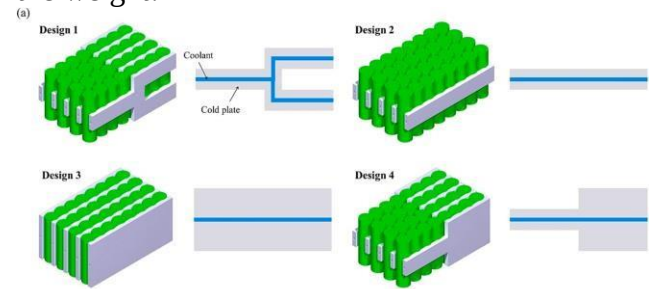


Figure 2 Wrench Shaped Mini Channel Cold Plate [9]

Wang et al. [10] have conducted experimental and numerical studies. In the study that carried out with liquid cooled aluminium plate, they investigated the thermal behaviour of modular 18650 LiB system in mass flow and series and parallel cases. It was aimed to transfer the heat generated in the battery to the fluid through the aluminium in contact with the batteries. Water was used as coolant with laminar flow. When the mass flow rate was between 20-140 ml/min, it was observed that the maximum temperature and temperature difference decreased as the flow rate increased. However, when the flow rate was greater than 80 ml/min, the temperature drop rate decreased. In the analyses carried out with parallel cooling, the maximum temperature and temperature difference were 37.67°C and 5.76°C , while these values were 7.55°C and 6.74°C lower compared to series cooling. Therefore, parallel cooling is quite effective compared to series cooling. Finally, the effect of flow direction on parallel cooling was investigated and the maximum temperature was 37.74°C while the temperature difference was noted as 4.17°C . Considering that the ambient temperature and fluid temperature were 30°C throughout the experiment, the obtained data are quite satisfactory.

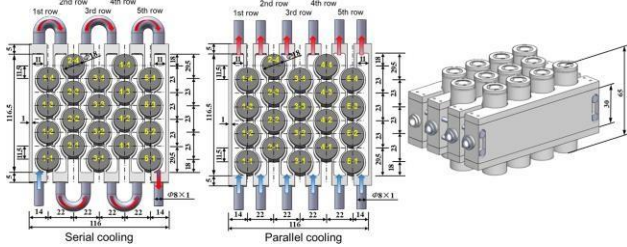


Figure 2 Aluminium Cold Plate [10]

Wang et al. [11] investigated the combined use of PCM and mini channel with the design called hybrid wavy mini channel cold plate (HWMCP). They numerically investigated the temperature distribution of the battery at different discharge rates, PCM thickness, coolant mass flow rate, different flow directions and different array combinations. The analysis consisted of 33 18650 LiB as battery modules. Water and composite RT44HC/expanded graphite were selected as coolant and PCM. In order to compare the effect of the presence of PCM, analyses were performed on wavy mini channel cold plate (WMCP) and HWMCP with only water flow. When comparing HWMCP and WMCP, results were obtained for water mass flow rate of 0.001kg/s and battery discharge rates of 3C and 5C. Although the mass flow rate of water decreased with the replacement of water with PCM, the maximum temperature decreased by 0.8°K and 1.3°K with HWMCP, respectively. In addition, 90% of PCM melted at the end of 5C discharge rate, while 40% melted at 3C discharge rate. PCM did not melt until 400th second at 3C discharge rate. For this reason, maximum temperature increased. However, temperature HWMCP showed more effective results with the melting of PCM. The effect of flow direction and flow rate was also examined for PCM thickness of 4 mm and number of channels through which water passes as 6. In case of 3 flows at the top and 3 flows at the bottom in different directions, there was a 4.4°K decrease in maximum temperature compared to flow in one direction. In addition, maximum temperature difference was 1.3°K. Analyses were performed in cases where flow rate was 0.0010 kg/s, 0.0012 kg/s, 0.0014 kg/s, 0.0016 kg/s. When the flow rate was increased from 0.0010 kg/s to 0.0016 kg/s, the maximum temperature decreased from 328.2°K to 323.3°K. The reason for this high temperature is that PCM did not melt. Only 8% of PCM melted at 0.0016 kg/s. The effect of early melting was investigated with PCM having 3 different phase change temperatures. In the previous analysis, the phase change temperature

was 314°K-317°K, while the maximum temperature decreased by more than 1°K when the phase change temperature was 306°K-309°K. This showed the effect of PCM melting temperature on the maximum battery temperature. The results showed that HWMCP provided better thermal management than WMCP. However, it should be noted that the battery temperature above 50°C increases the possibility of thermal runaway.

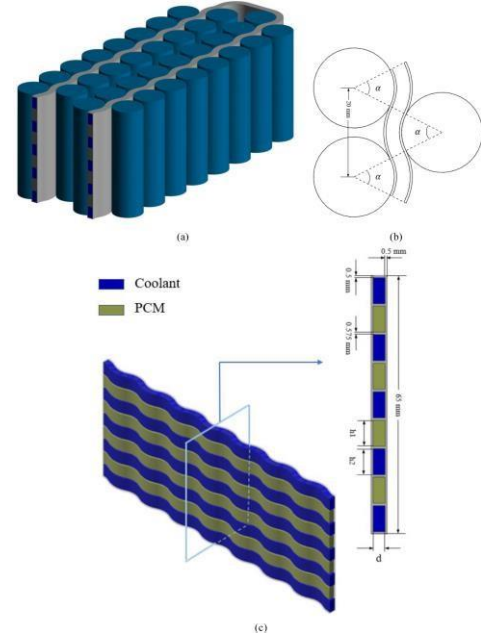


Figure 3 PCM and Liquid Cooling with Serpentine Mini Channel [11]

Li et al. [12] performed thermal analysis of a battery pack containing 24 cylindrical 18650 LiB. They used a heat conducting block (HCB) through which coolant (water) passes for heat dissipation. The channel through which water passes is 6 pieces of 1 mm x 4 mm dimensions. Other boundary conditions are as follows: ambient temperature between 25°C and 45°C; water flow rate 0.4 m/s; water temperature 25°C; discharge rate 2C. In the analysis performed at 45°C ambient temperature, the battery temperature dropped below 30°C after 50 seconds. Since the heat dissipation from the batteries was too much, the discharge rate was insufficient to heat the battery. For this reason, the maximum battery temperature remained constant. The effect of water inlet temperatures was also investigated in the cases where the ambient temperature was 35°C and 45°C. In all cases, while the maximum temperature difference remained below 5°C, the possibility of thermal runaway increased when the water inlet temperature exceeded 35°C. As a result, due to

the 135° contact angle between the HCB and the battery, the high heat transfer rate of the HCB and the high water inlet velocities, a very effective cooling was achieved and quite satisfactory temperature values were obtained despite the extreme conditions.

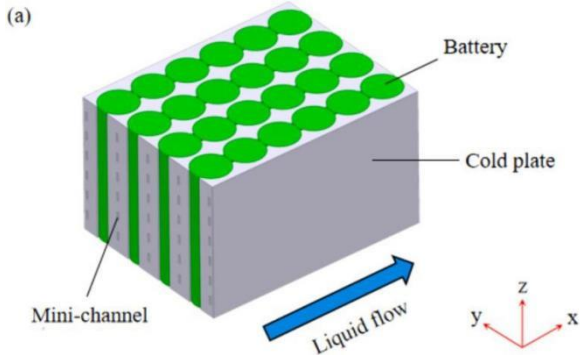


Figure 4 Mini Channel Cold Plate Cooling with 24 LiB [12]

Xin et al. [13] numerically investigated the temperature, weight and power consumption effects of air and water cooled 32 pieces of 18650 LiBs with different flow rates and geometries at 3C discharge rate. A heat conducting block (HCB) with cooler passing through it was used as the heat transfer element. Analyses were performed under with 2, 3 and 4 HCBs; 4mm, 6mm, 8mm and 10mm fluid diameters and constant mass flow rate conditions. It was concluded that 6 mm pipe diameter was the most suitable for HCB. In the analyses with 2 and 3 HCBs, the effect of the pipe diameter on the temperature was minimal. Considering the maximum temperature, temperature difference and pressure drop, 3 HCBs were preferred.

Analyses were made for the case where there was no flow in the HCB and for the case where there was flow with 7 different flow rates. Since the temperature difference between the water and the battery was low at the beginning of the discharge process, the amount of heat transfer was low. For this reason, a rapid increase in the battery temperature was observed. Over time, the temperature gradient increased and as a result, the maximum temperature came to equilibrium. While the increase in the flow rate reduces the maximum temperature, the rate of decrease in the temperature decreases. This shows that it is unreasonable to increase the flow rate too much. Although the water keeps the maximum battery temperature below 35°C , the battery temperature difference is over 5°C . In order to prevent this, the researchers have made an analysis for additional air cooling. In addition to the constant conditions

of 6 mm pipe diameter, 0.002 kg/s mass flow rate and 3 HCBs, analyses were made for air at different velocities. For an air mass flow rate of 1 m/s, the maximum temperature was 30.67°C and the temperature difference was 0.58°C . Though these results are very successful in preventing thermal runaway, it should be taken into account that energy consumption increases.

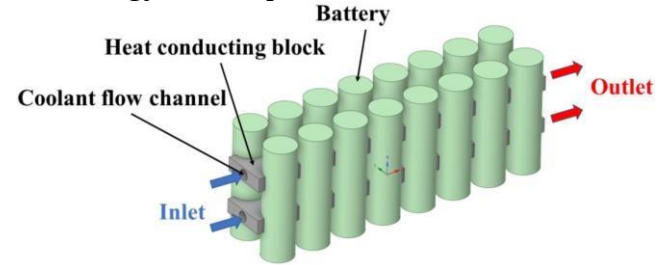


Figure 5 Air and Liquid Cooling HCB [13]

3.2 Prismatic Battery Thermal Management Systems

Mini channel provides the desired cooling requirement while occupying a minimum volume in prismatic batteries. Efforts to increase heat transfer in prismatic batteries focus on the use of mini channels with different shapes and different attachments. In this section, recent studies on mini channels in prismatic batteries are compiled. Dilbaz et al. [14] numerically performed the thermal analysis of 3 prismatic batteries with a capacity of 20Ah in their study with phase change material (PCM) and mini channel cooler. A rather extensive investigation was carried out in the cases of 3 different discharge rates (2C, 3C, 4C); water and Al_2O_3 nanoparticle added (0.5%, 1% and 2% by volume) nanofluid; 4 different geometry nanoparticles (Oblate spheroid, block, cylinder, and platelet); 4 different Reynolds numbers (250, 500, 750, 1000). The maximum temperature and maximum temperature difference were targeted to be below 50°C and 5°C in the study. In the analyses, when only RT-42 PCM was used at 4C discharge rate, maximum battery temperature and maximum temperature

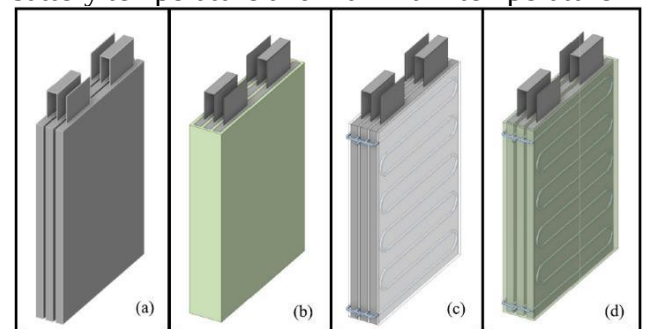


Figure 6 PCM and Serpentine Mini Channel Cooling [14]

difference were 45.736°C and 1.96°C, while 100% of PCM melted at 260 seconds. Analyses were performed when PCM and serpentine mini channel (diameter 1.5 mm) were used together. At 3C discharge rate, when Re number was 500 and platelet-shaped 2% Al₂O₃ nanofluid added coolant was used, the maximum temperature was obtained as 47.85°C. It was determined that platelet-shaped nanofluid gave the best result among other nanofluids.

Jaffal et al. [15] performed experimental and numerical analysis of prismatic battery for 1C and 2C discharge range, 45°, 60°, 75° and 80° rib angles and semi-circular (SCR), trapezoidal (TRAP), and triangular (TRAN) rib shapes. The reason for using ribs is to disrupt the boundary layer and improve heat transfer. The flow Reynolds number is designed between 200 and 1000 and the cross-sectional length of the channel through which the fluid passes is 4 mm×5 mm. Heat transfer from battery to the channel is performed with constant heat flux.

CFD analyses were first performed on 4 different angles of semi-circular shaped ribs (SCR), at 800 Reynolds number and 1C discharge rate. The best result among them was obtained as 27.46°C for SCCP-SCR-45°. In the analyses where the Reynolds number was increased, better cooling was provided and temperature uniformity was provided. It was also determined that decreasing the rib angle improved heat transfer and ensured that the maximum temperature difference of the battery was at the desired levels. At 1000 Reynolds number and 45° rib angle, the Nusselt number increased by 58% compared to the empty channel. Knowing how much the pressure drop is while such large increases in heat transfer are provided will be important for the efficiency of the ribs. The friction factor decreased as the Reynolds number increased. However, decreasing the rib angle increased the friction factor. Compared to the flow without ribs, the 45° rib angle at 100 Reynolds number caused the friction factor to increase by 106%.

To investigate the effect of rib shapes on heat transfer, and pressure drop analyses were performed for the channel at 45° rib angle. The results showed that the SCCP-TRAN-45° design gave the best results. It was also noted that the Nusselt number increased by approximately 71%, while the overall hydrothermal performance increased by 30%.

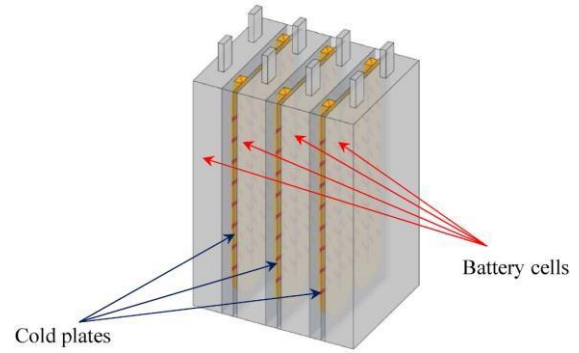


Figure 7 Effect of Different Ange Ribs [15]

Zhao et al. [16] numerically analysed 10 LiFePO₄ prismatic batteries with honeycomb liquid cooled cold plate (HLCP) design to determine the thermal behaviour. At the beginning of the analysis, the ambient temperature, coolant temperature and battery temperatures were input as 298.15°K and the flow character was laminar. Three different honeycomb geometries of HLCP with 3mm channel height and 8mm channel width were designed. The analysis results at 5C discharge rate and 0.1m/s velocity inlet showed that the maximum battery temperature was lower than 304°K with case 3, while the maximum battery temperature difference was 4.1°K. Analyses were performed for 5 different cases where the coolant entered the channel from 1, 2 and 3 points. In the first 3 cases, the inlet velocity was reduced as the number of channels increased to maintain the total flow rate. The velocities in Case4 and Case5 were designed as 0.2m/s and 0.3m/s. The results showed that the maximum temperature did not depend on the increase in the number of inlet points. However, it was observed that the maximum temperature difference decreased if the number of inlet points increased. But, since this decrease was not significant, it was not taken into account in further analyses. The maximum temperature decreased to 300.6°K by increasing the velocity to 0.3m/s. In order to better understand the effect of velocity, analyses were performed for 6 different inlet velocity values ranging from 0.01m/s to 0.5m/s. The results showed that increasing the inlet velocity more than 0.3m/s did not contribute significantly to the battery thermal management. In addition, the analysis performed on increasing the thickness of the HLCP showed that increasing the thickness without changing the flow rate did not contribute significantly to heat dissipation. Finally, it was observed that the flow direction had no effect on reducing the maximum temperature, but was successful in achieving a

uniform temperature distribution. As a result, the importance and effectiveness of mini channel use in thermal management of prismatic LiBs was revealed.

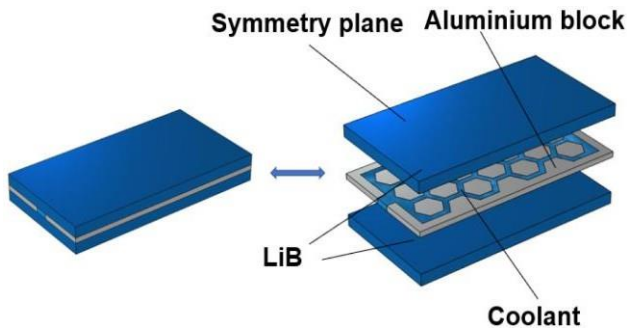


Figure 8 Honeycomb Shaped Mini Channel Cold Plate [16]

Li et al. [17] numerically investigated the effect of a new type of pin-fin added mini channel cold plate on battery thermal management performance increase. Prismatic LiB with a capacity of 45Ah was selected as the battery, which will serve as heat generator in the battery package. A design was proposed in which the coolant enters the mini channel from 5 different points and flows in parallel. The mini channel section lengths were 3mm×8mm, while the cold plate thickness was analysed as 4mm. CFD analyses were performed for coolant inlet temperature, pin-fin heights (PFH) and different pin-fin arrangements. In the analyses, the maximum battery temperature increase, maximum battery temperature difference and pressure drop were examined and the pin-fin efficiency performance was investigated.

Analyses were performed with the fluid at 3C discharge rate and 0.1m/s constant velocity in the mini channel without pin-fin (D1) and with pin-fin (D2, D3, D4, D5, D6). In the analysis, the ambient, battery and coolant channel inlet temperatures were selected as 298.15°K. The results showed that the fluid velocity increased as the PFH increased, as expected, since the cross-section narrowed. In addition, the pin-fin increased the fluid contact surface area and improved the heat transfer. For more detailed examination, analyses were performed at 2C and 3C discharge rates with 0.1m/s and 0.4m/s fluid velocities. It was noted that the D2 design, which has the highest pin-fin height, reduced the maximum battery temperature by 4.822°K at 0.4m/s and 3C discharge rate compared to D1. In the analysis performed at 2C discharge rate and 0.4m/s velocity, the maximum battery temperature difference remained below 5°K in

the all pin-fin arrangement analyses except D6. This value was 5.09°K for D6 and 4.139°K for D2.

The effect of Nusselt number and fanning-friction factor was also examined together to calculate the performance efficiency. In the analysis performed at 0.1 m/s inlet velocity, it was calculated that D2 design increased the Nusselt number by 83% compared to D1, but the fanning-friction factor increased by 238.9%. Therefore, heat transfer and friction coefficient should be evaluated together. The thermo-hydraulic performance of the best result D4 design was determined as 1.2935 and 1.4851 at 0.1 m/s and 0.4 m/s inlet velocities, respectively. With this result, the effectiveness of pin-fin usage in mini-channel battery thermal management was demonstrated.

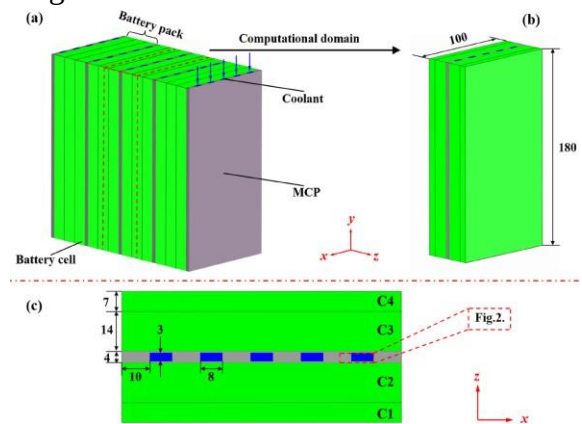


Figure 9 Pin-fin Added Mini Channel Cold Plate [17]

4 CONCLUSIONS

This paper compiles the latest studies on the use of mini channels in thermal management of LiBs. The results obtained are as follows;

- Mini channels took up very little space while transferring heat from the battery. Therefore, it's quite appropriate for battery packs.
- The efficiency coefficient increased by placing heat transfer enhancing elements (pin-fin, nanoparticle) inside the mini channel.
- Uniform battery temperature could be achieved by adjusting the fluid direction. However, its effect on the maximum temperature was minimal.
- As the fluid flow rate increased, the battery temperature approached a limit value and increasing the flow rate too much negatively affects power consumption.

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EFFECTS OF HYDROGEN ENERGY SHARE ON THE PERFORMANCE OF A COMPRESSION-IGNITION ENGINE RUNNING AT HIGH LOAD

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Abstract

This study examines the emissions characteristics of hydrogen-enriched diesel engines using CFD simulations. The results reveal that hydrogen enrichment improves brake thermal efficiency (BTE) by 11% and reduces soot and unburned hydrocarbon (UHC) emissions by 61% and 78%, respectively. However, NO_x emissions increase by 23% at high-load conditions with a 25% hydrogen energy share (HES). While hydrogen enrichment offers environmental benefits, further optimisation is needed to address the trade-offs, particularly the increase in NO_x emissions.

Keywords: Hydrogen engine, Dual-fuel engine, CFD combustion modelling, Emissions

1 INTRODUCTION

Transports account for 21% of global greenhouse gas emissions [1]. The widely employed engines in several industries, including road transport, agricultural vehicles, earth-moving machinery, rail, maritime propulsion, and stationary installations for electrical power production are compression-ignition (CI) engines due to their great fuel efficiency, torque, and durability [2]. Fossil fuels generally drive them which affects the environment badly. Currently, fossil fuels provide 84% of the world's primary energy [3], as indicated in Figure 1a. The energy industry also accounts for 81.5% of global greenhouse gas emissions (Figure 1b). Carbon dioxide (CO₂) and other greenhouse gases accumulate in the Earth's atmosphere, absorbing solar energy and insulating the planet. Humans are the major force behind global warming since fossil fuel consumption increases the accumulation of greenhouse gases, which are necessary for maintaining a habitable planet's temperature [4]. Fossil fuel combustion emits harmful air-quality pollutants such as NO_x, soot, UHC, and CO, as well as causing geopolitical and economic issues due to their limited availability. Regulations and timeframes aim to reduce emissions and phase out fossil fuels are set off. The Paris Agreement, signed by 196 states, aims to limit global average temperature rise to "well below" 2°C above pre-industrial levels and achieve a climate-neutral world by the middle of the

century through emission reductions [5]. Growing awareness of the environmental impact of burning fossil fuels and growing energy demand have helped renewable energy to become more and more popular recently [6]. To meet ambitious goals, shifting from fossil fuels to clean renewable energy sources is necessary. Hydrogen as a fuel has demonstrated the potential to be an alternative fuel for CI engines. Experiments have consistently shown that adding hydrogen to CI engines and converting them into dual-fuel CI engines may significantly reduce emissions of particulate matter, carbon monoxide (CO), and unburned hydrocarbons (UHC) [7, 8]. The effects on NO_x emissions are influenced by variables such as the proportion of hydrogen to diesel energy and the engine's load. Some research indicates that NO_x emission levels remain stable [9] or even decrease [10-13] following a transition to dual fuel. In certain instances, there is a direct correlation between NO_x emissions and the hydrogen-diesel energy ratio [13] whereas, at higher engine loads, an inverse relationship has been observed [10].

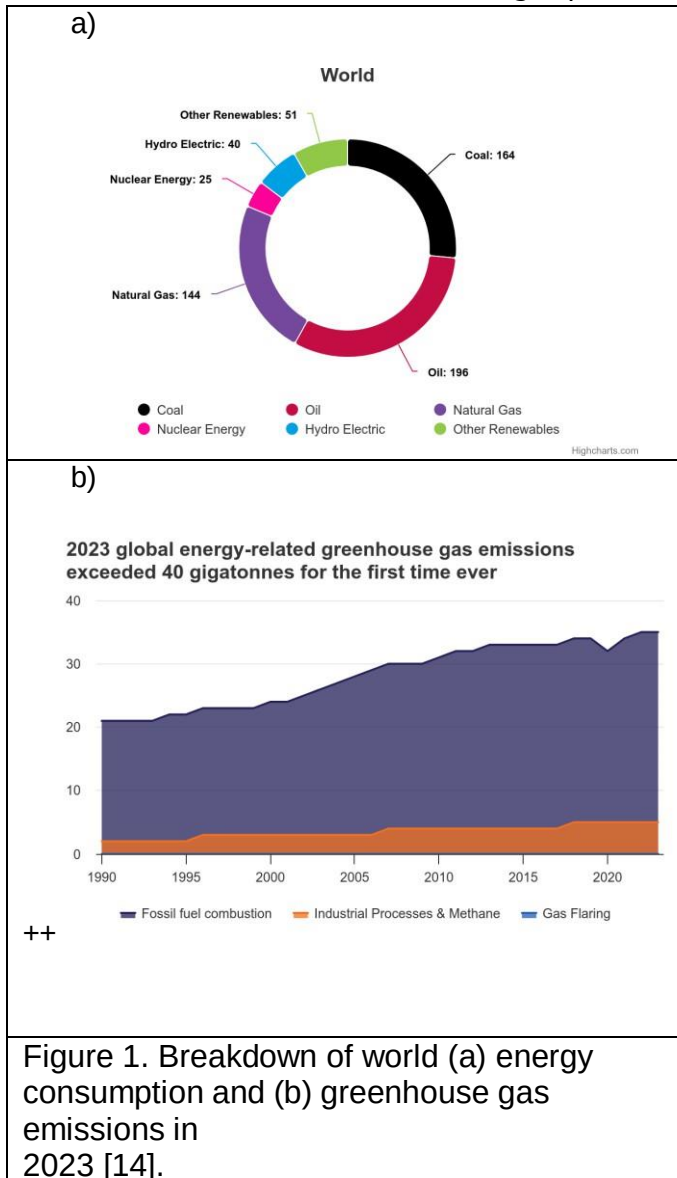


Figure 1. Breakdown of world (a) energy consumption and (b) greenhouse gas emissions in 2023 [14].

Injecting hydrogen into CI engines typically reduces emissions of CO₂, soot, CO, and UHC, while the effect on NO_x emissions varies based on factors like exhaust gas recirculation (EGR), injection methods (e.g., port and direct injection), operating conditions, hydrogen mass fraction, and diesel injection timing [15]. Engine geometry, such as compression ratio and size, also influences performance [16, 17]. Sharma and Dhar [18]'s analysis revealed that lower compression ratios reduce emissions, excluding NO_x, when hydrogen is injected through the intake manifold. Tripathi et al. found optimal crank angles for minimising emissions in a hydrogen-diesel dual-fuel engine to be 8 degrees BTDC for single injection and 16 degrees BTDC for pilot injection, with a 10% pilot mass fraction. Sharma and Dhar [18]'s experiments showed that adding hydrogen at high torque settings reduced UHC emissions by 11% and 3%. Jamrozik, Grab-Rogaliński [19] discovered

that a 30% hydrogen energy share increased in-cylinder pressure and heat release rate by 13% and 46%, respectively, while 25% hydrogen enrichment maintained engine performance. Khan, Wang [20] found that a 50% hydrogen mass fraction in a hydrogen-diesel blend improved brake thermal efficiency and torque by 5.6% and 25%, respectively. Overall, hydrogen enrichment in C.I. engines can reduce soot and carbon emissions, though its effect on NO_x emissions can vary.

Therefore, this study aims to examine the effects of HES on the performance of a hydrogen-diesel dual-fuel engine at high load. The following objectives will be investigated using 3D CFD:

- Analyse the impact of HES on BTE.
- Assess the effects of emissions such as NO_x, soot, and UHC.

2 METHODOLOGY

Three-dimensional unsteady Reynolds-averaged Navier-Stokes (URANS) computational fluid dynamics (CFD) simulations were conducted using ANSYS Forte 2023 R2 on the high-performance computing system at the University of Huddersfield.

2.1 Numerical Model

Using ANSYS Forte CFD, a tool designed specifically for modelling closed-cycle in-cylinder combustion processes, a numerical model was developed [21]. This simulation encompasses the period from intake valve closure to exhaust valve opening. The software operates under the assumption that the fluids involved behave as Newtonian fluids. The combustion process incorporates all chemical substances in both liquid and gaseous forms, quantified using the species conservation equation [21]. Fluid calculations follow fundamental conservation equations applicable to compressible fluids, namely mass, momentum, and energy conservation equations. The ANSYS Forte program utilises the Chemkin Pro solver for its combustion model.

The program gradually resolves the species' reactions based on their activation energies using reduced mechanisms derived from detailed chemical models. Diesel fuel properties were simulated using n-heptane (n-C₇H₁₆), while H₂ represented hydrogen. The reduced mechanisms, developed from skeletal kinetic models, consisted of 137 species and 1022 reactions. To

align with diesel-like properties, n-heptane was adjusted to mimic n-tetradecane (n-C₁₄H₃₀) in physical characteristics [21]. Spray properties were determined using an adaptive collision mesh model which reduces the dependability of the injector on the mesh size [40]. To simulate the combustion process starting from diesel fuel burning, the kinetic scheme must also encompass a sequence of reactions capable of describing methane and hydrogen oxidation. This study used the reduced n-heptane mechanism with 36 species for diesel and the GRIMECH 3.0 mechanism with 53 species for hydrogen combustion. Both mechanisms were merged in Chemkin Pro for dual-fuel combustion. The soot model implemented in Ansys Forte employs a two-step mechanism involving competing processes of soot formation and oxidation. Specifically, it incorporates the Hiroyasu model for soot formation [33] and the Nagle and Strickland-Constable model for oxidation [55].

A 1/7 sector mesh was employed to model the combustion chamber, considering the symmetry between the injector cylinder centre and the 7 nozzle holes, covering a 51.42° segment geometrically.

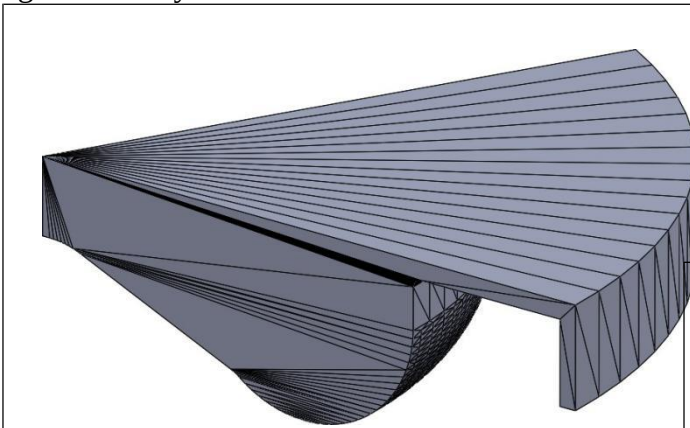


Figure 2. Sector Mesh of a diesel engine

2.2 Validations and Mesh Sensitivity Analysis

Figure 3 compares the pressure and HRR between the experimental reference [22] and four different mesh densities. All meshes reasonably capture the pressure and HRR profiles, accurately reflecting pre-combustion pressure, ignition delay, and initial heat release rate. The coarse mesh, however, fails to predict peak (Heat release rate) HRR and combustion pressure at high loads accurately and was

therefore excluded from further analysis. The medium and fine meshes better represent HRR but still slightly underpredict it, as well as the peak combustion pressure. Despite this, both meshes successfully capture overall trends, with the highly fine mesh offering only marginal improvements over the fine mesh. Consequently, the results are considered sufficiently independent of mesh density, and the fine mesh was selected for the remainder of the simulations due to its balance of accuracy and computational efficiency.

Figure 4 compares the emission predictions at the EVO in the simulations with the exhaust gases in the reference engine. The trends for UHC and NO_x at high load are well represented. However, the values are slightly overpredicted, which can be partly attributed to scaling the results with the gross indicated work output and measuring at EVO instead of directly from the exhaust gases due to simulation limitations. Discrepancies are notable in the UHC plot. Accurately capturing soot values is challenging due to the many intermediate combustion products involved, as noted by [23], suggesting the need for a more detailed reaction mechanism. Furthermore, the simulations show that the high-load primary diesel injection releases heat earlier, and the use of n-heptane as a diesel surrogate contributes to these discrepancies. More precise experimental results may also need taking soot into account in the initial gas composition at the IVC.

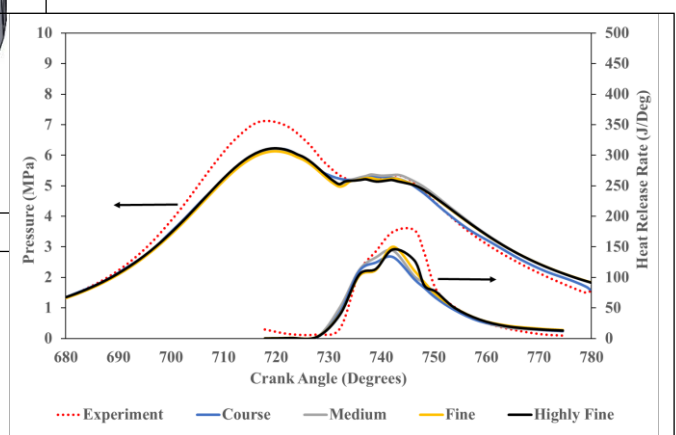


Figure 3. Experimental [22] and simulated in-cylinder pressure and HRR with different mesh densities

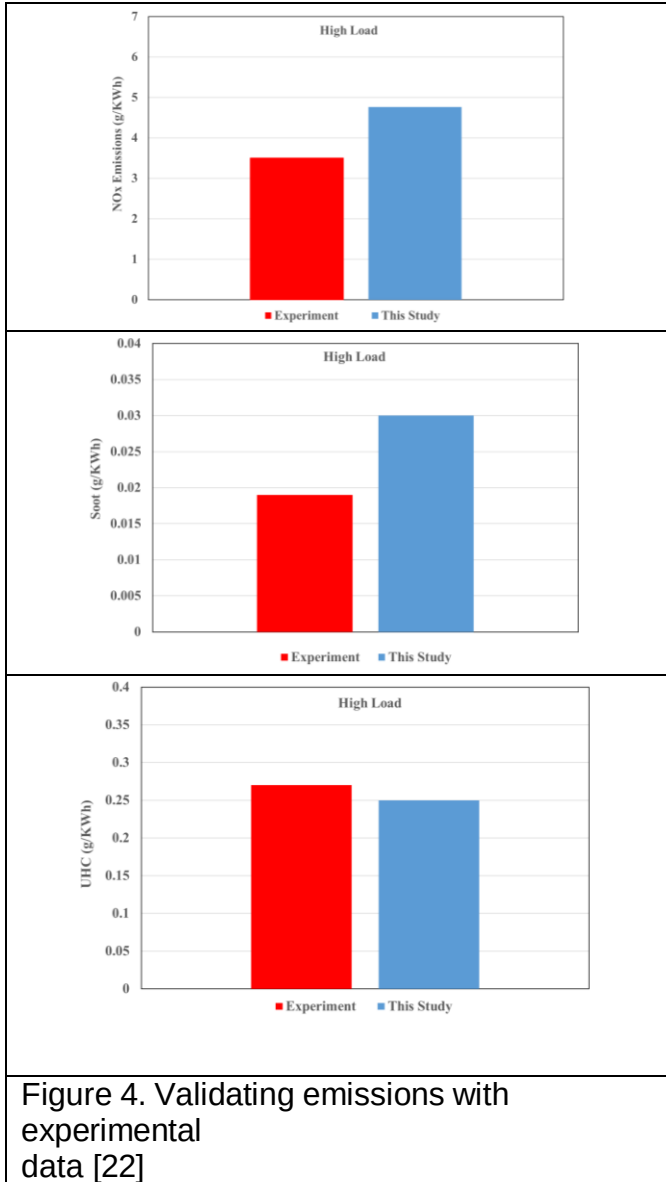


Figure 4. Validating emissions with experimental data [22]

3 RESULTS AND DISCUSSION

Figure 5 illustrates the impact of hydrogen enrichment on NOx emissions. The data reveal a significant increase in NOx levels when hydrogen is introduced, under high-load conditions. Specifically, the results indicate that the NOx emissions rise by approximately 23% with 25% HES. This observation underscores the relationship between hydrogen enrichment and NOx formation, suggesting that while hydrogen can enhance combustion efficiency, it also has the potential to elevate NOx emissions, at elevated load levels. Karagöz, Sandalcı [24] showed a similar pattern in their investigation. However, it can be handled by using exhaust gas recirculation, as explained in our previous study. Multiple reasons lead to increased NOx levels at high load. Increased combustion efficiency and energy release with more turbulence result in higher flame temperatures, which promote thermal NOx generation [25]. Furthermore, the

quicker combustion kinetics of hydrogen-enriched operation may shift combustion phasing closer to top-dead-centre, increasing peak cycle temperatures.

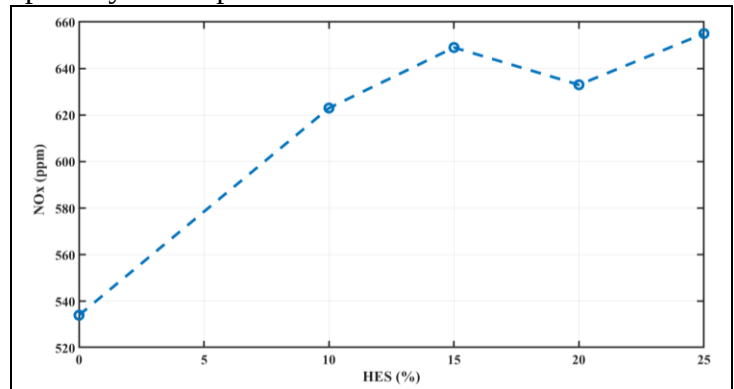


Figure 5. Effects of HES on the NOx emissions

Figure 6 demonstrates the reduction in soot emissions associated with the introduction of 25% hydrogen energy share (HES). The results indicate a substantial decrease in soot levels, with a reduction of approximately 61%. This finding highlights the effectiveness of hydrogen enrichment in mitigating soot formation, particularly at higher HES levels.

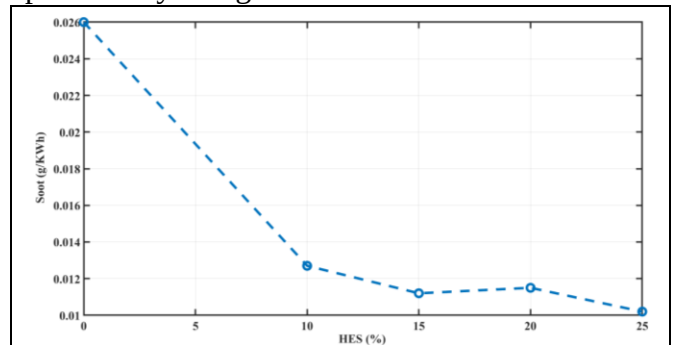


Figure 6. Effects of HES on the Soot Emissions

Figure 7 illustrates the effect of HES on UHC emissions. The data show that with a 10% HES, UHC emissions decrease significantly, by approximately 78%. This reduction highlights the efficiency of hydrogen enrichment in reducing UHC emissions, even at relatively low levels of hydrogen addition.

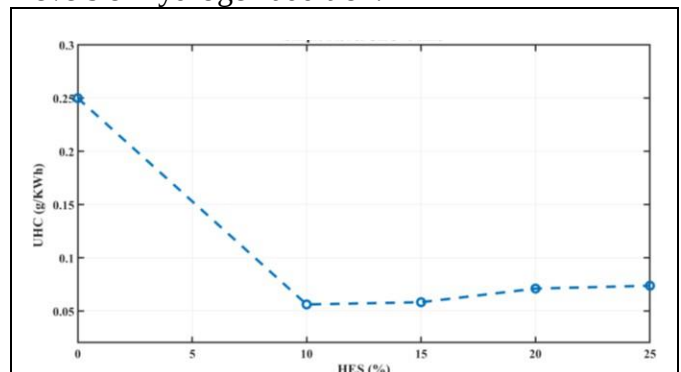


Figure 7. Effects of HES on the UHC

Figure 8 depicts the influence of HES on BTE. The results demonstrate that with a 15% HES, BTE increases by approximately 11%. This improvement indicates that hydrogen enrichment can significantly enhance the overall efficiency of the engine, particularly at this level of hydrogen integration.

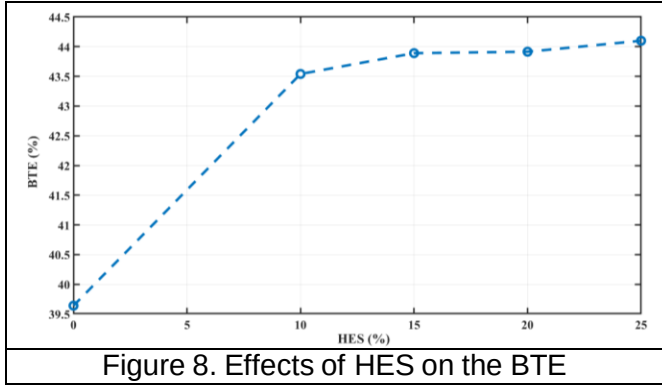


Figure 8. Effects of HES on the BTE

4 CONCLUSION

The study provides comprehensive insights into the effects of hydrogen enrichment in diesel engines, highlighting improvements. By employing CFD simulations, the research reveals that hydrogen-enriched dual-fuel engines can achieve substantial reductions in pollutants like soot and unburned hydrocarbons, as well as improvements in brake thermal efficiency. However, these benefits are accompanied by an increase in NO_x emissions, which poses a significant challenge. To fully leverage the environmental benefits of hydrogen, additional strategies are necessary to address the increased NO_x emissions.

- Hydrogen enrichment significantly improves combustion efficiency, with an 11% increase in BTE at a 15% HES.
- Substantial reductions in soot and UHC emissions are achieved, with soot decreasing by approximately 61% and UHC by 78% at a 10% HES.
- NO_x emissions increase notably, rising by about 23% under high-load conditions with a 25% HES, due to higher combustion temperatures and enhanced efficiency.
- Additional strategies, such as exhaust gas recirculation, are needed to mitigate the increase in NO_x emissions and balance the emission profile.
- Overall, while hydrogen-enriched dual-fuel engines present significant environmental advantages, further optimisation is essential

to address the trade-offs and maximise the potential benefits of hydrogen as an alternative fuel.

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A NATURE-LIKE TECHNOLOGY FOR THE RESTORATION OF TECHNOGENICALLY DISTURBED LIMESTONE QUARRY LANDS

M.S. Ivlieva

Abstract

The development of a limestone quarry has an impact on the entire natural complex of the surrounding area. Emissions into the atmosphere through liquid precipitation are filtered into the soil, forming man-made geochemical flows, under the influence of which anomalies in the content of heavy metals occur. As a result, the studied adjacent territory undergoes high environmental pressure. The paper presents the content of heavy metals in the upper horizons of rocks. Space images of the OneSoil program for the summer period of 2018 and 2023 according to the normalized vegetation index (NDVI) were used for the temporary analysis of vegetation cover in the zone of influence of the limestone quarry. For the mechanism of restoration of disturbed soils, a nature-like bioremediation technology is proposed, selected for the conditions of this study area. In the course of the work, the selection of the component composition of plants for intensive phytoextraction of increased heavy metal content was carried out, the consumption rates of seed material were proposed, and the optimal timing of work on biological reclamation of disturbed lands was determined.

Keywords: open-pit mining, nature-like technology, bioremediation, reclamation, phytoextraction, heavy metals.

Long-term anthropogenic impact on the environment during mining, it leads to an aggravation of the environmental situation. In the process of conducting open-pit mining, land is withdrawn from circulation, vegetation is destroyed, the hydrological regime of the territory changes, and the migration routes of animals and birds change. All components of geosystems are polluted, and natural objects are lost. In the zone of impact of the limestone quarry, the alienation of adjacent soils occurs for the storage of overburden in dumps. This is reflected in the change of landforms, the creation of new landforms of the technogenic landscape (pits, ridges), pollution of the atmosphere with dust, heavy metals and toxicants released during blasting along with the products of explosive decomposition and weathering of overburden. Simultaneously with the development of erosion processes, secondary geochemical flows arise around the dumps along the drain line.

The nature of their impact on adjacent soils and on biota depends on the chemical composition of overburden rocks. Chemical elements enter the soil through the atmosphere [2]. The dust containing carbonates and impurities of heavy metals spreads over considerable distances, where it then settles, getting into the soil affects its physico-chemical and mechanical properties, therefore the strongest effect is on the soil cover [4]. Rehabilitation of technogenically disturbed lands is relevant for industrial regions with developed industry, which include the Tula region.

The combined emissions from the quarry and the nearby cement production plant contain inorganic dust with a silicon dioxide content of less than 20%, the volume of which is about 200 tons/year. Nitrogen dioxide in the amount of 3,543 tons/ton, sulfur dioxide - 1,417 tons/year, carbon monoxide - 4,252 tons/ton are also present in emissions. In addition, heavy metals are present in atmospheric emissions: dust of divanadium pentoxide, cadmium oxide, cobalt, nickel, chromium, arsenic, dioxins.

Toxic and toxic substances in the emissions are mainly present due to the addition of slag to the cement production technology supplied from the metallurgical plant.

The main transporter of dissolved chemical elements are liquid atmospheric precipitation and meltwater. Flowing down the surface of dumps and tailings dumps and filtering through them beyond the dumps and tailings dumps, forming man-made geochemical flows. These flows affect adjacent soils sometimes at a distance of 30 km.

The concentration of dissolved substances in technogenic geochemical flows is highest near dumps and tailings dumps and decreases only at a considerable distance from them. This is due to the fact that various chemical elements settle on the soil surface along the flow path from its composition. The largest number of them fall out at the beginning of the stream, where an increased content of chemical elements is recorded in the soils. High concentrations of them are noted on

the flow path at some distance from the quarry at a distance of 0.3 to 6 km. This leads to the formation of concentric zones in the area of secondary (man-made) dispersion of chemical elements, including heavy metals and toxicants.

To identify the results of intensive and prolonged exposure to the chemical composition of soils and plants, X-ray fluorescence spectroscopy was studied using samples from the upper Verey horizon of the Moscow tier ds 19-1 (Table 1).

Table 1: The gross content of heavy metals in the soil of a limestone quarry, mg/ kg

Layer	Al ₂ O ₃	As	Cd	Co	MnO
ds 19-1	25,00	0,0000	0,0001	0,0036	0,03
Layer	Ni	Pb	Zn	Cu	Cr
ds 19-1	0,0103	0,0013	0,0092	0,0082	0,0108

Anomalies in the content of heavy metals occur under the influence of man-made geochemical flows. With the depth of the soil profile, their content changes (Table 2).

Table 2 Change in the content of heavy metals with depth, mg/kg

Layer	Al ₂ O ₃	As	Cd	Co	MnO
ds 19-1	25,00	0,0000	0,0001	0,0036	0,03
	Ni	Pb	Zn	Cu	Cr
	0,0103	0,0013	0,0092	0,0082	0,0108
ds 18-2	Al ₂ O ₃	As	Cd	Co	MnO
	25,24	0,0006	0,0001	0,0017	0,04
	Ni	Pb	Zn	Cu	Cr
	0,0062	0,0023	0,0079	0,0048	0,0086
ds 18-1	Al ₂ O ₃	As	Cd	Co	MnO
	26,96	0,0002	0,0000	0,0023	0,02
	Ni	Pb	Zn	Cu	Cr

	0,0053	0,0025	0,0097	0,0037	0,0086
ds 13	Al ₂ O ₃	As	Cd	Co	MnO
	8,61	0,0017	0,0002	0,0014	0,03
	Ni	Pb	Zn	Cu	Cr
	0,0054	0,0028	0,0038	0,0031	0,0078

Table 2 shows that the maximum concentrations of heavy metals are concentrated in different horizons, which indicates different mobility of heavy metals and binding to other elements. The distribution goes along the chain of Al₂O₃. Acid-base and redox conditions of soils have a great influence on the accumulation of heavy metals. Thus, under oxidizing conditions, some metals (lead, chromium) form sedentary compounds and accumulate. Other elements under oxidizing conditions remain in an easily mobile form and migrate deep into the mobile profile. Technogenic geochemical flows often carry a large number of mechanical suspensions and suspensions in their composition, which leads to the formation of surges of various capacities on the soil surface, often up to tens of centimeters. This causes a pulsation of soil formation processes and even a change in the morphological structure of the soil profile. [2]

The issue of environmental protection is of great importance and relevance today. Today, the remarkable development of the mining industry has changed the original landscape. The purpose of reclamation is to improve the state of the environment, restore the productivity of degraded lands so that in the future they can be used for their intended purpose. According to paragraph 1. GOST R 59057 – 2020 "Nature protection. Land. General requirements for land reclamation" disturbed lands of all categories, as well as adjacent land plots that have completely or partially lost productivity as a result of the negative impact of disturbed lands, are subject to reclamation. Biological reclamation of disturbed soils and

vegetation and the consolidation of soil surfaces has a long history in our country. There is no definite answer to many questions. There is no literature, there is no technology developed specifically for individual regions with different soil and climatic conditions.

Part of the surface of the deposit within the mining allotment is a developed quarry space filled with internal overburden dumps. Foci of forest in the watershed are often formed by secondary birch and aspen forests. The predominant tree species are oak, birch, aspen, from various grasses – meadow timothy, meadow clover, team hedgehog, meadow fescue, common spruce, wheatgrass.

To analyze the vegetation cover in the zone of influence of the limestone quarry, space images of the OneSoil program for the summer period of 2018 and 2023 according to the normalized vegetation index (NDVI) were used (Fig.1,2). The average NDVI index is 0.21, which corresponds to sparse and weak vegetation, lack of nutrients for biomass growth. The vegetation cover deteriorated markedly during the study period. The most disturbed area was identified, located south-west of the enterprise with the same predominance of the wind rose of the Tula region.

As a result, the studied adjacent territory undergoes high environmental pressure, leading to soil contamination. Man-made soils are characterized by their own set of agrochemical indicators that reflect the dynamics of fertility and allow it to be adjusted in the right direction. Currently, optimization of the soil structure is an urgent problem. Various bioremediation methods are used to restore disturbed soils.

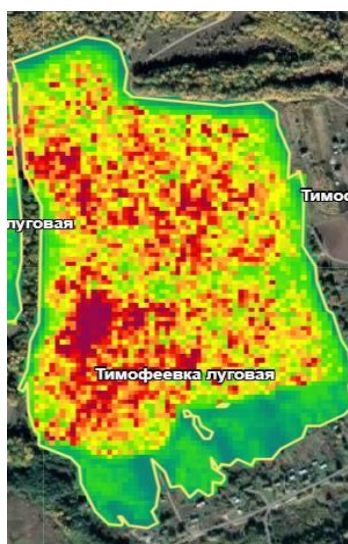


Figure 1. Space image of the NDVI index of Timofeevka lugovaya, June 2018

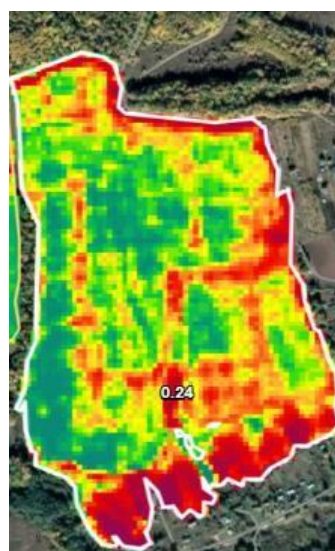


Figure 2. Space image of the NDVI index of Timofeevka lugovaya, June 2023

With an increase in the intensity of exposure to plants of any external environmental factor, they undergo a chain of changes in their physiological state in the direction of: stimulation of functions – adaptation – reversible damage – fatal outcome. As a rule, in most projects, reclamation measures are reduced to removing and preserving the fertile soil layer (PSP), applying it to disturbed areas, creating artificial soils – technozems, and conducting a biological stage of reclamation by sowing perennial grasses or planting tree crops. Despite the fact that this technology provides a fairly high level of efficiency and guarantees the restoration of vegetation to the surface of reclamation lands, work is often seriously hampered. The main obstacle to performing reclamation works with the application of PSP is the high cost of performing mining operations. It is necessary to carry out multiple surface planning and the movement of significant volumes of soils and materials of potentially fertile rocks. In modern socio-economic conditions, few enterprises can perform such work. It should also be noted that long-term storage of PSP in burts, repeated movement of PSP material and its layout by heavy technicians leads to a significant deterioration in the initial properties of PSP and a decrease in the efficiency of reclamation work. Therefore, enterprises engaged in the development of deposits often go to the violation of reclamation projects and carry out projects bluegrass – 8%, meadow timothy – 23%, boneless rump – 23%, red fescue – 23%, meadow fescue – 23%. For intensive phytoextraction of high content of heavy metals from the soil, it is proposed to use the following plants

according to a shortened scheme.

In many ways, the availability of nutrients to plants depends on many factors, the most important of which are the genetic characteristics of soils, their mineralogical and granulometric composition, the degree of acidity, climate, and biological characteristics of crops. Vegetation is the main element of the landscape, normalizing its natural functioning. On the other hand, the landscape destroyed by mining operations can actually be restored again with the help of vegetation, the process of formation of which can be regulated by man [3].

In the areas of undisturbed mining operations, it can be noted that mesophytes (42%) and basiphiles (38%) dominate, and near the face, biological diversity changes, with the predominance of oligotrophic plants (62%) and mesotrophs (22%). Together with this factor and the increased content of heavy metals in the soil, it is recommended to plant mixtures of herbaceous perennials that can quickly form sod, and plant native species of woody plants along the edge of the slopes.

For the best restoration of disturbed and polluted soils, the types of grasses should be selected in accordance with the natural characteristics of the region. The composition of the grass mixture: meadow bluegrass, meadow timothy, boneless bonfire, red fescue, meadow fescue (8:23:23:23:23:23).

For reproduction and introduction of seeds for bioregeneration, a typical grass mixture is used in the composition: meadow

Table 3
Phytoextraction of pollutants

Polluting substance	Battery Plant	Maximum accumulated concentration, mg/kg
Al	Solidago hispida [5]	6820
As	Agrostis tenuis (capillaris) [5]	2000
Cd	Thlaspi caerulescens [6]	3000
Co	Alyssum murale [7]	1320
Cr	Medicago sativa [5]	7700

Cu	Helianthus annuus L. [8]	8356
Mn	Ryegrass [9]	1020
Ni	Alyssum troodii [7]	17000
Pb	Brassica juncea [10]	26200
Zn	Thlaspi caerulescens [17]	52000

One of the criteria for assessing the potential fertility of technogenically disturbed lands is their overgrowth with higher plants: the intensity of overgrowth, the degree of projective coverage, the species composition of plants, as well as the features of their growth and development, which determines the prospect of biological reclamation of technogenically disturbed landscapes.

The calculation and technological map is used to make estimates for the restoration work. It contains a list of measures for the reclamation of disturbed lands, a list of units used in operation and information on the volume of restoration work. The procedure for drawing up calculation and technological maps is based on the technology of work, the result of which is the readiness of the site to transfer it

for agricultural use.

In order to optimize the design work, it is possible to use standard calculation and technological maps, which are developed based on the results of research in a given climatic zone, in a certain territory.

The volume of work performed is determined based on 1 ha of reclaimed area. The calculation and technological map for the biological reclamation of disturbed lands is presented in Table 4 with an indication of the technology for applying biochar to recultivated areas. The rate of application of seeds of perennial grasses is 150 kg/ha, nitroammophores (NPK 16:16:16) – 200 kg/ha.

Table 4 Technological map of reclamation of disturbed lands

No	Technological operations	Scope of work		Recommended inventory
		Unit of measurement	Per 1 ha	
1	Biochar	m ³	600	Mixer for bulk materials
2	Application of bio-carbon with a layer of 0.04 m on the recultivated surface	400 m ³	0,4	Trolleys, stretchers, shovel
3	Manual application of mineral fertilizers nitroammofoska	kg	200	Lawn Sprinkler Planter
4	Laying and fixing of the biomat	ha	1	Aluminum staples
5	Rolling	ha	1	ice rink
6	Watering if necessary	m ³	25	Watering can, motor pump

7	Fertilizing crops for 2 years with nitroammophonic	kg	30	Lawn Planter	Sprinkler
8	Sowing grass seeds randomly for the next year in problem areas	kg	22	Lawn Planter	Sprinkler

Table 5 Deadlines for carrying out work on the reclamation of disturbed lands

The stage of execution	Dates of the event
The preparatory stage	from 1 to 15 June
Technical stage	from 1 to 20 June
The biological stage	from June 20 to July 20

In the course of the research work, an assessment of man-made pollution of disturbed limestone quarry lands was carried out. The gross content of heavy metals in horizons close to the surface and concentrations in descending order are noted. The inherent natural stability of a landscape disturbed by long-term exposure is able to recover if one follows the conditions in which the origin of primary succession with plant species typical of the area took place. A similar technology is proposed to nature using biological plant materials peculiar to this territory, as well as a set of plants capable of phytoextraction. The selection of the component composition and consumption rates of seed material was carried out, the optimal timing of work on biological reclamation of disturbed and polluted lands was determined.

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CHEMICAL ANALYSIS OF THE CONCENTRATION OF HEAVY METALS, IN PARTICULATE MATTER, PM: 2.5 AND PM: 10 MG/M³, IN THE FLY ASH OF: TC "KOSOVO", COMPLEX "TREPÇA" AND FACTORY "FERRONICELI", IN THE CITIES: KASTRIOT, MITROVICA, DRENAS AND PRISTINA - CORRELATION WITH EU STANDARDS

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ABSTRACT

Kosovo is a very specific country, geographically, surrounded by all sides with the range, which is fundamentally protected, however, from the influence of the global climate, but in fact, how can this be defined when in many cases we encounter Pristina, as a city that has the primate in the world, of the day-to-day pollution of the environment, what is it that causes all this contamination, with a weak economy, why all this contamination, we have them, they are too weak filters (or have not installed them at all), then old vehicles, forest cutting, lakes contamination, above all, our awareness of a clean environment is lacking, almost `will be ours. Therefore, in this project, we will present our findings, based on chemical analysis, in the cities; Pristina, Mitrovica, Obliq, the cities considered as the most polluted, therefore, the impact on the health of residents and many other environmental impacts, in the areas analyzed will bring a realistic picture of environmental pollution, a perimeter of approximately 60km, including a triangle of the three cities analyzed.

Keywords: Heavy metals; Air, Cars, Households, Thermal power plant

EMPLOYING THE TREND ANALYSIS FOR MODELLING THE ENERGY-RELATED CARBON DIOXIDE EMISSIONS OF TURKIYE

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Abstract

Among the various human activities that emit greenhouse gases (GHGs), the primary cause of global warming, energy represents the largest source of emissions. For this reason, the majority of the existing studies have concentrated on the energy-related GHG emissions (E-CO₂), especially carbon dioxide (CO₂) emissions in order to suggest an effective tool to assist the countries in mitigating and managing the GHG emissions. Therefore, this study introduces a modelling study, employing the trend analysis (TA) for the E-CO₂. In the study where Turkiye is adopted as a case, total population and E-CO₂ are selected as the independent and dependent variables respectively. The proposed model is, then, statistically validated and forecasting accuracy is measured through several indices. Additionally, the E-CO₂ of Turkiye is forecasted for the foreseeable future. The results show that the TA can be utilized as a tool to successfully forecast the E-CO₂. Additionally, the verification and forecasting accuracies of the developed models indicate that the future E-CO₂ of Turkiye may be forecasted up to 93% accuracy. Furthermore, the forecasting results demonstrate that the total E-CO₂ of Turkiye will reach to almost 584 million tons by 2035.

Keywords: Total population, Energy-related CO₂ emissions, Model, Forecast, Turkiye place with almost 30%.

INTRODUCTION

It is widely accepted that climate change that is caused by GHG emissions poses significant risks such as rising sea levels, the potential for inundation of low-lying areas, melting of glaciers and sea ice, changes in rainfall patterns and the incidence of extremely high temperatures. These expected consequences of climate change have an impact on human health, ecosystems, key economic sectors such as agriculture, and water resources [1]. The primary drivers of climate change are the increases in energy use, global economic activities, and emissions of six key gases (namely methane, carbon dioxide, nitrous oxide, hydrofluorocarbons, perfluorocarbons, and sulphur hexafluoride) that are released as a result of these processes [2]. Among the key gases, carbon dioxide (CO₂), which can both be occurred naturally and is a by-product of fuel combustion, is the largest contributor to GHG emissions worldwide [3]. In 2022, the world's total GHG emissions reached 54 billion tons of carbon dioxide equivalent (BtCO_{2eq}), of which 38.5 BtCO_{2eq} or almost 72% was CO₂ emissions. The top six largest emitters were responsible for roughly 62% of total GHG emissions (Fig.1.). It is evident from the Fig.1 that China came in first

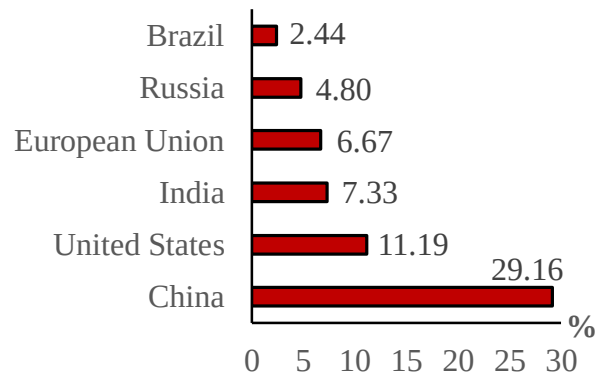


Figure 1. The top six largest GHG emitters in 2022 [4]

Located in a strategically advantageous geographic location between Asia and Europe, Turkiye has continued to maintain her status as a rising star in the region. She has over 85 million populations, representing 1.07% of the world total. As of the latest data from WBI (2024), her gross domestic product exceeded 1 trillion US dollars, with an annual growth rate of 4.52%, which was above the world's average annual growth rate of 2.72% in 2023. Additionally, Main energy resources of Turkiye are given in Table 1. One can infer from

the related Table that There are substantial coal reserves in Turkiye among the non-renewable resources. In addition, she has significant amount of renewables such as wind, hydropower and geothermal-biomass as well.

Table 1. Energy resources of Turkiye [5,6]

Resources	Amount	Share (%)
Oil (Billion tonnes)	-	-
Natural gas (Billion m ³)	544	0.29
Coal (Million tonnes)	11525	1.1
Nuclear (TWh)	-	-
Hydropower (TWh)	63.9	1.5
Wind (TWh)	34.1	1.5
Solar (TWh)	20.5	1.2
Other renewables* (TWh)	19.5	2.5

* Geothermal and biomass; TWh: Terawatt-hours

Moreover, in 2023, when the world's primary energy consumption (PEC) amounted to 620 exajoule, it was 7 exajoule in Turkiye, constituting 1.1% of the world's total PEC. The fossil fuels (FFs) dominated the PEC of Turkiye, with 81.30%. The FFs was followed by the renewables and hydropower with 10.17% and 8.53%. As it can be seen that the renewables are the second largest energy resources in Turkiye's PEC. Turkiye continues to be popular as a growing country worldwide, according to current indicators. GHG emissions do, however, also rise in tandem with this growth. In other words, in 2022, Turkiye's total GHG emissions were 687.53 million tons of CO_{2eq}, 481.25 of which were CO₂ emissions. In the same year, 420.4 million tons of GHG emissions were emissions from energy consumption. That is, 61% of the total GHG emissions resulted from the energy consumption. On the other hand, the current amount of total and energy-related GHG emissions represented 1.28% and 1.22% of the world's total and energy-related GHG emissions as well respectively [5,6]. With her share in total GHG emissions, Turkiye was among top fifteen emitters in the world. Turkiye's current situation in terms of GHG emissions indicates that it is necessary to take measures to reduce relevant emissions and eliminate future concerns as other emitters in the world. In light of this, recent years have seen the development of GHG emission forecasting models,

particularly for CO₂. Numerous scholars have used a variety of techniques from traditional to artificial intelligence to develop forecasting models for GHG emissions worldwide [7]. However, it is still vital to have realistic forecasting models of GHG emissions in order to implement the necessary controls and reductions. In addition, artificial intelligence based techniques have certain drawbacks such as black box in, when the development of the models and applied in real-world scenarios due to their complex structures. Thus, it might be more appropriate to use less precise and simpler modeling techniques to address the relevant issues. In this regards, this paper employs trend analysis (TA) to derive forecasting model for the energy-related CO₂ (E-CO₂) emissions of Turkiye using the total population (TP) as the independent variable.

DATA and methodology

Data Description

In the current study, the TP and E-CO₂ emissions were selected as the independent and dependent variables respectively. Their time span from 1980 to 2023 were utilized for the modelling study. The data for both the TP and E-CO₂ emissions were taken from publicly accessible and officially recognized online sources [WBI, 2024; EI, 2024]. Basic descriptive statistics of the selected variable are recorded in Table 2. It can be seen that the E-CO₂ emissions and TP on average are 188.10 and 61.38 respectively. Additionally, the largest values for both the variables are 341.1 and 78.2 for E-CO₂ emissions and TP, whereas the minimum values are 74.2 and 44.08.

Table 2. Results for the descriptive statistics

	Min	Max	Mean	SD	Skew ¹	Kurt ²
E-CO ₂	74.20	341.1	188.1	79.07	0.36	-0.95
TP	44.08	78.2	61.38	10.2	-0.06	-1.16

¹Skewness; ²Kurtosis and number of variables is 36

As it can be seen that Table 2 includes the skewness and kurtosis values as well. These values are indicators for the variables distribution in order to be employed statistical analysis. For an observed series to be considered symmetric or normally

distributed, the normal values for kurtosis and skewness must be zero (the ideal one). Nonetheless, some academics claim that the observed series is also assessable to a normal distribution if both values fall within ± 1.5 [8]. Based on the skewness and kurtosis in Table 2, the results suggest that every observed series has a normal distribution. In addition to the descriptive statistics of the selected variables, Fig.2 illustrates the trends of the selected variables for Turkiye. It evident from the related Figure that the TP and E-CO₂ of Turkiye have been trending increasing despite a small decrease in the E-CO₂ in 2019 due to the most probably coronavirus pandemic-COVID-19.

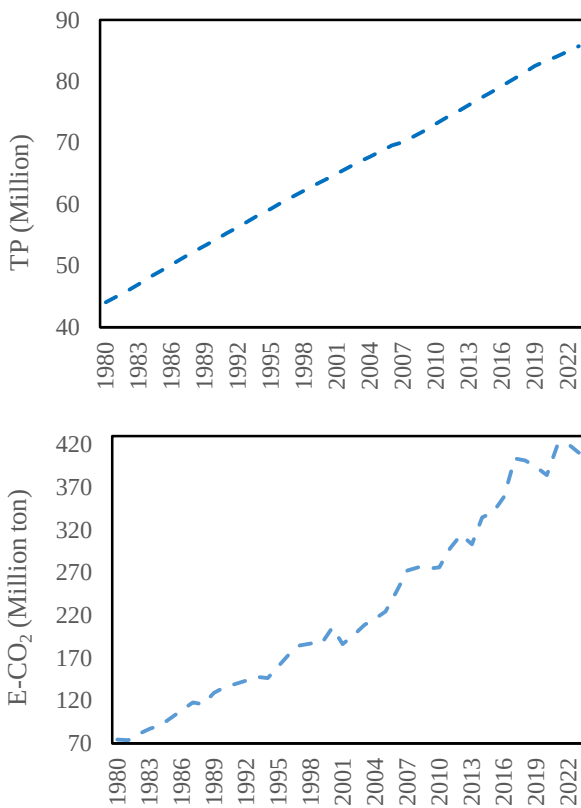


Figure 2. Trends of the E-CO₂ and TP of Turkiye [5,9]

Methodology

Owing to its primary advantages, which include ease of use and the ability to make projections using any accessible data, the TA was employed to derive the forecasting model for the E-CO₂ of Turkiye in the current study. When employing the TA, the historical trends of the variables play significant role in deriving the forecasting models. Therefore, the E-CO₂ of Turkiye were assumed to follow their historical trend throughout the analysis. In the study, one part of the data which equals

almost 82% of the total, was used for the training the model. The rest was utilized for the testing the derived model. Based on the mathematical illustrations that are given in Table 3, forecast models were developed using the SPSS software.

Table 3. Mathematical equations of the models developed through the TA

Model type	Equation
Linear	$y = a + b \cdot (t)$
Logarithmic	$y = (a) + \ln(t)$
Power	$y = (a) \cdot (t)^b$
Exponential	$y = (a) \cdot e^{b(t)}$
Inverse	$y = (a) + (b) \cdot \left(\frac{1}{t}\right)$
Growth	$y = e^{[(a)+(b) \cdot (t)]}$
S	$y = e^{[(a)+(b) \cdot \left(\frac{1}{t}\right)]}$

where; y is the E-CO₂ (million tons), a is the intercept or the constant, b is the slope, and t is the TP.

Following model development, a number of statistical tests were run to ensure the models' veracity and performance accuracy. Statistical indices for verification of the derived model are the coefficient of determination (R^2), the t-test, the F-test and the predicted versus the observed data were utilized for the verification, while those for forecasting accuracy of the derived model are mean absolute deviation (MAD), mean square error (MSE), root mean square error (RMSE), relative root mean square error (RRMSE), maximum absolute relative error (erMAX), and mean absolute percentage error (MAPE). All these statistical tests were carried out at the 95% confidence level. Table 4 gives the formulas for the performance metrics, used to measure how accurate the derived models are.

RESULTS And discussion

Model Development, Verification and Performance Accuracy

Forecasting models in all equation forms, presented in Table 3, were firstly developed and then, the best models were selected, based on mainly their MAPE and RRMSE values. It is worth to note that linear, logarithmic, power and S models give also good forecasting accuracies according to their MAPE values. However, only both of them, growth and

exponential functions, presents excellent forecasting accuracies, compared to the classifications in Table 5. Therefore, only two of the model functions have been proposed (Eqs. 1 and 2). The best models to forecast the E-CO₂ are explained by growth and exponential functions whose equation are given below.

Table 4. Metrics for assessing the models' efficacy

$MAD = \left(\frac{1}{n} \sum_{i=1}^n X_i - Y_i \right)$
$MSE = \frac{1}{n} \sum_{i=1}^n (X_i - Y_i)^2$
$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (X_i - Y_i)^2}$
$RRMSE = \frac{RMSE}{\bar{O}} \cdot 100$
$erMAX = \max \left(\left \frac{X_i - Y_i}{Y_i} \right \right)$
$MAPE = \frac{1}{n} \sum_{i=1}^n \left(\frac{ X_i - Y_i }{Y_i} \right) \cdot 100$

where; n is the total number of data, X_i is the predicted E-CO₂, Y_i is the actual E-CO₂, $\bar{O}$ is the mean value of observed data.

$$y = (11.705) \cdot (e)^{(0.043) \cdot (TP)} \quad (1)$$

$$y = e^{[(2.46) + (0.043) \cdot (TP)]} \quad (2)$$

where; y is the E-CO₂ (million tons) and TP is the total population (million).

The MAPE and RRMSE values were determined as 6.5 and 0.38 respectively for both exponential and growth functions. Results for other error analysis, employed for testing the forecasting accuracies of the proposed models are recorded in Table 6. It is evident that the proposed models have small relative errors, indicating the high accuracies in forecasting the E-CO₂.

Table 5. Forecasting abilities of the MAPE and RRMSE [10,11]

MAPE (%)	RRMSE (%)	Forecasting ability
$MAPE \leq 10$	$RRMSE < 10$	Excellent
$11 \leq MAPE \leq 20$	$10 < RRMSE < 20$	Good
$21 \leq MAPE \leq 51$	$20 < RRMSE < 30$	Reasonable
$MAPE > 51$	$RRMSE \geq 30$	Poor

Table 6. Performance metrics for the proposed models

Statistical Indices	Growth	Exponential
MAD	26.25	26.25
MSE	2.34	2.34
RMSE	1.53	1.53
RRMSE	0.38	0.38
erMAX	0.10	0.10
MAPE	6.50	6.50

Table 7 presents the validation results for the proposed models. The R^2 values of both proposed models demonstrate that TP and E-CO₂ have a substantial degree of association. Additionally, in comparison with the tabular F- and - t values, the proposed models' values are significantly greater. These results verify the statistical significance of the proposed models and the individual variables included in the derived models at the 95% confidence level. Furthermore, Fig.3 shows a significant correlation between the predicted and actual trends, indicating that the proposed models are capable of providing an accurate E-CO₂ forecast under the study's conditions. In summary, these verification results indicate that the proposed models have statistical significance.

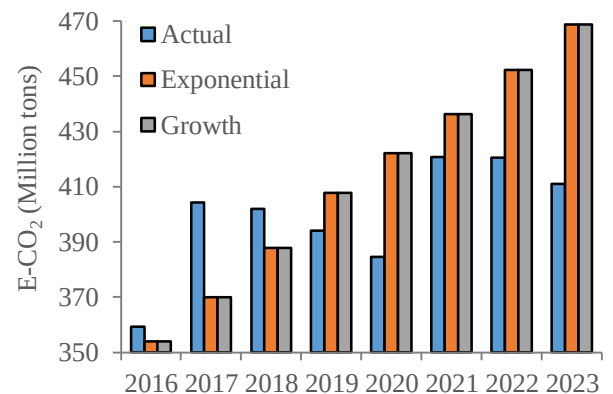


Figure 3. Actual vs Predicted E-CO₂

Table 7. Statistical verification results of the proposed models

	$t_{\text{calculated}}$	t_{table}	$F_{\text{calculated}}$	F_{table}	R^2
Growth					
Constant	41.999	1.69	2156.34	4.12	0.9
TP	46.436	0	1	5	8
Exponential					
Constant	17.072	1.69	2156.34	4.12	0.9
TP	46.436	0	1	5	8

Forecasting the E-CO₂ from 2025 to 2035

Turkiye's E-CO₂ for the years 2025 to 2035 are projected using the proposed models in this section of the study. Here, the UN's predicted data [12] on the TP was used, and the forecasting results are shown in Fig. 4. Turkiye's E-CO₂ are expected to rise in the foreseeable future for both proposed models, based on Fig. 4. To put it another way, Turkiye's total E-CO₂ will reach about 584 million tons in 2035, up 2.64 percent on average annually and 42 percent overall, when compared to data in 2023.

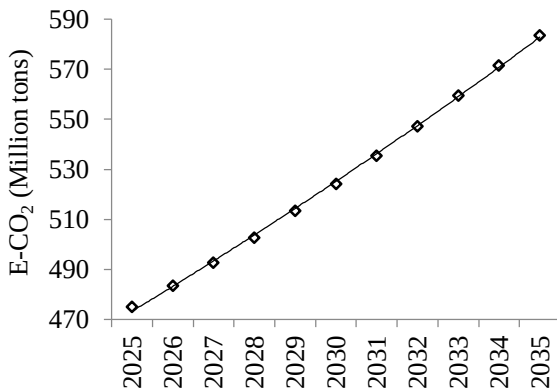


Figure 4. Forecasted results for the E-CO₂ of Turkiye

CONCLUSIONS

The current study where TA was employed to derive models for estimating Turkiye's E-CO₂, yields the following conclusions.

- It was determined that the TA is capable of derive models in order to forecast the E-CO₂ for Turkiye effectively.

- It was seen that the statistical verification and forecasting accuracy indices support the proposed models' successful usability for the E-CO₂ of Turkiye, with a forecasting accuracy up to 93%.
- It was projected that the E-CO₂ of Turkiye will increase by almost 42% totally in 2035, when compared to data in 2023.
- It was finally concluded that the E-CO₂ in Turkiye will continue to increase along with her energy consumption.

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FORECASTING METEOROLOGICAL DROUGHT USING ARTIFICIAL NEURAL NETWORKS

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Abstract

Drought is a disaster that occurs when precipitation falls below normal levels for various reasons for many years and causes the hydrological and ecological balance to deteriorate. The location, time, and duration of droughts cannot be predicted exactly. Drought is different from other natural events because it is an event that starts very slowly, develops over months and even years and affects very large areas. It is also quite difficult to determine the beginning, end, effects, and results of drought. Therefore, it is a very important to make a prediction in advance to minimize the possible effects of droughts and to minimize possible damages. Various indices have emerged to predict drought and are widely used in drought analysis. One of these indices is the Standard Precipitation Index (SPI). An important aspect of choosing SPI in this study comes from its ability to calculate drought levels for different time scales. In this study, drought prediction was conducted by using SPI12 values calculated using monthly precipitation data recorded between 1981-2020 in the city center of Kayseri by using artificial neural networks (ANN). A multi-layer perceptron type ANN model with one hidden layer was selected. Model training was accomplished by using 70% of the data and a scaled conjugate gradient backpropagation algorithm. The remaining 30% of data were used for model testing. The activation functions of the ANN model and the number of neurons in the hidden layer were determined by trial-and-error method. The performance of the model was evaluated by calculating the root mean square error (RMSE) between predicted and observer SPI12 values. The analysis showed that ANNs can be used for drought prediction.

Keywords: Drought prediction, Standard Precipitation Index, Artificial Neural Networks,

THE EFFECT OF FLOW RATE ON THERMAL, ELECTRICAL AND OVERALL PERFORMANCE OF SOLAR HYBRID PVT PANELS

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Abstract

Global energy demand is projected to rise by over 30% by 2035, emphasises the need for sustainable energy solutions. Solar energy, the most abundant and clean resource, offers a dual advantage through Photovoltaic (PV) cells and thermal panels, which convert sunlight into electricity and useful heat, respectively. However, the low electrical conversion efficiency of commercial PV cells, typically ranging from 12% to 18%, necessitates improvements in system design. Hybrid Photovoltaic Thermal (PVT) panels, which simultaneously produce electricity and thermal energy, offer a promising solution by cooling PV cells to enhance electrical conversion efficiency while capturing heat. This study experimentally investigates the impact of flow rate on the thermal, electrical, and overall performance of PVT panels, revealing that optimising flow rate is essential for maximising efficiency. By adjusting the flow rate, the balance between thermal and electrical outputs can be fine-tuned, ensuring the efficient operation of PVT systems. The findings underscore the importance of flow rate as a controllable parameter in the design and operation of solar PVT systems, which is critical for meeting future energy needs sustainably.

Keywords: Solar energy, Photovoltaic/Thermal, PVT

1 INTRODUCTION

Energy demand has increased a steadily in last decade and global consumption is expected to rise by over 30% by 2035 [1]. Solar energy is the most available and abundant clean source that can be used in the building sector. Solar energy can be converted into various forms; PV cells can convert the sunlight directly to electricity and thermal panels can convert it to useful heat. Although Solar PV cells can absorb approximately 80% of the solar energy yet electrical conversion efficiency of PV cells are quite low with the record efficiency 24.7%; commercial PV has even lower efficiency around 12% to 18% [2]. The rest of irradiation is converted to heat that increases the PV cells temperature and causing a further decrease in PV efficiency. Therefore, PV cells temperature is needed to be reduced. Solar hybrid PVT panels can be used for cooling the PV cell and simultaneously produce electricity and useful heat with the same area. Since PVT panels are producing electricity and thermal power, there are some factors effecting the fraction of thermal and electrical power production from the panel. The inlet temperature and the flowrate are the controllable operational parameters that effect the ratio of the electrical, thermal and overall performance of panels.

Experimental investigation is needed to evaluate the effect of flow rate on the thermal, electrical and overall performance of PVT panels.

2 Methodology -Experimental set up

The schematic design of experimental set up in outdoor conditions is illustrated in Figure 1.

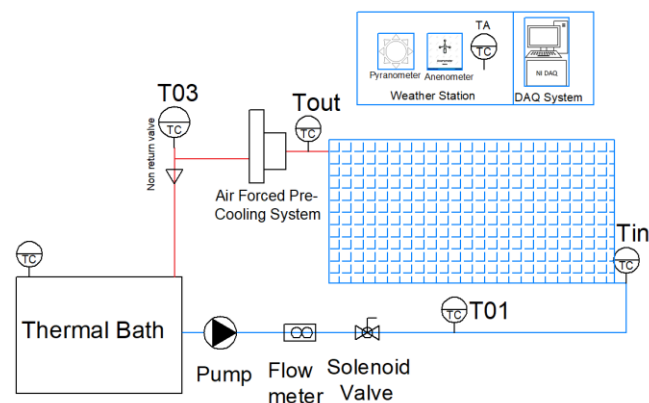


Figure 1. Experimental set up layout for PVT characterisation test rig.

The test rig was designed by following the EN 12975 standards to conduct characterisation of PV/T panels under real environmental conditions. The hydraulic system was chosen as a closed-loop circulating the fluid through the panels and returning to the thermal bath (Grant LTC4) which provided a desired inlet

temperature. Circulating the fluid and regulating the flowrate within the system, a PWM pump (Wilo-Yonos PICO-STG) was integrated. The actual flow rate was measured by ultrasonic flowmeter (Cynergy UF08B) in-line subsequent to the pump's operation. Solimpeks Powertherm PV/T panel utilised in this study encompasses an absorber area measuring 1.427m² with nominal electrical power of 180Wp, characterised by a nominal voltage of 35.15 V and a nominal current of 5.12A[3]. For the measurement, K type thermocouples (RS PRO) were used to measure inlet, outlet and ambient temperatures. A pyranometer (Kipp&Zonnen CMP10) for irradiation and an anemometer for wind speed were used for weather station. All the measurement were connected to DAQ system with NI equipment. The electrical performance were measured with PV 200 device that provided the IV curves for different flowrate.



Figure 2. Photo of the test rig at outdoor condition at Heriot Watt University, Edinburgh, Scotland.

All the test were performed at outdoor conditions at solar noon time (July, 2021) to ensure the irradiation was around 1000W/m². The inlet temperature was maintained at a constant value of approximately 21 °C while the ambient temperature was 15-16 °C. Measurements were taken only after the system reached a steady state, with altering the flow rate as controllable parameter. Due to a time lag in changing flowrate and temperature response of PVT panels, sufficient time was allowed for steady state conditions to ensure accurate data collection.

Flowrates ranging from 0.4 lpm to 2.4 lpm with 0.2 step increment were tested to evaluate its effect on the performance of PVT.

3 RESULTS AND DISCUSSION

The temperature uplift is the most important parameter on both thermal and electrical performance since it is used to calculate useful heat for thermal power and mean cell

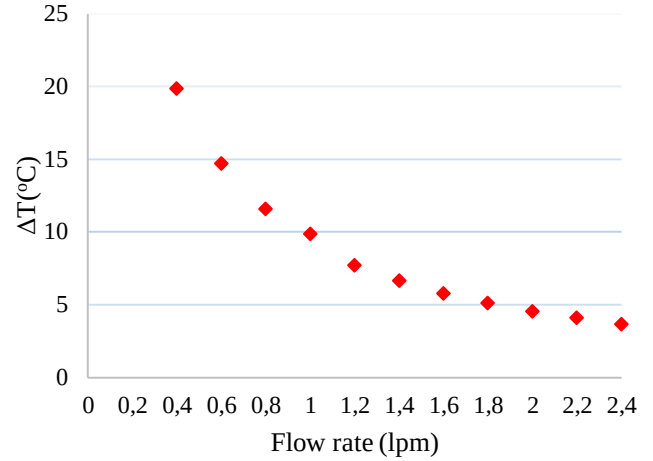


Figure 3. Temperature uplift for different flow rate.

The inlet temperature of the panel is maintained at a constant value of 21°C for all flow rate tests, enabling the evaluation of flow rate's impact on thermal performance. The lowest flow rate of 0.4 lpm yielded the highest outlet temperature of 41.03°C, resulting in a ΔT of 19.87°C. The highest flow rate of 2.4 lpm produced the smallest ΔT of 3.68°C, with an outlet temperature of 26.63°C. The figure illustrates a clear trend of decreasing ΔT as the flow rate increases. This observation aligns with a prior study by Fayaz et al. [4] which investigated flow rates ranging from 0.5 lpm to 3 lpm in 0.5 lpm increments. Fayaz et al.[4] reported a maximum fluid outlet temperature of 57.4°C at 0.5 lpm and a minimum of 33.1°C at 3 lpm, presenting their experimental findings from PV/T.

The ΔT decreased sharply from 19.87 °C to 14.75 °C with the highest drop of 5 °C by increasing the flow rate from 0.4 to 0.6 lpm. Similarly, it followed with 4 °C decrease for changing the flowrate from 0.6 to 0.8 lpm. Subsequent to the 1 lpm flow rate, the reduction in ΔT remained confined within a range of less than 2°C up to a flow rate of 2 lpm, reaching its lowest point with a diminution of 0.5°C or less subsequent to exceeding the 2 lpm threshold.

The thermal power output was computed with the measurement temperature uplift and flow rate, the thermal efficiency of the panel is a ratio of thermal power to the total incoming irradiation.

$$Q_{th} = m c (T_o - T_i) \quad \text{Eq.1}$$

$$\eta_{th} = \frac{Q_{th}}{G A} \quad \text{Eq.2}$$

4 CONCLUSION

Q_{th} : Thermal Power output (W)
 m : Mass flow rate (kg/sec)
 c : Specific heat capacity (kJ/kg-K)
 T_i : Inlet temperature (K)
 η_{th} : Thermal efficiency
 G : Solar Irradiance (W/m^2)
 A : Panel area

The electrical output from the panel was measured for each flowrate after the panel reaching the steady state conditions.

Table 1. Electrical Performance values for different inlet temperature.

Flowrate (lpm)	T_{mean} °C	P (W)	V_{oc}	I_{sc}	V_{mpp}	I_{mpp}
0.4	31.1	151	41.25	5.01	32.6	4.66
0.6	28.79	156	41.4	5.15	32.6	4.79
0.8	27.03	164.5	41.6	5.43	33.2	4.97
1	26.38	169	41.55	5.58	32.5	5.21
1.2	27.17	155.5	40.55	5.32	31.8	4.89
1.4	27.03	154.5	40.55	5.28	31.8	4.86
1.6	26.56	153.5	40.6	5.22	31.6	4.86
1.8	25.74	151.5	40.8	5.14	31.9	4.77
2	25.09	151	40.9	5.06	32.1	4.7
2.2	24.84	148.5	41.1	4.94	32.4	4.59
2.4	24.79	147	41.15	4.89	32.7	4.51

The electrical performance of the PV/T panel is related with the V_{oc} , which is directly influenced by the temperature of the PV cells. While V_{oc} decreases with higher PV cell temperatures, the I_{sc} shows a slight increase. Since the inlet temperature remains constant for all flow rates, there was a moderate variation in the outlet temperature. Consequently, the V_{oc} decreased slightly due to the rise in the mean panel temperature, which only ranged from 24.79 to 31.10°C. The overall performance of the panel is the sum up of the electrical and thermal efficiencies.

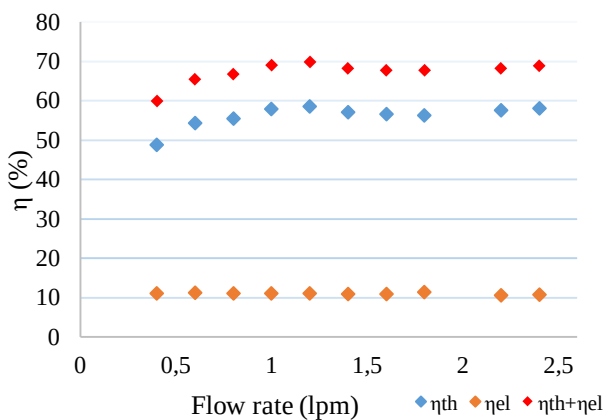


Figure 4. Electrical Thermal and Overall efficiency of PV/T for different flow rates.

The overall efficiencies exhibit a congruent pattern with the thermal efficiencies, as the variation in electrical efficiencies remained relatively modest in comparison to the thermal efficiency across various flow rates.

The flow rate of the working fluid in solar PVT panels significantly impacts their electrical, thermal, and overall performance. A higher flow rate typically enhances the thermal performance by improving heat dissipation from the panel, leading to lower operating temperatures. This reduction in temperature can positively influence the electrical performance, as photovoltaic cells generally operate more efficiently at lower temperatures. However, excessively high flow rates may result in diminishing returns, as the increased energy required to pump the fluid could offset the gains in thermal efficiency. Furthermore, the temperature gain from a panel is a crucial parameter in designing the overall system, as the integration of panels with a thermal storage unit is deemed necessary. Moreover, achieving an adequate temperature difference is essential to effectively charge the storage unit. Conversely, a lower flow rate might lead to higher temperatures, potentially decreasing the electrical output due to overheating, while also reducing thermal energy capture. Therefore, optimising the flow rate is crucial to achieving a balanced and efficient operation of solar PVT panels, maximizing both electrical and thermal outputs.

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THE EFFECT OF CLEANING PHOTOVOLTAIC PANEL SURFACES USING A CLEANING ROBOT ON PANEL EFFICIENCY: AN EXPERIMENTAL STUDY

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Abstract

The share of solar energy, which has an important place among renewable energy sources, in total energy production is increasing worldwide. Solar energy systems consist of photovoltaic (PV) panels and thermal energy collectors. PV panels directly convert sunlight into electrical energy, while thermal energy collectors utilize sunlight to produce hot water or steam. In addition to being an environmentally friendly energy source, these systems are vital for sustainable energy supply. One of the most important factors affecting the efficiency of PV panels is pollution. When panel surfaces become dirty, the amount of absorbed radiation decreases, leading to reduced output power. This study aims to determine, through measurements, the extent of production increase achieved by cleaning PV panel surfaces. To clean the 199,017 panels at the Aşağı Kaleköy Auxiliary Solar Power Plant in Bingöl Province, a robot with a cleaning performance rate of 1-3 MW/day is used. To eliminate the influence of other external factors, the cleaning process is conducted within a single day, allowing for a clear assessment of the impact of cleaning on production. The results indicate that cleaning can lead to power output increases of up to 6.19%, depending on the level of contamination.

Keywords: Solar energy, Pollution on PV panels, Efficiency of PV panels.

1 INTRODUCTION

The escalating demand for energy in our contemporary world is primarily driven by factors such as population growth, industrial and technological advancements, and an increase in living standards associated with evolving technologies. Meeting the increasing energy needs has become one of the foremost objectives for countries. Various energy sources are employed for this purpose. However, the use of fossil fuels increases atmospheric carbon dioxide levels, leading to environmental issues, notably the greenhouse effect [1,2]. Considering the limited nature of fossil fuels, the need for alternative energy sources becomes more evident. Consequently, there has been a growing focus on renewable energy sources, accompanied by intensive efforts to maximize their efficiency [3-5].

Solar energy stands out as a clean, environmentally friendly, and perpetual primary energy source. The solar radiation intensity on the surface of the sun is approximately 6.33×10^7 W/m² [6]. Beyond the Earth's atmosphere, the solar radiation intensity is conventionally considered constant at 1370 W/m² [7]. On the Earth's surface, this intensity varies between 0 and 1100 W/m² [8]. Approximately 30% of the

incoming radiation is reflected from the atmosphere. Of the remaining 70% reaching the Earth's surface, it is converted into heat energy and subsequently re-emitted [9]. Photosynthesis utilizes only a fraction of the total solar radiation, typically ranging from 3% to 6% [10,11]. The solar energy reaching the Earth's surface in a year is equal to 1.22×10^{14} tons of equivalent coal or 0.814×10^{14} tons of equivalent oil [12].

Advancements in technology have led to a decrease in the cost of solar energy systems, facilitating their widespread adoption. This utilization, initially aimed at meeting the energy needs of rural residences where electricity is unavailable, has expanded into various areas, including agricultural and industrial activities.

One crucial factor determining the amount of energy to be obtained from PV systems is panel efficiency. Several factors influence panel efficiency, some intrinsic to the panel itself, such as cell type and material properties. External factors, such as temperature, radiation levels, shading, incident light angle, and soiling, are also significant.

One of the primary factors affecting the output current and voltage of PV panels is irradiance. Panel output voltage logarithmically changes with solar irradiance, while panel output current

is directly proportional to solar irradiance. Another factor influencing panel efficiency is the angle of incidence of sunlight. Panel efficiency decreases during the first and last hours of the day and on cloudy days, depending on the angles of incident light.

A portion of the incident light on PV panels reflects from the surface, resulting in reflection losses. Constructing panel surfaces from materials with lower light reflectance will enhance panel performance. Under average irradiance, over 90% of the light incident on the panels is absorbed, while the remaining portion is reflected. However, only approximately 15-20% of the absorbed light is converted into electrical energy.

Another important factor affecting efficiency in PV systems is shading. Clouding is natural shading, and trees, buildings, and electricity poles also cause shading on the panels. In addition to all these, panels may shade each other because of the PV system's design. Shading situation must be considered during the design of PV systems. Even a 20% shading of the panel surface can lead to losses of up to 30%. Some studies have reported that losses due to shadowing can reach 50% [13].

The deposition of particles like sand, dust, algae, water, and dirt on the PV panel surface blocks and scatters incident light on the cells. Losses due to contamination vary based on geographical features and climatic conditions. Panel soiling leads to an approximate efficiency loss of around 10%. However, in areas with low precipitation and high dust levels, efficiency losses can reach 30-45%. The tilt angle of panels is typically adjustable based on the latitude of the location, commonly set between 15-20 degrees in practice [14]. Researchers have conducted numerous studies to mitigate or minimize the adverse effects of efficiency reduction and decreased operational lifespan associated with panel soiling [15-17].

This study aims to determine the effects of polluting on energy generation in PV systems. To achieve this goal, 13 PV arrays, each consisting of 27 panels, at the Aşağı Kaleköy Auxiliary Resource Solar Power Plant within the Aşağı Kaleköy Dam and Hydroelectric Power Plant in Bingöl Province, were cleaned using a cleaning robot on different days. The power values before and after cleaning were measured and compared, thereby revealing the impact of

the cleaning process on the output power of the system.

1.1 Literature Review

Hammoud et al., who studied the effectiveness of wet cleaning using robots, presented the results of their study. This study was carried out on a part of the 1 MW solar power plant in Zahrani, a coastal region of Lebanon. The robot has been designed and tested to clean the panels in this switchboard. The panels were cleaned between 15 June and 30 September 2018, and the power values produced were compared with the power values obtained without cleaning in the same period of 2017. The results revealed that the cleaning procedure had a positive effect on solar panel efficiency, with an average increase of 32.27% in electricity production [18].

Parrott et al. carried out automatic, robotic dry cleaning of solar panels in Saudi Arabia using silicone and rubber brushes, and as a result of the relevant study, they saw that the performance of a PV system increased by approximately 0.25% per day. Additionally, it was observed that the tested robotic system did not cause any significant damage to the panels [19].

Mousavi et al. designed, manufactured, and tested a suction robot called MFv01 with two sets of brushes to clean the surface of the PV array. They revealed that MFv01 has higher cleaning quality compared to Antonelli and Ecoppia T4 robots. Additionally, they revealed that MFv01 is better than Antonelli and Ecoppia T4 robots in terms of cleaning speed [20].

Syed et al., in their study, examined the effects of climatic conditions and pollution on PV module performance. Studies show that dust accumulation has a significant impact on module performance as it reduces the light transmittance of the PV module. The study summarizes past, current, and promising approaches to reducing environmental impacts and pollution. They have shown that the combination of the electrostatic cleaning method and micro/nanoscale surface functionalization method has the potential to counteract the negative effects of dust accumulation, especially in arid regions [21].

By Kayri et al., another study on the subject was conducted in Batman in 2021 to investigate the effect of dusting on panel efficiency. In this study, they measured the energy values produced by a clean PV panel and a PV panel with 5-day, 1-month, and 6-month-old dust

accumulated on its surface. According to the data obtained as a result of the study, the difference between the clean panel and the panel exposed to 5-day dusting is 5.26%; There was a difference of 28.49% less energy production between the panel exposed to dust for 1 month and 78.38% difference between the panel exposed to dust for 6 months [22].

In the study by Ghazi et al., it has been argued that various innovative methods are used to clean the surface of dirty PV panels, but the cleaning mechanism should be demonstrated with a holistic approach in different climatic conditions. The dust distribution pattern in different regions of the world has been evaluated and it has been determined that the Middle East and North Africa Regions have the worst dust accumulation regions in the world. Finally, a set of recommendations and guidelines for a suitable cleaning system for different climatic zones and characteristics are presented, especially for PV system installers [23].

Dahlioui et al., a study was conducted to provide an ecological solution for cleaning PV modules. The study area is located in the city of Rabat in northwestern Morocco. To examine the effect of dew water formed on the surface of the windshield on the cleanliness of the PV modules, systematic pollution rate measurements were carried out. Experiments were carried out on glass surfaces exposed to real outdoor conditions. The contamination rate was made by measuring the radiation transmitted and received by the glass. At approximately sunrise, the subsequent permutation of the glass from horizontal to a 30° tilt angle favors the flow of dew droplets. Then, the effectiveness of cleaning was investigated. A comparison of dewwater flux and fouling losses of fixed glass and variable glass is presented. Pollution losses for fixed glass were found to average 9.3% over the exposure period, while variable glass was only 3.3%. In other words, losses due to contamination for fixed glass are three times higher than for variable glass with cleaning using raw water [24].

The effects of dust on PV panel efficiency and the factors that manage dust accumulation on the panel were reviewed by Fardila et al. Dust is one of the unchangeable environmental factors and can cause physical damage, a decrease in incoming solar radiation, and decrease in PV panel efficiency due to temperature increase. As

a result of 20 g/m² dust accumulation on a PV panel, the measured short circuit current decreases by 15–21%, the open circuit voltage decreases by 2–6% and the efficiency decreases by 15–35% [25].

2 PV SYSTEMS

2.1 Structure of the PV Systems

PV systems transform sunlight into electrical energy. Solar cells were first investigated by Becquerel in 1839 [26]. The energy from sunlight is carried by photons. When photons strike the panel's surface, a portion of them is absorbed by the panel, resulting in the generation of energy.

The PV cell shown in Figure 1 is made of semiconductor materials that absorb sunlight and generate an electric current. Electrons in the upper layer of the cell move to the lower layer with the assistance of solar energy. The movement of electrons between the two layers enables the generation of an electric current.

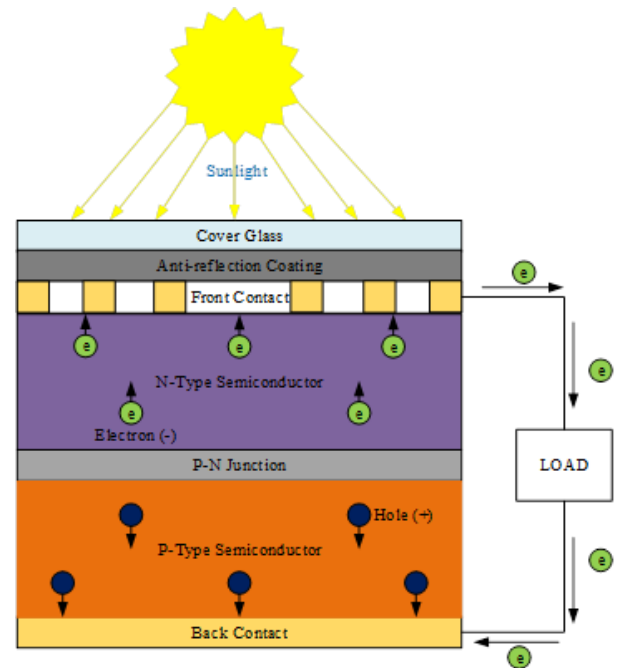


Figure 1. The operating principle of the PV cell

The PV cell current (I_{Ph}) varies directly with the intensity of incident solar radiation on the cell [27].

$$I_{Ph} = [I_{sc} + k_{i-sc} \cdot (T_{Ph} - T_{ref})] \cdot \frac{G}{G_{ref}} \quad (1)$$

Here;

I_{Ph} : PV cell current

I_{sc} : Short circuit current under conditions of 25 °C and 1000 W/m²

k_{i-sc} : Short-circuit current temperature coefficient
($k_{i-sc}=0,0017 \text{ A/}^{\circ}\text{C}$)

T_{ph} : PV cell temperature in Kelvin

T_{ref} : Reference temperature value ($T_{ref}=298,15 \text{ }^{\circ}\text{K}$)

G : Amount of solar radiation (W/m^2)

G_{ref} : Reference solar radiation amount
($G_{ref}=1000 \text{ W/m}^2$)

A PV panel is a direct current (DC) electricity generator with multiple cells that absorb solar energy. When the panel is unloaded and exposed to maximum irradiance, the measured voltage across the panel terminals is the open-circuit voltage (V_{oc}). At maximum irradiance, the output terminals of the panel are short-circuited to measure the short-circuit current (I_{sc}). Open-circuit voltage and short-circuit current are fundamental parameters calculating the panel power. Figure 2 illustrates the I-V and P-V characteristic curves of a PV panel. As can be seen in the figure, the power is zero at short circuit current and open circuit voltage values. PV panel output current increases as the amount of radiation increases. Due to this increase, the I-

V characteristic curve moves upward. The maximum power point (P_{MP}) is the point on the curve where the slope is zero.

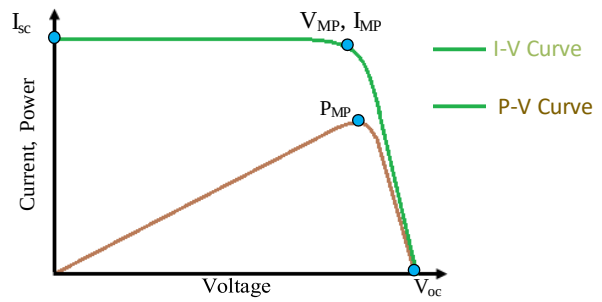


Figure 2. I-V and P-V characteristics of PV panel

The basic diagram of a PV system is presented in Figure 3. As can be seen in the diagram, a PV system consists of a PV panel, inverter, battery, charge controller, and loads.

When examining Equation 1, it is evident that solar irradiance directly influences the current generated in the PV cell and, consequently, the output power of the panel.

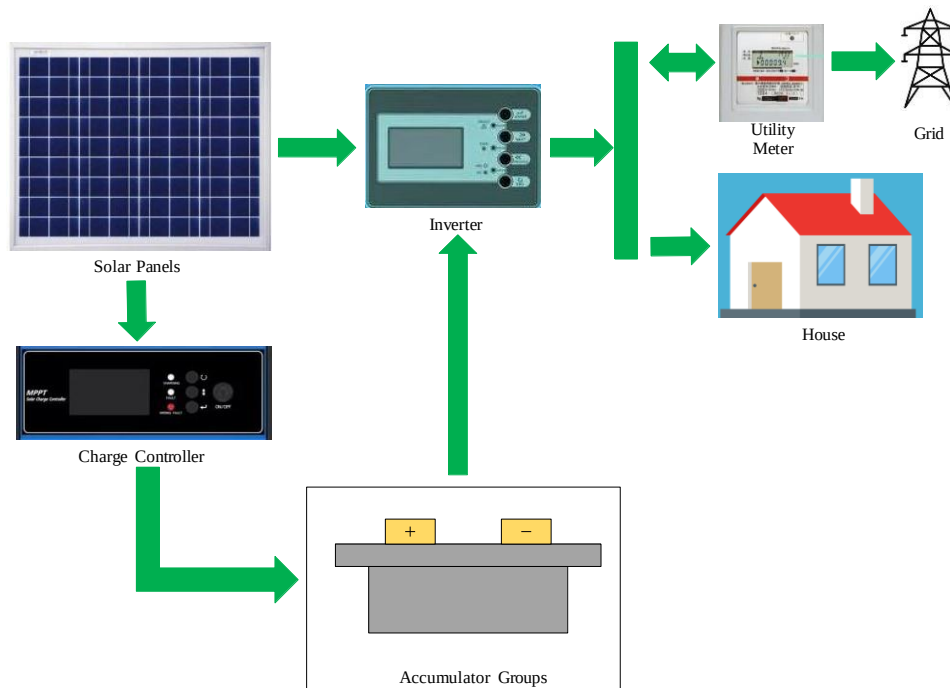


Figure 3. The fundamental diagram of a PV system

DC voltage is obtained at the output of PV panels and DC loads can be powered directly. To supply AC loads, an inverter is connected to the panel output to convert DC energy into AC energy. Due to variations in sunlight intensity throughout the day and under different seasonal conditions, the power generated from the panels also varies. For this reason, the power

generated from the panels may sometimes be insufficient or excessive. If the energy produced is more than the amount demanded, the excess energy can be stored in batteries. During periods of insufficient generation, the stored energy in the batteries can be utilized to continuously power loads.

Batteries should be exposed to a constant voltage while charging. Since the output voltage of PV panels is variable, it is not suitable to directly connect batteries to PV panels for charging. Additionally, once the batteries are fully charged, the voltage should be cut off. To eliminate all these problems, battery charge controllers are used. In PV systems where batteries are not used when generation is greater than consumption, the excess energy generated is given to the grid, and when production is insufficient, the required energy is drawn from the grid. Bi-directional meters connected to the distribution panel in PV systems record the values of energy drawn from and fed into the grid. This allows consumers and distribution companies to make payments to each other based on these values.

PV systems are divided into two main categories: off-grid and on-grid. In on-grid systems, the electrical energy generated from solar panels is converted into AC voltage with grid frequency using inverters. The excess energy that is not consumed is transferred to the grid. If the amount of energy consumed by the load is more than generated by PV panels, the load is supplied by the grid.

In off-grid systems, the electrical energy generated by solar panels is also converted into AC voltage using inverters. Excess energy not used by the loads is stored in batteries. During periods of insufficient energy production, the stored energy is converted back into usable form by the inverter. These systems require additional battery systems. So, they are relatively expensive. Additionally, due to storage losses, their efficiency is comparatively lower.

2.2 Efficiency of PV Systems

The efficiency of a PV system is defined as the ability to convert sunlight into electrical energy, typically expressed as a percentage. Efficiency determines the effectiveness of PV systems in generating electricity and depends on several factors. First, the intensity and duration of sunlight determine the amount of energy reaching the PV cells. Higher solar intensity and longer exposure generally lead to higher efficiency. Second, the materials and design of PV cells impact efficiency. The electron transport properties of semiconductor materials are key factors in cell efficiency.

Third, the treatment of the cell surfaces and back sides reduces reflection, allowing them to absorb more light and thus increasing efficiency. Finally, the matching and electrical connections among the components of PV systems also affect efficiency. With modern technologies, there's a constant increase in PV cell efficiency, making PV systems more attractive for commercial and industrial use. Therefore, the efficiency of PV systems is critical for the widespread adoption of solar energy and the promotion of sustainable energy transition.

PV systems use sunlight to generate electricity, but the intensity and characteristics of solar radiation play a determining role in system efficiency. The intensity of solar radiation sets the number of photons hitting the PV cells and thus affects the electrical current output of the system. Higher solar radiation intensity typically results in higher electrical current output, contributing to increased system efficiency. However, the characteristics of solar radiation are also important. For example, the wavelength and spectral composition of light are absorbed differently depending on the material properties of PV cells. Some PV technologies are more effective at certain wavelengths, while others perform better across a broader spectrum. Thus, the characteristics of solar radiation play a crucial role in the selection and design of PV systems. Additionally, the angular position of solar radiation affects the performance of PV systems. When sunlight is direct, PV cells perform at their maximum, while efficiency may decrease at different angles or on cloudy days. Therefore, the impact of solar radiation on efficiency should be considered in the design, positioning, and operation of PV systems. Research in the literature focuses on better understanding the effects of solar radiation and developing various methods to enhance the efficiency of PV systems.

3 MATERIAL METHOD

The efficiency of PV systems is one of the factors that requires regular maintenance and cleaning. Dust, pollen, bird droppings, and other pollutants accumulated on the surfaces of solar panels can prevent sunlight from reaching the panel surface, thus causing a decrease in electricity production. Therefore, regular cleaning of PV systems is important to ensure

maximum efficiency and performance. Traditionally, PV panel cleaning was carried out manually, but in recent years automatic cleaning robots have begun to be developed. These robots are generally designed to scan the panel surface, detect and clean contaminants. Using of automatic cleaning robots can reduce labor costs by saving manpower and making system maintenance more effective. Additionally, regular cleaning can extend panel life and reduce maintenance costs. However, the efficiency of cleaning robots may vary depending on their design features, the cleaning technology used, and application conditions. In some cases, especially in highly polluting environments or harsh weather conditions, manual cleaning may still be necessary. Therefore, the use and effectiveness of cleaning robots in PV systems should be carefully examined and evaluated by the application conditions. Research is ongoing to improve the design and performance of cleaning robots, making the maintenance of PV systems more efficient and economical.

The Aşağı Kaleköy Dam and Hydroelectric Power Plant project is situated approximately 2 km downstream of the confluence of the Yiğitler Stream and the Murat River, in Bingöl Province, Turkey. The construction of the dam, which spans the Murat River, was completed in December 2019. It was completed in December and has been generating 1,219.20 GWh of energy annually with an installed capacity of 500.00 MWe since the first quarter of 2020.

The Aşağı Kaleköy Auxiliary Resource Solar Power Plant (SPP) is located downstream from the Aşağı Kaleköy Dam, along the river regulation areas on the right and left banks, covering a total area of 1,100 dönüms (approximately 110 hectares). Commissioned in the last quarter of 2020, the Aşağı Kaleköy Auxiliary Resource SPP Facility, together with the Aşağı Kaleköy Dam and Hydroelectric Power Plant, has earned the title of Turkey's First Combined Renewable Energy Generation Facility. Furthermore, with 200,000 photovoltaic panels and an installed capacity of 79.99 MWm, the Aşağı Kaleköy Auxiliary Resource GES Facility is Turkey's largest solar power plant outside of the Renewable Energy Resource Areas [28].

3.1 Features of the Cleaning Robot Used

A cleaning robot powered by AC voltage was used in the study. The cleaning robot was powered by a mobile diesel generator. Pure water was used to increase the performance of the cleaning robot. Depending on the dirtiness of the cleaned panels, the speed of the robot was manually adjusted to be slower on dirty surfaces and faster on clean surfaces. A plastic bristle brush was used in the robot to prevent damage to the panel while cleaning. Some technical characteristics of the cleaning robot are shown in Table 1. The image of the cleaning process is shown in Figure 4.

Table 1. Cleaning Robot Features

Working system	Electric AC Motor
Length	4200 mm
Voltage	220 V AC
Brush length	4000 mm
Cleaning speed	10-30 Minute/Meter
Cleaning Performance	1-3 MW/Day
Temperature Operating Values	(+ 60)°C – (-10) °C
Water Consumption	8-20 Liter/Minute



Figure 4. The image of the cleaning process

There are 7371 arrays in Aşağı Kaleköy Auxiliary Solar Power Plant. Each array has 27 panels. In the plant, where there are panels of 4 brands, panels with the same features were used for the data in the study. The cleaned panels have a power of 400 W. The label values of the panels subjected to the cleaning process for this study are shown in Table 2.

Table 2. Cleaning Robot Features

Maximum Power (Pmax)	400 W
Power Selection	0~+5 W
Open Circuit Voltage (Voc)	48.7 (±5%) V

Short Circuit Current (Isc)	10.79 ($\pm 5\%$) A
Maximum Power Voltage (Vmp)	40.7 V
Maximum Power Current (Imp)	9.84 A
Weight	22.5 kg
Dimension (mm)	2008x1002x35
Fuse Current	20 A
Maximum System Voltage	1500 V
Operating temperature	45 $\pm$ 2 °C
Application Classification	Class II

4. RESULTS AND DISCUSSION

13 PV arrays, each consisting of 27 panels, were subjected to cleaning between 17.08.2021 and 23.08.2021. To eliminate the influence of external factors, the cleaning was performed at the same time each day under similar conditions. The output currents and voltages of the panels were measured to calculate the power values. Measurements made before and after cleaning are presented in Table 3 and Table 4, respectively. To facilitate easy comparison, the panel output powers are given together in Table 5. Additionally, the output powers are presented graphically in Figure 5.

Table 3. Values measured of PV Panels before cleaning

Date	Time	Temperature (°C)	Array No	Current Value (A)	Voltage Value (V)	Generated Power (W)
17.08.2021	12:01	36	1	8,957	1000	8.957,0
17.08.2021	12:01	36	2	8,784	1001	8.792,8
18.08.2021	12:01	36	3	8,844	1000	8.844,0
18.08.2021	12:01	36	4	8,611	1002	8.628,2
19.08.2021	12:01	36	5	8,668	1004	8.702,7
19.08.2021	12:01	36	6	8,713	1001	8.721,7
20.08.2021	12:01	36	7	8,912	1002	8.929,8
20.08.2021	12:01	36	8	8,884	1000	8.884,0
21.08.2021	12:01	36	9	8,798	1003	8.824,4
21.08.2021	12:01	36	10	8,587	1000	8.587,0
22.08.2021	12:01	36	11	8,684	1001	8.692,7
22.08.2021	12:01	36	12	8,779	1002	8.796,6
23.08.2021	12:01	36	13	8,836	1003	8.862,5

Table 4. Values measured of PV Panels after cleaning

Date	Time	Temperature (°C)	Array No	Current Value (A)	Voltage Value (V)	Generated Power (W)
17.08.2021	12:06	36	1	9,127	1000	9.127,0
17.08.2021	12:06	36	2	8,968	1001	8.977,0
18.08.2021	12:06	36	3	9,040	1000	9.040,0
18.08.2021	12:06	36	4	8,879	1002	8.896,8
19.08.2021	12:08	36	5	9,018	1004	9.054,1
19.08.2021	12:08	36	6	8,889	1001	8.897,9
20.08.2021	12:08	36	7	9,370	1002	9.388,7
20.08.2021	12:08	36	8	9,124	1000	9.124,0
21.08.2021	12:10	36	9	8,973	1003	8.999,9
21.08.2021	12:10	36	10	8,754	1000	8.754,0
22.08.2021	12:10	36	11	8,872	1001	8.880,9
22.08.2021	12:10	36	12	8,964	1002	8.981,9
23.08.2021	12:12	36	13	9,383	1003	9.411,1

Table 5. Power Values of PV Panels before and after cleaning

Array No	Power Values Before Cleaning (W)	Power Values After Cleaning (W)	Different (%)
1	8.957,0	9.127,0	1,90
2	8.792,8	8.977,0	2,09
3	8.844,0	9.040,0	2,22
4	8.628,2	8.896,8	3,11
5	8.702,7	9.054,1	4,04
6	8.721,7	8.897,9	2,02
7	8.929,8	9.388,7	5,14
8	8.884,0	9.124,0	2,70
9	8.824,4	8.999,9	1,99
10	8.587,0	8.754,0	1,94
11	8.692,7	8.880,9	2,17
12	8.796,6	8.981,9	2,11
13	8.862,5	9.411,1	6,19

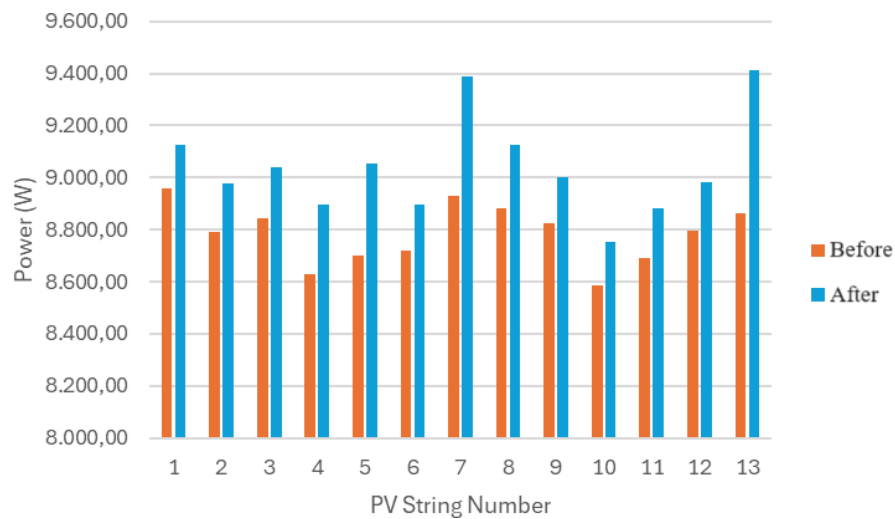


Figure 5. The image of the cleaning process

5. CONCLUSION

The 13 PV arrays at the Aşağı Kaleköy Auxiliary Solar Power Plant were cleaned between August 17 and August 23, 2021, at the same times each day. The cleaning process was carried out using a cleaning robot with a 4-meter brush length and a cleaning capacity of 3 MW/day. To assess the impact of cleaning on the output power of PV systems, current and voltage measurements were taken before and after cleaning, and power values were calculated. The measurements made and the power values obtained are presented in tables and compared graphically. As can be seen from

the values in the table, the increase in power output after cleaning reached 6.19%. Since the panels are located in a hydropower plant area, dust accumulation is relatively less compared to other rural areas. However, even under these conditions, a 6.19% increase is significant. Considering that the total installed power of the Solar Power Plant is 79.99 MW, the importance of the 6.19% increase that the cleaning process will provide will be better understood.

The performance of the robot used in the cleaning process enabled the cleaning process to be carried out very quickly. This rapid

cleaning process helped to illustrate the effects more clearly.

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ENHANCING SOLAR ENERGY FORECASTING THROUGH CHAOS THEORY AND ECHO STATE NETWORKS: A CASE STUDY OF THE KONYA EREGLI SOLAR POWER PLANT

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Abstract

This study explores the application of chaos theory and neural networks to forecast solar energy output from the Konya Eregli Solar Power Plant (SPP) in Turkey. The research primarily uses an Echo State Network (ESN) model, leveraging the False Nearest Neighbors (FNN) method to optimize the embedding dimension for accurate time series prediction. Time series data for this study include solar power production (endogenous data), ambient and solar cell temperature values (exogenous data). Initial findings reveal a high FNN ratio, indicating complex dynamics and the necessity for sophisticated modeling. Incorporating exogenous variables significantly reduces the FNN ratio, enhancing the representation of system dynamics. The optimized embedding dimension leads to an FNN ratio below 0.05, signifying effective capture of the time series' dynamics. Subsequent analyses use the ESN model on both the original and embedded data, demonstrating improved prediction accuracy with the embedded data. This study underscores the importance of embedding dimension optimization and the inclusion of exogenous variables in enhancing solar energy forecasting in the concept of chaotic modelling.

Keywords: Solar Energy Forecasting, Chaos Theory, Echo State Networks, Embedding Dimension Optimization

1 INTRODUCTION

Solar energy captures power from the sun using photovoltaic cells or solar thermal systems, providing a renewable and clean energy source. Its widespread adoption contributes significantly to Sustainable Development Goals (SDGs) by promoting affordable and clean energy (SDG 7), reducing greenhouse gas emissions to combat climate change (SDG 13), and fostering economic growth and innovation (SDG 8 and 9). Additionally, solar energy improves energy access in remote areas, enhancing quality of life and supporting sustainable communities (SDG 11). Through these contributions, solar energy plays a vital role in advancing global sustainability and resilience.

Solar energy output power refers to the electricity generated by solar panels over time (photovoltaic power), often analyzed as a time series to assess performance and variability. This output power can fluctuate due to factors like weather conditions, shading, and panel efficiency. Solar irradiance, on the other hand, is the power per unit area received from the sun in the form of electromagnetic radiation [1], which directly

influences but is distinct from the actual electrical output of solar panels, as the latter also depends on the conversion efficiency of the panels and other system losses. Generally, studies in the field of solar energy forecasting include two main categories. The first category refers to studies in which aim to forecast the irradiance or try to forecast the produced solar power by using irradiance time series, or by only exogenous variables. The second category includes studies which try to forecast generated power output by using historical values of the power output extracted from its time series data. This category is referred to as direct forecasting in this study.

1.1 Contributions of this work

This study presents a direct forecasting of solar energy production by integrating both endogenous and exogenous input variables into the forecasting models, rather than relying solely on meteorological variables. It implements chaotic analysis and trains an optimized Echo State Network (ESN) model on solar output energy generation time series data, a method capable of providing accurate forecasts that is often overlooked compared to support vector

machines and artificial neural networks. By comparing the ESN model's performance on both original and embedded data, the study demonstrates the superiority of the optimized, embedded data approach, highlighting the importance of proper data preprocessing and dimensionality optimization in achieving higher forecasting accuracy.

2 LITERATURE REVIEW

Most of the papers reviewed in this section rely on meteorological data or other external inputs, such as electricity market data, which are not directly related to the electrical setup. Consequently, these studies mainly concentrate on the meteorological aspects of energy conversion rather than on the electrical infrastructure. This focus may be because photovoltaic (PV) power production depends on operational parameters such as inverters and nonlinear and artificial parameters like panel temperature, which are much more challenging to model and predict compared to natural parameters. Considering all these factors makes forecasting in this area particularly difficult. Within the concept of direct forecasting models, the study of [2] provides a comprehensive and well-organized review, detailing how the relationship between input and output data impacts outcomes and emphasizing the benefits of optimizing these forecasting models.

Authors in [3] present a comprehensive Systematic Literature Review (SLR), focusing on the types of input data used in solar energy production forecasting and the most commonly implemented forecasting methods. This LSR indicates a couple of important points in the field of solar energy forecasting, which includes but is not limited to 1- Significant use of artificial neural network and Support vector machine methods comparing to other machine learning methods. 2- deficiency is use of electricity related data. 3- Lack of data pre-processing.

Forecasting is the most important optimization concept for improving energy efficiency and making accurate decisions [4]. On the other hand, Chaos theory, which emerged in the 1970s, is a fundamental aspect of nonlinear science [5]. According to Chaos theory, "Chaos is a long-term non-periodic behavior in a predictable system with a high sensitivity to initial conditions" [4]. This theory uncovers patterns within seemingly random and disorganized events, influencing and supporting many fields. As a result, chaos

research offers valuable solutions. Applications of Chaos theory are prevalent in various scientific domains, including wind farms [6], oil, gas, and solar photovoltaic systems [7].

3 MATERIALS AND METHODS

3.1 Chaos-based Neural Network: Echo State Network

Reservoir computing RC primarily draws from the concepts of recurrent neural networks but features a simpler training process. In RC, only the weights of the output layer are trained, while the other parameters are set randomly and remain untrained. Chaos-based neural networks integrate principles from chaos theory and neural networks, resulting in models skillful at handling complex behavior and recognizing patterns. Echo State Networks [8] are the most widely used approach for implementing the RC method [9]. ESNs have proven effective in predicting future steps in nonlinear time series and modeling chaotic dynamic systems, all while demanding minimal computing power [10].

3.2 False Nearest Neighbors

The false nearest neighbors (FNN) algorithm was initially created to identify the minimal dimension of a regression vector required to accurately reproduce the behavior of autonomous chaotic systems [11]. The concept of the FNN algorithm is based on geometry. When the regression vector contains sufficient information to forecast future output, two regression vectors that are close in the regressor space will also have similar future outputs. However, if the regression vector lacks enough terms to replicate the system's dynamics, certain neighborhoods in the regressor space will exhibit a wide variation in their associated future outputs. Trajectories that are close in the regression space but have significantly different outputs can be considered false neighbors. This occurs because their proximity is due to being projected onto a space with too few dimensions to accurately capture the system's dynamics [12].

3.3 Metrics of evaluation

The forecast results of our trained ESN model in this study are evaluated using the following criteria that are presented in Equation (1) to (5). Considering that $\hat{y}_i$ is the predicted value of the i -th observation y_i , and $\bar{y}$ is the mean of the actual values.

- Mean absolute error

$$MAE = \frac{1}{n} \sum_{i=1}^n |y_i - \hat{y}_i| \quad (1)$$

- Mean squared error:

$$MSE = \frac{1}{n} \sum_{i=1}^n (y_i - \hat{y}_i)^2 \quad (2)$$

- Root mean squared error:

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (y_i - \hat{y}_i)^2} \quad (3)$$

- Mean absolute percentage error:

$$MAPE = \frac{100}{n} \sum_{i=1}^n \left| \frac{y_i - \hat{y}_i}{y_i} \right| \quad (4)$$

- R-squared:

$$R_2 = 1 - \frac{\sum_{i=1}^n (y_i - \hat{y}_i)^2}{\sum_{i=1}^n (y_i - \bar{y})^2} \quad (5)$$

4 EMPIRICAL STUDY

4.1 Dataset

The data for this study is provided by Tegnatia Enerji, the company responsible for constructing the Konya Eregli Solar Power Plant (SPP), in Konya city, Turkey. This SPP has a capacity of 9.20 MWp and has been grid-connected since April 2016. Data includes the time series of solar power production for eight inverters in the field, from 2021-06-06 to 2022-12-08, having a 10-minute time interval. All the inverters reported in this dataset share the same features and exhibit similar performance. Therefore, to save space, only one inverter's production time series data is selected for analysis and modeling in this study. Collected data also includes the ambient temperature and solar cell temperature time series for the same time span. These two data sets are considered as exogenous variables for our model's input, which is further explained in section 5.2.

4.2 Data preprocessing

The collected data is preprocessed using Python programming with implementation of the following steps: removing the missing values, removing the outliers by using Local Outlier Factor (LOF) [13], and scale modification. Figure 1 depicts the visualization of the raw clean data.

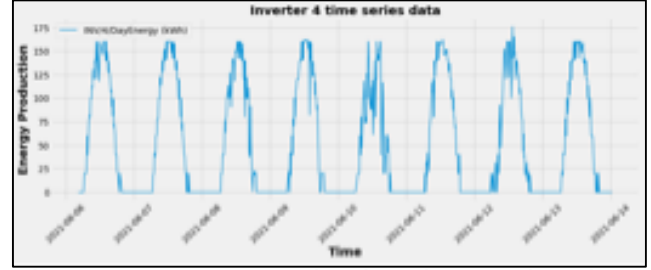


Figure 1. Energy production time series data

4.3 Experimental details

All the analysis are implemented in Python 3.10.13. Echo State Network model and false nearest neighbors' approach are employed using the "pyESN" and "scikit-learn" libraries respectively.

Implementing the FNN method for time series data in Python involves several key steps. Here is a detailed overview of the implementation:

1- Preparing the Time Series Data:

The time series data is ensured to be in a suitable format for analysis, such as a one-dimensional array or a Pandas Series object.

2- Embedding:

Time series data is embedded into a higher-dimensional phase space using time delay embedding. Appropriate embedding parameters, particularly the embedding dimension (m), are chosen in this step.

3- Calculate Nearest Neighbors:

A nearest neighbors' algorithm, in our case: brute-force algorithm, is used to find nearest neighbors in the embedded space.

4- Calculate False Nearest Neighbors:

Each point in the embedded space is perturbed slightly and the distance to its nearest neighbor is calculated. If the ratio of the perturbed distance to the original distance exceeds a certain threshold, the point is classified as a false nearest neighbor.

5- Calculate the FNN ratio:

This ratio offers insights into whether the selected embedding parameters accurately represent the underlying dynamics of the time series. It also indicates the percentage of points in the embedded phase space that are incorrectly identified as nearest neighbors after perturbation.

6- Plot Results:

By visualizing the results, the regions in the phase space where false nearest neighbors occur are identified.

5 RESULTS

5.1 FNN Ratio

By implementing the FNN method on the energy production time series, the obtained FNN ratio is obtained as: 0.77, which suggests that a significant portion of points in the embedded space are falsely identified as nearest neighbors when perturbed. Here are some possible interpretations for this ratio value:

- **Complex Dynamics:** A high FNN ratio suggests that the dynamics of the time series data are complex and possibly nonlinear. The presence of false nearest neighbors indicates that points in the embedded space are not truly nearby in the original phase space, which could be indicative of chaotic or nonlinear behavior.
- **Dimensionality Estimation:** The FNN ratio can also provide insights into the appropriate choice of embedding dimension (m). If the FNN ratio is high, it may indicate that the embedding dimension is insufficient to capture the underlying dynamics of the system. In such cases, increasing the embedding dimension might be necessary to reduce the FNN ratio and better represent the data in the embedded space.
- **Modeling Considerations:** High FNN ratios can have implications for modeling approaches, particularly for forecasting or modeling the underlying dynamics of the system. It suggests that simple linear models may not be sufficient and that more sophisticated nonlinear modeling techniques might be necessary to capture the complexities of the data.
- **Noise Sensitivity:** The FNN ratio can also be sensitive to noise in the data. If the data contains significant noise, it can lead to higher FNN ratios by artificially inflating the distances between points in the embedded space. In such cases, preprocessing steps such as denoising or smoothing might be beneficial.

5.2 Adding exogenous variables

The same defined FNN function is once more implemented, this time the structure of the input data is with consideration of two exogenous variables. Ambient temperature and solar cell temperature time series data are considered as exogenous input data. The target variable (endogenous variable) and exogenous variables are merged into a single dataframe and given to the FNN function as input. With this configuration the FNN ratio is reduced to 0.277. The difference in the FNN ratio between using

only the target variable and combining the target variable with the exogenous variables can provide valuable insights into the relationships and dynamics within our dataset, which are as the follows:

- 1- **Effect of Exogenous Variables:** The decrease in the FNN ratio when including the exogenous variables suggests that these variables contribute additional information that helps better capture the underlying dynamics of the system. By incorporating these variables, we may have reduced the noise or captured additional relevant features, leading to a more accurate representation of the system in the embedded space.
- 2- **Dimensionality and Embedding:** The exogenous variables may have provided complementary information that helps reduce the effective dimensionality of the system, resulting in a lower FNN ratio. This can be particularly relevant if the exogenous variables are correlated with the target variable or capture relevant aspects of the system's behavior.
- 3- **Modeling Considerations:** The lower FNN ratio obtained when including exogenous variables suggests that incorporating these variables may improve the performance of models or forecasting techniques applied to the data. Models that utilize both the target and exogenous variables may better capture the relationships and dynamics within the system, leading to more accurate predictions or analyses.
- 4- **Interactions and Relationships:** The decrease in FNN ratio could also indicate that the interactions or relationships between the target variable and the exogenous variables are meaningful and contribute to the overall dynamics of the system. Understanding these interactions can provide deeper insights into the underlying mechanisms driving the observed behavior.

5.3 Optimization of the embedding dimension

For the previous results the embedding dimension was set manually to embed the time series data into a higher-dimensional phase space. Determining the optimal embedding dimension for time series data typically involves using a method such as the false nearest neighbors (FNN) method itself, as well as other techniques like the mutual information or the method of delays (e.g., Cao's method).

In this section we use the FNN algorithm to optimize the embedding dimension. First, we set

the maximum dimension to 100 and then methodically alter the embedding dimension and determine the FNN ratio for each value. The ideal embedding dimension is generally identified as the smallest m value, where the FNN ratio either stabilizes or hits its lowest point. Figure 2 shows the FNN ratio as a function of the embedding dimension. This visualization shows us how the FNN ratio changes with different embedding parameters. The FNN ratio after optimization of the embedding dimension is changed from 0.771 to 0.01 for the single target variable of energy production, and also from 0.277 to 0.007 for the merged data of target variable and exogenous variables.

The obtained optimized ratio provides valuable insights into the effectiveness of the chosen embedding parameters for capturing the dynamics of the input time series data. A very low FNN ratio (below 0.05), such as 0.01 and 0.007 in both our cases, indicates that the embedding dimension and time delay are appropriate, with few false nearest neighbors, suggesting effective representation of the time series dynamics. This low ratio signifies that the embedding process successfully transformed the time series into a higher-dimensional space where nearby points reflect meaningful relationships, thus ensuring a reliable dynamics representation with the optimal embedding dimension of 70. This robust result suggests that the analysis is resistant to noise and perturbations, confirming that the observed structure in the embedded space accurately reflects the true underlying dynamics.

Since employing the exogenous variables led us to a more accurate representation of the system in the embedded space, we will continue the rest of our analyses in this study using the merged data of energy production time series (target variable) and two weather exogenous variables as the input data.

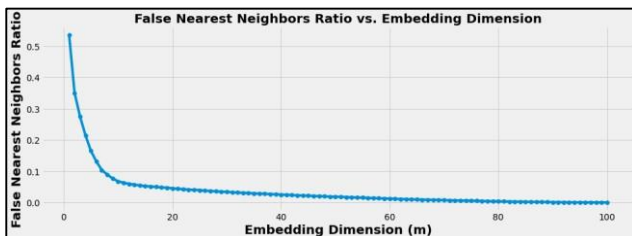


Figure 2. Relation between FNN ratio and embedding dimension

To understand the data structure and pinpoint areas with false nearest neighbors, we visualize the embedded phase space directly in Figure 3.

Given its inherent high dimensionality, principal component analysis (PCA) [14] dimensionality reduction method is essential to be employed. This technique enables us to project the data onto lower-dimensional spaces, facilitating clearer visualization and insight into the relationships among data points in the embedded phase space.

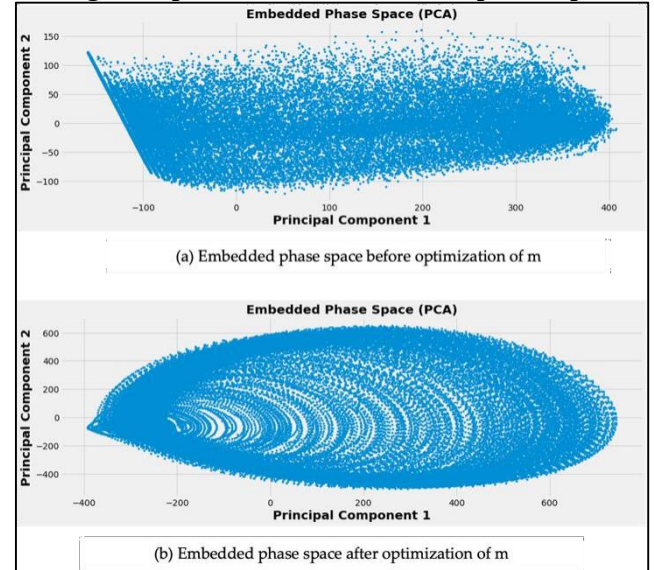


Figure 3. Embedded phase space. (a) Before optimization of m . (b) After optimization of m .

This visualization offers a lower-dimensional representation of the embedded phase space, enabling us to examine the data's structure and detect patterns or clusters. Clusters of closely grouped points suggest areas within the phase space sharing similar dynamics, whereas scattered points may highlight regions prone to false nearest neighbors.

It was mentioned that the reconstructed phase space with the optimum dimension, boosts confidence in utilizing the embedded data for constructing prediction models, by better maintaining the structure inherent in the original time series. This claim is proved with the analysis presented in the following.

5.4 Implementation of the ESN model on the original data

Echo State Network from the “pyESN” library in Python is defined on the original (non-embedded) solar energy production data, along with weather exogenous variables. The hyperparameters of the ESN model are optimized using the Tree-structured Parzen Estimator (TPE), which is a popular Bayesian optimization (BO) technique, and it is well-known for its outstanding performance in a wide range of applications [15]. The list of hyperparameters and their optimized

values, are presented in Table 3. The evaluation metrics assessing the performance of forecasting the original data with ESN model are presented in Table 1.

Table 1. Optimized ESN model performance on original time series data

MAE	MSE	RMSE	MAPE	R^2
4.94	78.27	8.85	0.16	0.96

5.5 Implementation of the ESN model on the embedded data

In this section we apply the optimized ESN model this time on the embedded data. Table 2 shows the evaluation metrics of the forecasting results. As it was claimed earlier, the prediction accuracy is improved compared to the implementation of ESN model on the original time series data.

Table 2. Optimized ESN model performance on embedded time series data

MAE	MSE	RMSE	MAPE	R^2
4.99	77.26	8.79	0.13	0.97

Table 3. Optimized values of the ESN model hyperparameters

Model	Hyper-Parameter	Optimized value (original data)	Optimized value (embedded data)
ESN	Number of reservoir units	1000	778
	Sparsity of the reservoir connections	0.403	0.021
	Spectral radius of the reservoir weights	0.840	0.357
	Magnitude of noise to be added to the reservoir activations	0.0007	0.054

6 CONCLUSION

This study demonstrates the successful application of chaos theory and Echo State Networks (ESNs) in forecasting solar energy output from the Konya Eregli Solar Power Plant in Turkey. By employing the False Nearest

Neighbors (FNN) method to optimize the embedding dimension, we significantly improved the representation of the time series data, leading to more accurate predictions. The incorporation of exogenous variables such as ambient and solar cell temperature further enhanced the model's performance by providing additional relevant information that reduced noise and improved the capture of the underlying system dynamics. The optimized embedding dimension achieved an FNN ratio below 0.05, indicating that the chosen parameters effectively represented the time series dynamics and demonstrated robustness against noise and perturbations.

The empirical results indicate that the optimized ESN model applied to the embedded data outperformed the model applied to the original non-embedded data. This highlights the importance of careful selection and optimization of embedding dimensions in chaotic modeling of solar energy systems. The improved prediction accuracy with the optimized model underscores its potential for enhancing solar energy forecasting, which is crucial for efficient energy management and planning. This study not only contributes to the field of renewable energy forecasting but also provides a robust methodology that can be adapted for similar complex, nonlinear time series prediction tasks in other domains.

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ENHANCING SURPLUS ENERGY PREDICTION FOR HIGH PENETRATION RENEWABLE ENERGY SYSTEMS USING REGULARIZED SUPPORT VECTOR MACHINES

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Abstract

As renewable energy sources become increasingly dominant in power grids, efficiently managing surplus energy is crucial for optimizing energy use and storage. Traditional approaches primarily focus on predicting energy load and weather conditions, often overlooking the direct prediction of surplus energy. This paper introduces a novel approach to surplus energy management through an Improved Support Vector Machine (ISVM) model, which integrates both L1 and L2 regularization techniques. The regularization parameters are optimized using the Firefly Algorithm (FA), a metaheuristic optimization method known for its effectiveness in complex parameter tuning. By directly predicting surplus energy, our method aims to improve forecast accuracy and better align energy production with storage and consumption needs. We develop a predictive model that integrates historical energy production, weather data, and load profiles, leveraging regularization to prevent overfitting and ensure robust generalization. The performance of our regularized SVM model is rigorously evaluated through extensive simulations and real-world case studies. The results demonstrate a significant enhancement in prediction accuracy. Specifically, the improved SVM model achieved a Root Mean Square Error (RMSE) of 7.606 and an R^2 value of 0.9834, compared to an RMSE of 12.167 and an R^2 of 0.9576 for the traditional SVM. This improvement leads to more efficient energy management and utilization, addressing key challenges in high-renewable-energy scenarios. The direct prediction of surplus energy proves to be a valuable tool for optimizing energy storage and grid stability. This work contributes significantly to the ongoing efforts to enhance energy management systems in the context of increasing renewable energy integration. By offering a more precise and effective approach to surplus energy forecasting, our study provides valuable insights for optimizing energy storage and improving overall grid stability.

Keywords: High penetration renewable energies, Surplus energy prediction, Support vector machine (SVM), Regularization Techniques, Energy Management Systems

1 INTRODUCTION

The transition to renewable energy sources is one of the most significant developments in the global energy landscape. Renewable energies, such as solar, wind, and hydro, are increasingly being integrated into national and regional power grids due to their environmental benefits and sustainability [1]. High penetration of these renewable sources offers numerous advantages, including reduced greenhouse gas emissions, decreased dependence on fossil fuels, and lower long-term energy costs [2]. However, the increased variability and intermittency associated with renewable energy sources pose

significant challenges to grid stability and energy management [3].

The fluctuating nature of renewable energy generation requires innovative solutions to ensure that the power grid remains balanced and reliable. For instance, solar energy production varies with the time of day and weather conditions, while wind energy is dependent on wind speed and patterns, which can be highly variable. As the share of renewable energy in the grid continues to grow, addressing these challenges becomes increasingly crucial [4]. The ability to effectively manage and utilize surplus energy generated during periods of high renewable output is essential for maintaining

grid stability and optimizing overall energy system performance.

Managing surplus energy effectively is pivotal in optimizing the benefits of high renewable energy penetration. Surplus energy occurs when the amount of energy generated exceeds the immediate demand. Efficient surplus energy management involves strategies such as energy storage, demand response, and energy redistribution [5]. By accurately forecasting surplus energy, operators can make informed decisions about storing excess energy in batteries, adjusting demand patterns, or feeding surplus energy back into the grid [6].

The proper management of energy not only enhances grid reliability but also maximizes the utilization of renewable resources and increase the reliability of the system [7]. It can lead to significant cost savings by reducing the need for curtailment (i.e., the practice of reducing energy production to match demand) and minimizing reliance on fossil fuel-based peaking power plants. Different types of energy storages such as batteries and hydrogen storage systems are utilized as effective solutions to efficiently manage the surplus energy [8] [9] [10]. Furthermore, effective surplus energy management supports the transition to a more sustainable energy system by ensuring that renewable energy is used to its fullest potential, thereby reducing overall carbon emissions and improving environmental outcomes [11] [12].

Predicting hourly surplus energy is a critical aspect of effective energy management. Accurate hourly forecasts enable grid operators to make real-time decisions about energy storage, consumption, and distribution. Hourly predictions provide granular insights into the fluctuations in energy production and demand, allowing for more precise and timely interventions. The ability to predict surplus energy on an hourly basis enhances the efficiency of energy storage systems by ensuring that excess energy is stored when available and utilized optimally. It also facilitates better demand response strategies, where energy consumption patterns can be adjusted based on anticipated surplus availability. By integrating hourly surplus energy predictions into energy management systems, operators can improve the alignment of energy supply with demand, leading to more reliable and cost-effective energy systems.

Existing research has primarily focused on predicting energy load demand and renewable energy outputs [13] [14]. Various methods, such as statistical modelling [15], time-series analysis, fuzzy based methods [16] [17], machine learning techniques [18], and neural network based methods [19] [20] [21] have shown their ability to predict nonlinear parameters.

Additionally, metaheuristic based algorithms increased the accuracy and improve the performance of prediction methods [22] [23] [24].

While these methods have provided valuable insights into energy prediction, they often fall short in directly forecasting surplus energy. Surplus energy prediction requires a more nuanced approach that not only considers the total energy generated and consumed but also accounts for the timing and magnitude of surplus occurrences. Traditional methods tend to focus on predicting energy load and generation without explicitly addressing the surplus component, which is critical for effective energy management in high-renewable scenarios.

This paper, aiming to fill this gap, presents a novel approach to predicting surplus energy by enhancing the performance of Support Vector Machines (SVM) through the application of regularization techniques. Our proposed method directly forecasts surplus energy, filling a gap left by previous studies that predominantly focus on load and generation predictions. By incorporating both L1 and L2 regularization, we aim to improve the accuracy and robustness of our SVM model. Regularization techniques help to prevent overfitting by penalizing excessively complex models and ensuring that the predictions are generalized well to new data. We employed the Firefly Algorithm (FA), as an efficient meta heuristic algorithm, optimize the related regularization parameters. Our approach offers a more precise tool for managing surplus energy in high-renewable scenarios, addressing the limitations of traditional prediction methods. The remainder of this paper is organized as follows: Section 2 details the methodology of our enhanced SVM model, including data collection, feature engineering, the application of regularization techniques, and FA algorithm. Section 3 presents the experimental setup and results. Section 4 discusses the implications of our findings. Finally, Section 5 concludes the

paper and proposes directions for future research.

2 IMPROVED SVM

SVM is a class of supervised learning algorithms used for classification and regression tasks. The primary objective of an SVM is to find the optimal hyperplane that maximizes the margin between different classes or, in the case of regression, the hyperplane that best fits the data with minimal error. The SVM algorithm can handle both linear and non-linear data through the use of kernel functions. Similar to other machine learning techniques, the dataset is split into two subsets: one for training and the other for testing. This division is essential for parameter adjustment and prediction tasks. The SVR formulation is outlined as follows: Given a data $\{(x_1, y_1), (x_2, y_2), \dots, (x_i, y_i), \dots, (x_n, y_n)\}$ where x_i and y_i represent the input vector and denotes the target value for n data points respectively, SVR constructs a function (Eq. 1) by minimizing a regularized risk function (Eq. 2) and (Eq. 3).

$$f(x) = \langle w, \phi(x) \rangle + b \quad (1)$$

$$R = \frac{C}{N} \sum_{i=1}^N (L(y_i, f(x))) + \frac{1}{2} \|w^2\| \quad (2)$$

$$L(y_i, f(x)) = \begin{cases} |y - f(x)| & \text{if } |y - f(x)| \geq \varepsilon \\ 0 & \text{otherwise} \end{cases} \quad (3)$$

In these equations, w is the weight vector, $\phi(x)$ represents the transformation into a high-dimensional feature space, and b is the bias term used in the decision function. The first part of the second equation quantifies empirical risk, computed using the epsilon-insensitive loss function described in the third equation. The second term, $\frac{1}{2} \|w^2\|$, represents the regularization component.

Regularization is a crucial technique in SVM to prevent overfitting and improve generalization. In SVM, regularization is achieved by adding a penalty term to the objective function, which constrains the model's complexity. The regularization term helps to balance the trade-off between maximizing the margin and minimizing the classification error. L2 regularization is applied to the SVM objective function to penalize large weight values, thereby controlling the model complexity. L1 regularization introduces sparsity in the model by penalizing the absolute values of the weights. While less common in standard SVM formulations, it can

be applied in hybrid models or modified SVM frameworks. Combining L1 and L2 regularization, known as Elastic Net regularization, provides a balance between sparsity and model complexity. The objective function is:

$$\text{Objective} = \frac{1}{2} \|w^2\| + \frac{C}{N} \sum_{i=1}^N (L(y_i, f(x))) + \lambda_1 \|w\|_1 + \lambda_2 \|w\|^2 \quad (4)$$

λ_1 and λ_2 are the regularization parameters for L1 and L2 regularizations, respectively.

3 METHODOLOGY

In this section the methodology used in the study is described. First the methodology steps are explained and then the FA algorithm as utilized technique to optimized the regularization parameters are detailed and formulated;

3.1 Improved SVM implementation

The following steps are utilized to predict the hourly surplus energy in a microgrid based on input data and using the improved SVM algorithm:

Step 1 - Data preparation: To enhance the SVM model for predicting surplus energy, we start with data preparation, including feature selection, normalization, and splitting the dataset into training and testing sets. Key features include historical energy production data, weather conditions, and energy consumption patterns.

Step 2 - Model training and hyperparameter tuning:

The regularized SVM model is trained using a dataset that includes features related to energy production and consumption. Hyperparameters such as C , λ_1 and λ_2 are optimized using FA optimization technique which is described later in this section. This process involves selecting the best combination of parameters to achieve the highest prediction accuracy.

Step 3 - Model evaluation

The performance of the regularized SVM model is evaluated using metrics such as Root Mean Squared Error (RMSE), and R-squared (R^2). R^2 measures the average magnitude of the errors between predicted and actual values. A lower RMSE indicates a better fit of the model to the data. These metrics provide insights into the accuracy and robustness of the surplus energy predictions (Eq.5, Eq.6).

$$R^2 = 1 - \frac{\sum_{i=1}^n (x_{actual} - x_{predicted})^2}{\sum_{i=1}^n (x_{actual} - \bar{x}_{predicted})^2} \quad (5)$$

$$RMSE = \sqrt{\frac{\sum_{i=1}^n (x_{actual} - x_{predicted})^2}{n}} \quad (6)$$

here, n and $\bar{x}_{predicted}$ are the number of the sample points and the mean of predicted point's values respectively.

3.2 Firefly Algorithm

The FA is a metaheuristic optimization technique inspired by the flashing behavior of fireflies[25] [26]. It is widely used for solving complex optimization problems due to its ability to handle non-linear, multi-dimensional, and multi-modal optimization tasks. The algorithm is based on the idea that fireflies attract each other with their flashing lights, and the attractiveness is proportional to the brightness of the fireflies [27] [28]. The FA utilizes this behavior to iteratively search for optimal solutions in the solution space. The Firefly Algorithm proceeds through the following steps:

- Initialization: A population of fireflies is randomly generated. Each firefly represents a potential solution in the parameter space of λ_1 and λ_2 . The initial positions (i.e., values for λ_1 and λ_2) are randomly selected within predefined bounds.
- Evaluation: Each firefly's fitness is evaluated based on the objective function, which in this case is the total regularized risk function of the SVM. The fitness is determined by the performance of the SVM model with the corresponding parameters.
- Attraction and Movement: Fireflies are attracted to brighter (i.e., better-performing) fireflies. The movement of each firefly is influenced by the attractiveness of other fireflies and their distance. The attractiveness is a function of the brightness, which decreases with distance. The movement is governed by Eq.7 and Eq.8:

$$\beta = \beta_0 \times e^{-\gamma d^{\lambda}} \quad (7)$$

$$X_i^{t+1} = X_i^t + \beta^{-\gamma d_{i,j}} (X_j^t - X_i^t) + \alpha_t \varepsilon_t \quad (8)$$

where, β_0 is the value of attractiveness. Also, λ and d balance the light absorption and the rate of

attractiveness based on the Euclidean distance of the two sample states.

- Update: The positions of fireflies are updated iteratively based on their attractiveness. The best solutions are retained, and the process continues until convergence or a maximum number of iterations is reached.

- Result: The optimal values for λ_1 and λ_2 are identified based on the best-performing fireflies. These parameters are then used to train the final SVM model.

4 RESULTS

In this section, we present the results of applying the improved SVM model with regularization techniques and the Firefly Algorithm. We first provide a detailed description of the data utilized for training and testing the model. Following this, we present the outcomes of the predictive analysis, including the performance metrics of the model and comparisons with baseline approaches. The dataset used for this study is sourced from a microgrid system detailed in references [29]. This dataset encompasses a comprehensive set of parameters crucial for modeling and predicting surplus energy. It includes measurements of photovoltaic (PV) output, solar irradiation, temperature, and load demand. PV output represents the electrical power generated by the photovoltaic panels, recorded at regular intervals. It reflects the direct contribution of solar energy to the microgrid. Solar Irradiation measures the amount of solar energy received per unit area. It is a key determinant of PV output and varies based on time of day and weather conditions. Also, ambient temperature data is included as it affects both the efficiency of PV panels and the overall energy consumption within the microgrid. In addition, the load demand represents the electrical load requirements of the microgrid, indicating the total energy consumption by connected devices and systems. The input data of the case study is provided in Fig.1.

Figure 2 illustrates the comparison between the actual and predicted surplus energy using various forecasting methods. The methods evaluated include the standard SVM, the proposed improved SVM with regularization and FA optimization, and LSTM networks. The results demonstrate that the proposed improved SVM model, which incorporates both $L1$ and $L2$ regularization techniques and is optimized using the FA, significantly outperforms the traditional

SVM and LSTM models in predicting surplus energy. The improved SVM shows a closer alignment with the actual surplus energy values, indicating higher predictive accuracy and better model performance. To quantify the performance of the different models, Table 1 presents the RMSE and R^2 values for each method.

In this study, the improved SVM achieved an RMSE of 7.606. This relatively low value indicates that the ISVM model provides predictions that are, on average, closer to the actual surplus energy values compared to other methods. In contrast, the LSTM model reported an RMSE of 15.444. This higher RMSE suggests that the LSTM model's predictions exhibit greater deviations from the actual surplus energy values. Also, the standard SVM produced an RMSE of 12.167, which is intermediate between the ISVM and LSTM results. This indicates that while the SVM model also provides relatively accurate predictions, its average deviation from the actual values is higher than that of the ISVM but lower than the LSTM.

Additionally, the R^2 value reflects how well the model explains the variance in the dependent variable, which in this case is the surplus energy. The ISVM model achieved an R^2 value of 0.9834, indicating that 98.34% of the variance in surplus energy is explained by the model. This high value demonstrates that the ISVM provides an excellent fit to the data, effectively capturing the patterns in the surplus energy predictions. In comparison, the LSTM model achieved an R^2 value of 0.9317. This value indicates that the LSTM model explains 93.17% of the variance in the surplus energy, showing that while it is effective, it does not perform as well as the ISVM. The standard SVM model recorded an R^2 of 0.9576, which means it explains 95.76% of the variance in surplus energy. Although this

value is lower than that of the ISVM, it still represents a strong explanatory power.

Table I: Evaluation metrics for different methods

Parameter	ISVM	LSTM	SVM
RMSE	7.606	15.444	12.167
R^2	0.9834	0.9317	0.9576

5 DISCUSSION

Efficiently managing surplus energy—i.e., the excess energy generated beyond immediate consumption needs—can enhance grid stability, reduce waste, and improve the economic viability of renewable energy systems. Accurate predictions of surplus energy allow for better planning and integration of energy storage systems, demand response strategies, and grid management solutions. In this study, we developed an improved SVM model optimized through regularization techniques and the FA algorithm, and compared its performance with standard SVM and LSTM models. Our proposed model significantly outperformed the traditional approaches in predicting surplus energy.

The improved SVM model achieved a lower RMSE of 7.606, indicating more precise predictions with an average deviation from actual surplus energy values that is significantly smaller than those obtained with SVM and LSTM models. Furthermore, the ISVM reached a high R^2 value of 0.9834, demonstrating its ability to explain 98.34% of the variance in surplus energy, which is superior to the R^2 values of 0.9576 and 0.9317 achieved by the standard SVM and LSTM models, respectively. The application of regularization techniques and the FA contributed to these improvements by reducing overfitting and optimizing the model parameters effectively. The ISVM's performance underscores the effectiveness of

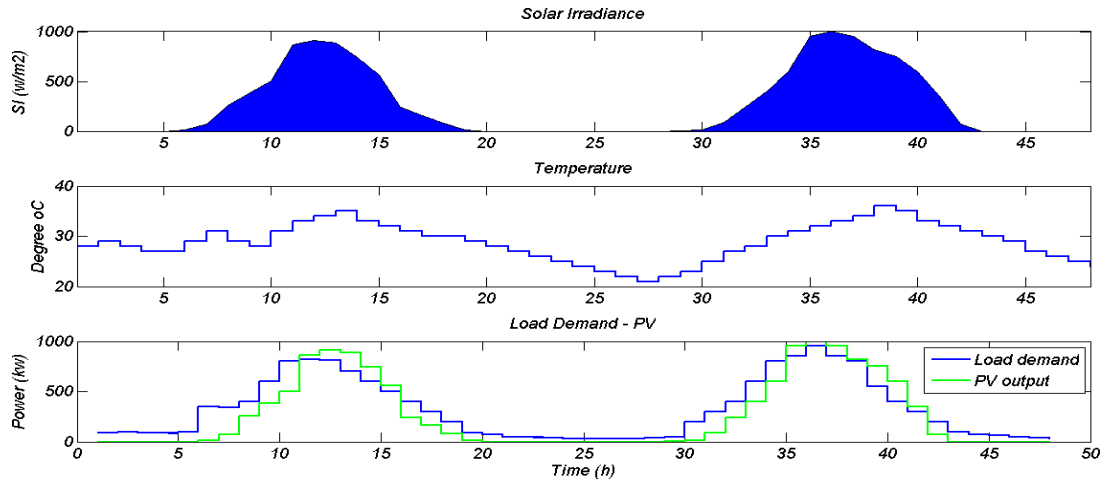


Figure 1. Input data (48 hours data)

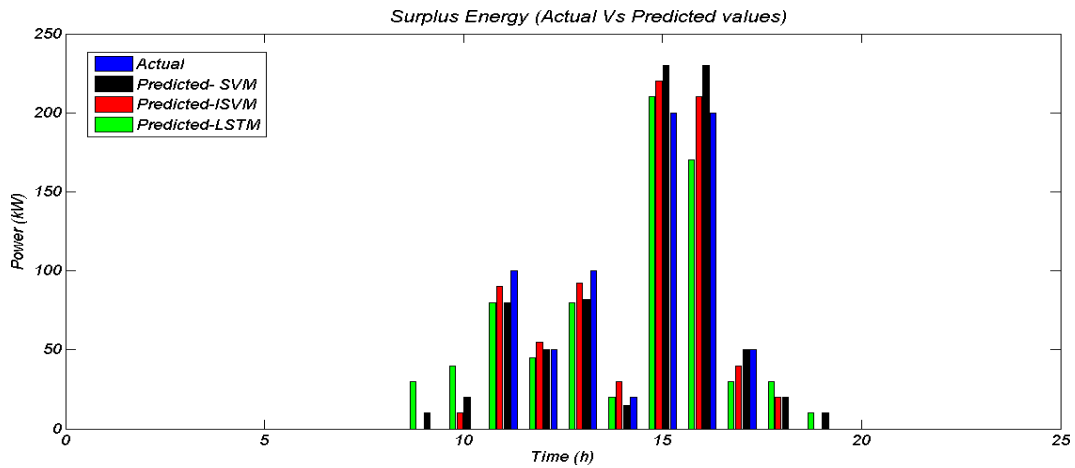


Figure 2. Predicted surplus energy for different methods

combining advanced optimization techniques with robust machine learning methodologies to enhance predictive accuracy in complex energy management scenarios.

Despite the notable achievements, there are limitations to this study that must be acknowledged. First, the performance of the ISVM model is heavily dependent on the quality and quantity of the input data. Also, the improved SVM model, with its regularization techniques and optimization algorithm, introduces additional complexity compared to standard SVM and LSTM models. While this complexity contributes to better performance, it also increases the computational cost and may require more sophisticated resources for implementation. In addition, the model's effectiveness was demonstrated on a specific dataset from a microgrid system. While the results are promising, further validation is

necessary across different datasets and types of renewable energy systems to ensure that the model's performance is consistent and reliable in various scenarios.

6 CONCLUSION

This study has made significant strides in advancing surplus energy management in the context of high renewable energy penetration. By developing an improved ISVM model, optimized through regularization techniques and the FA, we have demonstrated a substantial improvement in the accuracy of surplus energy predictions compared to traditional models such as the standard SVM and LSTM networks. The ISVM model achieved a remarkably low RMSE of 7.606 and a high R^2 value of 0.9834, showcasing its ability to provide precise predictions and a superior fit to the data. These results highlight the effectiveness of integrating

advanced optimization techniques with machine learning methodologies to enhance predictive performance in energy management applications. In summary, this work represents a meaningful advancement in the field of surplus energy management, providing a robust framework for improving predictive accuracy and supporting the transition towards more sustainable and efficient energy systems. The proposed ISVM model sets a new benchmark for surplus energy forecasting and offers a promising direction for future research in energy management and renewable integration. Future research could investigate how predicting the surplus energy can enhance the performance of energy storage systems.

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ENERGY EFFICIENCY AND ENVIRONMENTAL ASSESSMENT OF A BUSINESS IN A SMALL RURAL TOWN ON THE U.S./MEXICO BORDER IN TEXAS

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Abstract

The Staff of the Office of Outreach and Recruitment (OOR) at New Mexico State University has been evaluating a holistic approach to environmental issues by providing energy and environmental assessments to businesses since 1999, under the Pollution Prevention Grant Program. The OOR performed an on-site energy and environmental assessment for a steel rerolling mill specializing in manufacturing high-quality steel products. The assessment included an evaluation of the furnaces, lighting, recycling, mill processes, and water consumption. The team then presents their findings to the business's management and later prepares a report recommending improvement. The mill's outdated furnace operated 24 hours per day, five days a week. Switching to a modern furnace could save approximately 14,000,000 kWh of energy and reduce CO₂ emissions by 2,650 metric tons. Partnering with the University of Texas at El Paso, the team suggested implementing Lean Manufacturing to minimize waste from defects, transport, and motion. Implementing newer appliances would reduce electrical consumption by over 18,000,000 kWh, decrease greenhouse gas emissions by 8,176 tons, reduce solid waste by 13,974 tons, and have annual cost savings of \$9,936,647. Overall, improving the mill's environmental performance, operational efficiency, and cost-effectiveness, contributes to sustainable business practices.

Keywords: Environmental, Sustainable, Energy efficiency, Greenhouse emission

PARAMETRIC STUDIES ON A FREEZER WITH PCM

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Abstract

Ensuring food safety is paramount in cold storage applications. Temperature fluctuations in freezers can compromise food safety, leading to spoilage and potential health risks. This study investigates the utilization of Phase Change Materials (PCMs) in freezers to mitigate temperature fluctuations and enhance food quality. A numerical model developed in MATLAB/Simulink was employed to simulate the freezer's thermal behavior. The findings indicate that PCMs can effectively buffer temperature fluctuations, maintaining a consistent internal environment even during power outages or defrost cycles. This stabilization not only enhances the cold chain but also significantly extends the shelf life of frozen products, ensuring they remain safe for consumption over longer periods. Furthermore, the use of PCMs reduces the frequency and duration of compressor cycles, leading to lower energy consumption and potential cost savings.

Keywords: freezer dynamic modeling, SIMULINK, phase change material, PCM

1 INTRODUCTION

Phase change materials (PCMs) absorb or release a significant amount of latent heat during their phase transitions, such as from solid to liquid or vice versa. Using PCMs in freezers offers several important benefits, including enhanced temperature stability, energy efficiency, extended preservation, improved performance, cost savings, and environmental benefits. PCMs help maintain a consistent temperature inside the freezer, even during power outages or defrost cycles, by absorbing excess heat or releasing stored cold. One key advantage of PCMs is their ability to reduce the frequency and duration of compressor cycles. By absorbing heat during peak periods and releasing it during off-peak times, PCMs can effectively reduce the workload on the compressor, thereby lowering the energy consumption of freezers and leading to potentially significant cost savings. They also smooth out temperature fluctuations, reducing the need for the compressor to work as hard, which can decrease maintenance needs. In the event of a power failure, PCMs provide longer periods of stable temperatures, preserving the quality and safety of stored food items for extended durations. PCMs enhance the overall performance of freezers by reducing the load on the refrigeration system, potentially leading to a longer lifespan for the appliance and reduced

maintenance needs. The reduction in energy consumption and potential decrease in maintenance costs can lead to significant cost savings over the lifetime of the freezer. By improving energy efficiency, PCMs contribute to lower greenhouse gas emissions and a reduced carbon footprint for refrigeration appliances. Incorporating phase change materials into freezers is an innovative approach that leverages the thermal properties of these materials to optimize performance, increase energy efficiency, and enhance the reliability of food storage.

Karthikeyan et al. [1] studied how to enhance household refrigerator efficiency using phase change materials (PCMs) in various locations: the freezer, fridge, and condenser. Commercial PCMs (OM32, OM29, OM03, and HS3N) were used in slab form for the freezer and fridge and in packets for the condenser, arranged by melting temperature. After testing different configurations, the study found that the refrigerator's efficiency significantly improved when PCMs were used in all three locations. Ben Taher et al. [2] developed a validated physical model to study the energy efficiency of a residential refrigerator with multiple PCMs. They examined the effects of PCM thickness (3 to 7 mm), internal load (0 to 20 W), and external temperature (15 to 30°C) on performance. The

study concluded that the melting temperature and thickness of the PCMs significantly impact the refrigerator's autonomy and efficiency. Using multiple PCMs (*water and eutectic solution*) in parallel maintains the air temperature between 4 and 6°C, enhancing performance. Javeri-Shahreza et al. [3] evaluated the energy efficiency and thermal behavior of household freezers using PCMs. They developed a dynamic model incorporating thermodynamics, heat transfer, and a control algorithm to monitor PCM temperature and melted mass fraction. The model, which includes pressure-based hydraulic calculations, showed relative errors of 5.5% and 5.1% in power consumption compared to experimental data, with and without PCM, respectively. The study suggested that this fast and dynamic model is suitable for simulation, optimization, and control applications in refrigeration systems. Elsayed et al. [4] experimentally investigated the impact of pairing PCMs with frozen items (ice and fish) in a freezer. They highlighted the importance of PCMs during power outages under various environmental conditions. The optimal product-to-PCM mass ratio (PMR) for extended under-thawing durations was identified. The study introduced the Recovered and Saved Energy Ratio (RSER) to measure energy savings. The highest RSER for ice was 8.14% at a PMR of 4.0 in summer and 20.44% at a PMR of 1.0 in winter. For fish, the highest RSER was 12.5% in summer and 36.5% in winter at a PMR of 5.0. Current work aims to provide parametric results on the effect of the melting temperature of the PCM on the time-wise evolution of the temperatures in an empty freezer.

2 MATERIAL & METHOD

2.1 System Description

This study numerically investigates the freezer's dynamic behavior. For this purpose, an in-house SIMULINK model was developed, and the time-dependent temperature variations were validated against experimental measurements. Table 1 provides the freezer's specifications defined in the producer catalog [5].

Table 1. Specifications of the freezer [5]

Cooling system	Static
Refrigerant	R600a
Capacity	196 L
Daily energy consumption	0.613 kWh/day
Width	54 cm
Height	145.7 cm
Depth	57.5 cm
Number of compartments	5

Figure 1 shows the positions of the thermocouples inside the freezer. Six thermocouples are mounted on the evaporator surfaces, while five are placed at the center of the compartments to approximate the mean air temperature. Experiments are conducted with an empty freezer without the shelves.

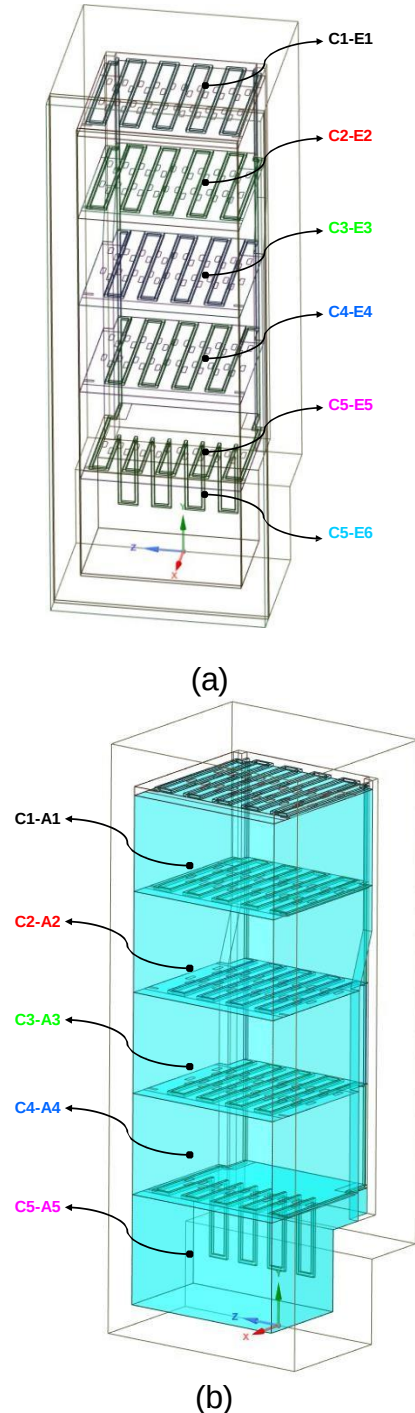


Figure 1. Thermocouple positions inside the freezer

2.2 Numerical Modelling

In the model, the freezer geometry is divided into five compartments. Energy balance equations for the air, phase change material, and evaporator volumes are formulated for each compartment, and the heat transfer mechanisms—radiation between surfaces and convection on surfaces—are defined according to the correlations provided in the literature. The net heat transfer through the inner surface of the insulation is transferred to a module that calculates temperature variations based on location and time within the insulation. Figure 2 shows a representative schematic of the heat transfer mechanisms across a selected compartment. PCM is located at the bottom of the tube-on-a-sheet type evaporator. The PCM-evaporator domain is considered a 2D-period model and discretized, as shown in Figure 3.

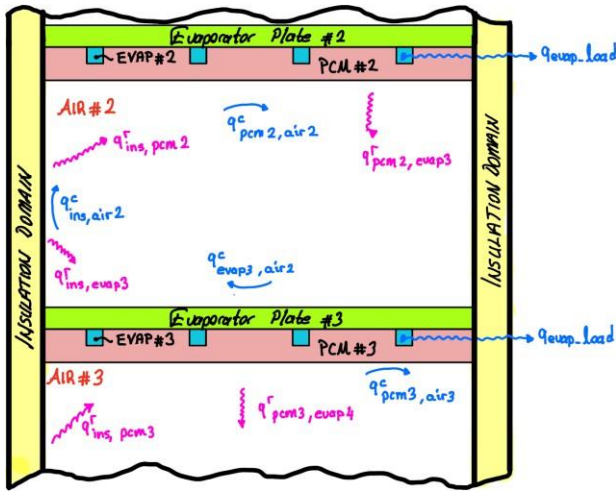


Figure 2. Heat transfer mechanisms across a compartment

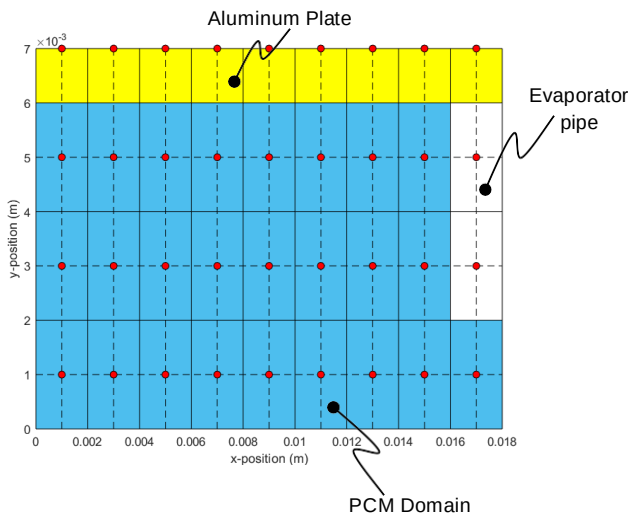


Figure 3. 2D model for PCM-Evap domain

For the air domain, the lumped-capacitance model is used with the following balance equation:

$$(mc \frac{dT}{dt}) = \sum_{in} q - \sum_{out} q$$

For the insulation domain, 1D heat conduction equation is defined as

$$\rho c \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} (k \frac{\partial T}{\partial x})$$

For the PCM-evaporator domain, 2D heat conduction equation is defined in terms of enthalpy as

$$\frac{\partial H}{\partial t} = \frac{\partial}{\partial x} (k \frac{\partial T}{\partial x}) + \frac{\partial}{\partial y} (k \frac{\partial T}{\partial y}) + \dot{q}_{load}$$

where $\dot{q}_{load}$ is valid in evaporator pipe domains, and it is defined as a function of the mean air temperature according to the experimental findings. The enthalpy-based balance equation is transformed into the temperature base by following the well-known temperature-transforming technique of Cao and Fagri [6]. In this technique, the enthalpy is defined as a piecewise linear function in solid, mushy, and liquid phases of the PCM as

The solid phase ($T < T_m - \delta T_m$)

$$H(T) = (\rho c)_s (T - T_m + \delta T_m)$$

The mushy phase ($T_m - \delta T_m \leq T \leq T_m + \delta T_m$)

$$H(T) = (\rho c)_m (T - T_m) + \rho \frac{h_{sf}}{2\delta T_m} (T - T_m) + (\rho c)_m \delta T_m + \rho \frac{h_{sf}}{2}$$

The liquid phase ($T > T_m + \delta T_m$)

$$H(T) = (\rho c)_l (T - T_m) + (\rho c)_s \delta T_m + \rho h_{sf}$$

The systems of ODEs are resolved in SIMULINK using the ode23 (Bogacki-Shampine) solver. A variable time-advancement technique is used for temporal discretization to reduce the solution time. A multi-step verification and validation approach is followed for subsystem models. The

experimental comparison is only provided in the next section of the current work.

3 RESULTS & DISCUSSIONS

The model's validity is demonstrated by comparing its predicted results with the measured data from the experimental setup. Figure 4 shows that the temperatures predicted by the model for each freezer compartment closely match the measured results. Given the freezer's pull-down duration and its on/off cycling behaviour, the model accurately predicts the temperature variations in the current freezer.

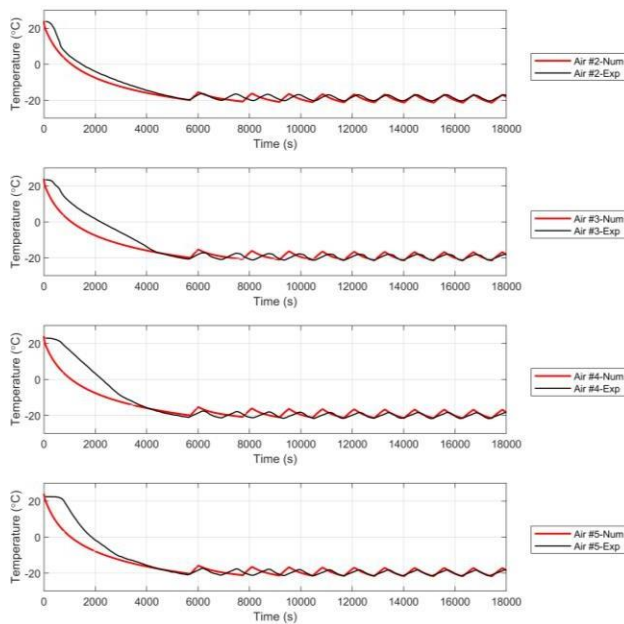


Figure 4. Validation of the numerical method

Figure 5 illustrates the time-dependent variations in the average air and evaporator temperatures for the scenario without PCM (w/o PCM). The freezer evaporator took almost 1.5 hours to reach the set temperature. After the seventh cycle, the cooling load was set to zero, and a power outage scenario was simulated. In this scenario, it took 36 minutes for the empty freezer to warm from -20°C to -5°C. The results were found to be consistent with the experimental data obtained from the empty freezer. Additionally, analyses were conducted on phase change materials (PCMs) with different melting temperatures to explore their impact on the freezer's dynamic behavior.

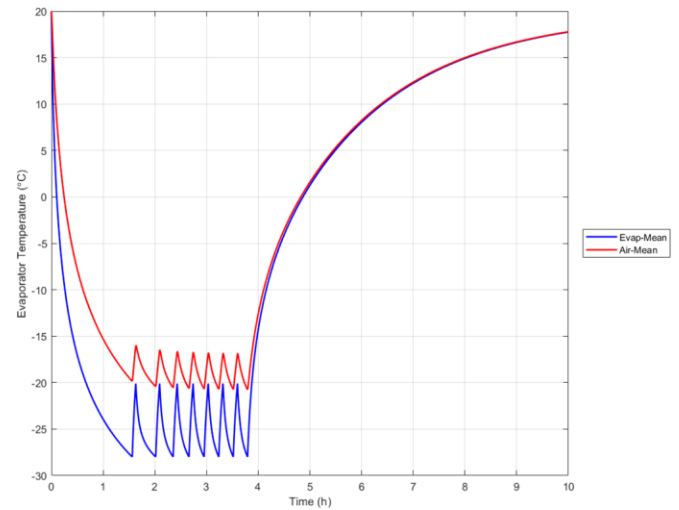


Figure 5. Power outage for the empty (w/o PCM) freezer

Figure 6 illustrates the effects of phase change materials (PCMs) with melting temperatures of -12.5°C, -15°C, -17.5°C, and -20°C on time-dependent average temperatures. The thermal properties of the PCM used are as follows: thermal conductivity 2 W/m·K, specific heat capacity 2000 J/kg·K, density 800 kg/m³, and latent heat of fusion 180 kJ/kg. The results show that the time required to reach the set temperature varies between 4 and 5.5 hours, depending on the PCM's melting temperature. The PCM's melting temperature creates plateau regions in the time-dependent temperature variation, with lower melting temperatures resulting in lower plateau temperatures. Incorporating PCM into the freezer affects the compressor's on/off frequency. For the empty volume, the compressor operates approximately four times per hour. However, in the freezer with PCM, this frequency is halved. Due to the increased heat capacity the PCM provides, the compressor's on and off times are longer than the empty volume. Considering the thermal behavior during a power outage, the temperature rise to -5°C is approximately 4 hours in the PCM-enhanced freezer due to the increased heat capacity. The PCM's melting temperature creates a plateau region of about 3 hours. For the PCM with a melting temperature of -12.5°C, the average air temperature during the plateau region is -7.5°C. For PCM melting temperatures of -15°C, -17.5°C, and -20°C, the plateau temperatures are approximately -10°C, -12.5°C, and -4°C, respectively.

ranges for extended periods, particularly in low-loading scenarios where the freezer's heat capacity is low. The study also demonstrates that consistent results can be achieved with the integrated system model developed in MATLAB/SIMULINK.

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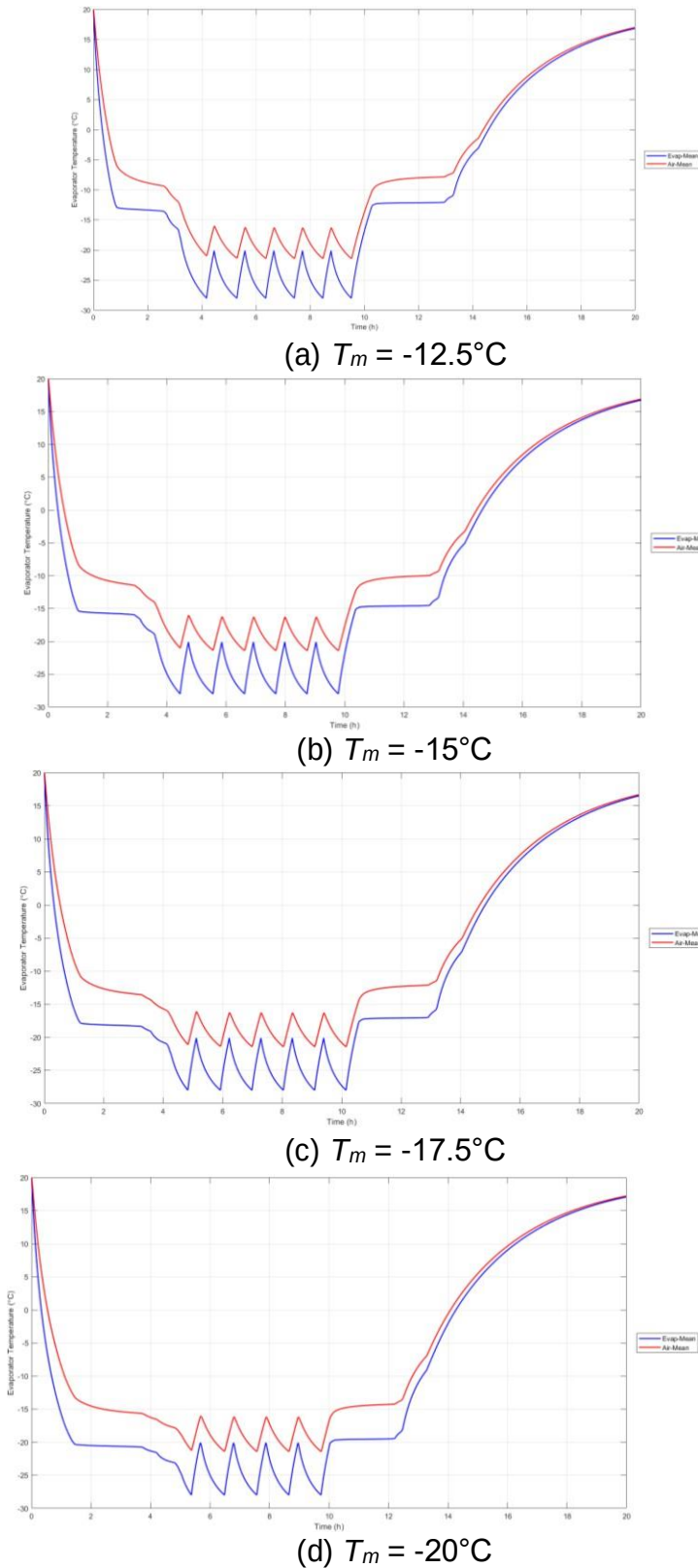


Figure 6. Power outage for the freezer with PCM (w/ PCM)

4 CONCLUSIONS

In conclusion, incorporating PCM into the freezer significantly prolongs the time required to reach the set temperature during the initial operation. However, this application offers the advantage of maintaining the air temperature within safe

VALORIZATION OF THE AQUATIC WASTED PTEROCLADIA CAPILLACEA BIOMASS INTO SUSTAINABLE VALUED PRODUCTS TO FLOURISH THE BLUE ECONOMY

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Abstract

As a solution for ecosystem bioremediation from the gigantic red seaweed proliferation across the Mediterranean shorelines, this work investigates the effective utilization of *Pterocladia capillacea* to produce different esteemed and viable bioproducts. The nutritional composition of approximately 6.88±0.31%, 20.15±0.2%, 42.16±0.3%, and 2.51±0.05% (w:w) protein, fiber, carbohydrate, and lipid, respectively, promotes its application in human food and animal fodder industries. Its N+P₂O₅+K₂O, undesirable heavy metals, organic carbon, and matter contents of 5.48±0.07%, 2.82±0.15 mg/kg, 16.11±0.15%, and 27.71±0.26% are in accordance with the Egyptian standard for organic fertilizer. Its calorific value of 16.16±0.5 MJ/kg and relatively low ash and heavy metals content are in accordance with the international standards for primary solid biofuel. Its relatively high holocellulose content of 44±0.5% (w:w) recommends its applicability in liquid biofuels sector. Further, via a pioneer practicing, a sequential, eco-friendly, and fully integrated bioprocess *Pt. capillacea* biomass is valorized into natural pigments of approximately 5.05±0.05 mg/g total chlorophyll, 2.12±0.05 mg/g carotenoids, phycobiliproteins of approximately 1.33±0.05 mg/g phycocyanin, 3.07±0.05 mg/g allophycocyanin, and 0.97±0.05 mg/g phycoerythrin, hydrocolloids of approximately 28.21±2.5% carrageenan and 20.46±1.5% agar, and finally cellulose of approximately 20.15±1.5%. Additionally, the extracted carrageenan proved an efficient antimicrobial action against pathogenic microorganisms that supports its use for water densification, food packing, and wound dressing.

Keywords: *Pterocladia capillacea* valorization; Fully integrated biorefinery process; Value-added products; Blue economy

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PROCESS ANALYSIS OF FLEXIBLE GASIFICATION BASED THERMOCHEMICAL CONVERSION CONCEPTS OF BIOGENIC RESIDUES AND WASTES INTO BIOMETHANE AND BIOCHAR

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Abstract

This study aims to provide the main performance estimates for new concepts and operation modes for bio-SNG and biochar production from biogenic residues and waste. Dedicated integrated process models were developed in Aspen Plus and simulation runs were performed for targeted cases studies, calculating the basic mass and energy flow parameters. Simulation results reveal the improved characteristics of the proposed proposed concepts for conversion to biomethane in a more efficient way compared to the reference scenario. The considerably reduced oxygen demand at the ATR owed to the improved catalyst played an important role on that. The co-production mode schemes showed promising results as concern the overall plant efficiency and the elevated total carbon utilization. Finally, the hybrid cases require an electrolyser with a capacity that is 70% smaller than that of the gasifier but more than 50% of carbon utilization and over 70% total plant energy efficiency can be achieved.

Keywords: Biomass gasification, bio-SNG, biochar, process simulation

1 INTRODUCTION

Biomass is a renewable energy source (RES) with the greatest potential to contribute to global energy needs and fight against climate crisis. Advanced biofuels that are derived from feedstock that are not competitive to food such as agricultural forest residues and biogenic wastes, is a promising option to replace fossil fuels with a sustainable and environmental friendly way.

Gasification is a key biomass conversion technology where syngas, as the main process product can be used as feedstock for the synthesis of products, including liquid and gaseous biofuels such as synthetic natural gas.

The global demand for natural gas is expected to increase in the coming decades, driven mainly by increasing power production from natural gas and as the “transition fuel” to the decarbonized era. Biomethane (or Bio-SNG) can be produced via either anaerobic digestion or gasification [6] and can reduce the environmental footprint of a natural gas network when it is injected to the pipeline. Although biogas plant is the commercially available technology to produced biomethane after upgrading, the capacity of such plants is limited to few MW_{th}. Large scale (decades of MW_{th}) bioSNG production can be realized via biomass gasification. Although

several studies have been dedicated in such biomass to SNG configurations, new advances in key components of the process such as the gasifier and the catalytic reformer are observed and deserve further investigation at system level. Process simulation analysis is a useful tool for a preliminary assessment of novel biorefinery concepts, evaluating the overall system performance in terms or energy and identifying the design aspects for optimal operation. Main goal of this study is to present a new, gasification based pathway that handles biogenic residues and wastes such as bark and SRF to convert them into biomethane, biochar and heat. Several cases with different operation mode, feedstock and configuration are modelled and simulated in Aspen Plus.

2 CONCEPTS DESCRIPTION

In the EU funded FlexSNG project [1], a flexible and cost-effective gasification-based process for the production of pipeline-quality biomethane (bio-based synthetic natural gas, bio-SNG), high-value biochar and renewable heat from a wide variety of low-quality biomass residues and biogenic waste feedstocks is developed. The gasification concept is based on “one plant, two modes” approach where the plant can switch

between: co-production of biomethane, biochar and heat (*co-production mode*), and maximised production of biomethane and heat (*maximization mode*). The key idea was that the single plant can adapt to changes in market conditions (e.g. demand of biochar) or feedstock availability and price by switching operation mode - thereby maximising plant revenue year round. Feedstock is first converted to raw syngas (and biochar) - using a mixture of oxygen and steam as fluidizing agents.

The overall system can be split into three main parts. The first one (gasification part) consists all the steps for the biomass conversion into syngas and biochar, including the drying and pre-treatment, the steam/O₂ gasification, the solids (ash and char) removal from raw syngas via gas filter and the tars removal via steam/O₂ blown autothermal reformer (ATR). Moreover, the pure (99.5% v/v) oxygen production through Air Separation Unit (ASU) is also considered. The second part consists the remaining syngas cleaning steps (two-stage water scrubber cooler for NH₃ removal, H₂S removal via activated carbon and ZnO sorbents), the methanation process and the bio-SNG purification via water and CO₂ removal. If needed, a shift reactor is interfered between the syngas compressor and the methanation reactors to regulate the H₂/CO molar ratio equal to 3.

The third steps includes the heat exchangers network for hot water/steam production from the excess heat valorization, and further use of them either within the process or externally for district heating.

2.1 Biorefinery

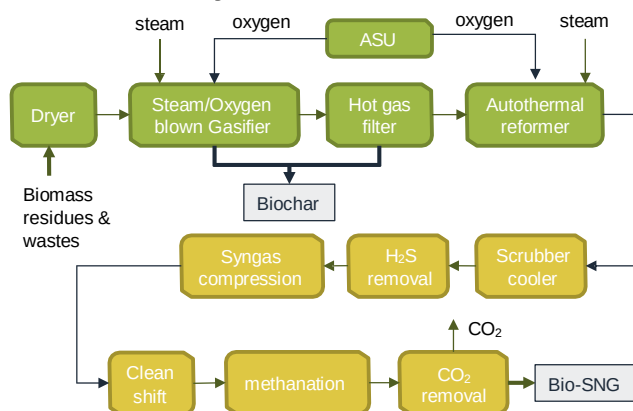


Figure 1. Biorefinery block flow diagram

Biorefinery plants (Figure 1) can be integrated with existing forest industries or agricultural sites using the sidestreams as feedstock and supplying

steam for industrial use. Such feedstocks are expected to produce biochar of good-quality that can be applied also for soil amendment applications.

2.2 Cityrefinery

The cityrefinery plants (Figure 2) are suggested to convert urban waste and biomass residues into high-value products in support of cities circular economy strategies. This feedstock potential in city areas consists of materials that are often difficult to recycle and thus poorly utilized, e.g. municipal solid waste (MSW), demolition wood, combustible fraction of construction wastes, residues from parks and horticulture as well as certain waste fractions from the surrounding industries and municipalities. This concept has two gasification lines. In line 1, woody biomass is gasified producing syngas and biochar according to co-production mode operational principles. In line 2, the produced char is co-gasified with waste for the production of syngas (maximization mode).

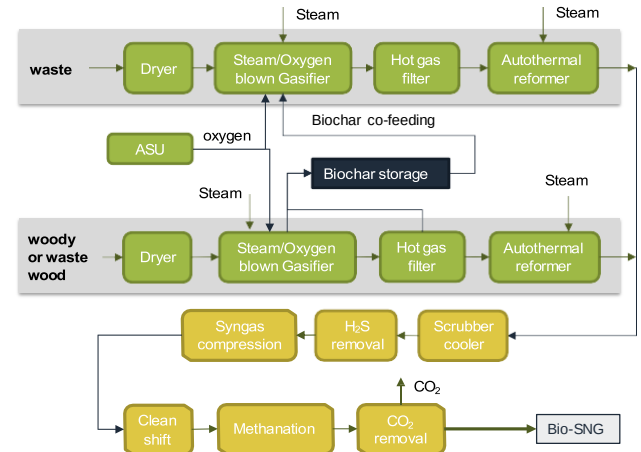


Figure 2. Cityrefinery block flow diagram

2.3 Hybrid

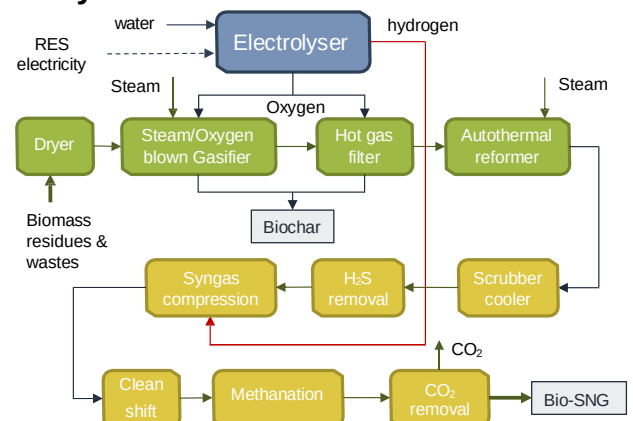


Figure 3. Hybrid block flow diagram

Finally yet importantly, the gasification/synthesis process can also be coupled with electrolysis (hybrid plant, Figure 3) that allows exploiting the surplus low-cost electricity available in the grid (typically in the summer season) and increasing the biomethane output of the plant by hydrogen boosting. In hybrid plants, electrolytic hydrogen can be used to boost biomethane production when low-cost electricity is accessible.

2.4 Reference case

In order to assess the performance improvements of the proposed concepts compared to other bio-SNG production pathways, a reference case study is introduced. This scenario consists a biomass to SNG process via gasification based on past studies [2], [3]. The basic aspects that make this reference case different from the previous ones are the different operation parameters and performance of gasifier and reformer, the sour WGS, the H₂S/CO₂ removal before methanation via Rectisol process and the different configuration at the methanation process.

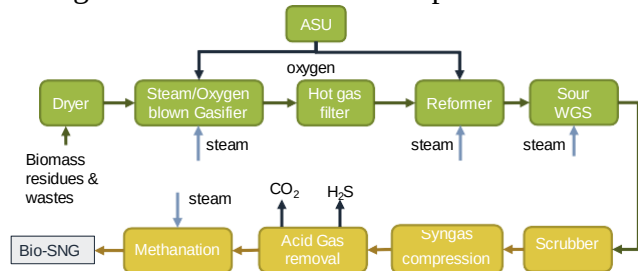


Figure 4. Reference case block flow diagram

Table 2. Simulation results for examined cases: flow rates (in kg/s) for basic streams

CASE	Ref	1	2	3	4		5	6
					line 1	line 2		
inlet streams								
wet biomass	11.63	11.63	11.63	11.84	5.82	3.17	11.63	11.63
dried biomass	6.84	6.61	6.61	6.58	3.31	2.70	6.61	6.61
steam for gasifier	1.90	2.48	2.66	2.46	1.33	1.35	2.48	2.66
O ₂ for gasifier	1.90	2.07	1.78	1.89	0.89	1.12	2.07	1.78
steam for ATR	1.24	0.65	0.68	0.69	0.12	0.58	0.65	0.68
O ₂ for ATR	1.24	0.81	0.85	0.87	0.19	0.49	0.81	0.85
steam for methanation	0.10	0	0	0	0		0	0
cooling water	914.40	261.10	280.56	175.00	313.89		300.00	291.67
outlet streams								
CO ₂ stream	6.82	7.2	6.57	6.32	6.31		5.11	4.97
ash	0.24	0.3	0.14	0.67	0.60		0.33	0.14
SNG	1.31	1.4	1.29	1.14	1.27		2.11	1.87
biochar	0.00	0.00	0.39	0.00	-0.19		0.00	0.39
wastewater	68.64	264.9	284.74	179.45	318.14		305.48	297.16

3 MODEL METHODOLOGY

The process models were developed in Aspen Plus. The gasifier/ATR modelling was based on equilibrium for the prediction of the main syngas components whereas for rest ones such as light hydrocarbons, tars and impurities (NH₃, COS, H₂S etc.) was based on data from relevant experimental campaigns [4]. More details about this modelling approach can be found in [5]. The examined cases are summarized in Table 1.

Table 1. Examined cases main specifications

Case	Feeds tock	Th. input (MW)	Concept	Gasific. mode ¹
1	Bark	100	Biorefinery	Max.
2	Bark	100	Biorefinery	Co-prod.
3	Straw	100	Biorefinery	Max.
4	Bark +SRF	50+50	Cityrefinery	Co-prod. & Max.
5	Bark	100	Hybrid	Max.
6	Bark	100	Hybrid	Co-prod.

¹ max: maximised production of biomethane and heat, co-prod: co-production of biomethane, biochar and heat

Moreover, the reference case was modelled according to process specifications in [3].

4 SIMULATION RESULTS

Table 2 summarizes the main streams flow rates of the examined cases.

As expected, the highest SNG production is observed at Hybrid cases (5 and 6) thanks to the considerable boosting in CH₄ synthesis from the electrolytic hydrogen.

The steam to biomass ratio was calculated for all cases and was found it increased compared to the reference case. Especially at the SRF/biochar gasification case, the steam to biomass ratio is 0.69 mainly because of the high steam requirements for the SRF/bio-char gasification.

It is important to mention that S/C ratio that was calculated for the reforming process was below 1 for woody biomass cases (forest residues and bark). Given also the fact that no coke formation was observed during the experimental campaigns, it is safe to say that the specific ATR technology offers the advantage of cracking the produced tars quite effectively with relevant low steam and oxygen requirements.

In Case 4, the produced biochar from the Line 1 (bark co-production) is less than the required biochar the Line 2 operation with the same heat input. This configuration makes more sense when a gasifier with a certain capacity is considered

that is able to operate either according to Line 1 or to Line 2 operating parameters consecutively. In other words, Line 1 should operate more hours than Line 2 in order to secure the required amount of biochar for the operation of Line 2 at the same load, without seeking for external biochar. A more detailed analysis on the operation planning for this concept should be analysed in follow-up study.

A schematic illustration of the main energy flows is seen at Sankey diagrams that are shown in Figures 5-7. The waste heat streams also include the heat losses at various process such as in gasification and reformer. Case 2 and Case 5, which are the cases that biochar is considered among the products, present the lowest waste heat, i.e. the lowest amount of energy that either lost or remain unutilized. Comparing Case 1 and Case 4 as the two ways for maximizing SNG production without the assistance of the electrolytic hydrogen, Case 1 configuration leads to a higher biomethane synthesis.

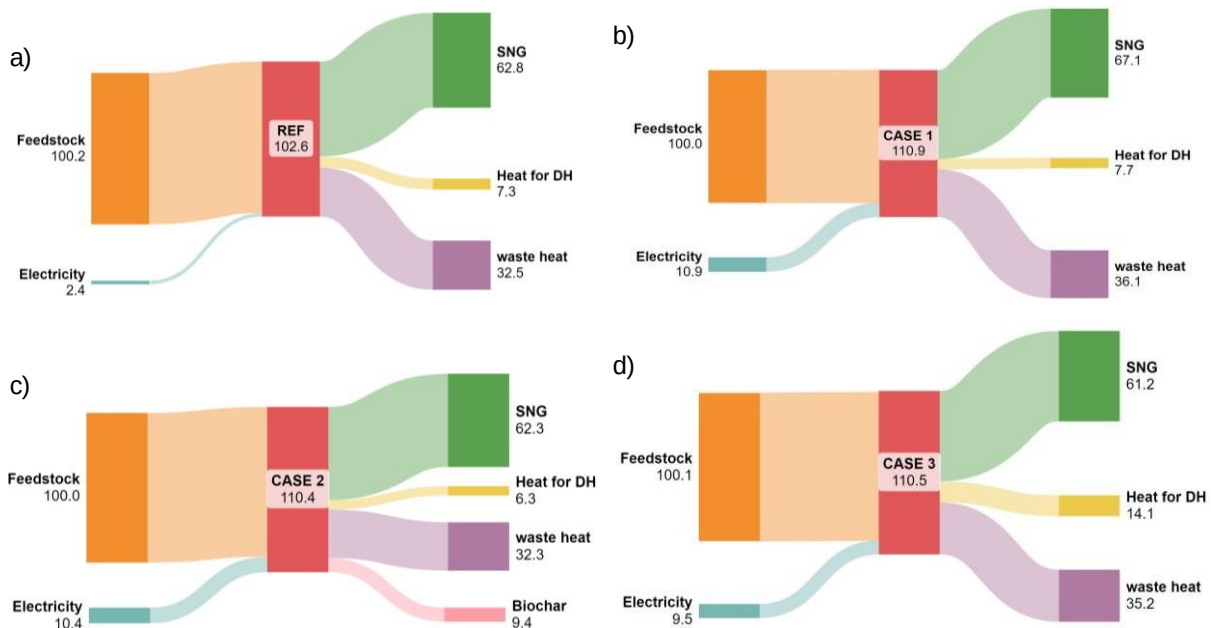


Figure 5. Basic inlet and outlet energy flows (in MW) in a) Reference, b) Case 1, c) Case 2 and d) Case 3 (made at sankeyMATIC.com)

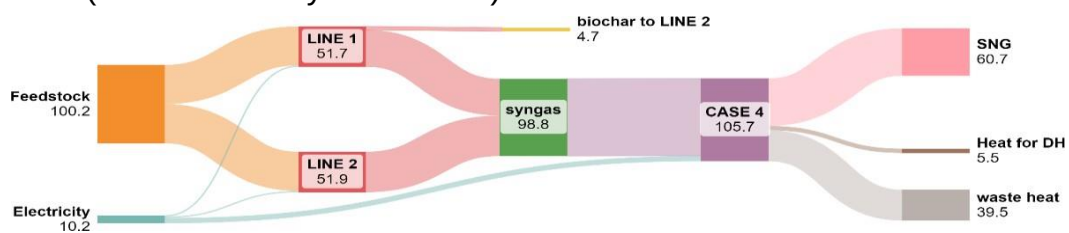


Figure 6. Basic inlet and outlet energy flows (in MW) in Case 4 (made at sankeyMATIC.com)

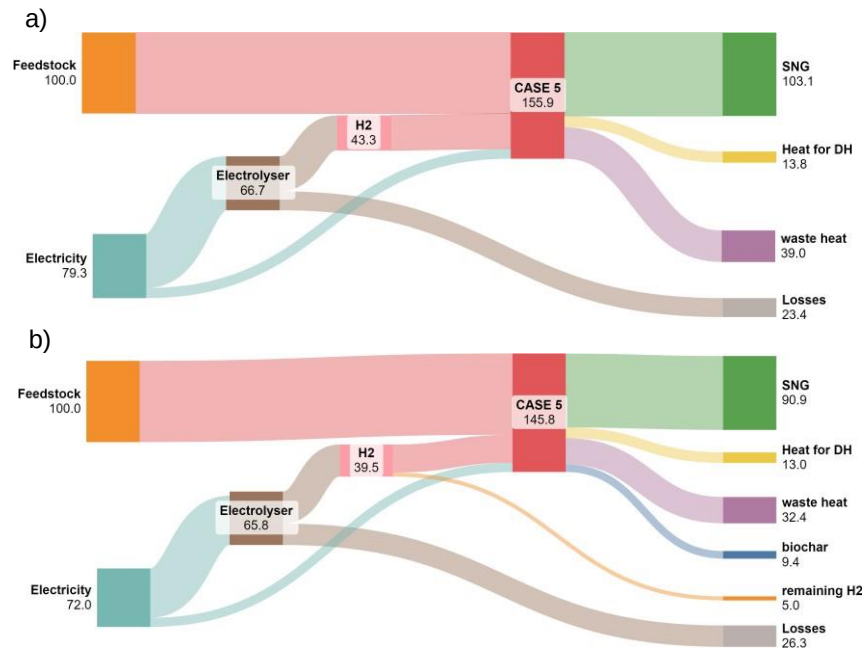


Figure 7. Basic inlet and outlet energy flows (in MW) in a) Case 5 and b) Case 6 (made at sankeyMATIC.com)

Table 3 Basic performance indicators for all examined cases

CASE	Ref.	1	2	3	4	5	6
Plant heat input (MW_{th})	100.2	100.0	100.0	100.9	100.2	100.0	100.0
Gasifier heat input (MW_{th})	111.4	111.6	111.6	100.9	111.5	111.6	111.6
Total oxygen demand (kg/MWh)	101.59	92.88	84.64	98.35	94.38	92.90	84.65
ASU consumptions (MW_e/MW_{th})	0.0267	0.0244	0.0223	0.0259	0.0248	-	-
Total steam demand (kg/MWh)	101.59	101.00	107.82	112.4	116.4	101.02	107.83
CGE after filter	82.8%	82.6%	76.7%	85.2%	76.2%	82.6%	76.7%
CGE after reformer	72.2%	75.6%	69.8%	75.5%	68.3%	75.6%	69.8%
H ₂ /CO ratio after reformer	1.34	1.43	1.61	1.6	1.6	1.44	1.61
Total electricity consumption (kWh _e /kWh of biofuels)	0.172	0.162	0.145	0.156	0.156	0.769	0.718
Conversion efficiency to bioSNG	56.4%	60.1%	55.8%	60.6%	54.4%	66.5%	62.2%
Conversion efficiency to biomethane, biochar and heat	69.4%	67.0%	70.0%	74.6%	63.6%	65.5%	71.3%
Total carbon utilization	31.8%	33.5%	41.0%	30.4%	43.3%	51.5%	55.3%

Table 3 summarizes the key performance indicators from the heat and mass balance calculations. In all cases, the plant heat input as it is expressed from the heat content of the initial biomass feedstock is the same. Apart from the straw case (Case 3) the gasifier heat input is greater because of the biomass pre-drying. Lower oxygen demands are observed in all Cases compared to the reference scenario. In co-production mode cases, this is because the lower gasification degree and the lower char conversion. In the maximization mode cases, this is attributed to the improved performance of

ATR. This oxygen demand reduction has a beneficial impact on both the reduction of ASU electricity consumptions and its size, leading to lower respective operational and investment costs. Apart from the hybrid mode cases for apparent reasons, the rest proposed cases present a reduction in overall electricity consumptions by 5.9% to 15.8%. Main reason for that is the absence of the energy demanding Rectisol process and the ASU energy demands. It is noteworthy that the gasifier operation pressure at Cases 1-6 is at 1.5 bar compared to the reference case (3.5bar) leading to higher syngas

compression duties. Nevertheless, the overall energy consumptions are reduced. It should be mentioned that the reference scenario converts a great amount of excess heat into electricity and almost 80% of the electricity demands are covered internally. As a result, the specific demand for electricity externally is 0.038 kWh_e/kWh of produced biofuel.

The proposed concepts improve the conversion efficiency of SNG production compared to the reference case by 10%. Although the gasification performance is kept at as high level as in the reference case as illustrated by the CGE after filter, part of this improvement is attributed to the better operation of the catalytic ATR. This is illustrated both from the better CGE after reformer and the increased H₂/CO after that. Another element is the very good exploitation of CO towards its conversion into CH₄ and the WGS is limited up to the desired level (i.e. to reach a H₂/CO=3).

The co-production modes present higher overall conversion efficiency than the respective maximization modes. Case 3 (straw) has highest overall conversion efficiency because of the absence of dryer that consumes a considerable amount of the excess heat. In addition, for the same case the lowest C utilization is observed due to lower heating content that requires a bit higher amount of oxygen than bark.

Moreover, the hybrid cases have the highest total C utilization because the syngas enter the methanator with a H₂/CO =3, no shift reaction is required and produced CO is converted entirely into CH₄.

5 CONCLUSIONS

This study presents the simulation results from the integrated models of new process configuration concepts for the production of biomethane, biochar and heat and the assessment of their performance in term of energy and exergy.

The simulation analysis reveals that the proposed advancements in the biomass conversion into biomethane and biochar can achieve higher bioSNG yields and lower oxygen demands compared to a conventional gasification based pathway, mainly owed to the improved performance of the catalytic ATR. Moreover, high conversion efficiency and good performance are also observed when more challenging feedstock are used such as SRF and straw. The

co-production mode is a promising approach to produce bio-SNG and biochar with quite high overall efficiencies. The hybrid concept can reach up to 70% overall efficiency and >50% total carbon utilization but the electricity demands for electrolytic hydrogen production are very high and comparable to the respective feedstock heat input (0.67 kWh_e/kWh of inlet biomass).

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EFFECT OF H₂ ADDITION ON BIOGAS MIXTURE IN A INDUSTRIAL BURNER

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Abstract

Biogas mixtures are of great importance in terms of clean and renewable energy sources. There are current studies to improve the combustion performance of biogas mixtures, which are prone to blowoff instability due to their low calorific values. In this study, a combustion test of a mixture containing 60% methane and 40% carbon dioxide by volume was carried out in an industrial biogas burner with a thermal power of 41 - 100 kW. In the experiments carried out, the thermal power was kept constant at 41 kW. In addition, the air was calculated according to the stoichiometric combustion equation and combustion was carried out with a 20% excess air coefficient. Following the experiment carried out with the biogas mixture, 10% volumetric H₂ gas was added into the mixture. As a result of the addition of hydrogen, data on the change in the flame temperature and pollutant emissions of the burner were obtained. The study results showed that the biogas mixture produced high CO emissions and low flame temperature due to the high CO₂ gas in it. On the other hand, as a result of the addition of H₂, there was an increase in flame temperature and a decrease in CO emission.

Keywords: Biogas, Hydrogen, Pollutant Emissions.

1 INTRODUCTION

Hydrocarbon fuels still provide a significant portion of today's energy production. Among these fuels, Methane stands out as having the lowest Carbon / Hydrogen ratio. On the other hand, methane gas can be extracted from nature as a fossil fuel or produced by renewable means. Although it contains high amounts of methane in biogas mixtures, it attracts the attention of researchers as a renewable and carbon-neutral fuel that also contains carbon dioxide. Despite these advantages of biogas mixtures, their stable combustion range is low due to their low calorific values. Researchers are currently working on increasing the flame stability of biogas mixtures.

Bykov et al. [1] investigated plasma-assisted biogas combustion in a swirl burner. Methane in biogas was replaced by volume between 25% and 60%. Study results showed that plasma support increased flame stability. On the other hand, under plasma assisted combustion

conditions, CO emissions decreased from 1550 ppm to 45 ppm. Devi et al., [2] made a comparative performance evaluation of biogas combustion in a porous radiant burner and a conventional burner. A biogas mixture created from cow manure containing 43-56% CH₄ was used as fuel. Study results showed that the porous burner provided a 38% improvement in combustion efficiency. In terms of pollutant emissions, much lower CO and NO_x emission values were measured compared to the traditional burner. Alabaş et al. [3] studied the dilution of the biogas jet flame with two different gases, N₂ and Argon. In the study, the thermo-acoustic combustion instability of the flame was tested. Study results showed that both N₂ and Aron dilution reduced flame dynamic instabilities. On the other hand, as a result of the increase in dilution rate, there was a significant increase in CO emissions.

Due to the low calorific value structure of biogas mixtures, their combustion in mixtures with different fuels is tested in studies in the

literature. In this way, a stable combustion is aimed. Mong et al. [4] investigated the biogas/ammonia flame characteristics in a swirl combustion. The results showed that the flame temperature decreased as the CO₂ in the biogas mixture was increased from 0% to 40%. The presence of CO₂ reduced both the flame speed and reactivity of the Ammonia/Methane mixture. Alabaş et al., [5] enriched the biogas mixture with both hydrogen and oxygen. Study results show that adding hydrogen to the biogas mixture increases flame stability. When the hydrogen addition rate was increased from 0% to 30% by volume, the CO emission value decreased from 5532 ppm to 130 ppm.

When these studies in the literature are examined, it can be seen that research on biogas mixtures is actual. These studies are generally carried out in numerical analyzes and pilot burners. In this study, enrichment of the biogas mixture with hydrogen was tested in an industrial burner.

2 METHODOLOGY

The experiments on enrichment of biogas mixture with hydrogen were carried out in the experimental setup shown in Figure 1. In the experimental system, the burner power can be changed between 41 kW and 100 kW. In this study, the burner power was kept constant as 41 kW. On the other hand, the industrial burner automatically operates with 20% excess air coefficient. The methane gas used in the experiments is supplied directly from the natural gas line. In order to be converted into biogas mixture, CO₂ gas is fed to the burner from an external tank. Hydrogen gas used to enrich the biogas mixture is stored in a steel tank. All these gases pass through mass flow controllers and are controlled instantly. In order to see the effect of hydrogen enrichment, 10% hydrogen addition was carried out by volume. As a result of all these experiments, the combustion chamber outlet temperature was obtained by means of a thermocouple placed at the combustion chamber outlet.

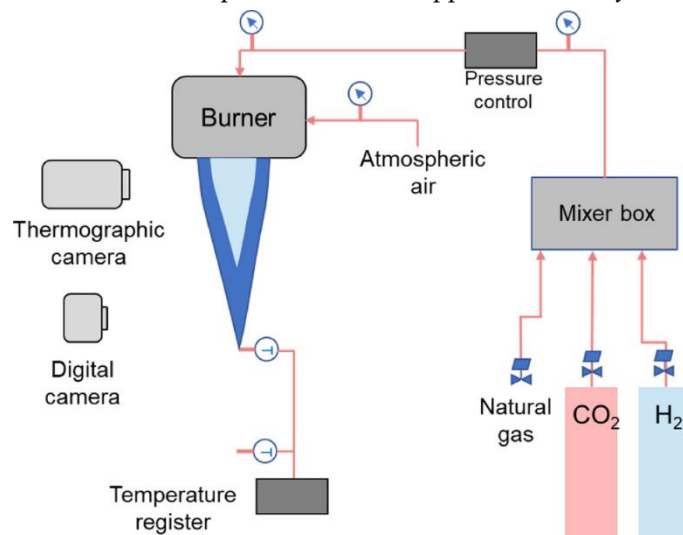


Figure 1. Schematic Desing of Experimental System

The burner used in the experiments is shown in Figure 2. This burner is a Bentone brand Biogas burner used in industrial applications.



Figure 2. Biogas Burner

3 RESULTS AND DISCUSSIONS

In this study, in order to see the effect of hydrogen enrichment, firstly a biogas mixture containing 60% CH₄ - 40% CO₂ was tested. Firstly, the combustion end temperature values were obtained under these experimental conditions. Then, the effect of 10% volumetric H₂ addition on the combustion end temperature and total efficiency was determined. The combustion end temperature of the biogas mixture containing 60% methane and the temperature value after hydrogen addition are presented in Figure 3. According to the values

obtained as a result of the experiments, it can be clearly seen that hydrogen addition increases the combustion chamber outlet temperature. This result is predictable due to the high adiabatic flame temperature of hydrogen [6]. However, in the combustion studies in the literature, the opposite situations can be seen due to combustion instabilities after critical values. It is seen that the industrial biogas burner used in this study can operate in full stability under 10% H₂ addition conditions.

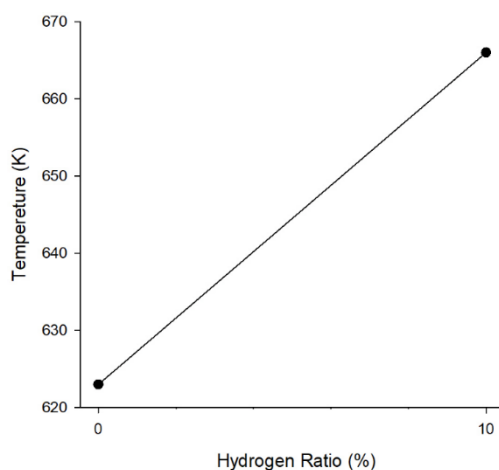


Figure 3. Outlet Temperature of Combustion Chamber

Another graph obtained from the results obtained in the study is presented in Figure 4. This graph shows the entropy changes of the air entering the combustion chamber in the cases of biogas mixture and hydrogen addition. The basic expectation in a gas turbine combustion chamber is to increase the enthalpy of the incoming air and ensure the flow of these high energy burnt gases to the turbine. According to the results obtained in the experiments, it is clearly seen that the addition of hydrogen increases the combustion chamber exit enthalpy.

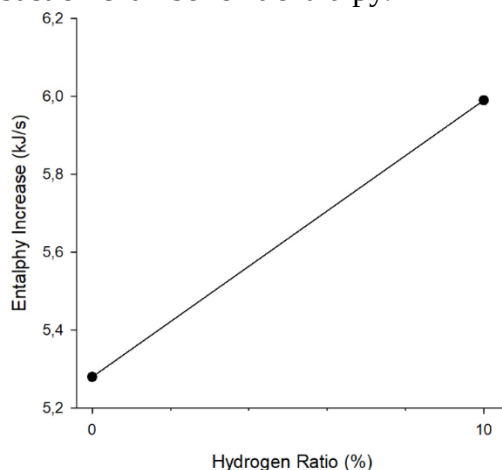


Figure 4. Enthalpy Increase in Combustion Chamber

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STUDY THE EFFECT OF SMOG ON THE ANATOMICAL AND PHYSIOLOGICAL BEHAVIOUR OF SOME SELECTED TREES

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Abstract

An emerging form of secondary pollution is smog emerging from the excessive combustion of fossil fuels, deforestation, industrialization, etc., and is the one of the major causes of eco-toxicity. Smog is having devastating effects in Asia which is now apparent in Lahore, Pakistan. As Lahore stands second most polluted city of the world the current study aims to analyze effect of smog on some tree species of Lahore. The selected trees include some native and indigenous species *Conocarpus lancifolius*, *Calotropis gigantea*, *Eucalyptus globulus*, *Nerium oleander*, *Polyalthia longifolia*, *Dalbergia sisso*, *Alstonia scholaris*, *Azadirachta indica*, *Ficus religiosa*, *Ficus benjamina*, *Syzigium cumini*, *Ficus benghalensis*, *Putranjiva roxburgii*, *Cassia fistula*, *Mangifera indica*, *Morus nigra*. Based on the air quality index values the impact of smog was analyzed from monitored and open sites. Leaf samples were studied for morphological, anatomical, and biochemical parameters. The morphological findings reveal differences between the two sites. In morphological analysis *Ficus benghalensis*, from both sites, exhibited significant variations in the leaf fresh and dry weights. Anatomical analysis reveal an increase in the size of leaf epidermal and mesophyll cells of *Ficus benjamina*, *Ficus benghalensis*, *Cassia fistula* and *Syzigium cumini* from monitored site. The leaf samples from open site show significant reduction in their cell sizes. Leaf samples of the open site possess shrunked, sunken and disturbed stomata. Biochemically, there was considerable difference in Relative water content (RWC) and (TCH) of leaf samples of monitored site rather than open site. *Ficus religiosa* and *Putranjiva roxburgii* show higher TCH content. In case of Ascorbic Acid (AA), *Alstonia scholaris* and *Eucalyptus globulus* show almost same AA content at both sites. The biochemical results represent *Cassia fistula*, *Alstonia scholaris*, *Ficus religiosa* and *Azadirachta indica* as the probable species to tolerate smog effects at a higher rate in comparison to all other listed trees. *Dalbergia sisso* and *Cassia fistula* show higher dust content at open site likely because of their augmented epidermis. These findings are useful in the selection of resistant plant species that are least affected by smog.

Keywords: Smog, Air quality index, Foliar anatomy

COMPARATIVE STUDY OF NUTRIENT AND HEAVY METAL BEHAVIOR ALONG OUED SEBOU

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Abstract:

The surface waters of the Oued Sebou are subject to dissolved loads such as heavy metals and nutrients from various sources. These loads differ according to whether they enter the river from point or diffuse sources. Point-source pollution is the direct discharge of pollutants into watercourses. Diffuse pollutants come mainly from municipal or agricultural sources but cover a wide range of activities. These pollutants are transported by runoff and end up in rivers, streams, and lakes. This study aims to compare the behavior of nutrients and heavy metals along the Oued Sebou to identify their origins. To this end, we conducted a sampling campaign at 12 sampling points along the Sebou River. We concluded from the analysis of the various elements that nitrogenous elements are mainly derived from diffuse inputs while phosphorus comes from both point and diffuse sources. Heavy metals behave differently as they come from point sources.

Key words: Oued Sebou, nutrients, heavy metals, diffuse pollution, point-source pollution, behavior.

ENVIRONMENTAL PERFORMANCE ASSESSMENT OF DIFFERENT CSP STEEL TYPES WITH SOL-GEL COATING

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Abstract

Sol-gel coatings have been extensively used as a passive protection agent for metallic elements in concentrated solar power (CSP) plants over the last decade. This type of ceramic coating is highly versatile and simple, allowing the use of low processing temperatures and precise control of the chemical composition. However, due to their nature and/or composition, they can present significant environmental issues. In this study, an assessment of the environmental performance of the three most common steel grades in CSP installations (316L, 321H and 347H) was carried out by extracting a series of samples, applying the sol-gel solutions 3YSZ and 3YSZ-5A, and subjecting them to a Life Cycle Assessment (LCA). For this purpose, the analytical software SimaPro 9.1 and the environmental database Ecoinvent 3.5 were used. In addition, based on the ReCiPe 2016 impact assessment method and the gate-to-gate temporal arc model, the environmental impacts of the dual midpoint-endpoint approach were modelled and quantified. The results showed 347H steel as the most unfavourable steel typology, obtaining its highest environmental penalty for the 3YSZ-5A coating in the Global Warming Human Health and Fine Particulate Matter Formation impact categories. These results will allow CSP managers to identify the optimal coating solution based on the steel type used, enhancing the sustainability of the facilities, ensuring their operability, and extending their lifespan.

Keywords: Ceramic coatings; Sol-gel; CSP; Steel facilities; Life Cycle Analysis (LCA)

1 INTRODUCTION

In recent years, a general trend has been observed in the use of molten salts as heat transfer fluid (HTF) in concentrating solar power (CSP) plants. This technology has enabled higher operating temperature ranges, leading to significant increases in enthalpy gradients and, as a consequence, a substantial improvement in technological competitiveness [1].

Within the molten salts developed to act as HTF, the most widely used in the industry is the binary mixture Balf-Haifa 60%-40% (NaNO₃-KNO₃), commonly known as "Solar Salt" [2]. The latter is characterised by its high density, high specific heat, low melting point, high

thermal stability, low viscosity in the molten state and low vapour pressure [3], as well as a competitive price [4]. However, according to several experiences with this fluid in CSP environments, solar salt can cause serious corrosion problems in different metallic elements of the solar plant (tanks, pipes, etc.) [5].

In this context, the use of ceramic coatings is conceived as an imperative need in the control of the aforementioned corrosion phenomenon, being one of the most widely applied passive protection methods in CSP plants [6]. Among these, sol-gel coatings have been one of the most widely used during the last decade, presenting greater acceptance in those formed by oxides,

such as TiO_2 , ZrO_2 , $\text{SiO}_2\text{-ZrO}_2$ and $\text{ZrO}_2\text{-CeO}_2$ [7]. This type of ceramic coating is very versatile, allowing the extension of the useful life and increasing certain capacities of the materials (wear resistance, thermal resistance, hardness, etc.) while maintaining their basic properties [8]. In addition, it allows the use of low processing temperatures, precise control of chemical composition and improvement of LCOE (Levelised Cost of Energy) by reducing O&M (Operating and Maintenance) costs [9]. However, due to their nature and/or composition, they could present significant environmental problems.

Currently, several scientific studies have addressed the influence of protective coatings on metallic CSP elements in relation to corrosion caused by molten nitrate salts [10]. In this line, authors such as Dorcheh and Galetz (2016) proposed and analysed the efficiency of aluminium slurries as a solution to the corrosion process suffered by P91 and 304 steels in molten nitrates [11]. Others such as Gómez-Vidal and Morton (2016) evaluated the use of SiO_2 coatings on SS347 working in contact with eutectic mixtures of carbonates and chlorides [12]. Finally, Audigié et al. (2017) proposed and developed aluminide slurry coatings deposited on P92 ferritic-martensitic steel [13].

In addition, over the last decade, a strong trend has been observed in the combined study of the corrosion performance and the mechanical and optical properties of different ceramic coatings on diverse metallic elements of CSP facilities. For example, authors such as Kirubarahan et al. (2018) studied the corrosion behaviour and mechanical properties of Ni-YSZ protective coatings in extreme temperature environments [14]. Others, such as Rossi et al. (2023), analysed the corrosion performance and optical properties of a protective multilayer structure based on tungsten (W), chromium (Cr), titanium (Ti), aluminium oxide (Al_2O_3) and silica oxide (SiO_2) for the protection of CSP plant receiver tubes [15]. Finally, authors such as Encinas-Sánchez et al. (2023) focused on the analysis of the corrosion performance of sol-gel coatings, more specifically, of 3% mol yttria-doped zirconia ($\text{ZrO}_2\text{Y}_2\text{O}_3$, 3YSZ) [16].

However, up to now, there are no authors who have included the environmental dimension in their studies on CSP protective coatings. The aim of this work is to evaluate the environmental performance of the three most common types of steel in CSP installations (316L, 321H and 347H) by extracting a series of samples from different systems and/or facilities (pipes, tanks, etc.) and coating them with the sol-gel solutions 3YSZ and 3YSZ-5A. Thus, the optimal coating solution can be identified depending on the steel type used, improving the sustainability of the facilities, guaranteeing their operability, and extending their useful life.

2 MATERIALS AND METHODS

In order to carry out the comparative analysis of the environmental impacts associated with the different types of steel and their sol-gel coatings, the Life Cycle Assessment methodological tool was used, which bases its procedures on the regulatory framework of the ISO 14040 [17] and ISO 14044 [18] standards.

In the modelling of the metallic samples and their corresponding ceramic coatings, SimaPro 9.3 software has been used to evaluate and quantify their characteristic environmental performance [19]. Ecoinvent 3.8 was used as the environmental database, which offers full-range life cycle inventories (LCI) and allows the use of different impact assessment methods [20]. Thus, the impact assessment method selected was ReCiPe 2016, which is internationally recognised and is characterised by its dual approach (Midpoint and Endpoint) [21].

Finally, 1 cm^2 of surface area has been established as a functional unit in order to adequately relate the inputs and outputs of the process and material flow that conform the different steel samples and their coating process. Table 1,

Table 2 and Table 3 present the data of the different LCIs, one for each type of steel.

Table 1. Life Cycle Inventory of AISI 316L metal samples and their coatings

316L Sample (g)	Sol-gel coating (mg)		Energy Consumption (kWh)		
		3YSZ	3YSZ-5A	3YSZ	3YSZ-5A
3.850	PrOH	0.471	0.651	0.427	0.436
	HNO ₃	0.060	0.088		
	AcY	0.092	0.014		
	TPOZ	0.177	0.040		
	AlSB	-	0.016		

Table 2. Life Cycle Inventory of AISI 321H metal samples and their coatings

321H Sample (g)	Sol-gel coating (mg)		Energy Consumption (kWh)		
		3YSZ	3YSZ-5A	3YSZ	3YSZ-5A
3.785	PrOH	0.766	1.058	0.497	0.505
	HNO ₃	0.098	0.143		
	AcY	0.150	0.023		
	TPOZ	0.287	0.064		
	AlSB	-	0.026		

Table 3. Life Cycle Inventory of AISI 347H metal samples and their coatings

347H Sample (g)	Sol-gel coating (mg)		Energy Consumption (kWh)		
		3YSZ	3YSZ-5A	3YSZ	3YSZ-5A
3.830	PrOH	0.825	1.140	0.559	0.572
	HNO ₃	0.105	0.154		
	AcY	0.161	0.025		
	TPOZ	0.309	0.069		
	AlSB	-	0.028		

3 RESULTS

Based on the modelling and simulation of the different metallic samples and their coating process, whose LCIs have been previously described in Table 1,

Table 2 and Table 3, the following environmental impact results have been obtained for the two analytical approaches characteristic

of the ReCiPe 2016 impact assessment method (Midpoint and Endpoint).

3.1 Results according to Midpoint approach

Figure 1 illustrates the individual scoring results, under the Midpoint approach, for the comparative analysis of the coated samples.

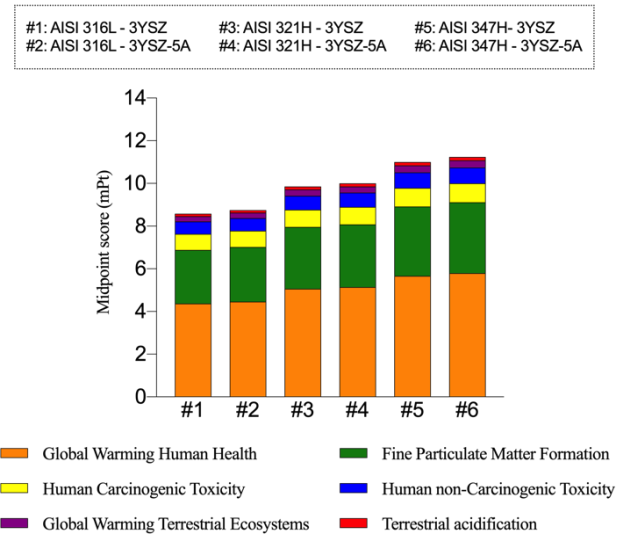


Figure 1. Impact analysis - Midpoint score.

3.2 Results according to Endpoint approach

Figure 2 illustrates the individual scoring results, under the Endpoint approach, for the comparative analysis of the coated samples.

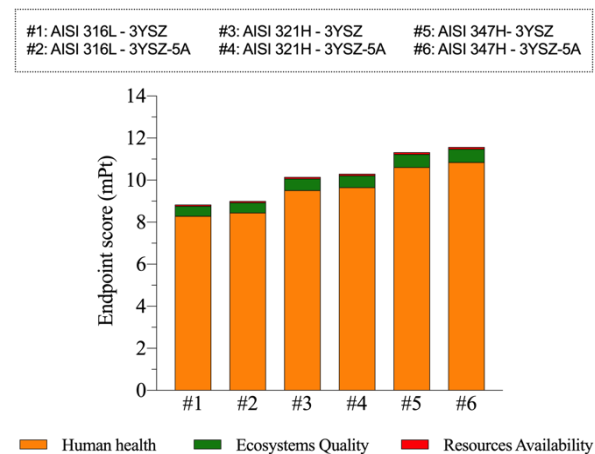


Figure 2. Impact analysis - Endpoint score.

4 DISCUSSION

Analysing the results obtained in the Endpoint approach (Human Health, Ecosystem Quality and Resource Availability), it can be concluded that the environmental impacts associated with the coated metal samples under study are mainly associated with the area of Human Health. This trend is present in the three steel typologies analysed for the 3YSZ and 3YSZ-5A coatings, with an average contribution of 93.76%. For the Ecosystem Quality area, the average contribution is lower, reaching 5.47%. Finally, the impact of the Resource Availability area was not significant (0.77%). This is due to the high availability of the resources, elements, and processes of which the different samples analysed are composed.

On the other hand, from the Midpoint approach, a common trend is observed in the results of the environmental impact of both sol-gel coatings. The environmental impact associated with the categories Fine Particulate Matter Formation, Global Warming Human Health, Human Carcinogenic Toxicity and Human non-Carcinogenic Toxicity account on average for 49.8%, 28.5%, 8.0% and 6.5%, respectively. The overall four categories together account for 92.8%. This represents 99.1% of the impact associated with the Endpoint damage area Human Health.

By comparing the results of environmental impact by steel typology, it can be seen how the AISI 316L typology presents the most favourable values (between 1.26 and 1.29 times more favourable than the 347H typology, the most unfavourable typology). These differences in environmental performance are mainly due to the presence of more demanding energy requirements (up to 1.22 times) in the pre-oxidation processes of AISI 347H metal samples.

Finally, by comparing the results obtained for both types of coating, it can be observed that the sol-gel 3YSZ coating presents the most favourable environmental impact values (between 1.01 and 1.02 times more favourable than the 3YSZ-5A coating). Furthermore, it can be observed that the main penalties of the 3YSZ-

5A coating compared to the 3YSZ coating are in the Human Health damage area and more specifically in the categories of Fine Particulate Matter Formation and Global Warming Human Health.

5 CONCLUSIONS

The LCA methodology has proven to be useful for implementing the environmental dimension in the decision-making process for the selection of sol-gel coatings in the protection of metallic elements of CSP plants, as it allows the identification of the most favourable types of coatings from an environmental perspective and according to the typology of the steel to be coated. Thus, the 3YSZ sol-gel coating is the most sustainable (between 8.84 mPt and 11.33 mPt), with values up to 1.02 times more favourable than the 3YSZ-5A coating (between 9.00 mPt and 11.57 mPt) and presenting the highest environmental impact scores in the AISI 347H steel typology (11.57 mPt).

Finally, this methodology is recommended to be used in the analysis and optimisation of new and existing coatings. In this way, the sustainability and climate neutrality of CSP facilities and their production processes is promoted, ensuring their operability and extending their service life.

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MODELLING BURDUR LAKE WATER LEVEL DYNAMICS USING ARTIFICIAL NEURAL NETWORKS: MULTI-LAYER PERCEPTRON APPROACH

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Abstract

An artificial neural network (ANN) model was developed for simulating water level dynamics in the Burdur Lake in Türkiye. Water levels in the Burdur Lake has changes considerably in recent decades due to the climate- and human-induced impacts. In this study, monthly water levels were simulated using a multi-layer perceptron type ANN model. The model inputs included precipitation, minimum, maximum and mean air temperature, relative humidity, wind speed data available from 1980 to 2023. The performance of the model was evaluated by calculating the Nash-Sutcliffe Efficiency (NSE), Percent Bias (PBIAS), RMSE-observations standard deviation ratio (RSR), Kling-Gupta Efficiency (KGE), Root Mean Squared Error (RMSE), Coefficient of Determination (R^2) between observed and simulated water levels. 50% of the data is allocated for model training, 25% for test and 25% for holdout. We optimized the model performance by analysing the effects of various input data sets, activations functions, model training algorithms. The analysis with different input datasets showed that the model was most sensitive to previous month water levels. The best result was obtained with hyperbolic tangent-identity activation functions and Scaled Conjugate Gradient optimization algorithm. With this configuration we obtained NSE as 0.993, PBIAS as 0.032, RSR as 0.081, KGE as 0.999, RMSE as 0.424 m, and R^2 as 0.993.

Keywords: Burdur Lake, Artificial Neural Networks (ANNs), Multi-Layer Perceptron (MLP), Modelling

1 INTRODUCTION

With the increase in water consumption and the growing pressure of climate change, availability of water has become one of the most critical issues of the 21st century. Water resources in the hydrological cycle are essential for humanity and critical for meeting municipal, agricultural, and industrial needs. They are also crucial for the sustainability of water-dependent ecosystems. Unfortunately, these resources are under serious pressure due to disruptions in the hydrological balance [1]. Additionally, global conditions such as climate change and water scarcity are worsening [2].

Water conservation studies are becoming more important to protect water resources. Methods such as integrated basin management [3], numerical water management [4], and drainage basin management [5] are a few techniques proposed for better managing water resources. Studies that focus on water availability [6, 7] and water quality [8, 9] have increased along with studies that make predictions about future conditions [10].

Modelling techniques play a significant role in water resources management. With the availability of more data from remote sensing devices [7] and field measurements [8, 11], the need for models has increased. In general models can be classified into two: (i) Data Driven Models [2, 10, 12], (ii) Physically-Based Models [10, 13]. Artificial neural networks (ANNs) are among the data-driven models, used frequently in modelling studies. ANNs have fast learning ability [14, 15] and they are also advantageous due to their ability to learn large and complex data, being adaptable, having the ability to adapt, and making predictions with high accuracy [16]. ANNs can include feedforward methods, where the output data is passed forward through the neurons to produce the final output, and feedback (or recurrent) methods, where the output data is redirected back into the network and used as input for the current or previous neurons to refine the output.

In the study, we developed an Multi-Layer Perceptron (MLP) type ANN model to simulate water level dynamics at Burdur Lake. Lake levels were predicted using the meteorological data as

input and employing data from the 1980-2023 period, during which strong water level fluctuations were observed.

2 MATERIAL AND METHODS

2.1 Study Area

Water stress resulting from climatic changes and artificial impacts on the hydrological cycle in Türkiye has reached significant levels [17, 18]. Burdur Lake is one of the ecosystems affected significantly by these changes.

Burdur Lake is a natural lake located in the southwest of Türkiye, between the Burdur provincial center and the districts of Isparta Gönen and Isparta Keçiborlu (Figure 1). The lake is situated in an area bordered by Söğüt Mountain to the northwest, the Suludere Yayladağ hills to the southeast, and alluvial plains to the southwest and northeast. The Burdur Lake Basin has an altitude of 1100-1200 meters above sea level and is located in the Western Taurus Mountains. The coordinates of the lake are between latitudes 37.65°-37.80° N and longitudes 30.06°-30.32° E,

with a surface area of approximately 153 km². The maximum depth of the lake is 110 meters [19]. The basin where Burdur Lake is located is a tectonic depression. Consequently, Burdur Lake is a closed basin with no hydrological outflow [20, 21]. Inputs to the lake include rainfall, streamflow, and groundwater inflow, while the only output is evaporation. The rivers that feed Burdur Lake include Bozçay, Suludere, Asar Stream, and Keçiborlu Stream. These rivers experience significant flow losses during the summer months, with some rivers drying out entirely.

The average annual precipitation in the basin is approximately 400 mm, and the average temperature is 14 °C. Summers in the Burdur Lake Basin are hot and dry, while winters are cool and snowy. According to the State Meteorology Service (MGM) Thornthwaite Climate Classification, the study area has a semi-dry and low-humid (2nd-degree mesothermal) climate [19, 22]. Meteorological time series for the basin are given in Figure 2.

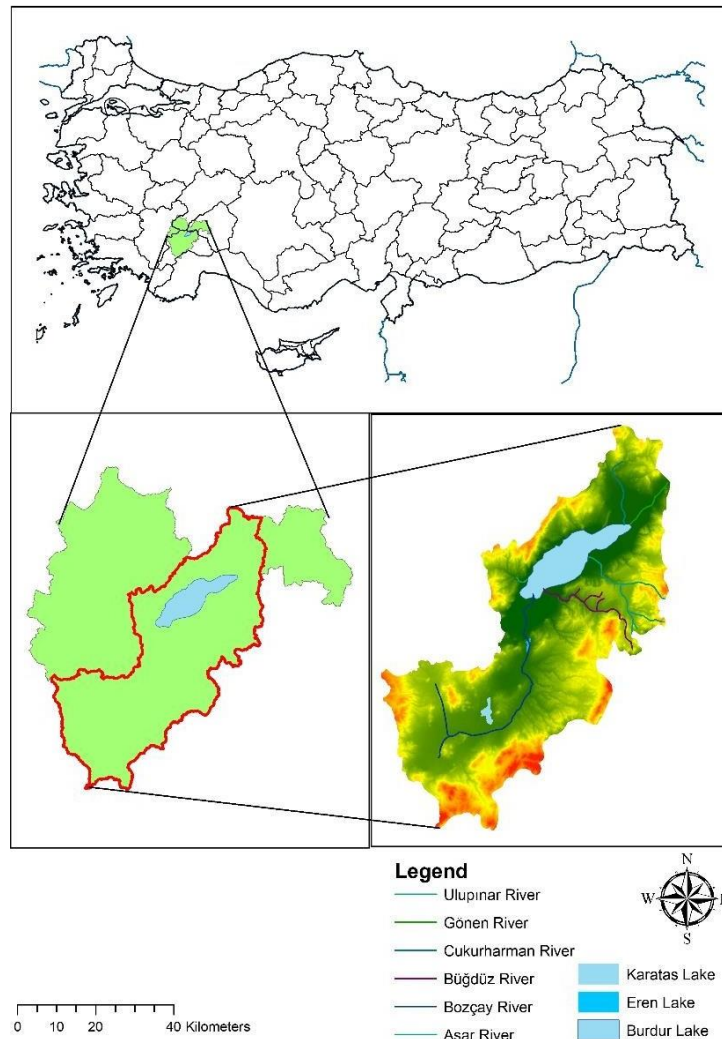


Figure 1: Study area

2.2 Data Collection

The data used in the study (Figure 2) were obtained from the State Hydraulic Works (DSI) and the State Meteorology Service (MGM). Data received from DSI Burdur Lake levels. The data

obtained from the MGM were precipitation, air temperature (average, minimum, and maximum), wind speed, and relative humidity. The data were available on the monthly timescale for the 1980-2023 period.

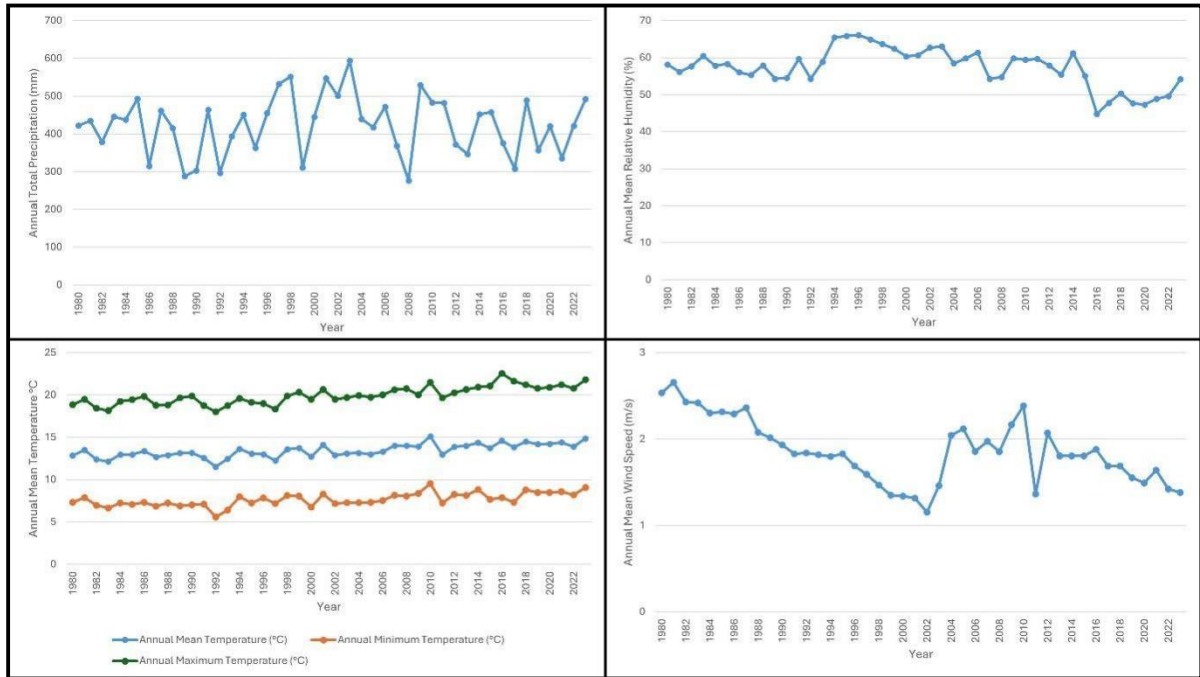


Figure 2: Meteorological data used in the analysis

2.3 Model Development

ANNs are mathematical models inspired by the working principles of the human brain. A classical ANN basically consists of five main structures. The first structure comprises input neurons that receive the input data. The second structure involves the weighting mechanisms used to analyse the data in the input cells. Following these two structures are the aggregation function and the activation function. The aggregation function collects the weighted data, while the activation function determines which of the collected data will be activated [15, 23]. Activation functions can be shaped according to the dataset, computational cost, and classification goal. Sigmoid (Logistic) Function, Tangent (Tanh) Hyperbolic Function, Rectified Linear Unit (ReLU) Function, Leaky ReLU Function, Softmax are the main activation functions that can be used with ANNs [23, 24].

Multilayer Perceptrons (MLPs) are a type of ANN with a feedforward structure. In other words, the output data from the neurons do not affect the neuron itself. Neurons are connected through hidden layers. ANNs incorporate an activation function and an output function in their structure. The settings used in the study for

optimizing the parameters of the model are given in Table. 1. The analyses were conducted using SPSS 22 software.

2.4 Model Evaluation

We calculated the Nash-Sutcliffe Efficiency (NSE), Percent Bias (PBIAS), RMSE-observations standard deviation ratio (RSR), Kling-Gupta Efficiency (KGE), Root Mean Squared Error (RMSE), Coefficient of Determination (R^2) for performance evaluation (Eq. 1-6). We used the criteria provided in Table 3 for RSR, NSE, and PBIAS. For KGE and RMSE, we aimed to obtain values closer to 0. For R^2 , we aimed to obtain values greater than 0.5 and close to 1.

3 RESULTS

In this study, we developed ANN models by using meteorological data (precipitation (PCP), Maximum Temperature (MaxT), Minimum Temperature (MinT), Average Temperature (MeanT), Relative Humidity (HUM), Wind Speed (WND)) and water levels in the previous time step (LVL) as input and water levels as the output. We run the models with different input data tests listed in Table 1.

Table 1: Tested Parameter Settings

Parameter Name	Options
Min Units Hidden Layer	1
Max Units Hidden Layer	50, 100, 150, 50/100, 10/50
Activation Function	Hyperbolic Tangent, Sigmoid
Output Layer Activation Function	Identity, Hyperbolic Tangent, Sigmoid
Rescaling of Covariates	Standardized, Normalized, Adjusted Normalized
Training	50
Test	25
HoldOut	25
Optimization Algorithms	Scaled Conjugate Gradient, Gradient Descent
Max Training Epochs	Compute Automatically

Table 2: Performance Ratings for RSR, NSE and PBIAS [25]

Performance Rating	RSR	NSE	PBIAS
Very Good	$0.00 \leq \text{RSR} \leq 0.50$	$0.75 < \text{NSE} \leq 1.00$	$\text{PBIAS} < \pm 10$
Good	$0.50 < \text{RSR} \leq 0.60$	$0.65 < \text{NSE} \leq 0.75$	$\pm 10 \leq \text{PBIAS} < \pm 15$
Satisfactory	$0.60 < \text{RSR} \leq 0.70$	$0.50 < \text{NSE} \leq 0.65$	$\pm 15 \leq \text{PBIAS} < \pm 25$
Unsatisfactory	$\text{RSR} > 0.70$	$\text{NSE} \leq 0.50$	$\text{PBIAS} \geq \pm 25$

First, we developed five scenarios with different input structures to evaluate the sensitivity of the system to different inputs. In Scenario 1, only precipitation data were used as the input. In this scenario, we could not attain the satisfactory model performance. In Scenario 2, in addition to the precipitation, and the lake level in the previous timestep was added as an input. We obtained a significantly higher performance compared to Scenario 1. The result was very good according to the criteria provided in Table 2. In Scenario 3, maximum, minimum and average temperatures were included as inputs in addition to precipitation and water level in the previous time step. In this scenario, although there was a partial decrease in NSE, R^2 , r values, an

improvement in PBIAS value was observed. In Scenario 4, in addition to parameters listed in Scenario 3, relative humidity was included in the input dataset. There was again a slight decrease in NSE and R^2 values, but higher improvement in PBIAS and KGE values. In the last scenario, Scenario 5, we added wind speed to the inputs. The results of this scenario showed a low level of decrease in all statistical methods. However, after this stage, since there were very small differences between the other scenarios and Scenario 5, and it was thought that this difference could change with the model settings, we optimized the conditions by using the inputs listed under Scenario 5.

Table 3: Settings used for sensitivity analysis

Min Units Hidden Layer	Max Units Hidden Layer	Activation Function	Output Layer Activation Function	Rescaling of Covariates	
1	50	Hyperbolic Tangent	Identity	Standardized	
Type of Training	Training	Test	HoldOut	Optimization Algorithms	Max Training Epochs
Batch	50	25	25	Scaled Conjugate Gradient	Compute Automatically

Table 4: Model results with different input datasets (PCP: Precipitation, LVL: Burdur Lake Level, MaxT: Maximum Temperature, MinT: Minimum Temperature, MeanT: Mean Temperature, HUM: Humidity, WND: Wind Speed)

Scenarios	Neurons Name	NSE	PBIAS	RSR	KGE	RMSE	R ²
Scenario1	PCP	0.009	0.508	0.995	-15.634	5.164	0.015
Scenario2	PCP LVL	0.994	-0.025	0.081	0.999	0.419	0.993
Scenario3	PCP MaxT MinT MeanT LVL	0.993	-0.018	0.081	0.999	0.423	0.993
Scenario4	PCP MaxT MinT MeanT LVL HUM	0.993	-0.015	0.082	0.999	0.424	0.993
Scenario5	PCP MaxT MinT MeanT LVL HUM WND	0.993	-0.022	0.082	0.999	0.425	0.993

We optimized the model further by using the input dataset used in Scenario 5. In this analyses, we used 50% of the data model training, 25% for testing and 25% as hold-out. As the pre-processing options, we evaluated normalization, standardization and adjusted normalization. As activation functions Hyperbolic Tangent and Sigmoid functions were included. As output activation functions, we analysed the applicability of identity, Hyperbolic Tangent and Sigmoid Functions. Model training was done using Scaled Conjugate Gradient and Gradient Descent algorithms. The maximum number of units in the hidden layer were selected as 50, 100, or 150.

The analyses showed that the best result was obtained with hyperbolic tangent-identity activation functions and Scaled Conjugate Gradient optimization algorithm. With this configuration we obtained NSE as 0.993, PBIAS as 0.032, RSR as 0.081, KGE as 0.999, RMSE as 0.424 m, and R² as 0.993. The best result obtained is shown in Figure 3.

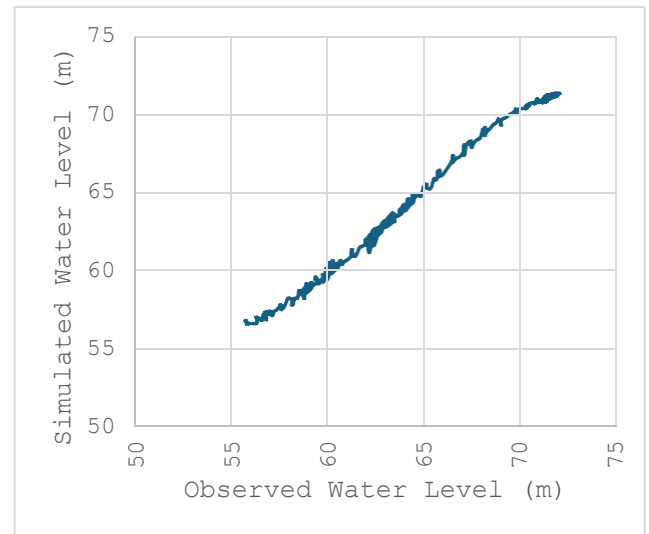


Figure 3: Observed-simulated water levels

4 CONCLUSIONS

In this study, we developed a MLP type ANN model for simulating water levels in the Burdur Lake. We obtained the best model performance when precipitation, maximum, minimum and mean air temperatures, relative humidity and wind speeds were used as inputs in addition to water levels in the previous time step. The model output was water level in the current timestep. We found that water levels in the previous time step

was the most critical input. This can be due to the presence of strong autocorrelation in the dataset. We detected a weak relationship between precipitation and the water level of Burdur Lake, which is an unexpected finding considering the role of precipitation in the hydrology of the lakes. This result suggests that artificial impacts on the lake hydrology reduced the effect of precipitation in water level dynamics.

An ANN model with one hidden layer was used. The method was optimized by using different configurations. The best result was obtained with hyperbolic tangent and identity activation functions and when scaled conjugate gradient was used as the training algorithm. With the best configuration, we could reach very good performance with all performance measures used.

This study showed that ANNs provide an effective method for simulating water level dynamics in lakes.

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RISK PRIORITIZATION OF PESTICIDES IN WASTEWATER BASED ON CONCENTRATIONS AND CONTAMINANT PROPERTIES

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ABSTRACT

The increasing food demand in parallel with the growing population requires additional needs for increasing the productivity of food products. Pesticides are chemicals that have been used for many years to reduce crop losses by killing pests. However, due to their toxicity, pesticides can be toxic to living organisms as well as other organisms, including air, water, soil and crops. In addition, these chemicals transported from the target area cause environmental pollution. As a result, the carried pesticides also reach the wastewater treatment plants.

In this study, prioritization was made with the scoring method based on the concentration, treatment efficiency, bioaccumulation and toxicity of pesticide detected in the Kayseri Advanced Biological Wastewater Treatment Plant. While the prioritization study was carried out, 19 pesticides analyzed at the influent and effluent of the wastewater treatment plant were included in the scope of the research. The measured pesticide types were ranked by scoring method using 4 criteria and the pesticide with the highest score was determined. According to the results, heptachlor-exo-epoxide received the highest score. This pesticide type received the highest 5 points from all 4 score types and finally received 20 points. The effects of these pollutants on the receiving environment need to be specially assessed.

Keywords: Wastewater, Pesticide Pollution, Pollutant Risk Prioritization

1. INTRODUCTION

As the population continues to grow, the demand for food correspondingly increases. This escalating need necessitates improved efficiency in food production. For many years, pesticides have been employed to protect crops from damage, thereby enhancing crop productivity. The World Health Organization defines pesticides as chemicals used to eliminate pests, including insects, rodents, fungi, and unwanted weeds [1]. It is estimated that approximately one third of agricultural products rely on the use of pesticides [2]. Pesticides are categorized in various ways, one of which is based on their toxicity levels. They can therefore be toxic to other organisms, including birds, fish, beneficial insects and non-target plants, as well as air,

water, soil and crops. In addition, these chemicals, which move away from targeted plants, cause environmental pollution [2]. These pesticides are eventually detected in wastewater treatment plants. It originates from non-agricultural uses of pesticides in urban wastewater treatment plants. These include turf management (golf courses, educational facilities, parks and cemeteries), industrial vegetation control (industrial facilities, electrical utilities, roads, railways, pipelines), public health (mosquito exclusion zones, rodent control areas and water areas) and non-agricultural crops such as commercial forestry, horticulture and plant nurseries [3].

Pollutants were present in significantly

high concentrations in raw wastewater (up to 684 ng/L for Diazinon) and persist in treated water after secondary and even tertiary wastewater treatment. It has also been observed that the removal of these pollutants in wastewater treatment plants is variable, often with low or negative efficiencies. Negative removal, that is, higher concentrations at the effluent, is explained as the deconjugation of metabolites of pesticides and/or conversion products, hydrolysis, and desorption from particulate matter during wastewater treatment [3].

It is very important to evaluate the risks posed by these pesticide types, whose sources are known, in the aquatic environment. In this respect, studies on the risk assessment of these pollutants individually are widely available in the literature. For example, in the Alqueva reservoir, the potential impact of pesticides on aquatic organisms belonging to the ecosystem was evaluated and the formation and risk assessment of 25 pesticides and some of their degradation products was conducted [4]. In another study, monitoring, risk assessment, and risk-based prioritization of 87 pesticides in wastewater from three WWTPs in Korea's Yeongsan River Basin were conducted, and a total of 59 pesticides were detected at concentrations ranging from 0.852 ng/L to 82,044 µg/L [5].

In addition, prioritization studies have been carried out to select these pollutants, which are numerous, for various reasons such as their inclusion in the monitoring program and the risk they pose to the environment and human health. Verlicchi et al. [6] prioritization methodology was applied according to 4 criteria (occurrence, persistence, toxicity and bioaccumulation) in order to include a limited number of pollutants with different characteristics that occur in the reuse of wastewater in monitoring programs.

On the other hand, studies have been conducted on pharmaceuticals that pose a

higher concern for the environment and human health when reclaimed water is used for irrigation. By prioritizing the formation data, persistence, toxicity and bioaccumulation data of 148 PhACs (Pharmaceutically Active Compounds), 47 compounds were identified [7].

The purpose of this study is to prioritize pesticides detected in the Kayseri Advanced Biological Wastewater Treatment Plant (Kayseri WWTP) using a scoring method based on concentration, treatment efficiency, bioaccumulation, and toxicity. The study evaluated 19 pesticides, including aldrin, alpha-hch, alpha-endosulfan, beta-endosulfan, dieldrin, gamma-hch, hexachlorobenzene, heptachlor, 2,4 DDE, 4,4 DDE, 2,4 DDD, 4,4 DDD, 2,4 DDT, 4,4 DDT, heptachlor-endo-epoxide, heptachlor-exo-epoxide, disulfoton, parathion-ethyl, and parathion-methyl, in the influent and effluent wastewater of the Kayseri WWTP. The risk ranking was conducted based on the concentrations of these pesticides detected in wastewater, their removal percentage after advanced biological treatment and the properties of pesticides in water. Thus, special studies can be carried out for pesticides determined to be high risk.

2. METARIALS AND METHODS

Kayseri Advanced Biological Treatment Plant (Kayseri WWTP) with a capacity of 110,000 m³/day, which was put into operation in 2004, was chosen as the study area. In the Kayseri WWTP, domestic wastewater generated in the Melikgazi, Kocasinan, Talas, Hacılar, and İncesu districts has been treated, and the treated water has been discharged into the Karasu Stream, which is connected to the Kızılırmak River [8].

The pesticides values in influent and effluent of Kayseri WWTP were obtained from the study of Ergin [9]. The data were analysed for the prioritization of pesticides measured between February 2018 and December 2018. While dieldrin and 4,4 DDD were detected in the influent during

certain periods and not found in the effluent, the remaining 17 pesticides were detected at least once in the effluent. For the 19 pesticides, a prioritization study was carried out according to the methodology used by Verlicchi et al. [6] for the selection of indicator pollutants of concern in the reuse of treated wastewater for irrigation. The selection of pesticides is determined by determined using four criteria: presence (C, ng/L) in the secondary effluent, persistence (P) during treatment (K, %), bioaccumulation (Log K_{ow}), and toxicity (PNEC_{FW}, µg /L).

3. RESULTS AND DISCUSSION

In the scoring made for 19 analysed pesticides, the higher the pesticide concentration in the wastewater, the higher the score. Heptachlor-endo-epoxide and

Heptachlor-exo-epoxide pollutants detected above 1000 ng/L received 5 points in the scoring. On the contrary, the higher the removal efficiency percentage, the lower the score. Pollutants with removal efficiency below 20% and pollutants that could not be detected in the effluent received 5 points. The higher the Log K_{ow} value, which is the octonal water distribution coefficient of the pollutant, the higher the score. This is due to the high bioaccumulation potential. The pollutant with a low PNEC_{FW} value has a higher score due to the high negative effect of the pollutant in water. PNEC_{FW} of these pollutants measured in Kayseri WWTP was quite low and all pollutants received the highest score. For the scoring criteria of pesticides, the criteria values given by Verlicchi et al. [6] were used

Table 1 Concentration, Persistence, Bioaccumulation, Toxicity Values of Pesticides Measured in Kayseri WWTP

Parameter	Occurrence (O)	Persistence (P)	Bioaccumulation (B)	Toxicity (T)
	Concentration (ng/L)	Removal efficiency after secondary treatment (%)	Log K _{ow} **	PNEC _{FW} (µg/L)*
Aldrin	400	36.1	6.5	0.01
Alpha-HCH	90	58.3	3.8	0
Alpha-Endosulfan	820	45.4	3.83	0.000005
Beta-Endosulfan	110	25.3	3.62	0.000005 ²
Dieldrin	20	>99 ¹	5.4	0.01
Gamma-HCH	70	21.4	3.72	0.02
Hexachlorobenzene	90	24.1	5.73	0.05
Heptachlor	160	57.8	6.1	0.0000002
2,4 DDE	450	25.6	6	0.00076
4,4 DDE	880	12.8	6.51	0.0004
2,4 DDD	50	38.9	6.02	0.0039
4,4 DDD	40	>99 ¹	6.02	0.0005
2,4 DDT	60	50,0	6.79	0.000006
4,4 DDT	160	39.9	6.91	0.01
Heptachlor-endo-epoxide	1540	33.5	5.4	0.0000002 ³
Heptachlor-exo-epoxide	2860	10.3	5.4	0.0000002
Disulfoton	620	35.8	4.02	0.082
Parathion-ethyl	800	37.2	3.83	0.05
Parathion-methyl	540	19.6	2.86	0.02

*Lowest $PNEC_{FW}$; the concentration of the pollutant at which no adverse effects will occur in the freshwater ecosystem.

**Log K_{ow} ; octanol water distribution coefficient, unit of measure for hydrophobicity or hydrophilicity of the pollutant.
1 Removal efficiency was not calculated due to undetectable pollutants in the effluent.

2 $PNEC_{FW}$ value is taken as the same as alpha endosulfan.

3 $PNEC_{FW}$ value was taken as the same as heptachlor-exo-epoxide.

Log K_{ow} values were obtained from the National Centre for Biotechnology Information [10] and Agency for Toxic Substances and Disease Registry [11] (for pesticides 3-4-9-11-13-15) and $PNEC_{FW}$ values were obtained from NORMAN Ecotoxicology Database [12]. Figure 1 shows the scores found for the prioritization of pesticides.

The pesticides monitored in Kayseri WWTP were scored according to Verlicchi et al. [6] scores and 3 pesticide types with 19 and 20 points were found. These are Heptachlor-exo-epoxide, 4,4 DDE, Heptachlor-endo-epoxide. These pollutants have the highest value with a concentration of 2860 ng/L, 880 ng/L, 1540 ng/L respectively and received 5 points. Likewise, the removal efficiencies calculated based on the values measured at the influent and effluent of the treatment plant were calculated quite low. 12 pollutants were found to be hydrophobic and therefore had a high tendency to accumulate in living organisms. The toxicity of all pollutants was found to be high.

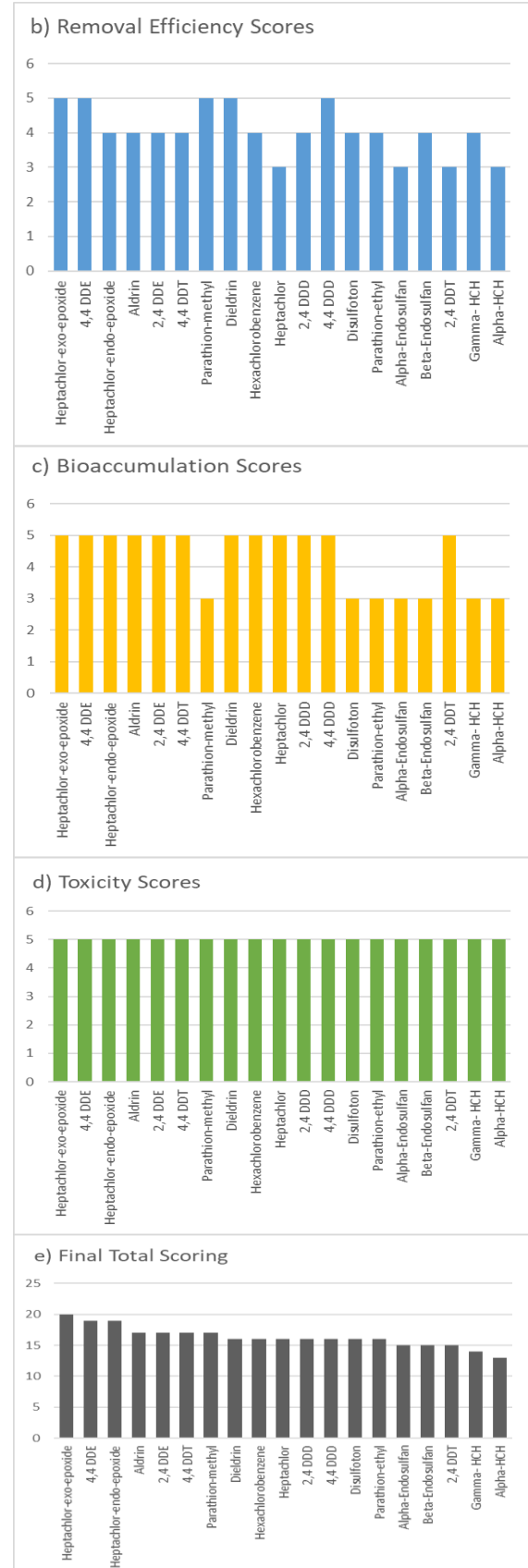
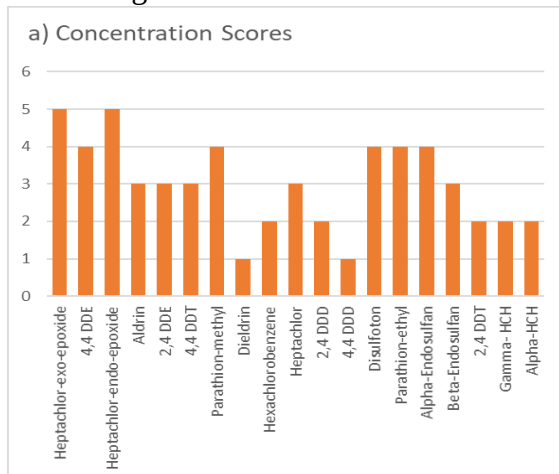


Figure 1. Scoring for Prioritization of Pesticides
a) Concentration Scores, b) Removal Efficiency Scores, c) Bioaccumulation Scores
d) Toxicity Scores e) Final Total Scoring.

4. CONCLUSION

In this study, the presence of pollutants for 19 pesticide analyses performed at the wastewater treatment plant in 2018 was prioritized according to pollutant properties. Pollutants were scored between 1-5 for 4 different criteria (concentration, removal percentage, toxicity and bioaccumulation). For 19 pesticides, the values ranged between 13-20. This shows that the lowest possible score of 4 was not found in this study and therefore the effects in the receiving environment may be high. It was determined that Heptachlor-exo-epoxide, which received high scores in each category, arrived at the wastewater treatment plant in high concentration, low removal after advanced biological treatment, high bioaccumulation and high adsorption.

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MAPPING THE FOREST: QUANTIFYING AND VISUALIZING THE DISTRIBUTION PATTERNS OF TREE SPECIES IN SHANGLA DISTRICT OF KPK, PAKISTAN

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Abstract

The current study reveals the quantitative description and floristic composition (distribution pattern of different tree species, density ha^{-1} , and basal area $\text{m}^2 \text{ha}^{-1}$), and the dbh size class structure of individual tree species around different forests of Shangla District. *Pinus wallichiana* and *Abies pindrow*, were the dominant species, whereas, associated species i.e. *Cedrus deodara*, *Picea smithiana*, *Pinus roxberghii*, and an angiospermic species *Quercus baloot* were also recorded in some forests. Each forest is discussed individually where species distribution, species abundance, and size of trees, were mainly influenced by the topographic condition of the area. The highest density was observed in the Yakh Tangy Poran side forest which occupied ($409.36 \text{ density ha}^{-1}$), whereas the highest basal area ($158.88 \text{ m}^2 \text{ha}^{-1}$) was recorded from the Yakhtangay-1 forest. The lowest density ($55.61 \text{ m}^2 \text{ha}^{-1}$ with $14.47 \text{ basal area m}^2 \text{ha}^{-1}$) was observed from Shangla Top forest near the Mangarkoot area. The pure forests of *Pinus wallichiana* observed in 23 locations exhibited the maximum number of species in the middle and large size classes followed by *Abies pindrow* which is the second dominant tree species observed in 9 sampling forest sites with associated species. The individual tree species *Pinus wallichiana* and *Abies pindrow* showed a highly significant correlation ($p < 0.001$) between density and basal area $\text{m}^2 \text{ha}^{-1}$ respectively. *Abies Pindrow* exhibited a highly significant correlation ($p < 0.001$) between density elevation and basal area and elevation. Correlation between overall basal area $\text{m}^2 \text{ha}^{-1}$ with topographic factor elevation also showed a highly significant correlation $p < 0.001$. Other tree species *Cedrus deodara*, *Picea smithiana*, *Pinus roxberghii*, and one angiospermic species *Quecus baloot* were present in less than six stands, therefore they were not correlated. The gaps in the early size class distribution indicate anthropogenic disturbance, poor regeneration potential, and deforestation in the Shangla District at a startling rate, therefore requires prompt action for protection and regeneration in these forests.

THE IMPORTANCE OF DRAIN SIZING IN THE STABILITY OF EMBANKMENT DAMS

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Abstract

According to statistics from the International Commission on Large Dams (ICOLD), a high percentage of recorded accidents involving embankment dams are related to the phenomenon of internal erosion due to seepage. The causes of these problems are related to the design of the structure or an error in the sizing of the drains.

To improve the overall stability of earth embankments, it is essential to control seepage into the embankment body and into the foundations. This is achieved by providing areas of high permeability within the embankment, known as 'drains'. Their role is to control the infiltration network due to the hydraulic load created by the reservoir.

The aim of this research was to analyse the infiltration into the body of the dam and its foundation with different lengths of drains. Numerical modelling was carried out using GEOSTUDIO software, SEEP/W analysis. The results showed that the length of the drain has a major influence on the variation of hydraulic gradients and leakage rates and consequently on the stability of the dam, hence the importance of respecting the drain sizing criteria.

Key word: Dam, infiltration, drain, stability

1 INTRODUCTION

Each dam must be considered as a unique project using more or less well characterised materials.

The design of an earth dam meets two main requirements: watertightness and stability. Whatever the permeability of an earth embankment, there will always be infiltration into its mass. There is no such thing as a perfect seal for this type of structure. The flow must be controlled so that the parameters associated with infiltration remain below the critical parameters (flow rate, interstitial pressures, hydraulic gradients, etc.).

The design of the drainage system is closely linked to the assessment of the permeability of the backfill. A drain is a thin element of granular material capable of collecting leakage flows to one (or more) precise points downstream where they can be measured. Placed in contact with the foundation, it drains the foundation and the backfill. Seepage control is therefore one of the

most important elements in the design of embankment dams.

In this article, a numerical modelling of an earth embankment is carried out, focusing on the effect of drain sizing on variations in hydraulic gradients and seepage rates.

2 MATERIALS AND METHODS

The numerical modelling was carried out using the GEOSTUDIO software, SEEP/W analysis, the earth dam consists of a homogeneous mass of isotropic permeability k , the height (H) of the dam is 60m, the water level (h) in the reservoir is 57m, the width (B) is 370m, 10m is the width of the dam at the crest. In our case, the homogeneous dam is formed by a mat of drainage material (horizontal drain) of constant thickness, this mat extending transversely over a width, starting from the downstream foot.

This research is dedicated to a study of infiltration in the body of the dam and its foundation using GEOSTUDIO software, SEEP/W analysis, seven different models will be studied, with lengths of 30 m, 45 m, 60 m, 75 m,

95 m, 105 m and 120 m. Hydraulic gradients and leakage flows will be assessed at the dam reference points for each model.

3 RESULTS AND DISCUSSION

3.1 Evolution of hydraulic gradients

The figures below illustrate the variations in hydraulic gradients at the dam reference points for the 30m, 95m and 120m length models.

Table 1 summarises the variations in hydraulic gradients at the dam reference points for all models.

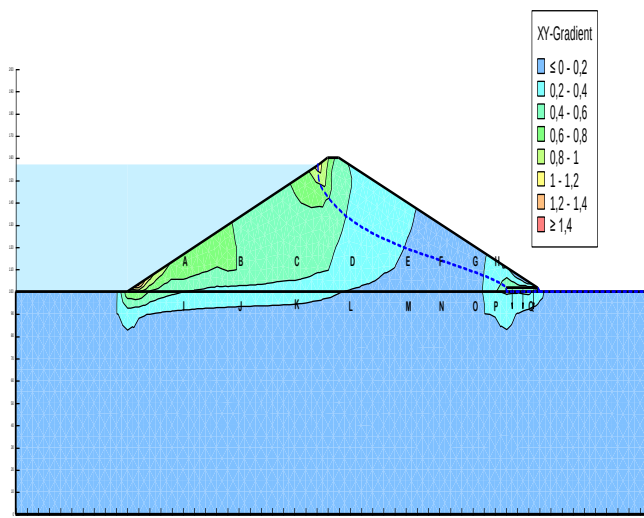


Figure 1. Variation of hydraulic gradient
 $L_{\text{Drain}} = 30\text{m}$

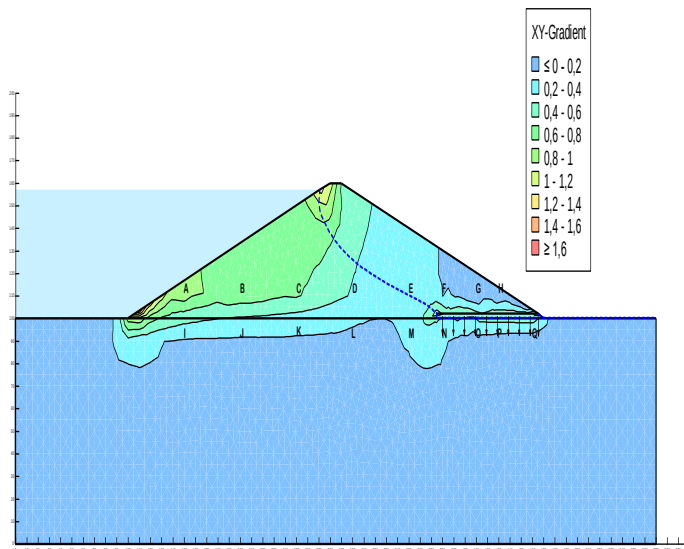


Figure 2. Variation of hydraulic gradient
 $L_{\text{Drain}} = 95\text{m}$

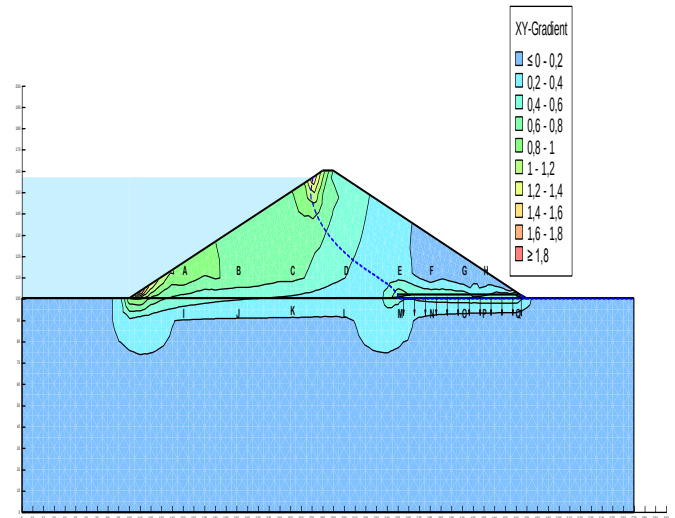


Figure 3. Variation of hydraulic gradient
 $L_{\text{Drain}} = 120\text{m}$

According to the results of the modelling, for points A, B, C, D, I, J, K and L the 7th model with $L=120\text{m}$ has the highest gradient values, while the 1st case with $L=30\text{m}$ has lower values. Points E, F, G, H, M, N, O, P and Q are located above and below the drain. From the curves shown in Figure 4, we can also see that the gradient values for the seven models are approximately equal to 0 at exactly these points G, H, P and Q. This means that the length of the drain has an influence on the variation of the hydraulic gradients.

Table 1. Variation in hydraulic gradients at reference points for each model

	Points		Hydraulic gradients						
	X	Y	30m	45m	60m	75m	95m	105m	120m
A	150	110	0,753	0,781	0,812	0,848	0,895	0,921	0,959
B	200	110	0,595	0,618	0,641	0,669	0,706	0,727	0,757
C	250	110	0,511	0,533	0,551	0,582	0,613	0,62	0,651
D	300	110	0,313	0,319	0,335	0,348	0,366	0,381	0,4
E	350	110	0,183	0,192	0,204	0,216	0,258	0,292	0,364
F	380	110	0,166	0,182	0,206	0,255	0,201	0,125	0,083
G	410	110	0,184	0,233	0,193	0,091	0,032	0,022	0,012
H	430	110	0,206	0,126	0,037	0,018	0,01	0,007	0,002
I	150	90	0,15	0,156	0,162	0,168	0,178	0,183	0,191
J	200	90	0,136	0,141	0,147	0,152	0,161	0,166	0,174
K	250	90	0,134	0,139	0,145	0,151	0,16	0,165	0,174
L	300	90	0,135	0,14	0,146	0,153	0,166	0,173	0,191
M	350	90	0,138	0,146	0,157	0,172	0,211	0,247	0,332
N	380	90	0,145	0,16	0,184	0,22	0,227	0,193	0,124
O	410	90	0,171	0,217	0,251	0,168	0,106	0,085	0,068
P	430	90	0,204	0,204	0,137	0,097	0,068	0,059	0,048
Q	460	90	0,13	0,091	0,071	0,056	0,042	0,036	0,03

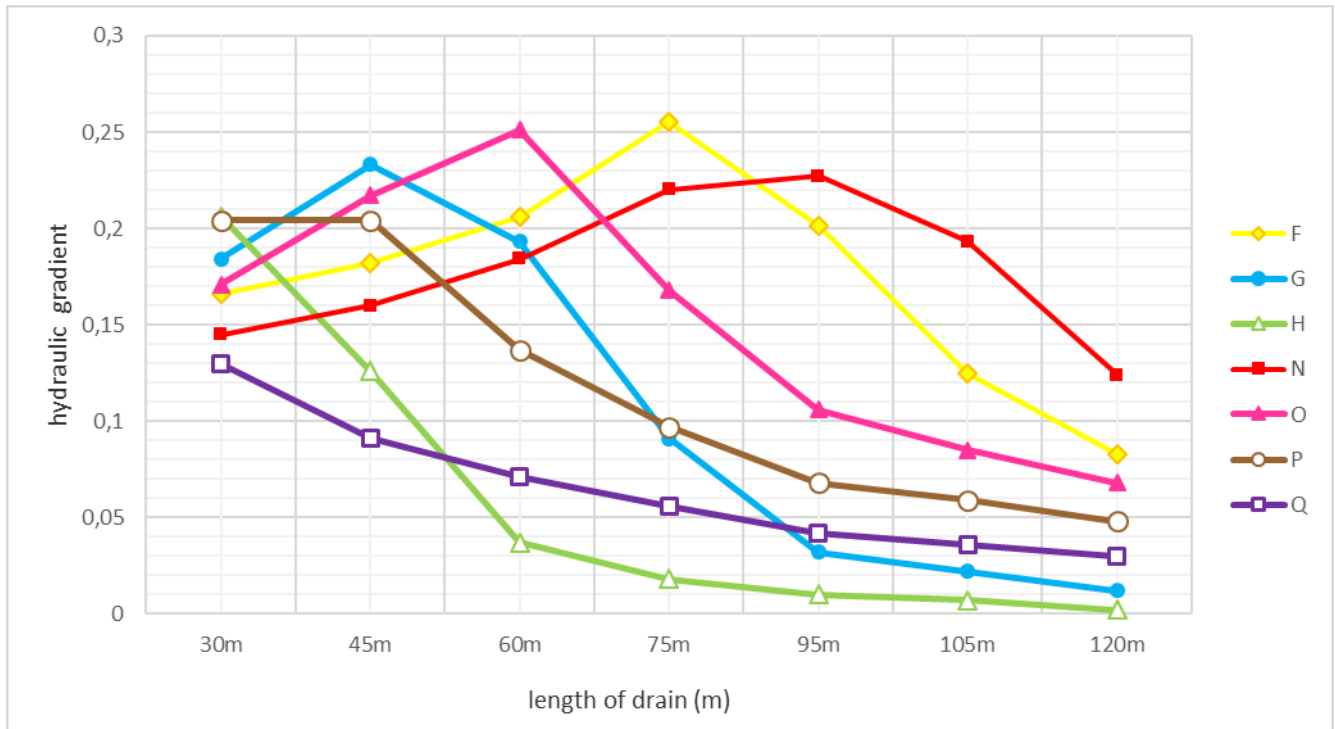


Figure 4. Hydraulic gradient variation curves for points in the downstream part of the dam.

3.2 Evolution of leakage flows

The figures below illustrate the variations in leakage flow at the dam reference points for the 30m, 95m and 120m long models.

Table 2 summarises the variations in leakage flow at the dam reference points for all models.

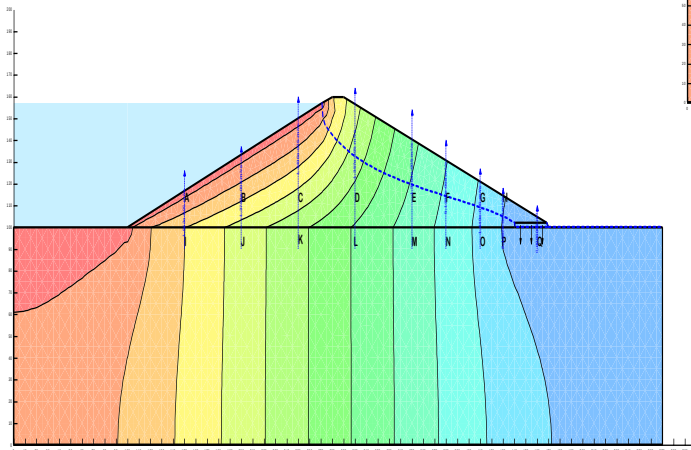


Figure 5. Variation of the leakage flow rate
 $L_{\text{Drain}}=30\text{m}$

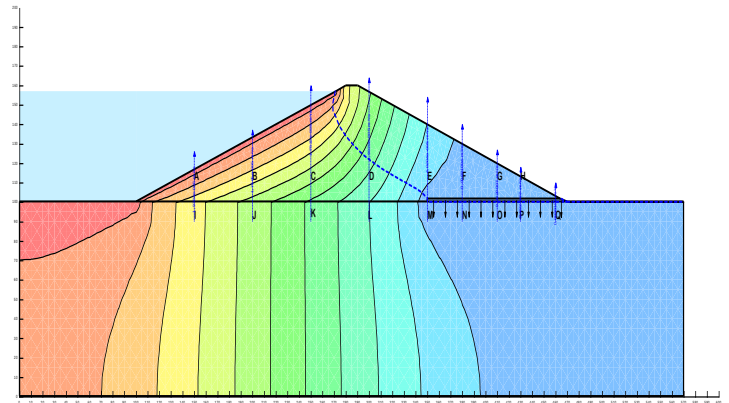


Figure 7. Variation of the leakage flow rate
 $L_{\text{Drain}}=120\text{m}$

According to the modelling results, the curves shown in Figure 8 are almost identical for points A, B, C, D and E, with a flow rate approximately equal to 0. The values vary for points F, G, H and Q.

The flow rate values at point Q, located in the downstream section, increase as the drain length is reduced. It can be seen that the three models 95m, 105m and 120m with discharge lengths in the order of B/4 to B/3 provide suitable flow values.

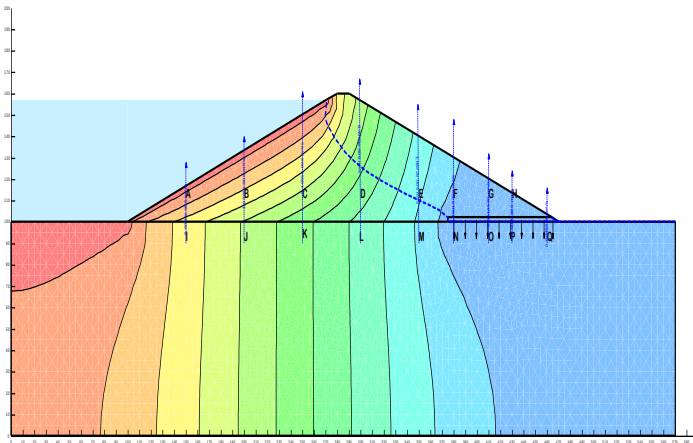


Figure 6. Variation of the leakage flow rate
 $L_{\text{Drain}}=95\text{m}$

Table 2 . Variation of the leakage flow rates at the reference points for each of the models

	Points		Leakage flow rate (m ³ /s)						
	X	Y	30m	45m	60m	75m	95m	105m	120m
A	150	110	0,0087.10 ⁻⁵	1,6028.10 ⁻⁵	1,6740.10 ⁻⁵	0,8528.10 ⁻⁵	1,8259.10 ⁻⁵	1,8790.10 ⁻⁵	0,0109.10 ⁻⁵
B	200	110	0,6885.10 ⁻⁵	1,4037.10 ⁻⁵	1,4833.10 ⁻⁵	0,7713.10 ⁻⁵	0,0085.10 ⁻⁵	1,6678.10 ⁻⁵	0,8787.10 ⁻⁵
C	250	110	0 ,6800.10 ⁻⁵	0,0094.10 ⁻⁵	1,4763.10 ⁻⁵	0,7638.10 ⁻⁵	0,0107.10 ⁻⁵	1,6105.10 ⁻⁵	0,8830.10 ⁻⁵
D	300	110	0,6895.10 ⁻⁵	0,4197.10 ⁻⁵	1,4763.10 ⁻⁵	0,7861.10 ⁻⁵	1,6645.10 ⁻⁵	1,7527.10 ⁻⁵	0,9812.10 ⁻⁵
E	350	110	0,6986.10 ⁻⁵	1,4603.10 ⁻⁵	0,7941.10 ⁻⁵	0,8655.10 ⁻⁵	1,9539.10 ⁻⁵	2,2877.10 ⁻⁵	0,0001
F	380	110	0,7359.10 ⁻⁵	1,5838.10 ⁻⁵	1,7849.10 ⁻⁵	0,0063. 10 ⁻⁵	0,0002	0,0006	0,0009
G	410	110	1,6610.10 ⁻⁵	2,0822.10 ⁻⁵	0 ,0003	0,0012	0,0017	0,0018	0,0019
H	430	110	1,2375.10 ⁻⁵	0,0008	0,0013	0,0027	0,0028	0,0026	0,0025
Q	460	90	0,0088	0,0058	0,0071	0,0051	0,0043	0,0039	0,0036

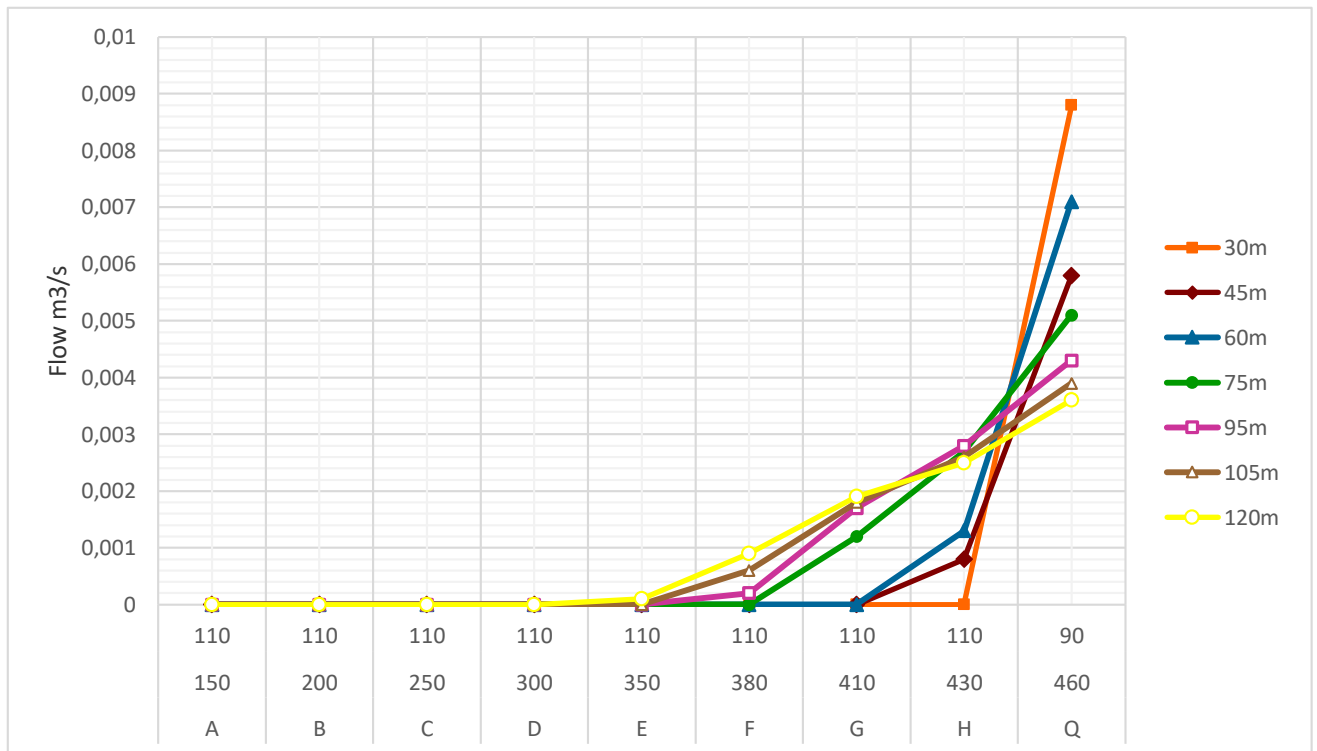


Figure 8. Flow variation curves for each model.

4 CONCLUSION

The seepage that can occur through earth embankments must be considered from two different perspectives. On the one hand, it can jeopardise the safety of the structure and compromise its stability if certain precautions are not taken against the risks posed by foxing and filtration pressures. Secondly, they result in a loss of water that needs to be reduced to a value that is determined by the overall economics of the project. In the context of this research and in terms of hydraulic behaviour, it is very important to comply with dam sizing criteria, as these have a significant impact on dam seepage.

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EFFECTS OF AMBIENT TEMPERATURE ON COMPRESSIVE STRENGTH OF RECYCLED THERMOPLASTIC MATERIALS USED IN WIND TURBINE BLADES

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Abstract

The significance of wind turbines in the realm of renewable energy has been steadily growing. It is known that the predominant focus of studies in this domain pertains to the lightness and strength of turbine blades. Composite structures are utilized to produce these blades with the desired lightness and strength. In these composite structures, resins are generally used as binding materials. The primary challenge associated with recycling wind turbine blades is the fact that the resins used in their production undergo irreversible chemical reactions. For this reason, the fact that giant wind turbine blades, that were installed 30 years ago and have reached the end of their service life, cannot be recycled and cause the formation of turbine waste dumps is an undesirable circumstance in terms of the clean energy concept. Using thermoplastic polymer materials instead of resins as the binder material for wind turbine blades is believed to contribute to the renewable and clean energy goals of the wind energy sector. Therefore, it is important to investigate the compressive strength of these polymer plastic materials. Furthermore, it is imperative to assess the impact of varying temperature conditions on the compressive strength of these materials, given that the blades are consistently exposed to sunlight in an outdoor setting. This study conducted compression tests on recycled plastic materials that can be used in wind turbine blades at various ambient temperatures to evaluate their compressive strength. The results of this study show that the use of these plastic materials as binders in turbine blades is possible in terms of compressive strength.

Keywords: wind energy; wind turbine blades; structural mechanics; recyclable composite structures; polymers

MODELLING HYDROLOGICAL PROCESSES IN THE KARTALKAYA RESERVOIR BASIN (KAHRAMANMARAS, TÜRKİYE) USING SWAT

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Abstract

This study aims to simulate hydrological processes in the Kartalkaya Reservoir Basin in Kahramanmaraş, Turkey. It also assesses the potential changes in water inflows to the Kartalkaya Reservoir due to land use/cover alterations following the February 6, 2023 earthquake. The Soil and Water Assessment Tool (SWAT) was used for model development. The observed streamflow data from two subbasins and data on water inflows to the Kartalkaya Reservoir were used for model calibration/validation. The calibration and validation was done on the monthly timescale using the SUFI2 algorithm available in the SWAT-CUP software. Model performance was evaluated based on Nash–Sutcliffe Efficiency (NSE), determination coefficient (R^2), and percent bias (PBIAS). The model successfully simulated flow dynamics in the basin. The analysis showed that an increase in imperviousness can increase inflows to the Kartalkaya Reservoir. The model developed in this study could be used in the future for simulating alternative land use/cover scenarios Kartalkaya Reservoir Basin.

Keywords: Hydrological Modelling, SWAT, Kartalkaya Reservoir, land use/cover change

1 INTRODUCTION

This study aims to simulate the hydrological processes in the Kartalkaya Reservoir Basin (Figure 1) using the Soil and Water Assessment Tool (SWAT). The Kartalkaya Reservoir Basin is an important water resource in Kahramanmaraş, Türkiye, providing water to meet agricultural, industrial, and domestic needs. The February 6, 2023 earthquake, centered in the Pazarcık and Elbistan districts of Kahramanmaraş, significantly impacted the region. This event caused notable land use/cover changes within the basin and has heightened the likelihood of further changes in the future.

A few studies in the literature have shown that earthquakes can cause long-term land use/cover changes. Chen and Nakatsugawa [1] showed that after the Hokkaido Eastern Iburi earthquake in Japan, forested areas turned into bare areas, leading to increased surface runoff and sediment transport. Zhang et al. [2] showed that landslides caused by major earthquakes changed the magnitude of peak flow of surface runoff in the Wenchuan earthquake example.

Land use/cover changes have been detected after some previous earthquakes in Türkiye [3]. Karadeniz and Sunbul [4] showed that urbanization and agricultural activities increased in the Düzce Plain after the 1999 Düzce

earthquake. Sunbul [5] showed that settlement and agricultural areas expanded in Sakarya after the 1999 Kocaeli earthquake, while forested and wetland areas decreased. These studies suggest that the Kahramanmaraş earthquake may also cause land use/cover changes in the future. In this study, the hydrological effects of possible land use/cover change scenarios were evaluated using modelling tools.

2 METHODOLOGY

2.1 Study area

The Kartalkaya Reservoir Basin (Figure 1), located in the Ceyhan Basin (Figure 1), which includes Kahramanmaraş and the surrounding provinces, is one of the important water resources of the region. The basin has an area of approximately 228.1 km². The reservoir was built on the Aksu Stream in 1965-1972 for flood control, drinking, and industrial water supply and agricultural irrigation. Kartalkaya Reservoir is important in terms of controlling possible flooding of settlements and agricultural areas. This reservoir is also used to provide irrigation water, thus increasing the productivity of agricultural areas in the region and providing significant support to farmers. Land use/cover in the basin consists of agricultural areas, sparsely vegetated areas and rangelands, forested areas, and rural settlements. Kartalkaya Reservoir,

which contributes to the economic and social development of the region, ensuring water

security for the people of the region, is a valuable natural asset for Kahramanmaras.

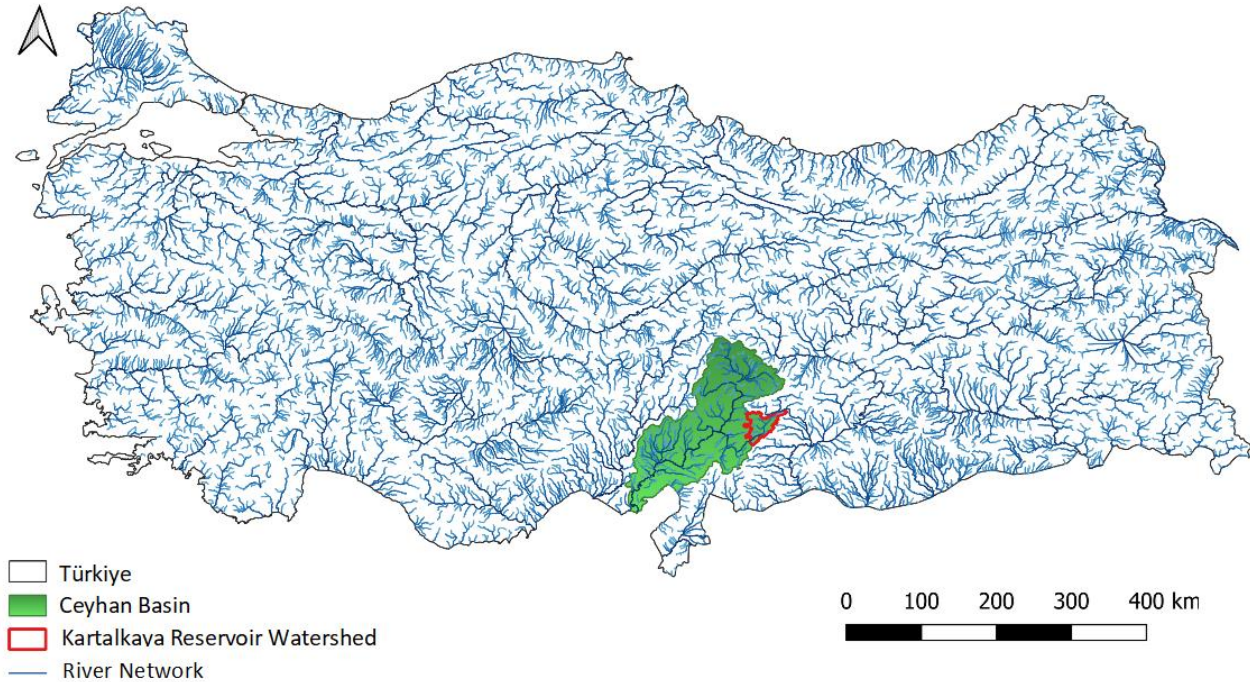


Figure 1. Location of Kartalkaya Reservoir Basin

2.2 Data Collection

Data necessary for developing the SWAT model were obtained from various sources. The Digital Elevation Model (DEM), providing essential topographic information, was obtained from the United States Geological Survey (USGS) (Figure 2). For representation of soil properties in the Basin, soil characteristics were extracted from the FAO-UNESCO World Soil Map (Figure 2). Land use/cover information was obtained from CORINE 2018 database (Figure 2). Meteorological data, including precipitation, air temperature, relative humidity, wind speed, and solar radiation, were obtained from the State Meteorology Service (MGM). Streamflow data and reservoir inflow data, crucial for model calibration and validation, were obtained from the State Hydraulic Works (DSI) (Figure 2).

2.3 Model Development

The development of the SWAT model proceeded through several stages [6]. Initially, the DEM was processed to define watershed boundaries and subbasins within the study area (Figure 3). This step was critical in understanding the topographical influence on hydrological processes. Subsequently, land use/cover and soil data were integrated into the model. By combining this information with slope data, Hydrological Response Units

(HRUs) were created, representing areas with homogeneous land use/cover, soil, and slope characteristics. In HRU creation, we used 5% area thresholds for land use/cover, soil, and slope. HRUs allowed for a detailed analysis of the basin's hydrological response. Overall, the model included 51 subbasins and 856 HRUs.

The next step involved the incorporation of climate data into the model. Meteorological data were essential for simulating the hydrological cycle within the basin, were added to the model. Calibration and validation of the model were conducted using streamflow data collected at two gauging stations operated by DSI (D02A002, D02A0026) and reservoir inflow data. The calibration period for streamflows spanned from 2006 to 2011, while the validation period covered 2012 to 2015. For reservoir inflow, we used the 2011-2016 period for calibration and the 2017-2022 period for validation. The SUFI2 algorithm within the SWAT-CUP software was employed for calibration, adjusting model parameters to match observed flow data [7]. We used Nash-Sutcliffe efficiency (NSE), determination coefficient (R^2) and percent bias (PBIAS) to evaluate the performance of the model [8]. p-factor and r-factor were used to evaluate the model's

performance in terms of uncertainty and reliability [7].

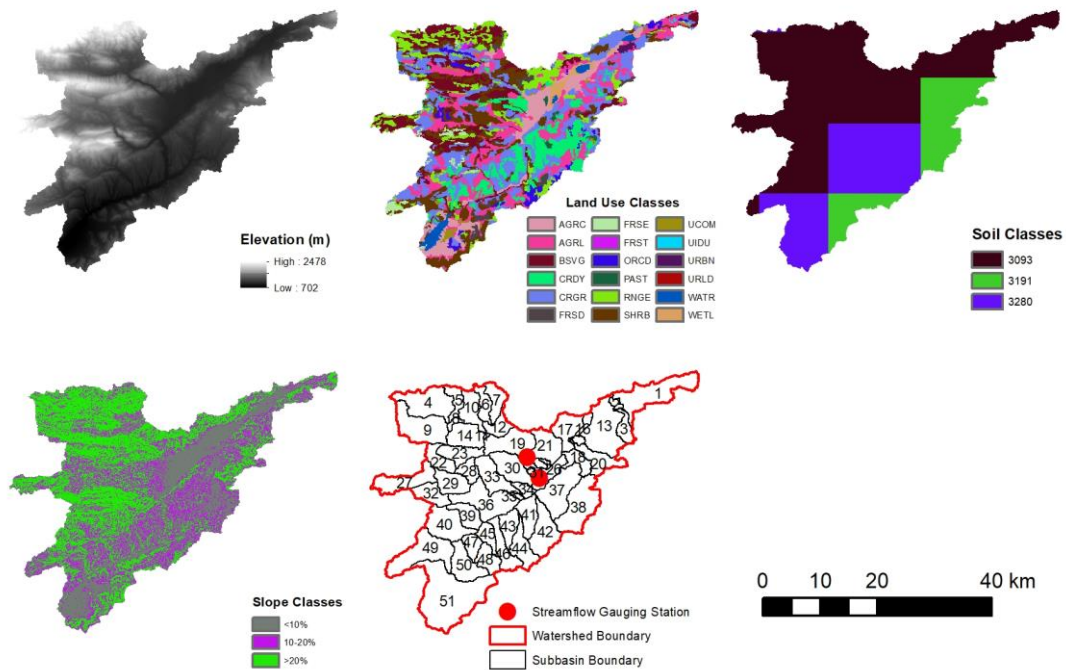


Figure 2. DEM, land use/cover, soil, slope and subbasins of the Kartalkaya Reservoir Basin

3 RESULTS

The parameters selected for calibration and validation of the SWAT model are presented in Table 1. We used a total of 25 parameters. During model calibration we run several iterations. Each iteration consisted of 500 models runs with different parameter values. Iterations continued until satisfactory model performance was attained.

Table 1. Parameters used for model calibration and validation

Parameter	Lower Limit	Upper Limit	Calibration Type
CN2.mgt	-0.2	0.2	r
Ch_K2.rte	5	130	v
Ch_N2.rte	0	0.3	v
ALPHA_BF.gw	0	1	v
GW_DELAY.gw	0	450	v
GWQMN.gw	500	5000	v
GW_REVAP.gw	0.02	0.2	v
RCHRG_DP.gw	0	0.3	v
GWHT.gw	0	10	v
REVAPMN.gw	0	500	v
SOL_AWC(1).left	-0.2	0.4	r
SOL_K(1).left	-0.8	0.8	r
SOL_BD(1).left	-0.5	0.6	r
SFTMP.bsn	-3	3	v
SURLAG.bsn	0	4	r
OV_N.hru	-0.2	0.2	v
SLSUBBSN.hru	-0.2	0.2	v
EPCO.hru	0	1.0	v
ESCO.hru	0	1.0	v
SNOCOVMX.bsn	100	500	v
SFTMP.bsn	-5.0	5.0	

SMTMP.bsn	-5.0	5.0	v
SMFMX.bsn	0	5	v
SMFMN.bsn	0	5	v
TIMP.bsn	0.9	1	v

The streamflow values simulated and measured at gauging stations D02A002 and D02A027 are presented in Figure 3 and Table 2 for the calibration and validations periods. The averages of the same periods are also presented in Table 2. During the calibration period (2006-2011), the NSE value was 0.76, the R^2 value was 0.79, and the PBIAS value was -13.2 at station D02A002. In the validation period (2012-2015), the NSE value was 0.62, the R^2 value was 0.62, and the PBIAS value was 6.7. In station D02A027, during the calibration period (2006-2011), the NSE value was 0.48, the R^2 value was 0.51, and the PBIAS value was -8.3. In the validation period (2012-2015), the NSE value was 0.19, the R^2 value was 0.40, and the PBIAS value was 17.3. According to Moriasi et al. [8], model performance is acceptable when the NSE value is greater than 0.5, the R^2 values are greater than 0.6, and the PBIAS value is between -25 and 25.p-factor and r-factor values were in the acceptable range. At stations D02A002 and D02A027, the model performance was acceptable or very close to this level during the calibration phase. However, for the validation period, the desired performance level was reached only at station D02A002. This could be

due to the effects of human activities on the hydrological system. The lakes located before the measurement station no. D02A027 and the

management of these lakes suggest that the hydrological conditions upstream of station no. D02A027 has been changed.

Table 2. R^2 , NSE, RSR, PBIAS, and KGE values in model calibration and validation and averages of measured and simulated values during these periods

Period	Variable	p-factor	R-factor	R^2	NSE	PBIAS	Observation Mean	Model: Average
Calibration	Streamflow (D02A002)	0.78	0.86	0.79	0.76	-13.2	2.89	3.27
	Streamflow (D02A027)	0.69	1.14	0.51	0.48	-8.3	2.94	3.19
	Inflow to Kartalkaya Reservoir	0.29	0.74	0.44	0.43	12.124	9.78	10.83
Validation	Streamflow (D02A002)	0.67	0.92	0.62	0.62	6.7	3.14	2.93
	Streamflow (D02A027)	0.64	1.29	0.40	0.19	17.3	3.53	2.92
	Inflow to Kartalkaya Reservoir	0.34	0.47	0.31	0.28	-18.39	12.04	14.25

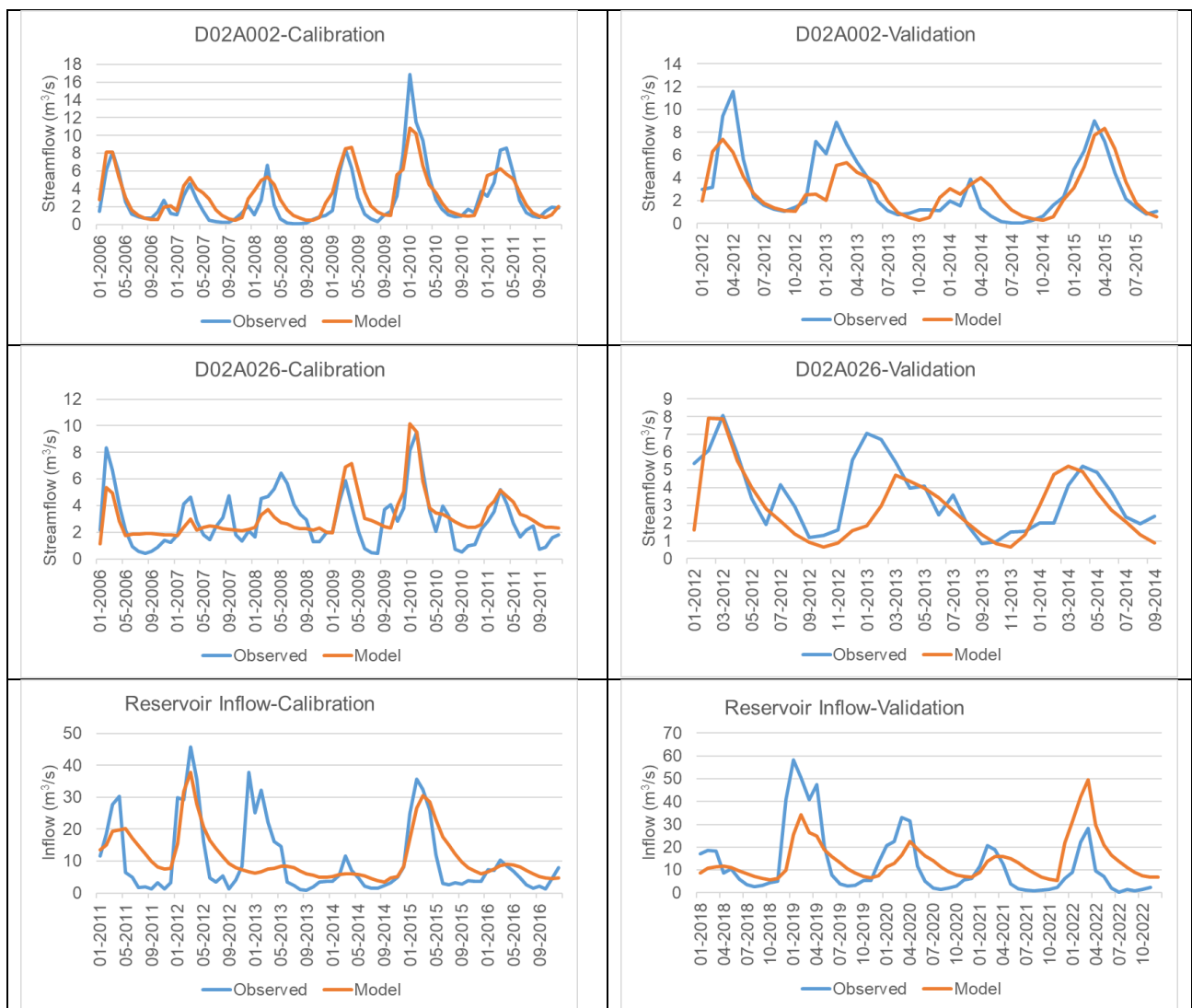


Figure 3. Model calibration and validation results

In terms of the inflow reaching Kartalkaya Reservoir, during the calibration period (2011-2017), the NSE value was 0.23, the R^2 value was 0.26, and the PBIAS value

was 2.5. In the validation period (2018-2022), the NSE value was 0.07, the R^2 value is 0.13, and the PBIAS value is 14.9. The inflow data reaching the reservoir are

the values estimated by DSI by calculation, so they can have uncertainties. These uncertainties can explain for the difference between the observed and simulated values. In addition, the reservoir inflows could be affected by impacts on the hydrological system upstream. Despite lower performance with NSE and R^2 values, in terms of PBIAS, the values show the adequacy of the model.

We run two scenarios to evaluate how an increase in imperviousness in the basin affect inflows to the Kartalkaya Reservoir (Figure 4). Analysis showed that a 10% increase in imperviousness can increase inflows to the Kartalkaya Reservoir by 9%. A 20% increase could cause on average 25% increase in inflows. These results suggest that changes in imperviousness can affect hydrological conditions in the Kartalkaya reservoir.

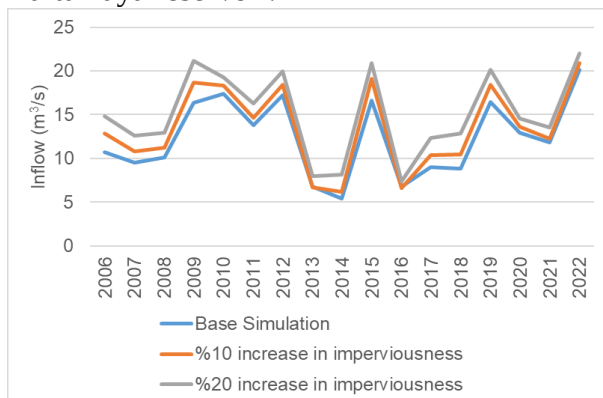


Figure 4. Simulation results

4 CONCLUSIONS

In this study, we developed a hydrological model for the Kartalkaya Reservoir Basin using SWAT. We also simulated the effects of changes in imperviousness in the basin. The model simulated hydrological dynamics in the basin, despite artificial impacts on the hydrological system. The scenario analyses showed that increase in imperviousness can increase water inflows to the reservoir. This study highlights the importance of using hydrological models like SWAT to assess the impacts of land use/cover changes on water resources. Future research should focus on long-term monitoring and adaptive management to

ensure the resilience of water resources in the Kartalkaya Reservoir Basin.

5 ACKNOWLEDGEMENTS

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CORPORATE CARBON FOOTPRINT CALCULATION: İNCESU MUNICIPALİTY EXAMPLE

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Abstract

Carbon footprint is a calculation tool used to indicate the amount of greenhouse gases released into the atmosphere directly or indirectly as a result of activities of individuals and organizations, such as energy consumption and transportation, in terms of carbon dioxide equivalent.

The carbon emission amounts of the service building of İncesu Municipality, which serves the İncesu District of Kayseri province, were determined and the carbon footprint was calculated based on the current number of personnel. The total carbon dioxide emission amount of the central service building between 2022 and 2023 is 72.2 tons of CO₂. It is seen that the carbon footprint value, which was 0.10 tons of CO₂/person/year in 2022, increased to 0.12 tons of CO₂/person/year by 2023. Accordingly, at the end of the 2-year period, the amount of carbon released into the atmosphere increased by 20% in terms of tons of CO₂. İncesu Municipality aims to keep the amount of carbon it releases into the atmosphere with the projects it will implement.

Keywords: Carbon Footprint, Sustainability, Smart Cities

Acknowledgment: Environmental Management

1. INTRODUCTION

One of the most important problems we face today is climate change. This problem is addressed to the United Nations Climate Change The Framework Convention on Change states that “in addition to natural climate change observed over comparable time periods, a change in climate resulting from human activities that directly or indirectly alter the composition of the global atmosphere defined as “change” (UNFCCC 1992). Climate change, population growth, industrialization, urbanization and energy demand Although its impact was felt more in the second half of the twentieth century due to reasons such as It has become an agenda item (IPCC 2022).

In the last twenty years, especially with international climate summits such as the 1997 Kyoto Protocol and the 2015 Paris Agreement, results have emerged in international climate policy that concern all countries of the world, and some regional, national or international measures have

begun to be taken in this regard. Previously, countries met in Stockholm in 1972, Rio de Janeiro in 1992, and Johannesburg in 2002 and accepted and evaluated the global effects of climate change (IPCC 2018).

Carbon footprint is used to indicate the amount of greenhouse gases released into the atmosphere directly or indirectly as a result of activities of individuals and organizations, such as energy consumption and transportation, in terms of carbon dioxide equivalent (Wiedmann and Minx 2008). In the Kyoto Protocol; Compounds consisting of gases such as CO₂, methane (CH₄), nitrogen oxides (N₂O), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs) and sulfur hexafluoride (SF₆) and which have the ability to retain heat in the atmosphere are defined as greenhouse gases. Information on these greenhouse gases is given in Table 1. CO₂ equivalent (CO₂ eq.) in the table; It states that other greenhouse gases, except CO₂, have the capacity to retain 20-

23,900 times more heat than the same amount of CO₂. By using this unit, all greenhouse gases are collected on a common denominator, making it easier to understand and compare emission calculations. According to this table, the most dangerous greenhouse gas appears to

be SF₆, and the least dangerous is CO₂. However, it has been stated that the opposite is the case because CO₂ is at a very high level in terms of quantity compared to other greenhouse gases (Downie and Stubbs 2012).

Table 1: Greenhouse gases based on the Kyoto Protocol (Downie ve Stubbs 2012)

Sembol	İsim	CO ₂ eşdeğer	Ana kaynak
CO ₂	Karbondioksit	1	Fosil yakıtların yanması, orman yangınları, çimento üretimi
CH ₄	Metan	21	Atık sahaları, petrol ve doğalgazın üretim ve dağıtımı, çiftlik hayvanlarının sindirim sistemlerinin fermantasyonu
N ₂ O	Nitröz oksit	310	Fosil yakıtların yanması, gübreler, naylon üretimi
HFCs	Hidroflorokarbonlar	140~11.700	Buzdolabı gazları, alüminyum eritme, yarı iletken üretimi
PFCs	Perflorokarbonlar	6.500~9.200	Alüminyum üretimi, yarı iletken üretimi
SF ₆	Sülfürheksaflorit	23.900	Elektrik iletim ve dağıtım sistemleri, magnezyum üretimi

In scenarios that limit global warming to 1.5 °C, it is estimated that industrial CO₂ emissions, which are currently 8 gigatons (Gt) annually, should be approximately 65-90% lower in 2050 than in 2010. Within the scope of the 26th United Nations Climate Change Conference (COP26) held in Glasgow, Scotland in 2021, with the 'net zero' industries mission to be jointly led by Austria and Australia, iron and steel, which is responsible for approximately 70% of industrial greenhouse gas emissions, Industries called heavy industries such as cement and chemicals are expected to contribute to the 'net zero' emission target by preventing approximately 60 Gt of CO₂ emissions by 2050 (IPCC 2018).

Approximately 65% of Turkey's electricity production in 2021 was provided by fossil fuels (TEIAS 2022). Considering that, as a developing country, Turkey provides most of its high energy demand from fossil fuels, it is inevitable that greenhouse gas

emissions will increase rapidly. It is of great importance to analyze national greenhouse gas emissions in order to carry out the necessary studies on climate change. With the greenhouse gas inventory study conducted throughout Turkey, annual greenhouse gas emissions are calculated and evaluated according to 1990 and shared. As seen in Figure 1, total greenhouse gas emissions in 2020 increased by 3.1% compared to the previous year, reaching 523.9 million tons (Mt) CO₂ eq. It was determined as (TUIK 2022). Although Turkey's total per capita emissions are lower than the average of the G20 countries, which are the largest economies in the world, the rate of increase is quite high (URL-1 2022). Carbon emission per capita in Turkey was 4.1 tons CO₂eq in 1990. Despite the population increase, 6.3 tons of CO₂ eq. in 2020. It has been observed that it has increased to the value (TUIK 2022).

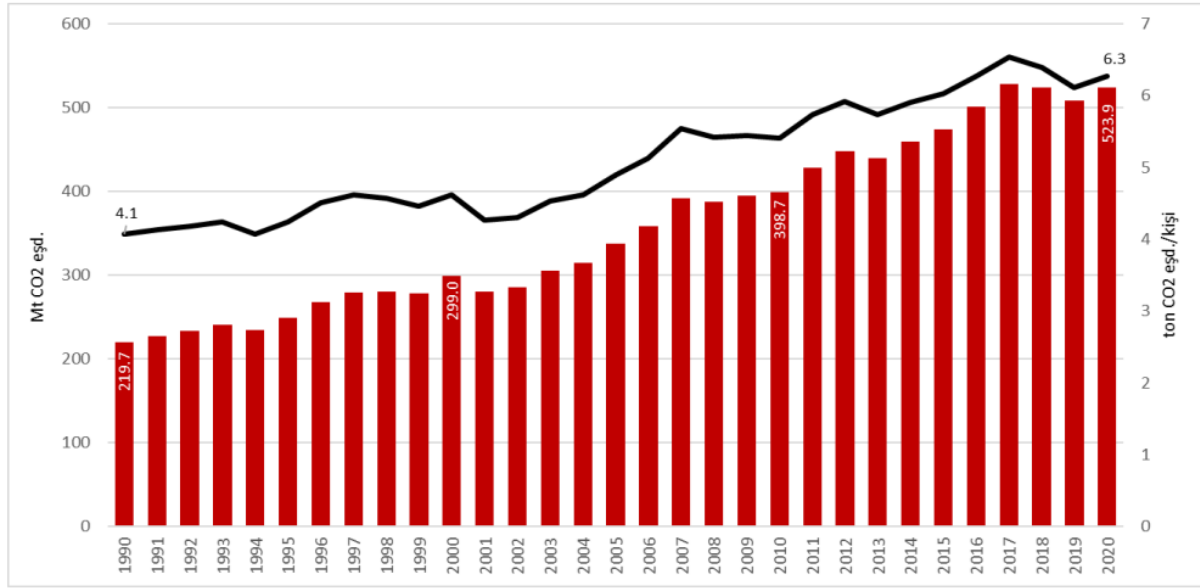


Figure 1: Total and per capita carbon emissions, 1990-2020 (TUIK, 2022)

In the Turkish greenhouse gas inventory study, emission amounts were calculated by sectors between 1990 and 2020, and greenhouse gas emissions for sectors are given in Table 2. As a result of the study, total carbon emissions will be CO2 equivalent in 2020. While the largest share comes from the energy sector with an average of 70%, the energy sector is followed by agriculture with 14%, industrial processes and product use with

13%, and the waste sector with 3% (TUIK, 2022).

When emissions are evaluated by sectors, the increase in all sectors attracts attention. When total greenhouse gas emissions are evaluated, there is an increase over the years. As an exception to this situation, a decrease was observed in the total amount of greenhouse gases in 2019 due to the restrictions during the COVID-19 pandemic period (TUIK, 2022).

Table 1.2.: Greenhouse gas emissions by sectors for the period 1990-2020 (million tons CO2eq.)

	1990	2000	2010	2015	2016	2017	2018	2019	2020	1990-2020 değişim %	2019- 2020 değişim %
Toplam emisyon	219,7	299,0	398,7	474,5	500,8	528,3	524,0	508,1	523,9	138,4	3,1
Enerji	139,6	216,0	287,8	342,0	361,7	382,4	374,1	365,4	367,6	163,3	0,6
Endüstriyel işlemler ve ürün kullanımı	23,0	26,3	49,0	59,2	63,5	66,4	68,0	58,6	66,8	190,5	14,0
Tarım	46,1	42,3	44,4	56,1	58,9	63,3	65,3	68,0	73,2	58,8	7,5
Atık	11,1	14,3	17,4	17,1	16,7	16,3	16,6	16,1	16,4	48,0	2,1

1.2. Corporate Sustainability

With the increasing effects of climate change, the concept of corporate sustainability has gained an important

place in the strategies of businesses. One of the strengths of this interest in corporate sustainability is the regulations designed to promote sustainable development goals.

The European Commission is actively involved in preparing policies and legislation to promote corporate sustainability responsibility. These range from “polluter pays” legislation to “producer responsibility” policies, “core labor standards” and “social management” and cover all stages from raw material sourcing to consumer products (Herzig and Schaltegger 2006).

Many companies are actively involved in sustainability efforts, trying to identify ways in which they can improve their bottom line in terms of sustainability and contribute to sustainable development. In terms of corporate sustainability, companies focus on all environmental, economic and social details and determine their target audiences (Lee 2012).

Incorporating sustainability into business practices is now yielding more and more positive results. In the latest reports of the World Business Council for Sustainable Development and the International Institute for Sustainable Development, the advantages of supporting sustainable development for the company are given below (Azapagic 2003; IISD 2002):

- Cost savings are achieved by improving material, energy and product efficiencies through clean production methods and innovation.
- It increases well-being and productivity by ensuring a safe and healthy environment for employees and the community, resulting in lower health and safety costs.
- Commitment to sustainable development increases a company's reputation and motivates employees within the company.

1.3. Corporate Carbon Footprint

In order to meet the long-term needs of people, natural resources must be managed with sustainable methods. In order to control climate change, global warming and greenhouse effects, different sectors

have independent and joint tasks (Şen 2022). There is great uncertainty about how the transition to a low-carbon labor market will end with resources depleting due to climate change. Many companies operating in different industry sectors have begun to see the carbon issue as one of the critical factors in supply chain management along with the production or service stage. For example, automobile manufacturers in the automotive sector, where the world's largest investments are made, have suppliers in many areas such as glass, plastic and metal. Since the automotive sector is greatly affected by its suppliers, it keeps the emission requirements and regulations of its suppliers under control (Lee 2011).

Corporate carbon footprint, corporate level carbon footprint, is the expression of greenhouse gases released into the atmosphere and causing climate change as a result of all activities of institutions such as production, service, processing in terms of CO₂ eq. (Ulusal 2021). Carbon footprint calculation, reporting and presentation are of great importance today for legal obligations, investor requests, customer demands, marketing strategies, necessity of emission trading mechanisms and corporate image (Üreden and Özden 2018).

2. Materials and Methods

This study utilizes energy consumption and natural gas consumption data from 2022 and 2023 to calculate the corporate carbon footprint of İncesu Municipality. The energy consumption and natural gas consumption data were obtained from the municipality's annual reports and energy bills. The CO₂ emissions amount was calculated based on the number of municipal employees.

For this study, initial steps included identifying sources and collecting data.

The annual electricity and natural gas consumption for İncesu Municipality for the years 2022-2023 is provided in Table 3.

Table 2.1.: İncesu Municipality's Annual Electricity And Natural Gas Consumption (İncesu Municipality's, 2024)

	Annual Electricity Consumption (kWh)	Annual Natural Gas Consumption (m ³)
2022	15582,74	16304,94
2023	18932,39	11326,92

The electricity emission factor was obtained from the Turkey Electricity Production and Electricity Consumption Point Emission Factors Information Form. The natural gas emission factor was obtained from the Turkish Statistical Institute.

The İncesu Municipality central service building has a total enclosed area of 2,599 m². Based on the annual total consumption figures and considering the usage areas, the electricity and heating intensities have been calculated.

3. Findings and Discussion

The annual energy consumption and associated CO₂ emissions for the İncesu Municipality central service building for

the years 2022 and 2023 have been calculated based on the provided data. Table 3 summarizes the annual electricity and natural gas consumption.

CO₂ emissions from electricity consumption were calculated using an emission factor of 0.478 kg CO₂/kWh. The total CO₂ emissions from electricity consumption in 2022 and 2023 were approximately 7.43 tons and 9.05 tons, respectively.

For natural gas, the emission factor was 0.515 kg CO₂/m³. The CO₂ emissions from natural gas consumption were calculated as 8.41 tons in 2022 and 5.84 tons in 2023.

Table 3.1.: CO₂ Emissions from Electricity and Natural Gas Consumption

Year	Electricity CO ₂ Emissions (tons)	Natural Gas CO ₂ Emissions (tons)	Total CO ₂ Emissions (tons)	Per Capita CO ₂ Emissions (tons)
2022	7.43	8.41	15.84	0,10
2023	9.05	5.84	14.89	0,13

3.1. Carbon Footprint per Employee

Assuming the total CO₂ emissions were 72 tons for both 2022 and 2023 and the per capita CO₂ emissions were 0.10 tons and 0.13 tons respectively, we can calculate the required number of employees as follows:

3.2. Comparison with Literature and Best Practices

The per capita emissions of 0.10 tons CO₂/employee in 2022 and 0.13 tons CO₂/employee in 2023 are relatively low compared to typical values reported for municipal buildings in similar contexts. For example, municipal buildings in other

regions often report per capita emissions ranging from 0.5 to 0.7 tons CO₂/employee, reflecting variations in energy use efficiency and emissions management strategies (Herzig and Schaltegger 2006; Lee 2011).

3.3. Discussion

The increase in carbon footprint per employee from 2022 to 2023 can be linked to changes in energy consumption patterns. Improvements in energy efficiency and conservation practices in 2022 might have led to higher emissions per employee, while the reduction in natural gas

consumption in 2023 contributed to lower emissions.

Despite the reduction in per capita emissions, there has not been a significant change in total CO₂ emissions. This underscores the need for more aggressive sustainability measures. Consistent with global trends, municipalities are increasingly focusing on reducing carbon footprints but face challenges in achieving substantial reductions (IPCC 2022; Üreden and Özden 2018).

3.4. Recommendations

To further reduce the carbon footprint, İncesu Municipality might consider implementing the following strategies:

- **Energy Efficiency Improvements:** Upgrading to more efficient lighting and HVAC systems.
- **Renewable Energy Integration:** Incorporating solar panels or other renewable energy sources to reduce reliance on fossil fuels.
- **Employee Engagement:** Promoting energy-saving practices among employees and encouraging sustainable behaviors.

4. CONCLUSION

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HYDRAULICALLY-EFFICIENT HYDRAULIC DESIGN FOR MULTI-OUTLET SUBMAINS-I: METHODOLOGY

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Abstract

Determining the actual energy (i.e., pressure head) profiles along the submain lines with a uniform slope is important for proper hydraulic design of water distribution systems. In practice, there are three general pressure head profiles (Type-I, Type-II, and Type-III) along the submain lines depending on different uniform line slope situations. Among all types of pressure profiles, the Type-II profile is considered as the optimal (or ideal) pressure profile which can produce the minimum pressure head difference for a given pipe length. This profile occurs when the total energy loss by friction is just balanced by the total energy gain due to uniform downslope. This paper presents a comprehensive analysis to identify the optimal pressure profile (Type II), to achieve the minimal point of the relative maximum pressure variation, Φ_H , which can be defined as the ratio of the maximum allowable pressure head difference ($\Delta H_{\max}$) to the total friction drop ($h_{f(L)}$). This minimal point is regarded as “*the most efficient pressure profile*” or “*ideal hydraulic design*” in the literature. For this purpose, an illustrative figure is developed to compare values of the relative maximum pressure variation versus the dimensionless energy-gradient ratio ($K_S = S_0/S_f$) for all types of pressure profiles. The present ϕ_H curve versus K_S values allows the design engineer to make a decision for the best alternative for selecting the K_S value, where for a given pipe slope (S_0) the K_S value can be selected to meet the minimum pressure variation [$K_S = 1$, $(\phi_H)_{\min} = 0.36$] or the range of pressure variation as close to the minimum point as possible. The implementation of the procedure based on the energy-gradient ratio (EGR) approach for all types of pressure profiles will be presented covering various design applications.

Keywords: Water distribution systems; Energy profiles; Pressure head distribution; Head loss.

INTRODUCTION

In water distribution systems, a sub-main line with multiple outlets can be regarded as a typical hydraulic structure, whose design is limited by the operating inlet pressure head (H_{0I}), desired uniformity criterion for water application, total friction drop at the end of line ($h_{f(L)}$), field topography, as well as outlet hydraulic characteristics. Analysis of the hydraulic design of multi-outlet submain

lines is important for the proper performance of these systems.

The energy-gradient ratio (EGR) approach is useful to identify first which type of pressure profile occurs for a given uniform design slope when other hydraulic variables are initially known, then comprehensively evaluate its hydraulic characteristics along the line. Knowledge of hydraulic properties for any type of pressure profile under consideration enables the design engineer to

evaluate pressure parameters through the line sections in a simple way based on the proposed EGR approach. The EGR approach is essentially based on a simple ratio, defined as “the energy-gradient ratio (K_s)” which can be explained as “the ratio of uniform pipe slope (S_0) to the friction slope (S_f) [or the energy-gradient line (EGL) slope] ($K_s = S_0/S_f$)”.

The design method, based on the EGR approach, was first presented by Gillespie et al. (1979), Wu and Gitlin (1979), and Wu et al. (1983), considering a single inlet submain line on uniform slopes. Gillespie et al. (1979) derived mathematical equations for pressure profiles resulting from the various possible combinations of friction drop and uniform slope situations. However, in their analysis a direct solution of most of the derived equations for determining the type of pressure profile is difficult. To simplify the implicit nature of their formulation, Barragan and Wu (2005) developed simple nomographs based on a trial-and-error procedure in which pipe (S_0) and friction (S_f) slopes can be estimated for different combinations of pipe diameter (D), total line length (L), and total inlet discharge (Q).

The most important difficulty, when recognizing the type of pressure profile, is the determination of energy-grade line slope (or friction slope) (S_f) which depends on the total inlet discharge (Q) and pipe diameter (D), since Q and D are unknown parameters in most design cases (Yitayew and Warrick 1988; Hathoot et al. 1993). Through the following analysis (Yıldırım and Singh 2013a), an improved EGR approach, based on the recent analytical development (Yıldırım 2006, 2007), encompassing different types of pressure head profiles (**Type-I**, **Type-II.a**, **Type-II.b**, **Type-II.c** and **Type-III**) concerning different uniform line slope situations, is presented. In the companion paper (Yıldırım and Singh 2013b), several design examples covering various uniform line slope situations

regarding different types of pressure profiles will be presented.

Determination of Energy-Gradient Line (EGL) along Submain Line with Multiple Outlets

The energy-gradient line (EGL) in a multi-outlet submain line will not be a straight line but a curve of the exponential type. Fig. 1 sketches a horizontal multi-outlet submain line with a single inlet (single line size system) and shapes of hydraulic (piezometric) (HGL) and energy-gradient (EGL) curves along its length (Yıldırım 2007).

Flow in a submain line is considered to be steady, spatially varied flow with decreasing discharge along the direction of flow (from upstream inlet to downstream closed end). Flow in a submain line is usually turbulent ($3,000 < R < 10^5$; R : Reynolds number). Sometimes fully turbulent flow ($10^5 < R < 10^7$) exists at the upstream end, and flow becomes laminar ($R < 2,000$) at the downstream reach where the flow velocity decreases to zero. The transition flow approximately occurs in the interval $2,000 < R \leq 3,000$, and the flow characteristics are indeterminate for the transition zone (Miller 1990).

The introduction of the Blasius friction factor [$f = aR^b$; a and b = empirically determined coefficients, $a = 0.316$ and $b = -0.25$ (von Bernuth and Wilson (1989), $a = 0.302$ and $b = -0.25$ (Provenzano et al. 2005); and R = Reynolds number] into the Darcy-Weisbach (DW) formula provides an accurate estimate of frictional losses produced by turbulent flow inside uniform pipes with low wall roughness and when Reynolds number changes within the range $3,000 < R < 10^5$ (Watters and Keller 1978; von Bernuth and Wilson 1989; von Bernuth 1990; Bagarello et al. 1995). In most of the submain lines with plastic material, the flow regime rarely exceeds these flow conditions.

To determine the total amount of actual energy losses along a submain line, head

losses through local singularities at the outlet connections must be additionally taken into account. These minor losses, $H_{s(L)}$, are usually calculated as if the pipe length were increased by the so-called equivalent length, l_e , i.e., a length of the same uniform pipe that would have the same head loss (Juana et al. 2002a). The total energy losses along the submain line, $H_{T(L)}$, includes friction ($h_{f(L)}$) and local ($h_{s(L)}$) head losses can be formulated as (Yıldırım 2006):

$$H_{T(L)} = h_{f(L)} + h_{s(L)} = F_S h_{f(L)} = \bar{F} F_S \left(K \frac{Q_I^m}{D^{m+3}} L \right) \quad (1a)$$

where

$$F_S = \left(1 + \frac{l_e}{s} \right) \quad (1b)$$

in which $\bar{F} = 1/(m+1) = 1/2.75$: the friction correction factor [m = flow or velocity exponent; for turbulent flow: $m = 1.75$ for the Darcy-Weisbach (DW) and $m = 1.852$ for the Hazen-Williams (HW) equations] taking into account continuous and uniform outflow along the submain line [for the $\bar{F}$ formulation based on uniform and discrete outflow from a finite number of operating outlets, see Eqs. (5a) and (5b) in Yıldırım (2006)]; F_S = the amplification or enlargement factor to be applied to the friction losses in the uniform pipe sections, in order to take into account the effect of local losses [note that for the case of neglecting local head losses, F_S is equal to one ($F_S = 1.0$)]; l_e = the equivalent length of a minor singularity (m) (Juana et al. 2002b, 2004); s = the distance between successive outlets along the submain line (m); K = constant [$K = a(4/\pi)^{(2+b)}/2g$]; the value of K is equal to 2.458×10^{-2} for the Blasius formula (von Bernuth 1990), and 2.35×10^{-2} from Bagarello et al. (1995); Q_I = the total inflow rate at the pipe inlet ($m^3 s^{-1}$); D and L = the pipe internal diameter and length (m), respectively.

The slope of the energy-gradient line (EGL) or the friction slope, S_f , can be written as (for $m = 1.75$):

$$S_f = \frac{H_{T(L)}}{L} = 8.94 \times 10^{-3} \times F_S \times \frac{Q_I^{1.75}}{D^{4.75}} \quad (2)$$

The pressure head change from the pipeline inlet to a given length, l , is a linear combination of the pressure head change due to friction and uniform slope along the pipeline. Applying the conservation of energy principle between pipe sections, $l = 0$ ($i = 0$) and $l = L$ ($i = 1$), the pressure head profile along the line, $H(l)$, can be determined in terms of the operating inlet pressure head, H_{0I} , from the recent analytical development (Yıldırım 2006):

$$H(l) = H_{0I} + H_{VI} [1 - (1-i)^2] - F_S h_{f(L)} [1 - (1-i)^{m\beta+1}] - p i \Delta S \quad (3a)$$

As an alternative derivation, $H(l)$ in terms of the required pressure head, $\bar{H}$, can be written as (for the relationship between Eq. (3b) and Eq.

(3a):

$$H(l) = \bar{H} + H_{VI} [1 - (1-i)^2] + h_{f(L)} \left[F_S [(1-i)^{m\beta+1} - 1] + \frac{m\beta+1}{m\beta+2} \right] - p \Delta S \left(i - \frac{1}{2} \right) \quad (3b)$$

where

$$M_B = \beta \times m,$$

$$\beta = 1 - 3.322 \times \log \left[1 + \frac{H_{VI}}{\bar{H}} + \frac{h_{f(L)}}{\bar{H}} \left[\left(\frac{m+3-0.5^{m+1}}{m+2} \right) - F_S \right] + \frac{1}{4\bar{H}} (p \Delta S) \right] \quad (4)$$

where $H(l)$ = the pressure head at a given section of length l from the pipeline inlet (m); $\bar{H}$ = the required average pressure head for the entire pipeline (m); $i = l/L$: the dimensionless distance as the ratio of length (l) from inlet to the total length (L); H_{VI} = the velocity head at the pipeline inlet (m); β = the nonuniform outflow exponent (Yıldırım 2006); $m\beta$ = the improved value of velocity exponent m from Eq. (4);

$\Delta S = S_0 \times L$ = the total head loss or gain due to the change in elevation at the closed end of pipeline (m); and S_0 = the line slope assuming to be uniform along the pipeline (m/m). In this procedure, the slope of a downhill pipeline is negative ($p = -1$), and the slope of an uphill pipeline is positive ($p = 1$).

For determining the energy profile, $H(l)$, Eq. (3b) has a greater practical importance than

Eq. (3a), since Eq. (3a) requires computation of the operating inlet pressure head (H_{OI}) in advance; whereas, Eq. (3b) can be directly used for the required average pressure head, $\bar{H}$, which is initially a known parameter in most usual design cases. In the proposed procedure, the pressure head distribution, $H(l)$, can be determined in terms of H_{OI} or $\bar{H}$ from Eq. (3a) or Eq. (3b), regarding two successive stages. In the first one, EGL can be evaluated from Eq. (3a) or Eq. (3b), assuming that the uniform outflow occurs along the line ($m\beta = m$; $\beta = 1.0$); then in the second improved stage, EGL can be exactly determined, based on the nonuniform outflow distribution, by introducing the improved value of the velocity exponent ($m\beta = m \times \beta$, $\beta \neq 1.0$) [Eq. (4)] into Eq. (3a) or Eq. (3b). It should be noted that in most usual design cases, the first initial approximation is sufficiently accurate with a little deviation; however, if a greater precision is required the second improved stage can then be implemented. For simplification of the derived procedure, the localized head loss along the pipe is regarded ($FS \neq 1.0$), whereas the change in kinetic head is neglected ($H_{vt} \cong 0$).

Types of Pressure Head Profiles for Different Uniform Line Slopes

When a submain line with multiple outlets is designed using a single inlet system and laid on a uniform slope (S_0), the pressure head profile along the line resulting from the total energy drop by friction, $h_{f(L)}$ [$h_{f(L)} = S_f \times L$; S_f : the slope of energy-gradient line or friction slope] and the total potential energy gain (or loss) due to uniform downslope (or upslope) at the end of the line, ΔS ($\Delta S = S_0 \times L$), can be classified into three general types (Type-I, Type-II and Type-III). The classification can be based on a dimensionless energy gradient ratio, K_S ($K_S = S_0/S_f$).

When the kinetic energy is considered to be small and neglected in a submain line, the shape of profile (pressure variation) will be simply a linear combination of the operating inlet pressure head (H_{OI}), total energy drop

due to friction, and total potential energy change (gain or loss) due to uniform line slope, as suggested by Wu and Gitlin (1973,1974), Howell and Hiler (1974), and Gillespie et al. (1979).

A comprehensive description of the energy relations for all types of pressure profiles is synthesized in Table 1, and is also shown in Figs. 2 and 3. From this table, the effect of the dimensionless energy-gradient ratio, $K_S = S_0/S_f$, on the maximum and minimum pressure values with their positions, can be clearly analyzed. There are five typical pressure head profiles (Type-I, Type-II.a, Type-II.b, Type-II.c and Type-III) under three general types as shown in this figure, and can be expressed (Gillespie et al. 1979, Wu et al. 1983, Barragan and Wu 2005) in what follows:

I. Pressure Profile Type I (Minimum Pressure at the Downstream Closed End of the Line):

As shown in Fig. 2(a), the pressure head decreases with respect to the submain length. This type occurs when the submain line is laid on zero or uphill slopes. In this condition, the dimensionless energy-gradient ratio is $K_S = S_0/S_f \leq 0$. The total energy is lost by both elevation change due to uniform upslope and by friction. The maximum pressure head, H_{max} , is at the inlet of line and is equal to the operating inlet pressure, H_{OI} ($H_{OI} = H_{max}$); the minimum pressure head, H_{min} , is at the closed end of line, and is equal to the downstream pressure head ($H_d = H_{min}$).

II. Pressure Profile Type II (Minimum Pressure along the Line):

As shown in Fig. 2(b), (c) and 3(d), the pressure head decreases from the upstream end with respect to the pipeline length, reaches a minimum point (i_{min}), and then increases with respect to the submain line. The minimum pressure head is located somewhere along the line ($0 < i_{min} = l_{min}/L < 1$), depending on the large interval of K_S , $0 < K_S = S_0/S_f < 2.75$.

a) Profile II-a: This type of pressure profile (Fig. 2b) occurs under the friction and slope

situation, where $0 < K_S = S_0/S_f < 1.0$. In this type, the total energy gain due to uniform downslope at the end of line is smaller than the total energy drop due to friction; so the downstream end pressure head (H_d) is still less than the operating inlet pressure (H_{0I}). The maximum pressure head is at the inlet ($H_{\max} = H_{0I}$); and the minimum pressure head is located somewhere along the line.

b) Profile II-b (Optimal Pressure Profile):

This is under the friction slope situation where the dimensionless energy-gradient ratio is $K_S = S_0/S_f = 1.0$. As shown in Fig. 2(c), this profile is similar to Profile II-a, but the profile is such that the downstream closed end pressure head is equal to the operating inlet pressure head ($H_{0I} = H_d$). The maximum pressure is at the inlet ($H_{\max} = H_{0I}$) as well as at the closed end of line ($H_{\max} = H_d$). The minimum pressure is located somewhere near the middle section of the line.

c) Profile II-c: This is under the friction and slope situation where the dimensionless energy-gradient ratio is $1.0 < K_S < 2.75$ for the Darcy-Weisbach (DW) or $1.0 < K_S < 2.852$ for the Hazen-Williams (HW) equation. This occurs when the line slope is even steeper, so the pressure at the end of line is higher than the operating inlet pressure (Fig. 3.d). In this condition, the maximum pressure is at the downstream closed end of line ($H_{\max} = H_d$), and the minimum pressure is located somewhere along the upstream segment of line.

III. Pressure Profile Type III (Minimum Pressure at the Upstream Inlet of Line):

This occurs when the submain line is on a steep downslope where the total energy gain by the uniform downslope is larger than the total energy drop due to friction for all sections along the line. As shown in Fig. 3(e), the pressure head increases with respect to the line length. This is caused by a steep downslope situation where the dimensionless energy-gradient ratio is $K_S \geq 2.75$ for the DW equation, or $K_S \geq 2.852$ for the HW equation. In this condition the maximum pressure is at

the downstream closed end of line ($H_{\max} = H_d$), and the minimum pressure head is at the pipe inlet and equal to the operating pressure head ($H_{\min} = H_{0I}$).

Among all types of pressure profiles, the Type-II profile is considered as the optimal (or ideal) pressure profile which can produce the minimum pressure head difference for a given pipe length as discussed earlier (Wu and Gitlin 1980; Wu et al. 1983). This profile occurs when the total energy loss due to friction is just balanced by the total energy gain due to uniform downslope (Profile II-b) as shown in Fig. 2(b).

Comparative Analysis of Pressure Head Profiles

Based on the procedure derived above for the design criterion, ϕ_H , a systematic comparison between different types of pressure profiles for different slope patterns will be presented in this section. Note that for simplification, $F_S = 1$ is considered in the related expressions for ϕ_H . For this purpose, the relative maximum pressure variation [$\phi_H = \Delta H_{\max} / h_{f(L)}$] [on the premier axis of y], and the minimum outflow (pressure head) point ($i_{\min} = l_{\min}/L$) [on the secondary axis of y] versus the dimensionless energy-gradient ratio ($K_S = S_0/S_f$) [on the x axis] were computed, as shown in Fig. 4.

In the present figure, there are different segments concerning five types of pressure profiles (**Type I**, **Type II.a**, **II.b**, **II.c** and **Type III**), concerning the related intervals of energy-gradient ratio, K_S . Each portion of this curve is individually determined based on the relationships for ϕ_H , derived for each type of pressure profile. As shown in Figure 4, the shape of ϕ_H distribution is linear through the zero/upslope zone ($K_S \leq 0$), whereas it has a curve form through the downslope zone [$0 < K_S < 1$, $1 < K_S < 2.75$ and $K_S \geq 2.75$ (for DW)]. This figure also illustrates the minimum outflow point ($i_{\min}$)

profile which starts decreasing from the downstream closed end ($i_{\min} = 1$) to the upstream inlet ($i_{\min} = 0$) as the K_S value increases from 0 ($K_S = 0$: **Type I**) to 2.75 ($K_S \geq 2.75$: **Type III**).

In the upslope zone (Type I: $K_S < 0$, $i_{\min} = 1$), the ϕ_H distribution linearly increases and yields values smaller than 1, which means the minimum pressure is at the downstream closed end, and the maximum pressure difference is smaller than the total friction drop [$\phi_H < 1$; $\Delta H_{\max} < h_{f(L)}$]. ϕ_H is finally equal to 1 [$\phi_H = 1$; $\Delta H_{\max} = h_{f(L)}$], for the value of $K_S = 0$ (Type I, $i_{\min} = 1$), which means the minimum pressure occurs at the downstream closed end, and the total friction drop is just balanced by the maximum pressure head difference [$\Delta H_{\max} = h_{f(L)}$].

In the first portion of the downslope zone (Type II.a: $0 < K_S < 1$), the ϕ_H curve yields smaller values than 1 ($0.36 < \phi_H < 1$), then reaches a minimum value ($\phi_{H\min} = 0.36$) for $K_S = 1$ (Type II.b). For this interval ($0 < K_S < 1$), $i_{\min}$ occurs near the pipe downstream section, $0.44 < i_{\min} < 1$, and finally reaches a critical value of 0.44, for **Type II.b** profile (for $K_S = 1$, $i_{\min} = 0.44$, $\phi_{H\min} = 0.36$). In the second portion of downslope zone (Type II.c: $1 < K_S < 2.75$), the ϕ_H profile increases again for the interval, $0.36 < \phi_H < 1.75$, with increasing values of K_S ; and the $i_{\min}$ profile occurs near the upstream section for the interval, $0 < i_{\min} < 0.44$.

As a remarkable result from Fig. 4, ϕ_H is equal to 1 ($\phi_H = 1$) which means that the maximum pressure head difference is just balanced by the total friction drop ($\Delta H_{\max} = h_{f(L)}$), for two different values of K_S . The first one is the Type I profile in which when $K_S = 0$, $\phi_H = 1$, $i_{\min} = 1$; and the second one is the Type II.c profile in which when $K_S \approx 1.9$, $\phi_H = 1$, and $i_{\min} \approx 0.2$. This practical consideration may give an idea to the design engineer when selecting the best alternative

among these two slope conditions for the submain line design.

In the third portion of downslope zone (Type III: $K_S \geq 2.75$), the ϕ_H profile linearly increases with increasing values of K_S , for the interval $\phi_H \geq 1.75$; and $i_{\min}$ just occurs at the upstream inlet point ($i_{\min} = 0$), which means the operating inlet pressure is equal to the minimum pressure, and the maximum pressure head difference is much higher than the total friction drop ($\Delta H_{\max} \geq 1.75 \times h_{f(L)}$), for the steep downslope case (Type III).

Discussion and Concluding Remarks

In the present paper, a comprehensive hydraulic analysis for different types of pressure head profiles is carried out, based on the improved energy-gradient ratio (EGR) approach. Practically, five typical pressure head profiles are observed along the submain line for various line slope combinations. When a submain line is designed for a uniform slope, the dimensionless “energy-gradient ratio ($K_S = S_0/S_f$)” can be efficiently used to identify the type of pressure profile with the corresponding hydraulic characteristics, and determine the proper values of the main pressure parameters through the energy-gradient line.

Considering a single inlet in a submain line on a uniform slope, pressure profiles resulting from the various combinations of friction drop and slope situations are derived. For a given uniform pipe slope, first the type of pressure head profile is primarily assigned, based on the EGR approach; then certain values of the main pressure parameters along the energy-gradient line [operating inlet pressure (H_{oi}), downstream end pressure (H_d), extreme pressures ($H_{\max}$, $H_{\min}$) with their specific positions along the line ($i_{\max}$, $i_{\min}$), total friction drop ($h_{f(L)}$), maximum pressure head difference ($\Delta H_{\max}$) and pressure variation (ϕ_H)] are also evaluated. Hence, the operating inlet pressure head is reformulated by incorporating different uniformity

patterns, by setting a multiplication factor, α , for the required average outlet pressure head, and β^* for the potential energy head change due to uniform line slope. The procedure is simplified by regarding the localized head loss along the pipe but neglecting the change in kinetic head.

The proposed procedure offers flexibility by directly computing values of the required hydraulic variables along the energy profile incorporating different uniformity patterns and without needing any additional hydraulic variables (pipe diameter, total inlet discharge, required average outflow, downstream end pressure head, total friction drop or outlet characteristics). The procedure performs better than the conventional procedures, and can be efficiently used for different types of pressure profiles in different line slope situations. Further investigation on the current hydraulic analysis will be presented in a companion paper encompassing various design applications, comparative analysis and verification.

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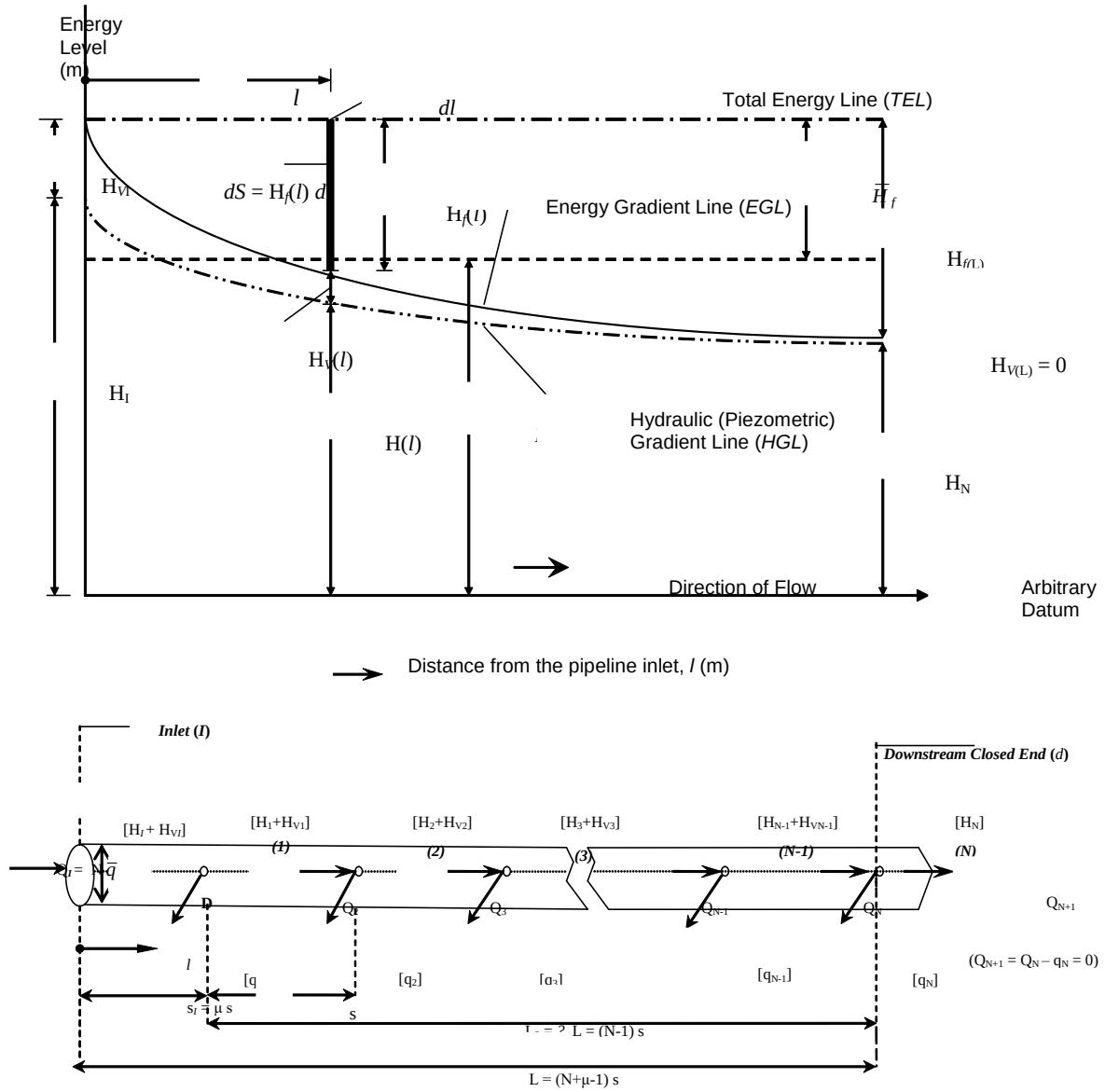
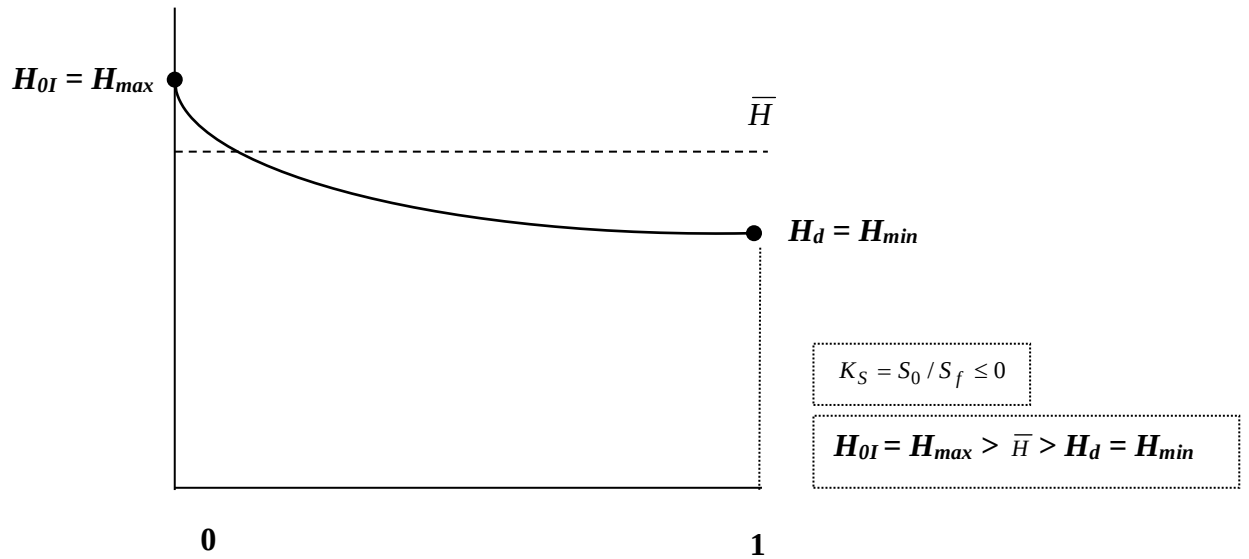
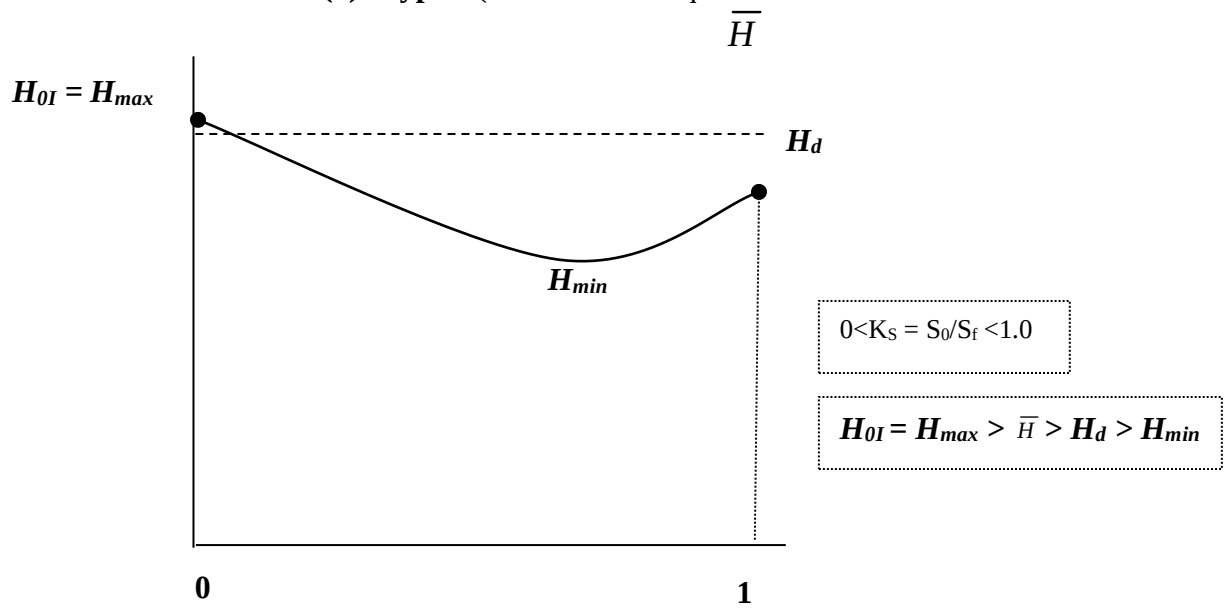


Fig. 1. Shapes of hydraulic (piezometric) gradient line (HGL), and energy-gradient line (EGL) along horizontal submain line with multiple outlets (Yıldırım 2007).



(a): Type I (Horizontal or Upslope)



(b): Type II-a (Gentle Downslope)

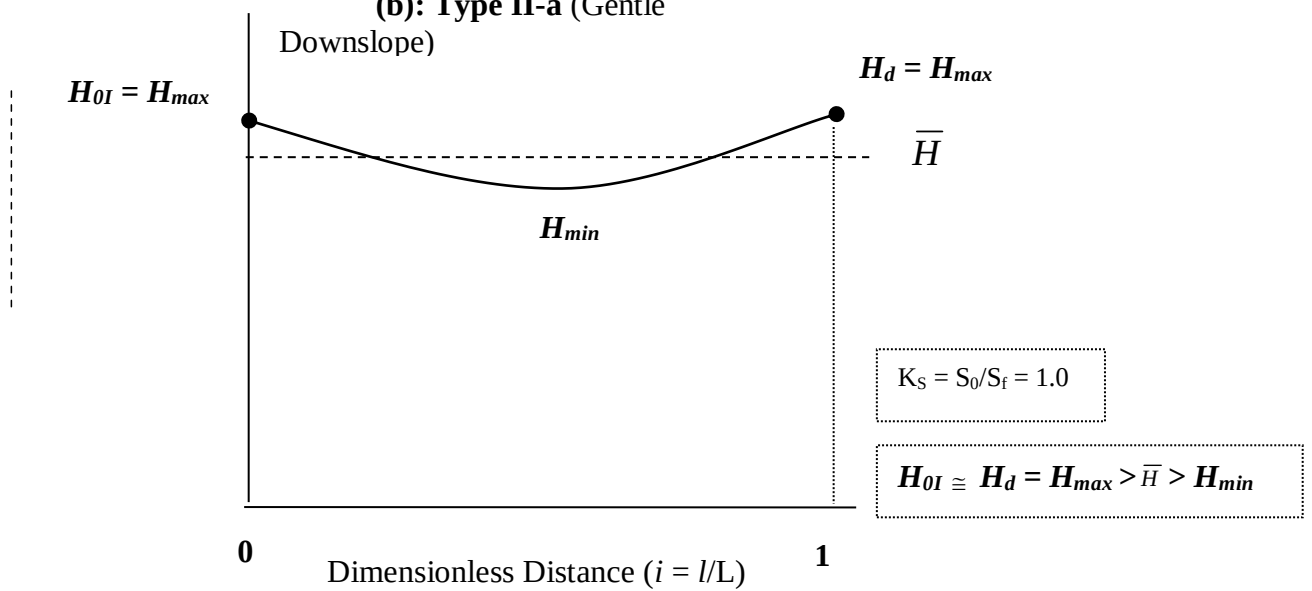


Fig.2. Pressure Head Profiles for (a): Type I, (b): Type II-a and (c): Type II-b

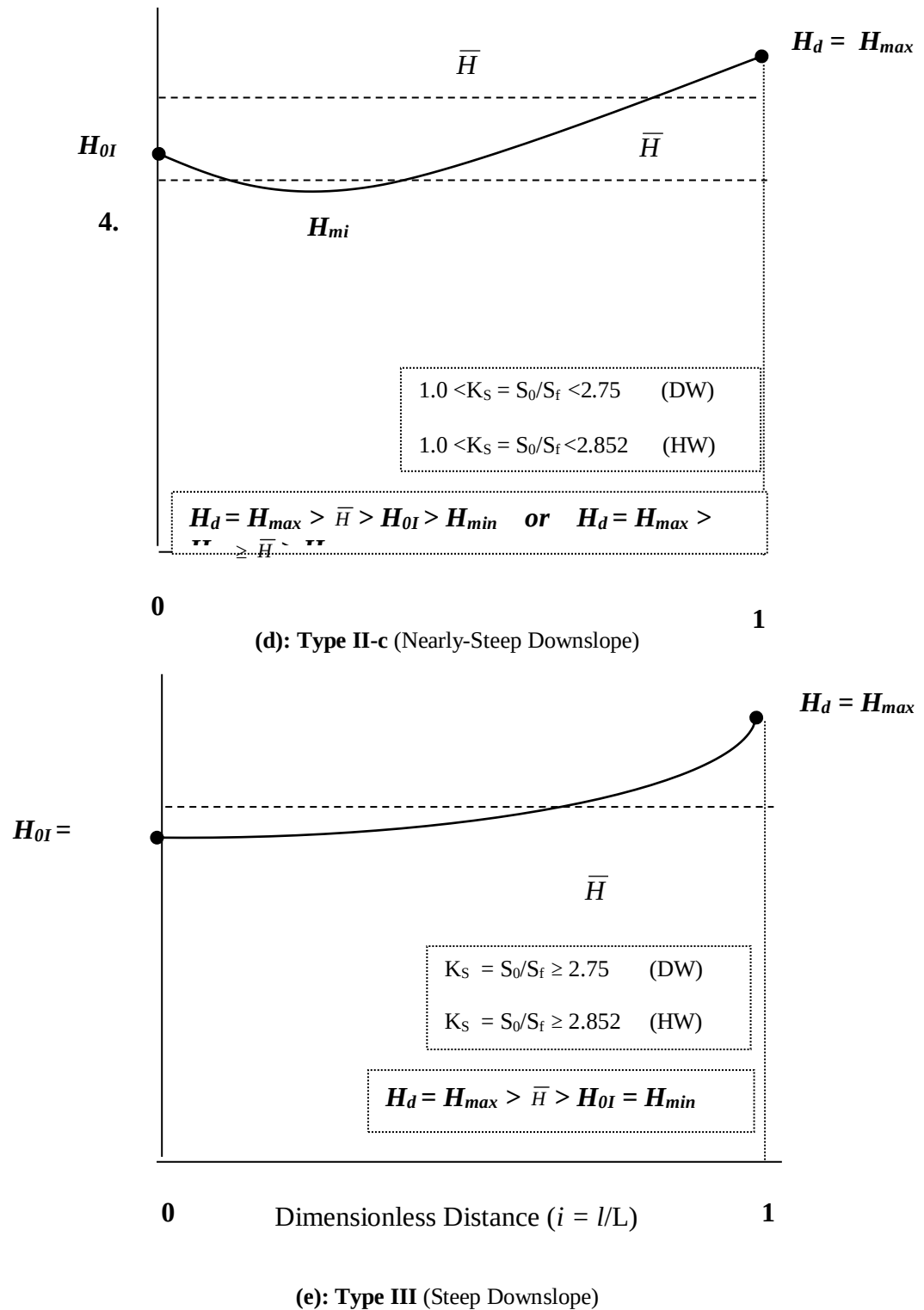


Fig. 3. Pressure Head Profiles in Downslope Situation for **(d):Type II.c** and **(e): Type III**

Table 1. Relationships and Design Intervals for Pressure Parameters for Different Types of Pressure Profiles Concerning Various Line Slope Situations

Slope Definition	Type of Pressure Profile	Relationships for Average ($\bar{H}$) and Extreme Pressure Heads (H_{0I} , H_d , H_{max} , H_{min})	Extreme Outflow Points (i_{max} , i_{min}) (also see Table 3)	Energy Gradient Ratio $K_S = S_0 / S_f$	Relationships for Relative Maximum Pressure Variation (Φ_H): $\Phi_H = \frac{\Delta H_{max}}{h_{f(L)}}$	
					Considering Local Losses [$F_S \neq 1.0$]	Neglecting Local Losses [$F_S = 1.0$]
Horizontal & Uphill	Type-I	$H_{0I} = H_{max} > \bar{H} > H_d = H_{min}$	$i_{max} = 0$ (inlet) $i_{min} = 1$ (downstream end)	$K_S \leq 0$ [$S_0 = 0$ and $S_0 > 0, S_f < 0$]	$K_S + F_S$ (HW, DW)	$K_S + 1.0$ (HW, DW)
Downhill (Gentle)	Type-II.a	$H_{0I} = H_{max} > \bar{H} > H_d > H_{min}$	$i_{max} = 0$ (inlet) $0.44 < i_{min} < 1$ (downstream segment)	$0 < K_S < 1$ [$S_0 < 0$, $S_0 < S_f$, $S_f < 0$]	$(F_S - K_S) + 0.357 \times F_S^{-0.57} K_S^{1.57}$ (DW) $(F_S - K_S) + 0.368 \times F_S^{-0.54} K_S^{1.54}$ (HW)	$(1.0 - K_S) + 0.357 \times K_S^{1.57}$ (DW) $(1.0 - K_S) + 0.368 \times K_S^{1.54}$ (HW)
Downhill (Efficient)	Type-II.b	$H_{0I} = H_d = H_{max} > \bar{H} > H_{min}$	$i_{max} = 0$ (inlet) and/or $i_{max} = 1$ (downstream end) $i_{min} \cong 0.44$	$K_S = 1.0$ [$S_0 < 0$, $S_0 = S_f$, $S_f < 0$]	$0.357 \times F_S^{-0.57}$ (DW) $0.368 \times F_S^{-0.54}$ (HW)	$0.357 \cong 0.36$ (DW) $0.368 \cong 0.37$ (HW)

				(DW) $i_{min} \cong 0.43$ (HW)			
Downhill (Nearly- Steep)	Type-II.c	$H_d = H_{\max} > \bar{H} > H_{0I} > H_{\min}$ and/or	$i_{\max} = 1$ (inlet)	$1 < K_S < 2.75$ (DW) [$S_f < S_0 < 2.75S_f$]	$0.357 \times F_S^{-0.57} K_S^{1.57}$ (DW)		$0.357 \times K_S^{1.57}$ (DW)
		$H_d = H_{\max} > H_{0I} > \bar{H} > H_{\min}$	$0 < i_{\min} < 0.44$ (upstream segment)	$1 < K_S < 2.852$ (HW) [$S_f < S_0 < 2.852S_f$]	$0.368 \times F_S^{-0.54} K_S^{1.54}$ (HW)		$0.368 \times K_S^{1.54}$ (HW)
Downhill (Steep)	Type-III	$H_d = H_{\max} > \bar{H} > H_{0I} = H_{\min}$	$i_{\max} = 1$ (downstream end)	$K_S \geq 2.75$ (DW) [$S_0 \geq 2.75S_f$]			
			$i_{\min} = 0$ (inlet)	$K_S \geq 2.852$ (HW) [$S_0 \geq 2.852S_f$]	$K_S - F_S$ (HW, DW)		$K_S - 1.0$ (HW, DW)
Note: <i>HW</i> : Hazen-Williams Equation and <i>DW</i> : Darcy-Weisbach Equation; <i>F_S</i> : Amplification factor to be applied to friction losses to take into account the effect of local losses (<i>F_S</i>) =							

HYDRAULICALLY-EFFICIENT HYDRAULIC DESIGN FOR MULTIOUTLET SUBMAINS-II: COMPARATIVE ANALYSIS

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Abstract

In water distribution systems, a sub-main line with multiple outlets can be regarded as a typical hydraulic structure, whose design is limited by the operating inlet pressure head (H_{0I}), desired uniformity criterion for water application, total friction drop at the end of line ($h_{f(L)}$), field topography, as well as outlet hydraulic characteristics. Analysis of the hydraulic design of multi-outlet submain lines is important for the proper performance of these systems.

An illustrative figure is developed to compare values of the relative maximum pressure variation versus the dimensionless energy-gradient ratio ($K_S = S_0/S_f$) for all types of pressure profiles. The present ϕ_H curve versus K_S values allows the design engineer to make a decision for the best alternative for selecting the K_S value, where for a given pipe slope (S_0) the K_S value can be selected to meet the minimum pressure variation [$K_S = 1$, $(\phi_H)_{\min} = 0.36$] or the range of pressure variation as close to the minimum point as possible. The implementation of the procedure based on the energy-gradient ratio (EGR) approach for all types of pressure profiles will be presented covering various design applications.

Keywords: Water distribution systems; Energy profiles; Pressure head distribution; Head loss.

Introduction

The main objective of this paper is to develop a procedure based an improved Energy Gradient Ratio (EGR) approach which is an improvement on the previous mathematical development (Yıldırım 2008) utilizing analytical approaches (Yıldırım 2006, 2007) and which covers different types of pressure head profiles (Type-I, Type-II.a, Type-II.b, Type- II.c and Type-III) (Gillespie et al. 1979, Wu et al. 1983, Barragan and Wu 2005) under different uniform line slope situations, while determining values of pressure parameters.

The design method, based on the EGR approach, was first presented by Gillespie et al. (1979), Wu and Gitlin (1979), and Wu et al. (1983), considering a single inlet submain

line on uniform slopes. Gillespie et al. (1979) derived mathematical equations for pressure profiles resulting from the various possible combinations of friction drop and uniform slope situations. However, in their analysis a direct solution of most of the derived equations for determining the type of pressure profile is difficult. To simplify the implicit nature of their formulation, Barragan and Wu (2005) developed simple nomographs based on a trial-and-error procedure in which pipe (S_0) and friction (S_f) slopes can be estimated for different combinations of pipe diameter (D), total line length (L), and total inlet discharge (Q).

The most important difficulty, when recognizing the type of pressure profile, is the determination of energy-grade line slope (or friction slope) (S_f) which depends on the total inlet discharge (Q) and pipe diameter

(D), since Q and D are unknown parameters in most design cases (Yitayew and Warrick 1988; Hathoot et al. 1993). Through the following analysis (Yıldırım and Singh 2013a), an improved EGR approach, based on the recent analytical development (Yıldırım 2006, 2007), encompassing different types of pressure head profiles (**Type-I**, **Type-II.a**, **Type-II.b**, **Type-II.c** and **Type-III**) concerning different uniform line slope situations, is presented. In the companion paper (Yıldırım and Singh 2013b), several design examples covering various uniform line slope situations regarding different types of pressure profiles will be presented.

Percentage of Average Pressure Head (δ_H)
and Relative Pressure Variation (ϕ_H)

The hydraulic design procedure for a submain line with multiple outlets usually establishes that the maximum difference in extreme outlet operating pressure heads along the pipeline is equal to the maximum allowable difference, $\Delta H_{\max}$. The uniformity criterion applied for the design of multiple outlet pipelines is that the maximum allowable difference in the outlet operating pressure head along the pipeline, $\Delta H_{\max}$, is less than a percentage of the average pressure head, δ_H :

$$\delta_H = \frac{\Delta H_{\max}}{\bar{H}} = \frac{(H_{\max} - H_{\min})}{\bar{H}} \quad (1)$$

where δ_H = the percentage of the maximum allowable difference in the outlet operating pressure heads to the average outlet pressure head (m/m); $\Delta H_{\max}$ = the maximum allowable difference in the outlet operating pressure head along the pipeline (m); and $H_{\max} - H_{\min}$ = the maximum difference in the extreme outlet operating pressure head along the pipeline (m). The usual criterion applied for the design of laterals is that the difference in outlet discharge along a single lateral is less than $\pm 10\%$. This corresponds to a maximum difference in the outlet operating pressure head of $\pm 20\%$ (Cuenca 1989).

Another useful design criterion is defined as the relative maximum pressure variation, ϕ_H ,

which is the ratio of the maximum allowable pressure head difference to the total head loss due to friction, and is given by the following expression (Barragan and Wu 2005):

$$\phi_H = \frac{\Delta H_{\max}}{h_{f(L)}} = \delta_H \times \frac{\bar{H}}{h_{f(L)}} \quad (2)$$

ϕ_H is an important indicator to practically determine the shape of pressure profile and evaluate the minimum pressure variation along the profile for different slope situations (Barragan and Wu 2005). In the following section, the extreme pressure heads ($H_{\max}$, $H_{\min}$) will be deduced for all types of pressure profiles to determine the maximum allowable difference in the outlet operating pressure, $\Delta H_{\max}$, the percentage of maximum allowable difference (δ_H), and the relative maximum pressure variation, ϕ_H . Table 1 presents a systematic comparison between the relationships for the average and extreme pressures with their locations along the line, and for the relative maximum pressure variation, ϕ_H , with the design case of considering ($F_S \neq 1$), and neglecting ($F_S = 1$) local head losses, for all types of pressure profiles in different slope situations, as discussed in the following section.

Evaluation for Ideal Hydraulic Design

An ideal hydraulic design is to obtain the minimum pressure variation, or a range of pressure variation as close to the minimum point as possible, for a given total friction drop (Barragan and Wu 2005). As illustrated in Fig. 4, among of all five types of pressure profiles, the one (**Type II.b**), which can produce the minimum pressure variation ($\phi_{H_{\min}} = 0.36$), occurs when the energy-gradient ratio is equal to 1 ($K_S = 1$), and $i_{\min} = 0.44$ ($l_{\min} = 0.44 \times L$). In this ideal design case, the ratio of the maximum pressure head difference, $\Delta H_{\max}$ to the total friction drop, $h_{f(L)}$ is a minimum point which is defined as “the most efficient pressure profile”, or “ideal hydraulic design”, however, it may not be feasible because of the restraints in the field. such as slope and layout of the submain unit (Barragan and Wu 2005).

The present ϕ_H curve versus K_S values (Fig. 4) allows the design engineer to make a decision for the best alternative for selecting the K_S value, in which for a given pipe slope (S_0) the K_S value can be selected to meet the minimum pressure variation [$K_S = 1$, $(\phi_H)_{\min} = 0.36$], or the range of pressure variation as close to the minimum point (near $K_S = 1$) as possible, then finally the friction slope S_f can be determined, depending on the K_S value, assigned in advance.

Conclusions

Based on the present analysis, the following conclusions can be drawn:

1. Among all types of pressure profiles, there is an “*ideal hydraulic design*” for downslope situation at which the dimensionless energy-gradient ratio is equal to 1 ($K_S = S_0/S_f = 1$), in which the ratio of maximum pressure difference to the total friction drop is a minimum [$(\phi_H)_{\min} = \Delta H_{\max} / h_{f(L)} = 0.36$], as shown in Fig. 4 (**Type II.b** profile). The present ϕ_H curve versus K_S values (Fig. 4) permits the design engineer to make a decision for the best alternative for selecting the K_S value, in that for a given pipe slope (S_0) the K_S value can be selected to meet the minimum pressure variation, or the range of pressure variation as close to the minimum point (near $K_S = 1$) as possible. Finally, the friction slope S_f can be determined, depending on the K_S value assigned in advance. For **Type-II.b** profile, the minimum outflow (or pressure head) occurs in the upstream pipe section, $i_{\min} = 0.44$ ($l_{\min} = 0.44 \times L$).

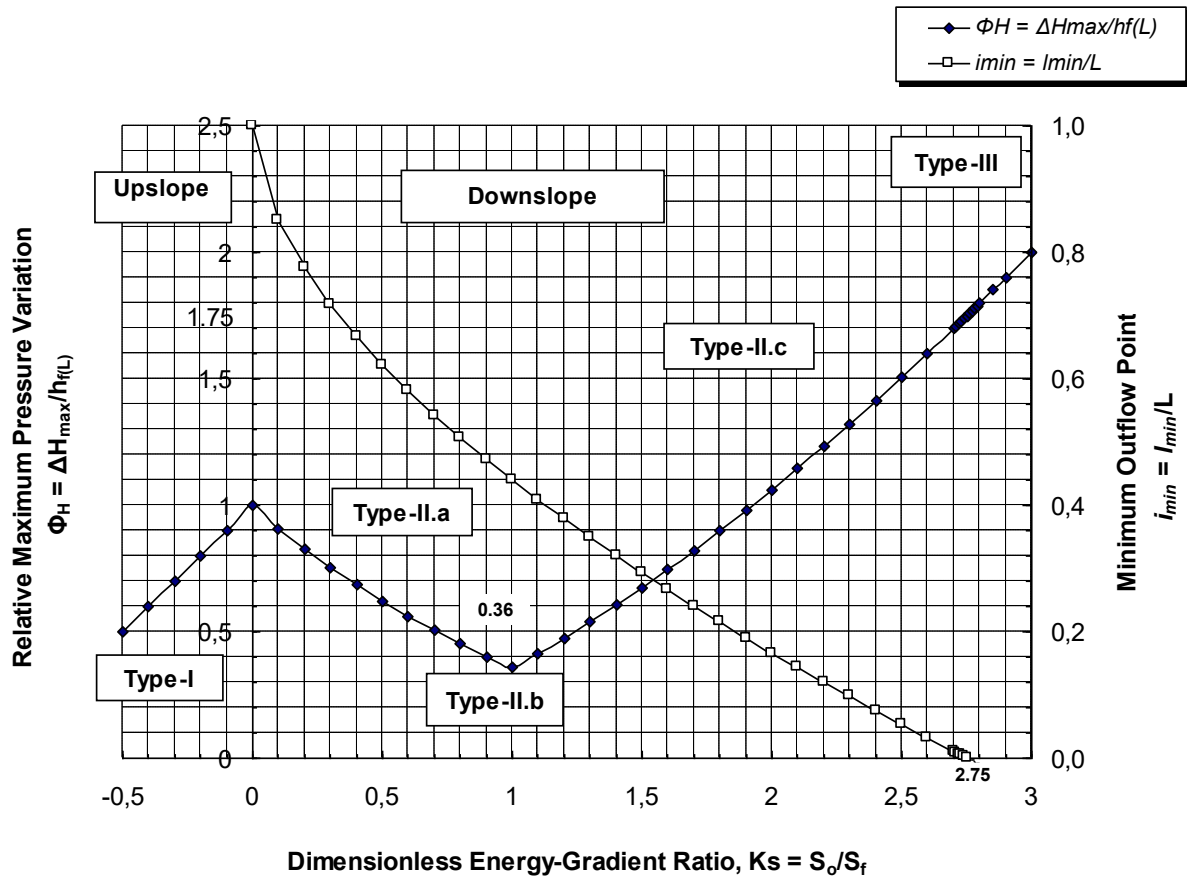
2. As a remarkable result from Fig. 4, ϕ_H is equal to 1 ($\phi_H = 1$) which means that the maximum pressure head difference is just balanced by the total friction drop ($\Delta H_{\max} = h_{f(L)}$), for two different values of K_S . The first one is the **Type I** profile in which when $K_S = 0$, $\phi_H = 1$, $i_{\min} = 1$; and the second one is the **Type II.c** profile in which when

$K_S \cong 1.9$, $\phi_H = 1$, and $i_{\min} \cong 0.2$. This practical consideration may give an idea to the design engineer to select the best alternative among these two slope conditions for submain line design. For **Type II.b** profile, the maximum, minimum and average pressure heads can be functionally expressed by simple relationships, in which when one of the extreme pressures or the average pressure head is required for design, the unknown pressure head can be directly determined, depending on the remaining two pressure heads initially known.

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DEVELOPMENT OF A DETAILED MULTIPHYSICS MODEL FOR THE DYNAMIC PERFORMANCES OF X-EV ON REAL DRIVING CYCLES

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Abstract

This study addresses the gap in literature regarding the performance characterization of x-EVs, specifically BEVs, in real-driving scenarios. A multiphysics numerical model, simulating the dynamic evolution of key parameters over different driving cycles, has been proposed and verified against both SoC measurements and standard performances over WLTP cycles, demonstrating good predictability. Subsequently, the application of this model with respect to the experimentally characterised urban, periurban, and extraurban cycles revealed that higher target velocities in extraurban profiles require more power from the battery. In contrast, urban and periurban cycles benefit from regenerative braking, with more frequent brake activations enhancing energy recovery. Lastly, the proposed model allowed to quantify the real environmental benefit related to the employment of BEVs with respect to traditional gasoline and diesel vehicles, whose performance is simulated on the same routes. Results showed a reduction in CO₂ emissions during Tank-to- Wheel operations equal to 10 kg_{CO2}, when BEVs are fully recharged with renewable electricity, and equal to 8 kg_{CO2} when using energy from the Italian national grid. These findings will help future studies on quantifying the benefits related to BEVs integration as distributed energy storage in a V2G layouts.

Keywords: x-EV, BEV, regenerative braking, numerical, model, CO₂.

1 INTRODUCTION

Carbon dioxide (CO₂) emissions represent one of the main causes of climate change and the consequent environmental crisis that the planet is facing. Over the past few decades, the ever-growing levels of CO₂ concentration in the atmosphere reached about 424 ppm in 2023 compared to 353 ppm in 1990 [1]. This has prompted scientists and governments to seek urgent and sustainable solutions to reduce the environmental impact of human activities. In 2022, the energy sector contributed the most to global CO₂ emissions [2], accounting for about 38% of the share. During that year, the transportation sector was responsible for the second largest share of global CO₂ emissions, amounting to just over 20%. Among these lasts, 71.7% regards road transport.

In the effort to reduce carbon emissions in the transport sector, Electric Vehicles (EVs) are steadily gaining a larger share of the market. They can be categorized as Battery Electric Vehicles, Hybrid Electric, Plug-in Hybrid

Electric Vehicles and Fuel Cell Electric Vehicles (BEV, HEV, PHEV, FCEV), or more in general, x-EV, and their spread can seriously tackle the carbon footprint of the transport system, especially if the electricity used for their recharge comes from the exploitation of renewable sources, also including green hydrogen from electrolyzers.

In the specific, BEVs configuration is the simplest one and cover nowadays the largest share of the market revenues. According to analyses by the International Energy Agency, the global market could reach between 50 and 75 million units by 2025 [3]. This expansion can negatively affect the power grid stability if it is assumed that numerous vehicles charge simultaneously.

Notwithstanding the still controversial driving experience of x-EVs with respect to traditional vehicles, the former are of particular interest since they can be integrated as energy storage systems, through proper technologies enabling the connection to the power grid (Vehicle-to- Grid, V2G paradigm) [4-6].

In this perspective, the correct characterization of the dynamic performances of these vehicles on real-case scenarios becomes fundamental, to correctly depict the technical and economic benefits that derive from their employment in V2G paradigm.

This objective can be achieved through the development of predictive numerical models, which according to their level of detail and accuracy, may provide help both in the design stage [7], as well as in the fast identification of the most optimal solution aimed at maximizing related benefits [8].

The state-of-the-art offers several studies regarding the detailed modelling of BEVs and the analysis of their performances on different driving cycles. Stabile et al. [9] performed a detailed analysis of the power demand of an urban concept lightweight BEV when applied with reference to driving profiles related to the Shell Eco-marathon competition. The model comprised a simple thermo-electro-mechanical model of the DC motors, motor controller and of the lithium-ion battery pack. Subsequently, Ballo et al. [10] extended the model validity by adding a proper formulation to consider wheel rolling resistances and a detailed parametrization of the throttle command. Mallouh et al. [11] provided a comprehensive and detailed modeling for the powertrain of a medium-size BEV, to reproduce the transient and dynamic vehicle responses with respect to three US EPA drive cycles. Ragone et al. [12] performed a computational study for the State of Charge (SoC) estimation in BEV combining electrochemical-degradation-thermal modeling of battery and ML algorithms. The test cases considered for model validation refer to six EPA driving cycles.

As seen, many works which dealt with the accurate modelling of the complete BEV were applied with reference to standard driving cycles. However, real-world driving conditions vary significantly from the standard used for regular testing, as they feature sudden changes in acceleration due to different driving styles and traffic conditions.

It is worth mentioning the paper of Wei et al. [13] where a real vehicle speed profile in Beijing, China was collected for the online estimation of the vehicle remaining driving range. However,

no information about road altitude variation were collected, while the vehicle model presented a simplified characterization of the battery, motor and air resistances. Similarly, Mamo et al. [14] collected real driving cycles in the city of Addis Ababa in Ethiopia. However, these data served for the identification of a minimum energy consumption condition through the development of statistical clustering methods for BEVs.

Therefore, the need to precisely characterize and quantify parameters as the battery discharging power, as well as the energy availability provided by the vehicle, with particular reference to real driving cycles, is the main aim addressed by present work.

With respect to the literature, the novel aspect regards the development of an accurate model for the dynamic analysis of performances of several BEVs, applied to reproduce vehicle performances with reference to real-case scenarios related to urban, periurban and extraurban driving profiles. The characteristics of these cycles (velocity and altitude profiles) were measured during experimental campaign run in the city of Naples, Italy, for the correct initialization and verification of the model.

This extensive study allows to reproduce the performances of the entire vehicle through accurate modelling of the energy fluxes that take place between each of the components that are part of the electric (battery, electric motor, inverter) and mechanical (motor, wheels, brakes differential, gear transmission) circuits on-board, allowing to also quantify the effective environmental gain that is related to the use of these vehicles with respect to traditional means of transportation.

2 CASE STUDY

2.1 Driving cycle profiles and technical characteristics of BEVs under study

In this work, the performance of electric vehicles was evaluated using driving cycles acquired during measurement campaigns on both urban, periurban and extraurban routes. During these campaigns, velocity and altitude profiles were recorded via GPS signal. As better highlighted in next sections, these experimental data are crucial since they allow the dynamic simulation model

to evaluate the performance of each component of the vehicle using a PID controller which follows the objective velocity profile. The routes considered as reference for the simulations are shown in Figures 1. Specifically, they are:

- Urban route - Riviera di Chiaia area (Naples city). The traced route reproduces a typical urban route in the Riviera di Chiaia area (Figure 1.a). Figure 2.a shows the velocity and road slope profiles, characterized by an average speed of 14.4 km/h and a peak of 45 km/h (maximum speed of the vehicle in question).
- Periurban route - Pompeii - Sorrento. The route begins near a green area on the edge of the Sarno River on the outskirts of Pompeii, and reproduces a typical suburban tourist route up to Piano di Sorrento (Figure 1.b). The speed and altitude profiles shown in Figure 2.b are characterized by an average speed of 35 km/h and a peak of 55.2 km/h.
- Extraurban route - Naples – Caserta. The route includes short city stretches and long motorway routes (Figure 1.c). The speed and altitude profiles shown in Figure 2.c are characterized by an average speed of 54.8 km/h and a peak of 160.2 km/h.

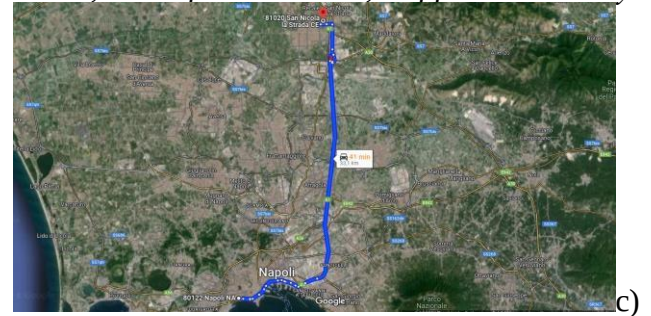


Figure 1. Driving cycles under study: a) urban; b) peri-urban; c) extra-urban.

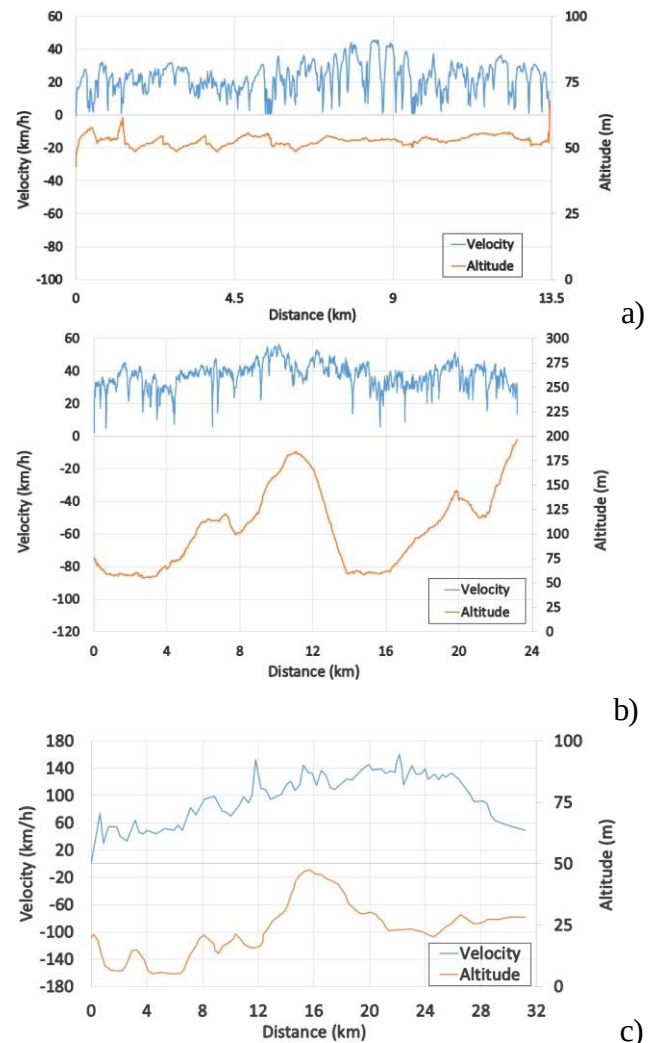


Figure 2. Velocity and altitude profile as collected from experimental test campaigns: a) urban; b) periurban; c) extraurban driving cycle.

The vehicles examined in this case study are all of the BEV type: the 2020 Citroen Ami, the 2019 Nissan Leaf, the 2020 500e Hatchback and the 2020 Tesla Model Y. Their technical and geometrical specifications are reported in Table 1. Vehicles were chosen among different categories – in terms of nominal motor power or vehicle weight - to help in achieving comprehensive results.

Table 1. Main geometrical parameters of the BEVs under study [15].

	Citroen Ami 2020	Fiat 500e 2020	Nissan Leaf 2022	Tesla Model Y 2021
Curb Weight [kg]	471	1365	1580	2072
Nominal Weight [kg]	700	1690	1995	2532
Frontal Drag Coefficient [-]	0.31	0.31	0.28	0.31
Vehicle Frontal Area [m²]	1.61	2.42	2.14	2.20
Wheelbase [m]	1.73	2.32	2.71	2.89
Wheel Height [m]	0.101	0.101	0.120	0.101
Wheel Weight [kg]	7	8.3	10	12.4
Wheel Diameter [m]	0.35	0.38	0.30	0.53
Wheel Friction Coefficient [-]	0.95	0.95	0.95	0.95
Vehicle Length [m]	2.41	3.63	4.51	4.75
Motor Nominal Power [kW]	6	87	110	95
Maximum Power [kW @ RPM]	6 @ 9000	87 @ 9000	110 @ 9000	95 @ 9000
Maximum Torque [Nm @ RPM]	40 @ 3500	220 @ 3500	320 @ 3300	400 @ 3500
Battery Cell Configuration	12s1p	96s2p	96s2p	96s4p
Nominal Cell Voltage [V]	3.8	3.7	3.6	3.7
Nominal Cell Capacity [Ah]	120	52	55	4
Total Battery Capacity [kWh]	5.4	37.3	39.0	75.0
Battery Voltage [V]	45	355	350	357
Gear Ratio [-]	10:1	9.6:1	8.2:1	9.7:1
Nominal Range [km]	75	35	270	514

WLTP Specific Consumption [Wh/km]	73.3	118	144	171
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3 MODELLING AND SIMULATION

3.1 Dynamic Model of Battery Electric Vehicle

The development of the multiphysics model of the x-EV is carried out within the AVL Cruise M environment, a multidisciplinary vehicle system simulation tool for mobility concept analysis, subsystem design and layout, and virtual component integration [16].

In the next subsections, more information about the modelling of each component is provided, always with reference to BEVs.

The model accounts for the whole structure of the vehicle, owning a vast library related to the vehicle components under interest and allowing the mechanical and functional links between these elements. The modular structure of the BEV modelled is shown in Figure 3, where all the connections among the components considered in the model are highlighted. It can also be observed, as already said, how the model needs a reference route profile to be reproduced as objective.

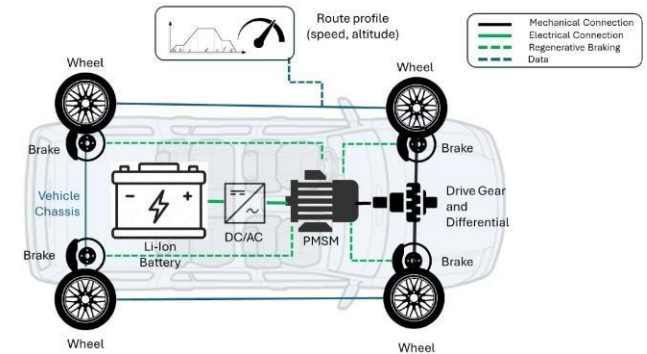


Figure 3. Modular structure of a BEV vehicle.

Electric Motor Model

The electric motor is modelled using a straightforward map-based method, based on the definition of the full load torque in relation to the engine rotational speed. In this work, both the first (motor mode with positive angular rotation) and fourth (generator mode with positive angular rotation) quadrants are

modelled, due to the presence of the regenerative braking system on each vehicle.

The first step involves both defining the type of electric machine installed on the vehicle (asynchronous or permanent magnet synchronous motor – PMSM) in the latter case, a correction to the requested torque based on the operational temperature of the layout is applied) and the efficiency of the inverter (a necessary component for the proper management of energy flows between the battery and the motor) as the requested torque and the machine's rotational speed vary.

In detail, in each integration time step, the model:

- defines the Signal Load parameter – equal to -1 (machine in Generator mode) or 1 (machine in Motor mode) depending on the sign of the vehicle's acceleration, the latter based on the instantaneous speed value to be achieved;
- identifies the machine's maximum torque in both generator and motor modes, based on the Torque-Speed characteristic curves provided as input to the model;
- the current supplied or requested by the machine, given the angular speed value at the previous time step, is evaluated according to the equations:

$$T \cdot w = V \cdot I + P_{\text{loss}} \quad (1)$$

$$T \cdot w + P_{\text{loss}} = V \cdot I \quad (2)$$

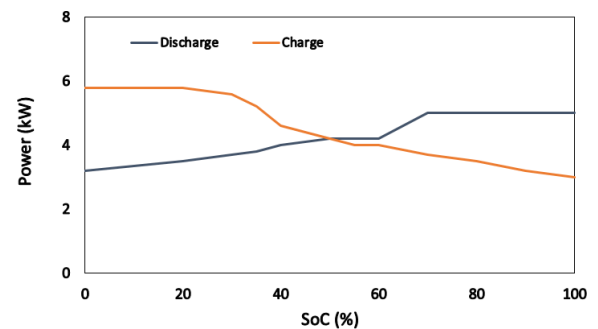
respectively for a negative or positive signal load. In the equations, T is the torque in Nm, w is the machine's angular speed at the previous time step (in rad/s), V is the voltage (in Volts), and I is the current (in Amperes). The losses P_{loss} (in Watts) are calculated based on the system efficiency defined as input in the map-based approach;

- lastly, the actual torque value is updated based on the estimated current and is sent back to the Electric Machine component as a dimensionless Demanded Load signal which updates the system's rotational speed. The resulting torque is also provided to the Drive Gear and Differential component for the transmission of motion to the wheels.

It is worth saying that the Tesla Model Y is equipped with two electric motors, one on the front axle (induction motor), the other on the rear axle (PMSM) to provide power to all four wheels. For this vehicle, the energy logic implemented in the model, aimed at managing the operations of these two engines, were set to guarantee a provision of 100% power from the rear motor unless traction or the amount of acceleration requires assistance from the front engine. The maximum power output between the two engines has been split at a ratio of 60/40, this last identified after a parametric study aimed at achieving a vehicle consumption in accordance with the vehicle technical specifications.

Battery

The battery pack model utilizes an equivalent electrical circuit approach, based on series and parallel connections of individual storage cells. This model can predict the voltage response to a current at a specific SoC and temperature. Each cell is depicted as a voltage source, defined by the Open Circuit Voltage (OCV) of the storage cell, and an Equivalent Series Resistance (ESR), which represents the dissipative forces during charging and discharging [17]. Moreover, the model requires in input the charge/discharge power curves as a function of the SoC. The former is derived from literature data, while the latter were inferred from the author's extensive experience and validated through plausible assumptions. They are shown in Figure 4.



a)

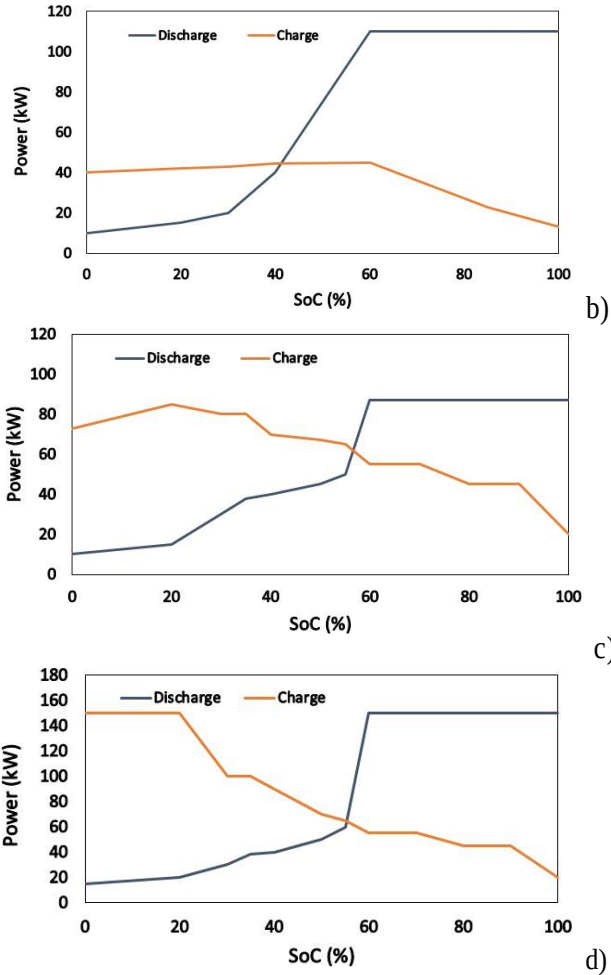


Figure 4. Battery curves of charge/discharge for a) Citroen Ami; b) Nissan Leaf; c) Fiat 500e; d) Tesla Model Y.

Drive Gear and Differential

The Drive Gear component solely defines the relationship between the rotational speed of the electric motor and that of the wheels. The Differential component compensates for discrepancies in the rotational speeds of the drive wheels: between the inner and outer wheels while cornering and between different drive axles on vehicles. Except for rare exceptions, the differential is a bevel gear transmission unit. When the bevel gears on the left and right sides (the most common arrangement) are of equal size, the differential gears act as a balancing arm to equalize the torque distribution between the left and right wheels, ensuring different rotational speeds for the two.

Chassis-Wheels-Brakes

Vehicle dynamics require the precise definition of the car's characteristic dimensions, including the vehicle's curb weight and driver weight, the

frontal area and drag coefficient for estimating aerodynamic resistance, and the position of the centre of gravity and wheels (mutual distances and height from the ground) for estimating resultant forces. Regarding the wheels, it is essential to define the tire radius, weight, moment of inertia, and the static and dynamic friction coefficients, which will be used to estimate the rolling resistance torque using the formula:

$$M_{\text{roll}} = W_{\text{wheel}} \cdot c_{\text{wheel}} \cdot r_{\text{wheel}} \quad (3)$$

where W_{wheel} is the weight of the wheels, c_{wheel} is the friction coefficient, and r_{wheel} is the tire radius. For the brakes, the model requires the brake radius r_{brake} , brake contact area A_{brake} , friction coefficient μ_{brake} , moment of inertia, braking efficiency η_{brake} , and the characteristic curve linking pedal pressure to braking force to calculate the braking torque using the equation:

$$T_{\text{brake}} = 2 \cdot P_{\text{brake}} \cdot A_{\text{brake}} \cdot \eta_{\text{brake}} \cdot \mu_{\text{brake}} \cdot r_{\text{brake}} \cdot c_{\text{brake}} \quad (4)$$

Driver System

The driver system is designed to realistically emulate the driving behaviour of a human driver. In this study, a simplified driver model was used, whose primary goal is to minimize the error between the desired reference speed and the vehicle's actual speed. Depending on the sign of the difference between these two variables, the system generates an acceleration or braking command to ensure the vehicle follows the desired speed profile. The model employs a PID controller, whose parameters have been optimized through a calibration approach in order to accurately tracks and replicates the desired speed profile.

When vehicle deceleration is required, the driver presses the brake pedal, which causes a change in the operations of the electric propulsion system, switching from motor to generator mode. This process allows for the recovery of braking energy, which is feed back to the battery pack.

3.2 Model Verification

The model verification has been performed with respect to measurements in terms of battery discharge, with reference to the performances of the Citroen Ami 2020 vehicle when employed in

the urban driving cycle. The vehicle has been provided by the innovative startup DG Twin S.r.l., which also performed the experimental campaign where measurements in terms of driving speed and altitude profiles, as well as the battery SoC reduction, were collected.

By implementing the model with both the vehicle specifications (Table 1) and the velocity and altitude road data, the evolution of the SoC discharge was obtained as output and compared with experimental measurements, as shown in Figure 5. The numerical result well follows the experimentally obtained data, with a maximum deviation at 3000 seconds equal to 2.8% (SoC equal to 50% from experimental measurements, 48.6% according to the numerical model), while the average error settles at a value of approximately 1.13%.

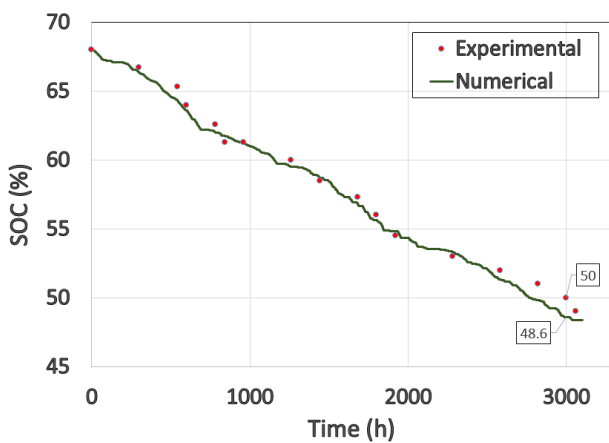


Figure 5. Comparison between the experimental (red circles) and numerical (continuous green curve) evolution of SoC discharge – Citroen Ami on urban cycle.

Subsequently, the multiphysics numerical model has been also applied to compare the estimated specific consumption of all vehicles (Table 1) with reference to the Worldwide harmonized Light vehicles Test Procedure (WLTP) driving profile, this last shown in Figure 6.

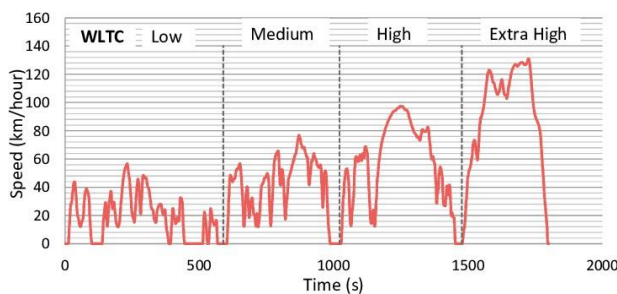


Figure 6. WLTP driving cycle.

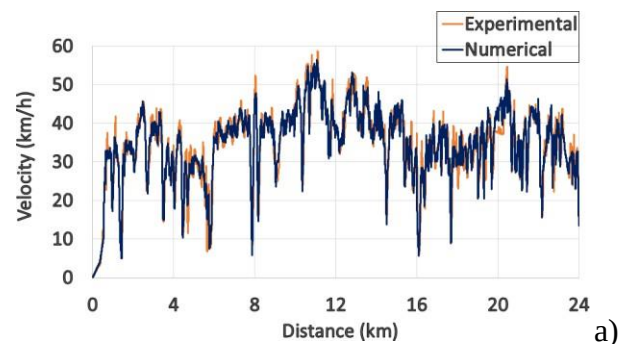
Verification has been performed by calculating the energetic consumption of all BEVs in accordance with the correct standards set by the procedure [18]. The following Table 2 shows the comparison between the rated consumption as reported by the vehicle's datasheet and the numerical results, accounting for an average error equal to 4 %.

Table 2. Comparison between the rated consumption reported on datasheet and the numerical results.

	WLTP Specific Consumption (Wh/km)		
	Datasheet	Numerical	Error - %
Citroen Ami	73.3	69.4	-5.32
Nissan Leaf	144	140	-2.78
Fiat 500 e	118	116	-1.69
Tesla Model Y	171	177	+3.5

4 RESULTS

Once the model verification has been accomplished, the multiphysics model has been applied to reproduce the performances of all the BEVs under study on the three reference cycle routes. It must be mentioned that the Citroen Ami analysis against the extraurban driving cycle is not reported, as the vehicle technical characteristics are not sufficient to achieve the high velocities measured in this operative condition. With specific reference to the periurban case, Figures 7 show the comparison between the target speed profiles with respect to the one depicted from the numerical model. The good agreement between these variables derives from a reliable definition of the PID controller parameters.



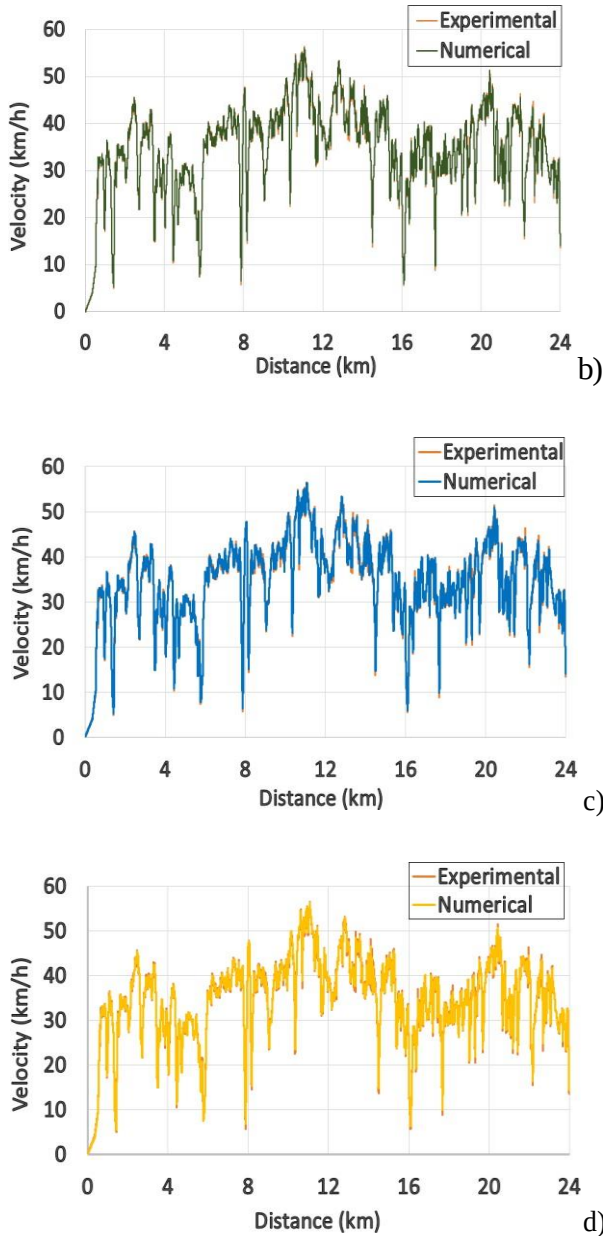


Figure 7. Comparison between the target speed profiles and numerical model profile for the periurban routes. a) Citroen Ami; b) Nissan Leaf; c) Fiat 500e; d) Tesla Model Y.

Therefore, Figures 8 and 9 show the evolutions of the SoC and of the power to/from the battery for the three routes of interest. As expected, for all vehicles the SoC tends to decrease much more rapidly during the extraurban route, by virtue of the higher speeds that the vehicles reach in these contexts, which leads to a significant increase in the power delivered by the engine. In particular, it can be affirmed how the management of the SoC becomes crucial on extraurban routes, where it is essential to optimize the use of the available energy to prevent the battery from discharging excessively

and guarantee the autonomy necessary to complete the journey. The lower energy consumption associated with the urban and periurban routes derives from the combined action of two factors.

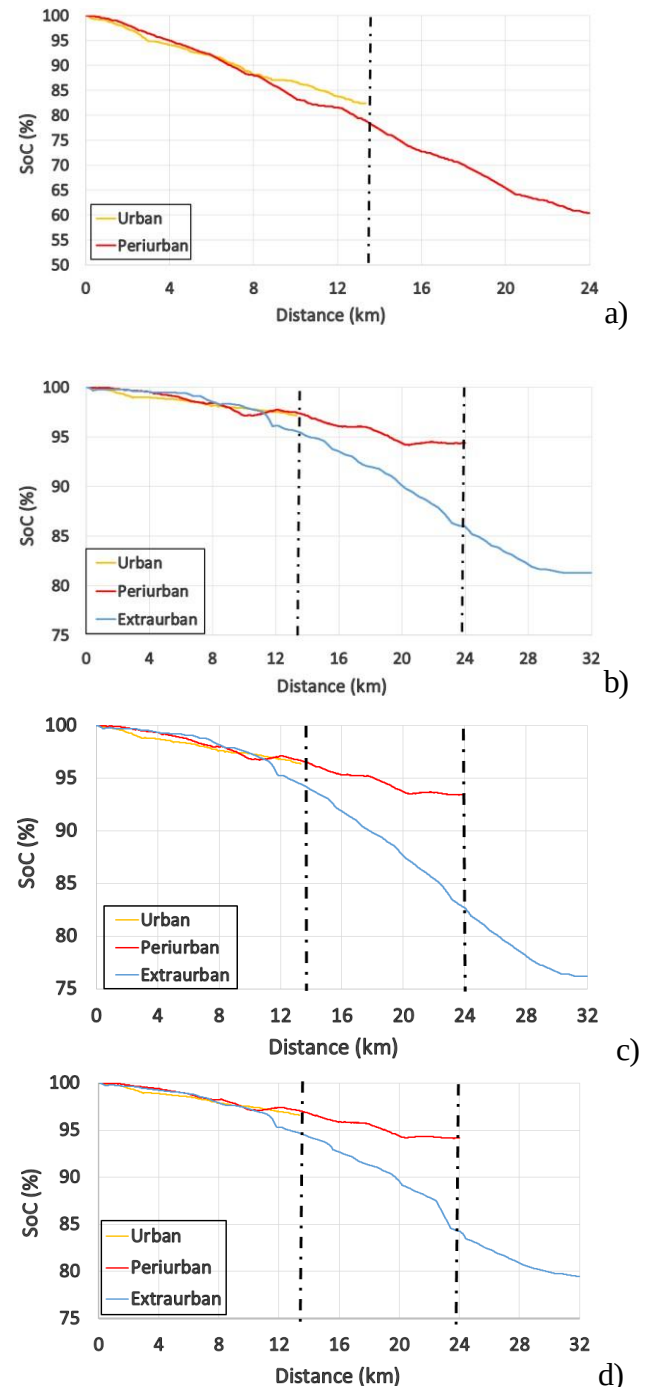


Figure 8. Comparison between the evolution of the SoC for the analysed routes. a) Citroen Ami; b) Nissan Leaf; c) Fiat 500e; d) Tesla Model Y.

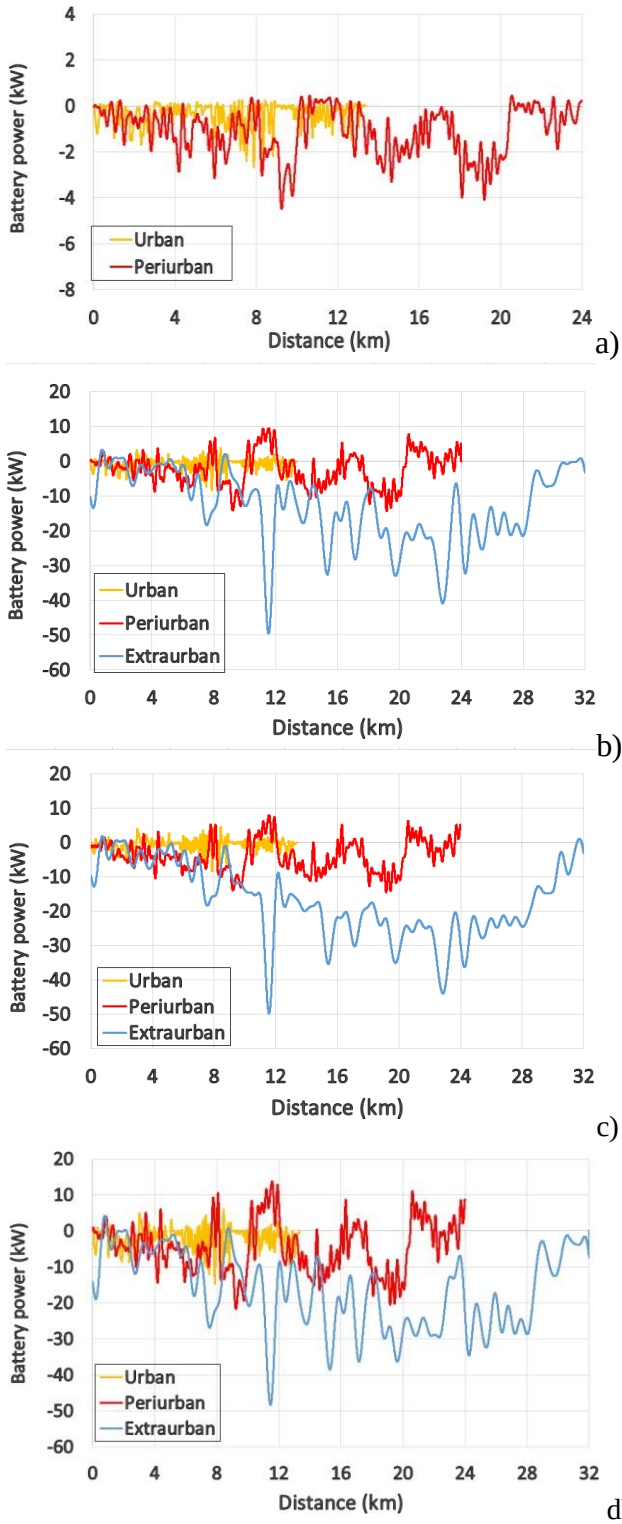


Figure 9. Comparison between the power to/from the battery for the analysed routes. a) Citroen Ami; b) Nissan Leaf; c) Fiat 500e; d) Tesla Model Y.

Taken the Nissan Leaf case as reference, it can be said that:

- the power withdrawn from the battery (Figure 9) is lower: during the urban and periurban routes, the peak power

requested from the battery is respectively equal to 10 kW and 15 kW, compared to the 50 kW peak required for the extraurban route;

- there are greater recharges resulting from regenerative braking, as consequence of more frequent phases of activation of the brake pedal.

With respect to this last aspect, authors also performed simulations where the regenerative braking has been deactivated, with the aim of weighting its effects over the average battery consumption. The results in Table 3, in terms of SoC attained at the end of each route, enlighten an average gain for the urban, periurban and extraurban cases respectively equal to 0.3, 1 and 0.27 kWh.

Table 3. Final SoC and related energy recovery for each route with and without regenerative braking.

		Citroen Ami	Nissan Leaf	Fiat 500e	Tesla Model Y
Urban	Reg. Brak. (%)	82.3	97.2	96.7	96.8
	No Reg. Brak. (%)	81.9	96.3	96	96.1
	ΔE (kWh)	0.02	0.3	0.3	0.5
Periurban	Reg. Brak. (%)	60.7	94.4	93.5	94.2
	No Reg. Brak. (%)	60.1	91.3	91	92.1
	ΔE (kWh)	0.03	1.2	1	1.6
Extraurban	Reg. Brak. (%)	-	81.3	76.2	79.5
	No Reg. Brak. (%)	-	80.8	75.8	79
	ΔE (kWh)	-	0.2	0.2	0.4

4.1 Environmental Benefits

Lastly, the environmental benefits that is associated to the employment of BEVs on real driving conditions with respect to traditional vehicles – fuelled with gasoline or diesel – are studied in detail. Therefore, the software environment, employed for the previous

analyses, has been also considered for the development of two further vehicle's models, where a map-based approach is followed for the characterization of performance, and the related CO₂ emissions, of gasoline/diesel-fuelled Internal Combustion Engines (ICEs). The environmental impact has been quantified considering a Tank-to-Wheel (TtW) approach. In the specific, the vehicles and engines characteristics set in the models are shown in Table 4 and are based on validated examples provided by the software.

Table 4. Main parameters of the ICEs (gasoline – Diesel) of reference.

	Gasoline	Diesel
Curb Weight [kg]	1450	1450
Nominal Weight [kg]	1930	1930
Vehicle Length [m]	3.8	3.8
Motor Nominal Power [kW]	144	87
Maximum Power [kW – RPM]	144 @ 6000	87 @ 4500
Maximum Torque [Nm – RPM]	235 @ 4100	180 @ 2200
Specific Consumption [L/100km]	14	6.3

Therefore, the model is applied to reproduce the performance of these vehicles on the reference routes, and the related avoided CO₂ emissions are estimated both considering the case in which BEVs are charged both from renewable sources, and the case where charging occurs from the Italian National grid. In the former case, the associated CO₂ production on a tank-to-wheel approach is assumed equal to zero, while in latter case, authors considered that the electricity production in Italy derives from the exploitation of renewable sources just for the 36.8%, [19], thus the environmental impact associated to the recharging has been quantified considering a conversion factor equal to 0.330 kgCO₂/kWh, [20].

Based on this data, the CO₂ emissions of BEVs are compared with the two reference ICE vehicles on the three routes analysed.

Figure 10 shows a comparison histogram of the amount of CO₂ emitted by each vehicle on all routes. Battery electric vehicles, when recharged from the Italian grid, have much lower emission

levels than gasoline and Diesel vehicles, with an average reduction compared to gasoline and Diesel vehicles of 75% and 56% respectively.

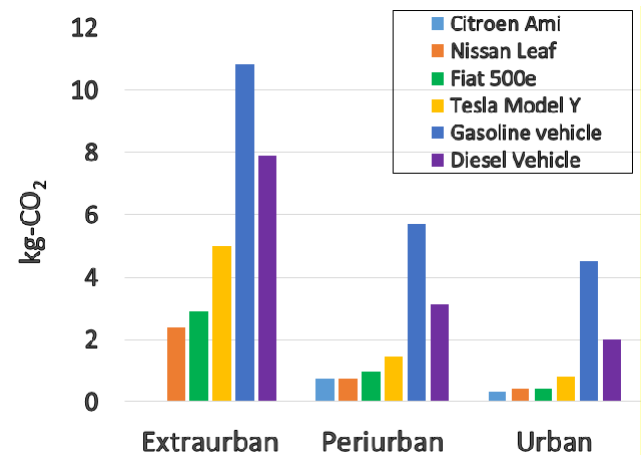


Figure 10. Comparison of CO₂ emissions of BEVs with ICE vehicles for the three routes analysed.

5 CONCLUSIONS

Present work aimed at fulfilling the literature gap about the correct identification of the performance of different BEVs when employed in real-driving scenarios, these last depicted from experimental campaigns on different routes in the city of Naples – Italy. Indeed, actual driving scenarios greatly differ from the standard test cycles typically used for these scopes, as they involve abrupt shifts in acceleration caused by varying driving habits and traffic situations.

The proposed multiphysics numerical model, which reproduces the dynamic evolution of the main parameters of interest over different driving cycles, showed good predictability during verification both against collected measurements – the SoC reduction on urban cycle reproduced with a related average error of 1.13%, and technical datasheet consumption – with an average error among the four vehicles tested on WLTP cycle equal to 4%.

Subsequently, the application of the numerical model in reproducing vehicles performance with respect to urban, periurban and extraurban cycles better enlightened how the higher objectives velocities characterizing the latter profile required higher power withdrawn from the battery, while the urban and periurban cycles mostly benefit from the energy gaining associated to the regenerative braking system, by virtue of the more frequent activations of the brake pedal.

Lastly, with respect to the performances of other two traditional vehicles, fuelled with gasoline and diesel and whose characteristics are depicted from both literature and model examples, enlightened how the employment of BEV leads to a substantial reduction of the amount of CO₂ emitted in the atmosphere. With specific reference to the comparison with the gasoline-fuelled vehicle, the related environmental gain is at maximum equal to 10 kg_{CO2} - when the vehicles are recharged from electricity coming from renewable sources – and equal to 8 kg_{CO2} when the Italian energetic mix is considered. The results of this work will lay the foundation of future studies where the integration of these systems as distributed energy storage sources in a V2G paradigm will be analysed in detail.

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MULTI-OBJECTIVE OPTIMIZATION OF HESS TOPOLOGY AND SIZING FOR METRO VEHICLES USING NSGA-III

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Abstract

This study investigates the best Hybrid Energy Storage System (HESS) design for metro vehicles, considering both cost and energy efficiency. The HESS combines supercapacitors and hydrogen fuel cells, arranged in either serial or parallel configurations. Using the Non-dominated Sorting Genetic Algorithm III (NSGA-III), a powerful optimization tool, the research balances conflicting goals of cost reduction and energy loss minimization, while also meeting practical constraints like vehicle weight and passenger capacity. NSGA-III is chosen for its ability to handle multiple objectives, efficient sorting, and diverse solutions. Results highlight the superior performance of the parallel HESS configuration in improving energy management and cost-effectiveness for metro systems.

Keywords: HESS, NSGA-III, Metro Vehicle, Optimization, Energy Storage, Supercapacitors, Hydrogen Fuel Cells

INTRODUCTION

The increasing energy demands and environmental concerns in urban rail transit systems necessitate the development of efficient energy storage solutions. Hybrid Energy Storage Systems (HESS) combining batteries, supercapacitors, and hydrogen fuel cells offer a promising approach to enhance energy efficiency and reduce operational costs. Supercapacitors provide high power density and quick charge/discharge capabilities, while hydrogen fuel cells offer high energy density and long-term storage solutions.

Hydrogen fuel cells have been utilized in rail applications due to their ability to provide a continuous power supply over long periods, making them suitable for long-distance and high-frequency operations [1]. Supercapacitors, on the other hand, are ideal for managing the rapid power fluctuations and regenerative braking energy common in rail systems [2]. The integration of these two technologies can significantly enhance the performance and efficiency of rail transit systems [3].

This study aims to optimize the topology and sizing of HESS for metro vehicles using NSGA-III, considering both serial and parallel configurations. The optimization targets cost minimization and energy loss reduction, subjected to constraints on vehicle weight, passenger capacity, and available HESS volume.

NSGA-III (Non-dominated Sorting Genetic Algorithm III) is particularly suitable for solving multiobjective optimization problems, especially

when dealing with a large number of objectives. It uses a reference point-based approach to maintain diversity in the solution set and ensure a well-distributed Pareto front. NSGA-III's efficient sorting mechanism, diversity preservation through reference points, and scalability make it an effective tool for high-dimensional optimization problems [4, 5].

In comparison, several state-of-the-art evolutionary multi-objective optimization algorithms offer different strengths and are also widely used:

1. **MOEA/D (Multi-Objective Evolutionary Algorithm based on Decomposition):**
 - a. **Decomposition Approach:** Breaks down a multi-objective problem into a set of single-objective subproblems [6].
 - b. **Neighborhood Structure:** Utilizes neighborhood information for solution diversification.
 - c. **Applications:** Effective in optimizing individual objectives within the overall problem framework.
2. **SPEA2 (Strength Pareto Evolutionary Algorithm 2):**
 - a. **Fitness Assignment:** Calculates fitness based on domination and density information [7].
 - b. **Archiving:** Uses an external population to archive good solutions.
 - c. **Applications:** Excels in maintaining a diverse set of high-quality solutions for multi-objective problems.
3. **MO-CMA-ES (Multi-Objective Covariance Matrix Adaptation Evolution Strategy):**

- a. **Adaptation Mechanism:** Adjusts the covariance matrix of solutions adaptively [8].
- b. **Applications:** Highly effective for continuous optimization of energy storage components.
4. **RVEA (Reference Vector Guided Evolutionary Algorithm):**
 - a. **Reference Vectors:** Uses reference vectors to guide the search process [9].
 - b. **Angle-based Selection:** Selects solutions based on their angles to reference vectors.
 - c. **Applications:** Efficient in balancing multiple conflicting objectives.
5. **HypE (Hypervolume Estimation Algorithm):**
 - a. **Hypervolume Indicator:** Uses hypervolume as a fitness indicator [10].
 - b. **Monte Carlo Simulation:** Reduces computational load using Monte Carlo simulations.
 - c. **Applications:** Suitable for problems where hypervolume is a critical measure of solution quality.

These algorithms, like NSGA-III, offer effective solutions for various multi-objective optimization problems and are preferred in different application areas based on specific needs and problem characteristics.

Materials and Methods

Problem Formulation

The optimization problem for HESS topology and sizing is formulated with the following objective functions and constraints:

Objective Functions:

1. Minimize total cost (C): $C = C_{initial} + C_{maintenance} + C_{replacement}$
2. Minimize energy loss (E): $E = E_{transmission} + E_{conversion}$

Constraints:

1. Vehicle weight (W): $W_{vehicle} + W_{HESS} \leq W_{max}$
2. Passenger capacity (P): $P_{actual} \geq P_{required}$
3. Available volume for HESS (V): $V_{HESS} \leq V_{max}$
4. Dynamic performance requirements.

HESS Topology:

- **Serial configuration:** Battery, supercapacitor, and hydrogen fuel cell connected in series.
- **Parallel configuration:** Battery, supercapacitor, and hydrogen fuel cell connected in parallel.

The problem involves balancing the trade-offs between these conflicting objectives while satisfying all constraints. Supercapacitors offer quick energy release and absorption, ideal for handling the fluctuating power demands during metro operations. Hydrogen fuel cells provide a higher energy density, suitable for longer-term energy supply. The combination of these technologies in various topologies requires careful consideration of their individual and collective performance characteristics.

NSGA-III Algorithm Adaptation

NSGA-III is a multi-objective optimization algorithm designed for problems with a large number of objectives. Its adaptation to the HESS optimization problem involves the following steps:

Algorithm Steps:

1. **Initialization:** Generate an initial population of possible HESS configurations.
2. **Evaluation:** Compute the objective functions for each individual.
3. **Non-dominated Sorting:** Sort the population based on Pareto dominance.
4. **Reference Point Generation:** Generate reference points to guide the search towards the Pareto front.
5. **Selection:** Select individuals based on their distance to reference points.
6. **Crossover and Mutation:** Apply genetic operators to generate new solutions.
7. **Replacement:** Form a new population by replacing less fit individuals.

NSGA-III is particularly suitable for solving multi-objective optimization problems for several reasons:

- **Scalability to Many Objectives:** NSGA-III is designed to handle optimization problems with a large number of objectives. It uses a reference point-based approach, which helps in maintaining diversity in the solution set and ensuring a well-distributed Pareto front.
- **Reference Points:** The algorithm uses a set of reference points to guide the search process. These reference points are predefined and help in

maintaining diversity among the solutions, especially when the number of objectives is high.

across the Pareto front, ensuring that different trade-offs between objectives are explored.

- **Efficient Sorting Mechanism:** Like NSGA-II, NSGA-III also employs a non-dominated sorting mechanism to classify solutions based on Pareto dominance. This helps in finding a diverse set of Pareto-optimal solutions.
- **Diversity Preservation:** NSGA-III includes mechanisms to preserve diversity in the population. The reference points help in spreading the solutions

- **Flexibility:** The algorithm is flexible and can be adapted to different types of multiobjective optimization problems, including those with conflicting objectives.

Overall, NSGA-III is a robust and widely used algorithm for multiobjective optimization, especially suitable for problems with more than three objectives, where traditional methods might struggle to maintain diversity and convergence.

Algorithm Code:

```
def nsga_iii(pop_size, generations,
crossover_rate, mutation_rate):
    pop = init_population(pop_size)
    for generation in range(generations):
        offspring = crossover(population,
crossover_rate)
        mutate(offspring, mutation_rate)
        comb_pop = population + offspring
        fronts = non_dom_sort(comb_pop)
        pop = select_pop(fronts, pop_size)
        assign_ref_points(fronts)
    return population
```

Input Parameters:

- Population size
- Number of generations
- Crossover rate
- Mutation rate

Output Parameters:

- Optimal HESS configurations
- Pareto front of solutions

FINDINGS

The optimization results indicate that a parallel HESS configuration with specific sizing of

supercapacitors and hydrogen fuel cells achieves the best trade-off between cost and energy loss. The optimal solutions show a significant reduction in both initial investment and operational energy losses compared to traditional energy storage systems. The serial configuration, while effective, did not perform as well as the parallel configuration in terms of energy efficiency and cost reduction. The Pareto front obtained from NSGA-III provides a range of optimal solutions, allowing decision-makers to select the most suitable configuration based on specific operational priorities. The integration of hydrogen fuel cells and supercapacitors in a parallel topology offers enhanced energy management capabilities, ensuring reliable and efficient metro operations. Detailed simulations and analyses show that the parallel configuration outperforms the serial configuration in dynamic performance and long-term sustainability.

Comparison of Algorithms

The table below summarizes the comparison between NSGA-III and other state-of-the-art evolutionary multi-objective optimization algorithms in terms of optimization success and computational efficiency:

Table 1. NSGA-III Performance Comparison

Algorithm	Scalability	Success Rate	Time Efficiency	Application Areas
NSGA-III	High	Excellent	Moderate	Overall problem optimization
MOEA/D	High	Very Good	High	Individual objective optimization
SPEA2	Moderate	Good	Moderate	Maintaining diverse high-quality solutions
MO-CMA-ES	High	Excellent	Low	Continuous optimization of energy storage

				components
RVEA	High	Very Good	High	Balancing multiple conflicting objectives
HypE	Moderate	Good	High	Hypervolume-based solution quality

CONCLUSION

This study demonstrates the effectiveness of NSGA-III in optimizing the topology and sizing of HESS for metro vehicles. The optimized solutions enhance energy efficiency and reduce costs, contributing to more sustainable urban rail transit systems. The combination of supercapacitors and hydrogen fuel cells in a parallel configuration offers significant improvements in energy management and operational efficiency. Future work will focus on real-world implementation and testing of the proposed HESS configurations, exploring further refinements in energy management strategies and integrating additional components such as renewable energy sources to enhance the sustainability of metro systems. Additionally, the impact of different driving cycles and operational conditions on the performance of the optimized HESS will be investigated to ensure robust and versatile solutions for metro applications. Other multiobjective optimization algorithms will also be explored to compare and potentially enhance the optimization outcomes.

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EXPERIMENTAL INVESTIGATION OF DIESEL, AQUEOUS AMMONIA AND CNG BLENDS ON PERFORMANCE AND EMISSIONS IN A COMPRESSION IGNITION ENGINE

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Abstract

This study explores the effects of aqueous ammonia (NH₃) and compressed natural gas (CNG) blends on the performance and emissions of a compression ignition (CI) engine under constant operational conditions. Using a torque setting of 300 Nm and a rotational speed of 660 rpm, the engine was initially tested with pure diesel to establish baseline performance metrics and emission profiles. Following the baseline tests, the diesel was also blended with 10% NH₃ to form the first experimental fuel mixture. The engine's performance, including brake thermal efficiency and fuel efficiency, as well as its emission levels—specifically nitrogen oxides (NO_x), carbon monoxide (CO), and unburned hydrocarbons (HC)—were closely monitored. Subsequently, the ammonia concentration was increased to 20%, while the diesel proportion was adjusted to 80%, and the engine's response to this higher NH₃ content was analyzed.

In addition, a separate test was conducted by blending 10% CNG with the initial pure diesel, 10% NH₃ and 90% diesel mixture and the 20% NH₃ and 80% diesel mixture. This combination aimed to assess the impact of adding CNG to the NH₃-diesel blend on the engine's performance and emissions. The results of this study provide insights into how ammonia and CNG blending influence CI engine performance and emissions, potentially offering pathways to enhance fuel flexibility and reduce environmental impact.

The results show that for the same power output, operating under the same conditions, the NH₃-Diesel mixture showed increase in the brake specific fuel consumption (BSFC) as the amount of NH₃ is increased. Adding CNG to the mixture blend showed a decrease in brake specific fuel consumption. In the experiments, a blend of Diesel-CNG10% showed the lowest BSFC. In the case of the Brake Thermal Efficiency (BTE), the highest was observed for the Diesel-CNG10% blend.

For emissions, increasing the amount of ammonia added to the diesel mixture showed an increase in NO_x, CO and HC emissions while a reduction in CO₂. Reduction in CO₂ and NO_x, an increase in both CO and HC emissions was noted when CNG was added to either the pure diesel or the NH₃-Diesel mixtures.

The results indicate that while ammonia-CNG blends can reduce CO₂ emissions significantly compared to pure diesel or CNG, they present trade-offs in terms of engine performance and NO_x emissions.

Keywords: Ammonia, Compressed Natural Gas, Diesel, Compression, Engine Performance, Emissions, Fuel Efficiency

INVESTIGATION OF USING THE GROUNDWATER TREATMENT SLUDGE AS A COAGULANT FOR BREWERY INDUSTRY WASTEWATER TREATMENT: A CIRCULAR ECONOMY APPROACH

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Abstract

Coagulation process has caused to the large amounts of chemical sludge generation in drinking water treatment (DWT). From this perspective, the utilization of DWT sludge has been encouraged to obtain sustainable waste management. This study has aimed to investigate the DWT sludge utilization for industrial wastewater treatment as a component of coagulant. Groundwater treatment has been applied using coagulation process as the drinking water treatment and alum ($\text{Al}_2(\text{SO}_4)_3$) has been as the coagulant for the groundwater treatment. Then an alum-based sludge has been occurred in the result of coagulation process. This alum-based sludge has been used for the coagulation of brewery industry wastewater as the coagulant instead of ferric chloride and addition to ferric chloride (FeCl_3). Three experimental designs have been performed. The Scenario-I is the industrial wastewater treatment using only alum-based sludge as the coagulant. The Scenario-II is the industrial wastewater treatment using ferric chloride as a coagulant. And the Scenario-III is the industrial wastewater treatment using sludge supported ferric chloride. According to the experimental results, sludge addition (24.5 ± 1.5 mL dewatered sludge/L wastewater) has boosted the average removal efficiency of chemical oxygen demand (COD) from 69% to 83.5%. Also, total suspended solid (TSS) substances removal efficiency has improved from averagely 73% to 85% while adding the sludge. The virtual operational costs (VEC) have been accounted based on chemical consumption and sludge transfer and disposal activities. Economic amendment index (EAI) has been developed related to operational costs. The results revealed that the DWT sludge addition has reduced the overall operational costs by 15.5%. This study has confirmed that the sludge of groundwater treatment has been used as an effective coagulant for the industrial wastewater treatment and decreased the overall operational costs in terms of circular economy perspective.

Keywords: Coagulant, Drinking Water Sludge, Industrial Wastewater Treatment, Circular Economy

INTRODUCTION

Many policies and strategies have been developed for sludge management and recovery in terms of circular economy approach, in recent years [1,2,3,4]. The utilization of sludge has many environmental benefits in recent years in terms of techno-economic perspective [4,5,6]. The coagulation process has led to the huge amounts of sludge production at drinking water treatment (DWT) plants [5,6,7,8]. The utilization of DWT sludge has been encouraged to obtain sustainable waste management [9,10].

Drinking water treatment sludge is a by-product in the result of the coagulation-

flocculation process using aluminium or iron-based materials to precipitate many substances from water supplies. Owing to its large production rate and its disposal costs, many researchers has focused on using this waste substance in various applications. It could be an efficient and low-cost material for environmental applications [9]. From this perspective, groundwater treatment has been applied using coagulation process as the drinking water treatment and alum ($\text{Al}_2(\text{SO}_4)_3$) has been as the coagulant in this study. Then an alum-based sludge has been occurred in the result of coagulation process. This alum-based sludge has been used for the coagulation of brewery industry wastewater as the coagulant instead of ferric chloride and assisted coagulant

to the ferric chloride.

This study has aimed to investigate the DWT sludge utilization for pilot-scale industrial wastewater treatment as a component of coagulant. In this study, the virtual operational costs have been accounted based on chemical consumption and sludge transfer and disposal activities in terms of circular economy approach. Economic amendment index (EAI) has been developed related to these operational costs.

MATERIALS AND METHOD

Groundwater samples have been obtained from Uğraklı resources in Harran Plain. For the coagulation process, alum has been used in the dose of 20 mL/L. This alum-based DWT sludge has been dried at 103°C for 2 days and then 550 °C for 8 hours. Then, this dried sludge has been utilized as the coagulant for the brewery industry wastewater treatment.

Three experimental investigations have been performed in this study. The Scenario-I is the industrial wastewater treatment using only alum-based sludge as the coagulant. The Scenario-II is the industrial wastewater treatment using ferric chloride as a coagulant. And the Scenario-III is the industrial wastewater treatment using sludge assisted ferric chloride. Also, SEM and XRD analyses have been performed for the DWT sludge to define the characterization as the coagulant.

Table 1. Experimental Planning

Experimental design	Coagulant
Scenario-I	DWT sludge
Scenario-II	Ferric Chloride
Scenario-III	DWT sludge + Ferric Chloride

Box-Behnken design methodology has been applied to determine the optimum coagulant dose for the brewery industrial wastewater treatment. According to Box-Behnken design, 24.5 ± 1.5 mL dewatered sludge/L wastewater has been used as the coagulant for the industrial wastewater treatment. The removal efficiencies have been reported according to COD and TSS

parameters related to brewery wastewater. All water and wastewater analysis have been performed according to the Standard Methods [11]. The brewery industry wastewater has a highly organic content. The COD value of influent is 5478 mg/L and TSS is 2498 mg/L.

Finally, the virtual operational costs (VEC) have been figured out based on costs related to chemical consumption (OC_{CC}) and sludge transfer and disposal activities ($OC_{ST,D}$) (Eq.1.). Economic amendment index (EAI) has been developed related to these inputs.

$$VEC = OC_{CC} + OC_{ST,D} \quad (1)$$

$$EAI (\%) = (VEC_I - VEC_{II}) / (VEC_I) \quad (2)$$

Where:

VEC_I : Operational costs related to groundwater treatment when sludge has been disposed+ When only ferric chloride is used at the industrial wastewater treatment plant (Euro/month)

VEC_{II} : Operational costs related to groundwater treatment when sludge has not been disposed used as the coagulant for the industrial wastewater treatment+ When sludge addition is applied as a coagulant at the industrial wastewater treatment plant (Euro/month)

3 RESULTS AND DISCUSSION

This study has recommended a perspective on the DWT sludge utilization as a coagulant for industrial wastewater treatment to remove COD and TSS. The results have showed that 24.5 ± 1.5 mL dewatered sludge/L wastewater of sludge addition has improved the removal efficiency of chemical oxygen demand (COD) from averagely 69% to 83.5%. Also, suspended solid (TSS) substances removal efficiency has improved from averagely 73% to 85% while adding the sludge. Figure 1 shows the removal efficiencies related to experimental designs. From these results, it is clear that DWT sludge addition has boosted the industrial wastewater treatment performance.

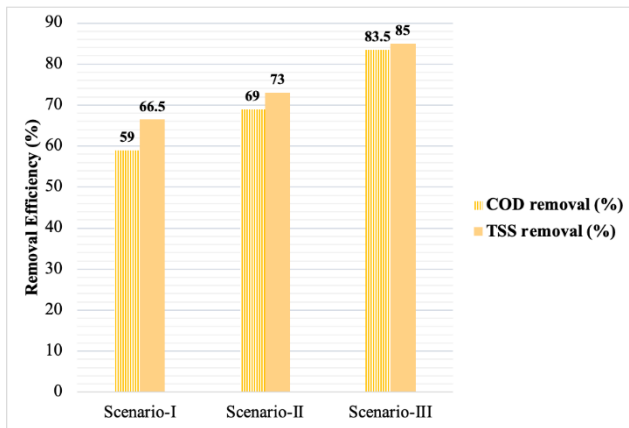


Figure 1. COD and TSS removal using different coagulants

Also, an economic performance assessment has been carried out using operational costs. The results revealed that the DWT sludge addition has reduced the overall costs by 15.5%.

In the literature, there is a limited perspective on this topic. Ahmad et al. (2016) has recommended the used of water treatment sludge and its reuse as coagulant [8]. Gülhan et

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al. (2023) has investigated the use of water treatment plant sludge in high-rate activated sludge systems. They reported similarly favourable effect on using sludge for activated sludge system [9]. A study by Abo-El-Enein et al. (2017) has recommended the DWT sludge as an adsorbent for heavy metal removal [10]. Kang et al. (2022) has investigated the use of aluminum-based water treatment sludge as coagulant for animal farm wastewater treatment [12]. They similarly higher pollutant removal efficiency.

4 CONCLUSIONS

This study has confirmed that the DWT sludge of groundwater treatment has been used as an effective coagulant for the industrial wastewater treatment and decreased the overall operational costs in terms of circular economy perspective. Therefore, case studies, based on practical application of DWT sludge in full-scale drinking water plants and industrial wastewater treatment plants, for determining the dosage, particle size, and reuse of this valuable waste on using as a coagulant should be highly investigated in future research in terms of circular economy aims and perspective.

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Control of DC-DC Buck Converter with Hybrid Controller Created Using ANN and PID in MATLAB/Simulink Environment and Integration to Electrolysis System

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Abstract

Solar energy systems have made significant progress among renewable energy sources today. These systems are used directly or indirectly in many applications according to the needs. In our study, the conversion of photovoltaic (PV) systems to the desired voltage-current values using a DC-DC buck converter, hybrid controller design for this conversion to be made at maximum efficiency and finally integration into electrolysis systems are discussed. The main purpose of the converters used in such systems is to obtain constant current and voltage at the desired level. The feedback control of these systems is done with PID systems known as proportional-integral-derivative controllers. In this study, a hybrid modeling simulation was created by integrating artificial neural network (ANN) modeling, which is frequently used in research and applications recently, into the traditional PID controller. In the study, it was aimed to obtain 5 V output voltage from the system by using a solar panel with 18.7 V and 1.18 A maximum outputs and a DC-DC buck converter. It was aimed to feed the electrolysis system with the obtained 5V-4.4A and to produce hydrogen. Finally, a comparison of an uncontrolled system and a controlled system designed by taking the same conditions and values into account was made and the necessity of the controlled system was revealed.

Keywords— Solar Panel, Controller, Buck Converter, MATLAB/Neural Network Fitting, Electrolysis System

INTRODUCTION

Traditional fossil fuels pose a major problem for our present and future due to their limited use and the damage they cause to the environment. It is very important to eliminate this problem and encourage environmentally friendly resources. Renewable energy sources such as solar, wind, hydroelectric, biomass and geothermal energy have gained importance in recent years due to their unlimited supply and minimal damage. Advances in their production and use have made them applicable in various areas such as homes, industry and vehicles [1]. Population growth, increasing technology and industrialization speed have led to an increase in the need for fossil fuels and therefore the search for alternative energy sources to limited fossil fuels.

Due to these factors and suitable climate and land conditions, interest in solar, wind and geothermal energy production facilities is increasing in our country. Especially solar photovoltaic panel systems are preferred and their areas of use are increasing. These systems are directly affected by environmental conditions. Changes in criteria such as radiation, temperature, fluctuations in

maximum power point (MPP) and shading affect panel efficiency and unit energy cost. Maximum power point tracking (MPPT) systems, which are used to get the best efficiency from the system against these changes, are used to be a solution to all these issues [2], [3], [4]. Since the systems, which have a very important role in optimizing energy production, work with a controller logic, they are also associated with many structures.

To perform PWM control in MPPT systems, algorithms such as disturbance and monitoring (P&Q), incremental conductance (IC) [5], hill climbing (HC), fractional open circuit voltage (FOCV), constant voltage (CV), artificial neural networks (ANN) [6], fuzzy logic control (FLC), particle swarm optimization (PSO), sliding mode control (SMC) and extreme overcall control (ESC) are used, and also proportional-integral-derivative (PID), proportional-integral (PI), proportional derivative (PD), proportional (P), fuzzy logic (FL), artificial neural networks (ANN) and hybrid controller models are used to ensure the stability of the system [7]. Controller models are shown in Figure 1.

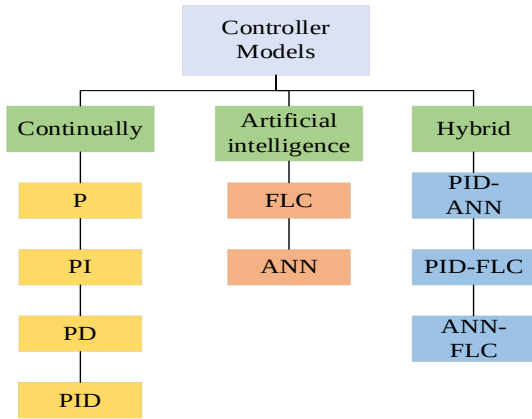


Figure 1. Continuous, AI-powered and hybrid controller models.

Controller models can be chosen according to the structure and operation of the system and can be designed according to the desired situation depending on factors such as the system's response time, error rate, delay time and stability [8].

When the studies in the literature are examined, Idrissi et al. designed a PI-ANN hybrid controller for photovoltaic systems [9]. Arrar and Xioaning studied energy management in microgrids using ANN, PID and BM controllers [10]. Rai et al. made a study on the design and implementation of electric vehicle models with PID and ANN-based controllers [11]. Dakhell et al. created a simulation model of ANN and PID controller for direct current servo motor using MATLAB/Simulink [12].

In this study, the design, simulation analysis, comparison with an uncontrolled system and integration to the electrolysis system of a direct current (DC)-DC synchronous buck converter system, whose general usage areas are renewable energy production systems, electrolysis systems, heating systems, industrial systems, UPSs, motor speed control applications and many other power electronic systems and whose purpose is to reduce the high input voltage to the desired voltage, are discussed. In this system, which has a hybrid control system created with the YSA-PID controller, the 20 V input voltage is reduced to 5 V by generating the necessary switching signal. MOSFET switching operation is performed with the PWM signal controlled by the hybrid controller. The necessary information for the PWM signal is produced by controlling it

with the determined process sequence in the YSA-PID controller created in accordance with the information received from the system output and our reference value. Thanks to the switching operation, the energy charging-discharging operation is performed on the inductance and the input voltage is reduced. Since low voltage and high current are targeted, a synchronous converter is preferred in order not to experience any loss in efficiency and the design is made accordingly. It is aimed to produce hydrogen by integrating an electrolysis system as a load at the output of this analyzed system.

SOLAR PANEL AND ITS PARAMETERS

Photovoltaic panel systems consist of series and parallel semiconductor silicon cells that enable us to convert solar energy into electrical energy [13]. When sunlight falls on the panel, photons are absorbed and electrons in the silicon material are released, creating an electron flow. As a result of this event in each cell, small amounts of currents combine to form the system output. The designed system is shown in Figure 2, and the desired level of output voltage control can be achieved thanks to the DC-DC converter used in the system.

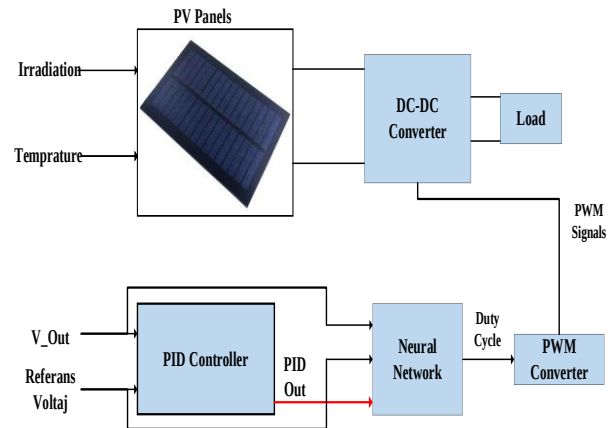


Figure 2. DC-DC converter and PID-ANN hybrid controller model.

In this study, a 20 W photovoltaic panel, DC-DC buck and PID-ANN hybrid MPPT system was designed to reduce 20 V PV voltage to 5 V. Table 1 shows the parameters used in the PV panel design.

Table 1. Solar Panel Parameters and Values

Parameters	Values
Parallel Arrays	4
Series-connected Modules Per Array	9
Maximum Power	20 W
Cells Per Module (N_{cell})	36
Open Circuit Voltage (V_{oc})	21.59 V
Short Circuit Current (I_{sc})	1.28A
Maximum Power Point Voltage (V_{mp})	18.2 V
Maximum Power Point Current (I_{mp})	1.1 A
Temperature Coeff. of V_{oc} (%/deg.c)	-0.2727
Temperature Coeff. of I_{oc} (%/deg.c)	0.061743

CONTROLLER MODELS

Control systems are very important in industrial systems and applications in terms of ensuring the stability of the system and analyzing error values. The most important purposes of these systems are to control the system outputs with the desired reference value and to perform operations according to special conditions in a flow direction. Two types of control methods are frequently used.

3.1. Open Loop Control

In this control system, the controller is unaware of the system output and only controls according to the given reference information. Systems such as traffic lights, washing machines and dishwashers can be given as examples [14]. The general block structure of the open-loop control system is shown in Figure 3.

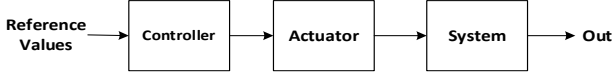


Figure 3. Open-loop control system.

3.2. Closed Loop Control

Feed Forward Closed Loop Control System

In this control system, the controller creates a prediction system after measuring and evaluating a disturbing variable that affects or may affect the system output and ensures system stability by making adjustments accordingly. The general block structure of the feed forward control system is shown in Figure 4.

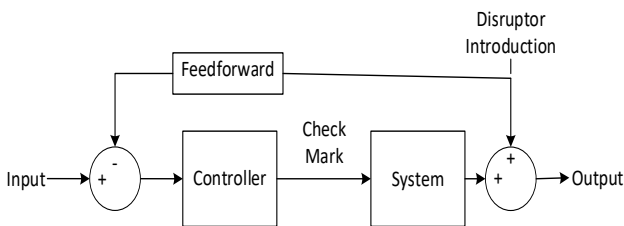


Figure 4. Feedforward control system.

In this study, the ANN algorithm from feedforward control systems is considered. A multilayer feedforward artificial neural network model is shown in Figure 5.

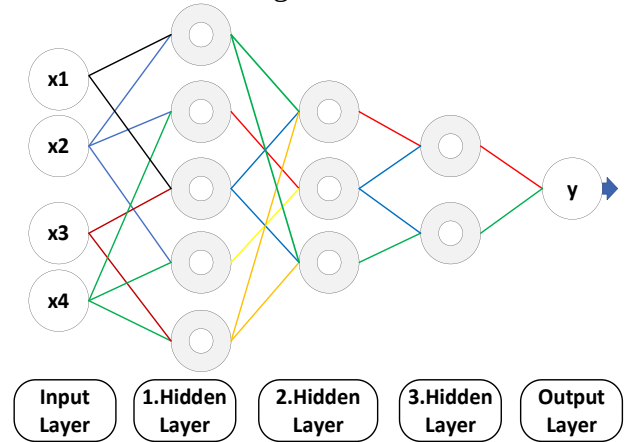


Figure 5. Feedforward neural network model.

Feedback Closed Loop Control System

In this control system, the controller calculates an error value by receiving feedback from the system output through sensors and comparing it with the input data and can make adjustments for a more stable output according to this value. Feedback control systems are also divided into two. These are discontinuous control systems and continuous control systems [15]. The general block structure of the feedback control system is shown in Figure 6.

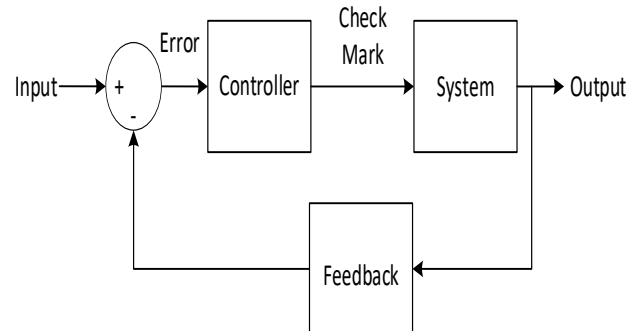


Figure 6. Feedback control system.

In this study, the PID controller from feedback control systems is considered. The PID controller, whose general block structure is shown in Figure 7, is a controller system used to minimize the error value resulting from feedback. The desired output is obtained by trial and error method using proportional (K_p), integral (K_i) and derivative (K_d) coefficients.

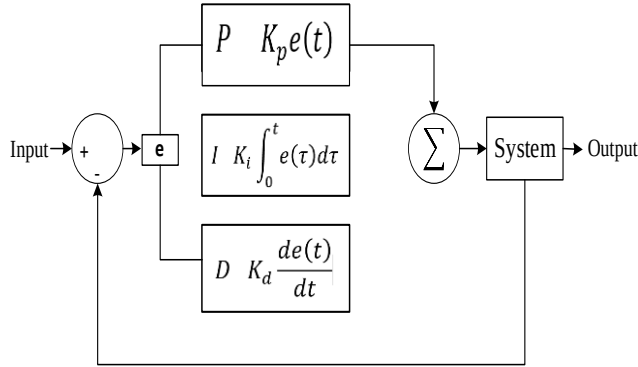


Figure 7. PID systems.

$$u(t) = K_p e(t) + K_i \int_0^t e(\tau) d\tau + K_d \frac{d}{dt} e(t) \quad (1)$$

The proportional value is found by multiplying the error by K_p .

$$\text{Error} = \text{Reference} - \text{Input} \quad (2)$$

$$P = K_p * \text{Error} \quad (3)$$

The aim here is to reduce the error.

The integral value is found by adding the result obtained by multiplying the temporal average of the error with the K_i coefficient in each temporal transformation.

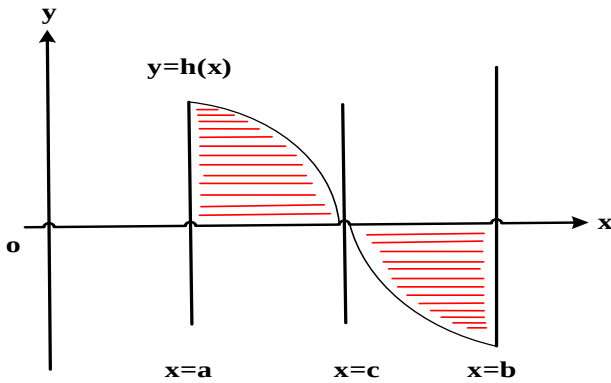


Figure 8. Integral, the field of error.

$$I = I + (K_i * \text{Error} * dt) \quad (4)$$

The aim here is to find the area of the error shown in Figure 8.

The derivative value is found by multiplying the K_p value by the Error difference and taking the derivative.

$$E_d = \text{Error} - \text{Error}_e \quad (5)$$

$$D = (K_d * \text{Error}_e) / d_t \quad (6)$$

The aim here is to calculate the time between two samples. If there is no change in the error during the time, the derivative is equal to zero [16].

DC-DC CONVERTER MODELS

The circuits that convert the DC input voltage to a different DC output voltage are called DC-DC converters. These converters perform voltage conversion in DC circuits. The main purpose of a DC-DC converter is to provide the desired output voltage level, which can be higher, lower, or isolated from the input voltage. DC-DC converters are widely used in a variety of applications where different voltage levels are required. Some common applications include power supplies for electronic devices, battery charging systems, renewable energy systems, automotive electronics, telecommunications equipment, and industrial machinery.

A DC-DC converter usually consists of switching elements such as transistors or semiconductor switches to control the system flow. These switching elements are rapidly turned on and off to create a square wave-like waveform as shown in Figure 9.

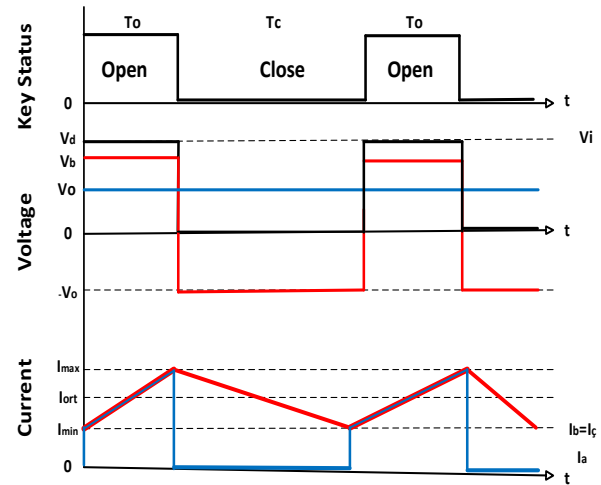


Figure 9. Input-output voltages and coil current waveforms according to the switch state of the DC-DC buck converter.

DC-DC converter regulates the output voltage by managing the duty cycle. The most commonly used converters are the buck converter, boost converter, buck-boost converter, and fly-back converter. When choosing a DC-DC converter, output voltage targets, power efficiency, current ratings, cost, and other application-specific conditions should be considered.

When choosing the DC-DC converter that we will use, these situations were taken into consideration and the DC-DC buck converter, which is used to reduce the input voltage to the desired output voltage, was preferred.

The simple circuit diagram of the DC-DC buck converter is shown in Figure 10.

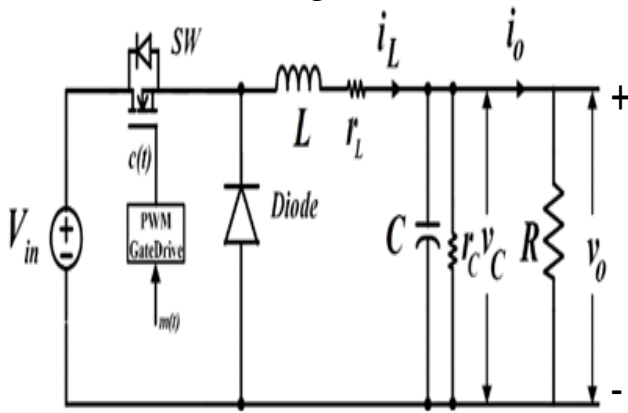


Figure 10. DC-DC buck converter.

ELECTROLYSIS

Systems that use electrical energy to cause a chemical change in a substance are called electrolysis systems. Electrolysis is generally preferred in systems such as metal production, water electrolysis, chlorine and sodium hydroxide production, electroplating, electro refining and electrowinning, batteries, fuel cells, analysis and testing, wastewater treatment, electrolytic capacitors and electrolytic etching [17].

The water electrolysis system is based on the principle of separating water into hydrogen and oxygen gas. The hydrogen obtained can be used as a clean and sustainable fuel source, especially in the context of renewable energy [18]–[20].

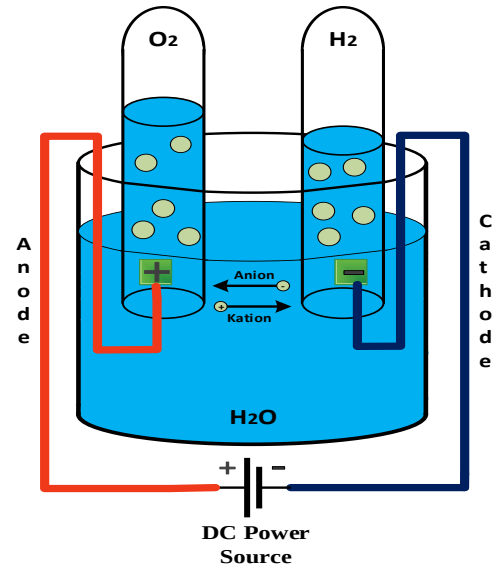


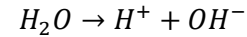
Figure 11. Water electrolysis system.

5.1. Electrolysis Event

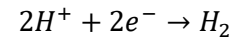
When the power supply is connected to the ends of the electrodes, anions are collected at the anode and cations are collected at the cathode end. As a result of this collection, cations take electrons to neutralize themselves, while anions reaching the anode give electrons to neutralize themselves.

The working principle of electrolysis can be listed as follows:

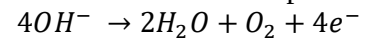
1. First, the water molecules around the cathode react to form OH^- and H^+ ions.



2. While OH^- , one of these ions, moves towards the anode, the H^+ ion neutralizes by taking an electron from the cathode and reacts with another neutral H molecule, forming H_2 gas and hydrogen gas at the top of the tube.



3. The OH^- ions coming to the anode react to form water molecules and oxygen gas. The oxygen gas formed as a result of this reaction begins to accumulate at the top of the tube.



The designed electrolysis system is shown in Figure 12.



Figure 12. Hydrogen production system.

SIMULATION RESULTS

In this section, a PID-ANN hybrid-controlled DC-DC buck converter was designed and tested using MATLAB/Simulink. The system was designed to reduce the PV panel voltage from approximately 20 V to 5 V. The parameters used in the system and the capacitor, coil and resistance values obtained as a result of the calculation are given in Table 2.

Table 2. System Parameters and Values

Parameters	Values
Input Voltage	18.2 V
Output Voltage	5 V
Input Current	1.1 A
Power	20 W
Frequency	20 kHz
Inductance (L)	1m H
Capacity (C)	150u F
Load (R)	10 Ω
Temperature (T)	25 $^{\circ}$ C
Solar Irradiation (G)	1000 W/m ²

Figure 13 shows the design of the ANN-PID hybrid controlled synchronous DC-DC buck converter made in MATLAB/Simulink environment. To understand and analyze this system more easily, it is divided into three sections: PV Panel, DC-DC buck converter and ANN-PID hybrid controller.

The first section aims to obtain the input voltage required for the system from the PV panel. Therefore, instead of variable values, the required irradiance (900-100 W/m²) and temperature (25-35 $^{\circ}$ C) ranges were used as panel data to obtain 20 V input voltage.

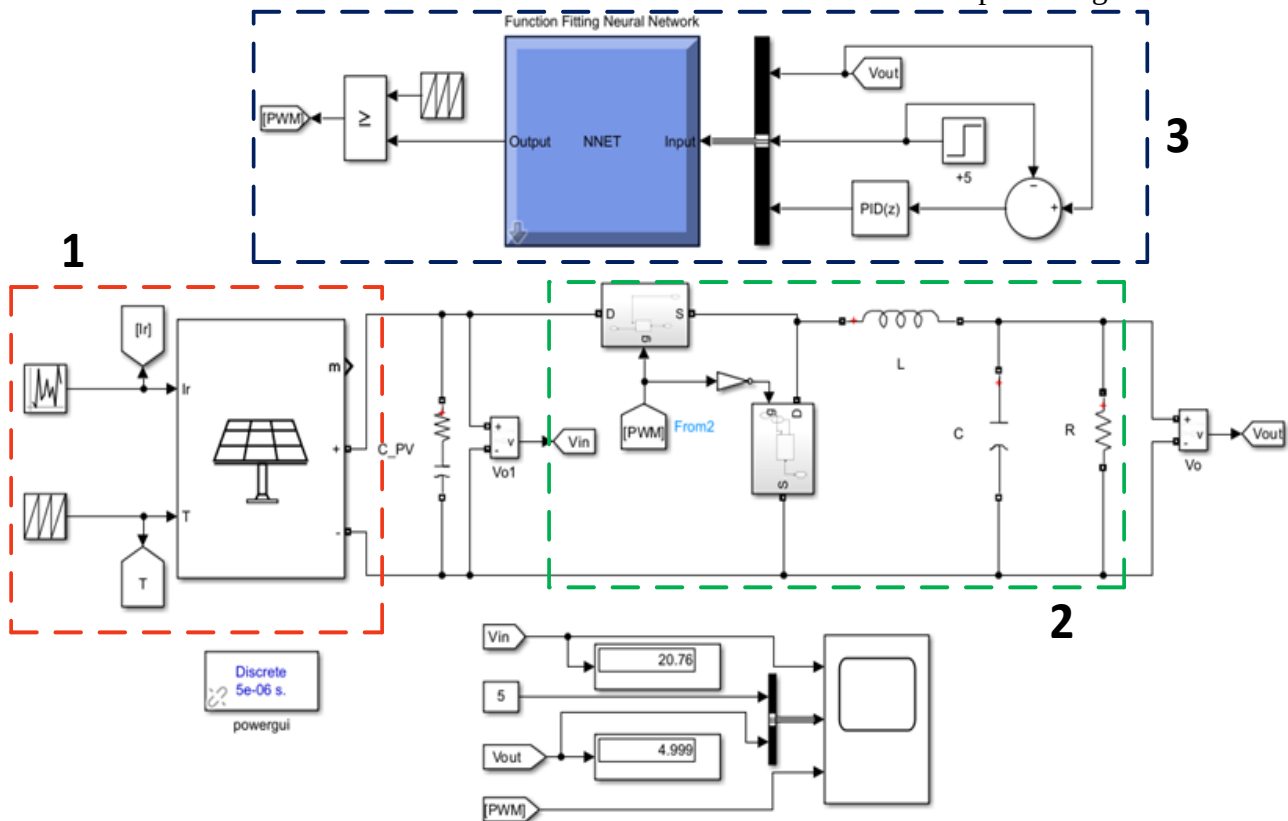


Figure 13. Design of ANN-PID hybrid controlled DC-DC buck converter in MATLAB/Simulink.

In the second part, since a synchronous structure was preferred instead of MOSFET as the switching

element and diode as the protection element, a DC-DC buck converter was designed using a second MOSFET, coil, capacitor and resistor elements. The values of the elements used in the circuit are obtained from Equations 7, 8 and 9.

$$D = \frac{V_o}{V_i} \quad (7)$$

$$L = \frac{(1-D)R}{2f} \quad (8)$$

$$C = \frac{(1-D)V_o}{8Lf^2\Delta V_i} \quad (9)$$

In the third section, a hybrid controller was designed using ANN-PID to generate and control the switching signal. First, a simple PID controller system was designed for the controller whose block diagram is shown in Figure 14. This system was run and data for the ANN algorithm was obtained. V_{out} , V_{ref} and duty ratio were used as input data. It was aimed to obtain a duty ratio as output from this system.

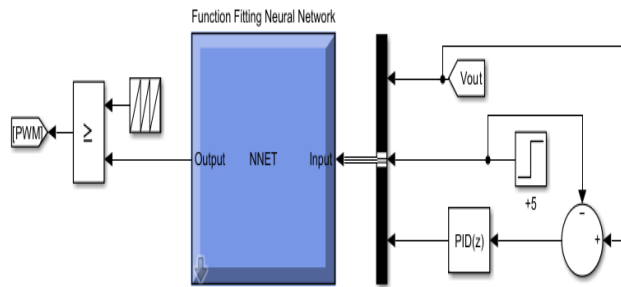


Figure 14. ANN-PID hybrid controller.

The obtained data were trained by separating them into training (75%) and test (25%) data in the Neural Network Fitting interface in the MATLAB/Simulink application. In this training phase, the two-layer feedforward network structure shown in Figure 15 was preferred and 98% success was achieved as a result of the training. The block structure of these trained data was integrated into the system as shown in Figure 14 and the simulation was run.

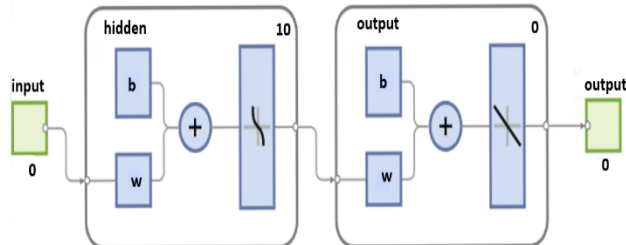


Figure 15. A two-layer feedforward network structure with sigmoid hidden neurons and linear output neurons suitable for regression tasks.

The radiation and temperature graph required for the operation of the solar panel is shown in Figure 16. These values are the values that allow the panel to operate at maximum efficiency.

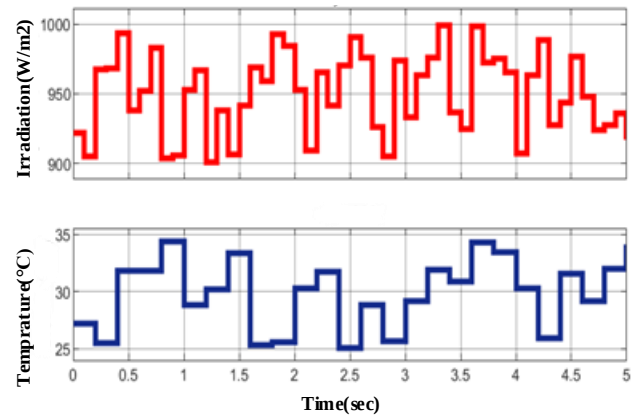


Figure 16. Ambient radiation and temperature values.

The PWM signal generated to perform the switching task is shown in Figure 17. This signal operates at a duty ratio of approximately 25%. The PWM signal is obtained by comparing the duty ratio obtained from the ANN-PID hybrid controller with a ramp signal.

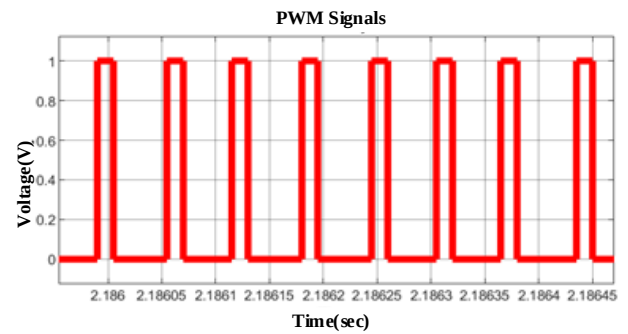


Figure 17. PWM signal generated to drive MOSFET.

Figure 18 shows the voltage and current graphs on the coil.

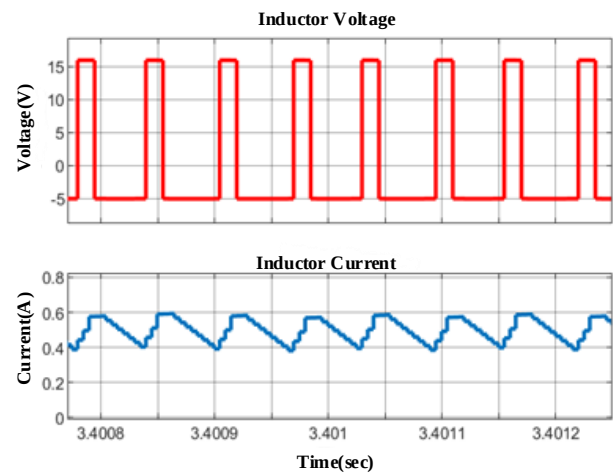


Figure 18. Inductor, current and voltage ratings.

Figure 19 shows the graphs showing the input and desired output voltages of the system and the reference voltage. When these graphs are examined, we can see that the desired results are obtained from the system.

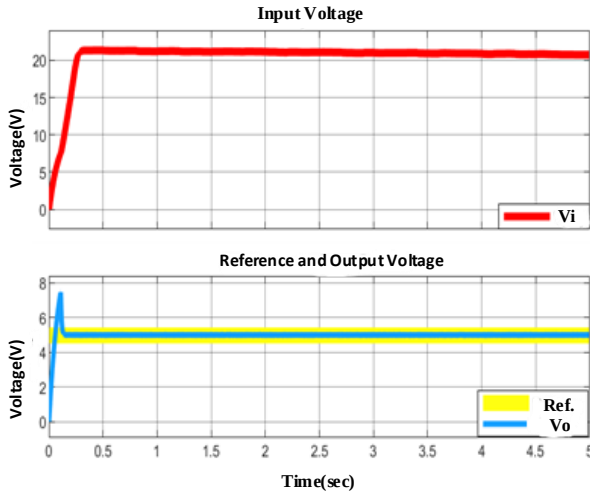


Figure 19. Input voltage, reference voltage and output voltage values.

Figure 20 shows the DC-DC buck converter model designed without a control system.

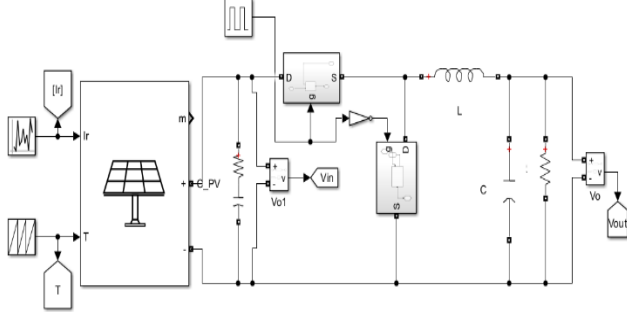


Figure 20. Design of uncontrolled DC-DC buck converter in MATLAB/Simulink application.

The input, reference and output values of the uncontrolled system are shown in Figure 21.

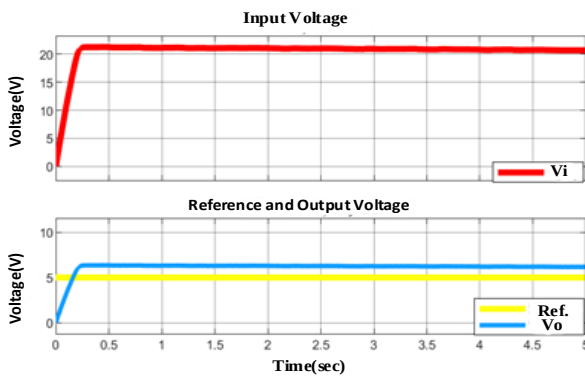


Figure 21. Input, reference and output voltage values of the uncontrolled system.

When these two results are compared, it is seen that the controlled system, namely the ANN-PID controlled system, reaches the desired value by establishing a relationship between the input and output to capture the output value of 5 V. However, the uncontrolled system aims to obtain a result from the system by using only the input data. As a result, it cannot provide stability in the output voltage.

CONCLUSION

As a result, the ANN model was trained using the DC-DC buck converter and MATLAB/Neural Network Fitting application and integrated into the DC-DC buck converter system. The graphical outputs in the design were obtained using the MATLAB/Simulink application.

The voltage-current values obtained from the DC-DC buck converter were integrated into the system designed for hydrogen production and hydrogen production was aimed. It was observed that the 5V-4A values obtained from this system were not at the desired level for hydrogen production. In order to obtain efficiency from such an electrolysis system, it was determined that a design with at least 15-20A values should be realized and the desired results could be obtained by using the appropriate electrolyte material. In addition, this design, which has a controlled system, can obtain the desired output voltage based on the reference value. However, it was determined that an uncontrolled system could not provide this stability in output voltage.

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INVESTIGATION OF HALF-METALLIC DICHALCOGENIDE ALLOY FOR HIGHLY SELECTIVE GAS ADSORPTION

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Abstract

Half-metallicity is a unique feature of spin polarized materials that enables its utilization for spintronics applications due to switching between the metallic and semiconducting behavior upon changing the spin orientation. Half-metallicity of dichalcogenides of the composition MoXY and their capacity for adsorption of different gases will be discussed in this presentation. Transition metal doping of MoXY monolayer introduces significant variations in the band gap, and it enhances its selective adsorption of gases. The work involves analysis of the effect of doping on the gas adsorption energy and distance, charge transferred between a structure and a gas molecule, band structure, and density of states (DOS). The band structure of MoXY reveals substantial variations in its electronic properties upon doping with new bands developed near the Fermi level. Transition metal doping of MoXY dichalcogenide monolayer is a promising pathway for engineering its band gap and utilization for applications related to selective and sensitive gas detection.

Keywords: Chalcogenide; MoXY; DFT; gas sensor

IMPROVING PEDIATRIC DOSE MEASUREMENTS WITH DEEP LEARNING MODELS FOR ACCURATE INTERNAL DOSIMETRY IN NUCLEAR MEDICINE

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Abstract

Animal models play a crucial role in the development of new radiopharmaceuticals in nuclear medicine. To calculate the absorbed dose in small animal internal dosimetry, an accurate and widely available database of S-values is necessary. This study aims to provide a dataset for calculating S-values for commonly used radionuclides, based on the mouse phantom and using the Monte Carlo simulation code GATE for all simulations.

For benchmarking, a simulation was first conducted using the Digimouse phantom and a Tc-99m source, and the results obtained were compared with published results.

Subsequently, the phantom was used to calculate the S-values for eleven radionuclides used in nuclear medicine for diagnostic and therapeutic purposes. Finally, the phantom (26.9 g) was resized to simulate two mouse geometries: 19.6 g and 35.9 g while maintaining voxel size. Similarly, datasets were generated to evaluate variations in S-values for the 20 organs. The results were compared to published Digimouse data, which showed good agreement.

This study systematically evaluated S-values for eleven radionuclides in three mouse geometries and examined the impact of organ mass variations on calculated S-values. The methodology for calculating S-values in organ-based voxelized phantoms is detailed in this study. Moreover, it provides a comprehensive database for internal dosimetry in mice for radiopharmaceuticals used in small animal PET and SPECT studies.

EXPERIMENTAL INVESTIGATION OF EMISSION AND PERFORMANCE VALUES OF GASOLINE BLENDS IN RCCI DIESEL ENGINE

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Abstract

Petroleum-based energy is used more than ever before, which is rapidly increasing environmental pollution. Although electric vehicles are common today, internal combustion engine vehicles are still the majority. Although catalytic converter methods are used to reduce emissions in internal combustion engines, they cannot reach the desired level, making it necessary to work on internal combustion engines. RCCI is one of the most effective methods used to reduce harmful gases produced during combustion before they occur. In our study, the RCCI method was applied by adding gasoline to a 3-cylinder, 4-stroke diesel engine with the code LOMBARDINI brand LDW 1003. In this method, low reactivity fuel is sprayed into the engine from the intake manifold and high reactivity fuel is sprayed into the cylinder. Low reactivity fuel was injected at the desired time and amount in terms of crank angle by means of a software. The studies were conducted with LFR fuel (gasoline) at 3 different injection timings (10 CA, 20 CA, 30 CA) at 1500, 2000, 2500 and 3000 rpm with the engine at full load. In the experiments, in-cylinder pressure, power, torque, fuel consumption and NO_x, HC, O₂, CO and CO₂ exhaust emission values were collected. The results show that as the amount of fuel injected increases, fuel consumption decreases by up to 6.4% and CO₂ decreases by up to 5%, although torque and power decreases lightly.

Keywords: Energy, Power, Combustion, RCCI, Fuel

1 Introduction

With the increase in the world population and the development of technology, the need for energy is increasing more than ever. Today, we still provide the vast majority of our energy needs from oil. This rate is much higher for the transportation sector than for other sectors. The increase in energy production from oil brings with it environmental problems. NO_x, CO and HC emissions from internal combustion engines have been greatly reduced by the use of catalytic converter-style exhaust gas treatment systems. However, these systems are not yet able to reduce harmful emissions to the desired levels.

Reactivity-controlled compression ignition (RCCI) is an alternative combustion strategy with significant advantage potential in

expanding thermal exchange along with reducing NO_x and soot emissions. In this combustion method, low-reactivity fuel such as gasoline is sprayed from the engine's intake manifold and sent into the cylinder, then high-reactivity fuel such as diesel is sprayed directly into the cylinder and combustion is carried out. As seen in the figure 1, more homogeneous combustion occurs because combustion starts at more than one point in the cylinder. This results in cleaner emissions.

In recent years, LTC, which has attracted attention in internal combustion engines, has focused on achieving lower combustion temperatures to keep NO emissions low and avoiding regional rich fuel applications to keep soot production under control. Thus, it is thought that LTC can regulate the balance in pollutant

emissions (NO and soot) while maintaining thermal efficiency. This will be possible thanks to the use of high rates of EGR (Exhaust Gas Recirculation) and longer mixing times compared to conventional combustion [].

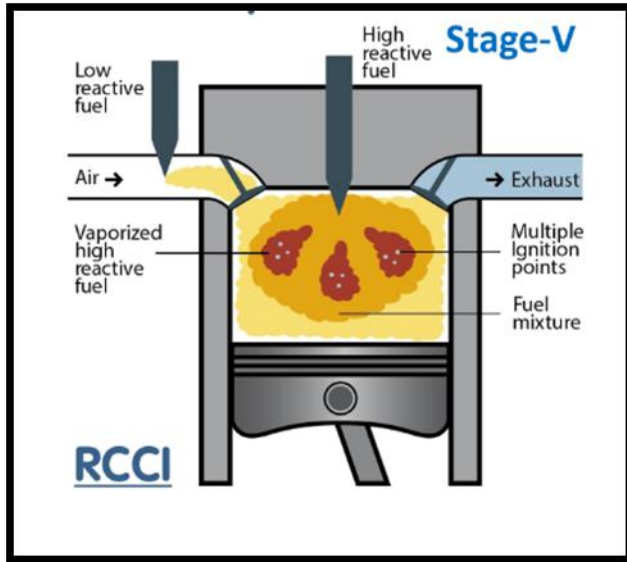


Figure 1: RCCI Combustio[2]

Zhu et al. present an experimental study on the combustion and emission characteristics of Reactivity Controlled Compression Ignition (RCCI) combustion with n-heptane/gasoline-like fuels on a single-cylinder engine. The effects of injection timing and premix ratio are investigated. The experimental results show that with the advancement of direct injection timing, the ignition delay for all three fuels increases, and ethanol has the longest ignition delay. For the three different fuels, CO (carbon monoxide) and soot emissions decrease gradually, while NO_x emissions increase. However, HC (hydrocarbon) emissions decrease in parallel with gasoline, but first increase and then decrease with alcohol fuels. When comparing gasoline and ethanol with the same premix ratio and direct injection timing, the combustion stage with ethanol as the port fuel occurs later than gasoline, especially with a higher premix ratio. Furthermore, ethanol has lower NO_x and soot emissions than gasoline, indicating that ethanol as an alternative fuel can improve emissions in RCCI combustion mode [3].

Review article presents a detailed analysis of the effect of methanol on the performance, combustion and emission (NO_x, CO, HC and soot) characteristics of conventional CI engine

combined with dual-fuel combustion mode. This study focuses on the use of methanol in dual-fuel mode, an advanced engine combustion mode. Firstly, the issues of methanol production and solubility of methanol in diesel are briefly discussed. This study discusses the soot and nano particle emissions from methanol-fueled CI engine, which is one of the main concerns in the current emission legislation. It has been found that the use of methanol in CI engine has the potential to improve performance and at the same time provide significant reduction in NO_x, CO, soot and nano particle emissions compared to pure diesel operation. However, while unburned HC emissions are reduced in methanol-diesel blended fuel operation, HC emissions are higher in methanol-diesel dual fuel operation [4].

Panda et al. injected methanol from the port. In the conventional dual fuel mode, diesel was directly injected as a single injection pulse and the injection timing was adjusted for maximum efficiency. RCCI combustion mode could only be supported by an early diesel injection followed by a late diesel injection. By appropriate adjustment of diesel injection parameters, Methanol-Diesel energy share (MDES) in RCCI combustion mode could be increased from 45% in dual fuel mode to 56%. The increased amount with the second diesel injection occurred close to TDC, resulting in thermal efficiency and good combustion stability. NO level was about 95% lower in RCCI mode, soot emission decreased by about 78% and thermal efficiency increased from 36% to 38% in dual fuel mode at a constant MDES. Overall, significantly lower NO emissions and comparable soot, HC and CO emissions were achieved with higher thermal efficiency than conventional dual fuel mode [5].

Natural Gas (NG) with high octane number and low C/H ratio is beneficial for Reactivity Controlled Compression Ignition (RCCI) engines in terms of controlling the boost rate and reducing emissions. Therefore, a detailed 3D combustion model was developed in ANSYS-Forte environment on a real single cylinder diesel engine scanned image for RCCI engines of NG and then validated with the ordinary data of the same engine. Then, the effect of NG premixtures (Rp, 15%, 30% and 45%) on the

combustion and emission characteristics of RCCI engine was analyzed at 20% load and 2400 rpm. The results showed that the heat release rate and cylinder pressure decreased with the swelling of R_p , and the ignition delay (ID) increased. It was also observed that NO_x and HC emissions of R_p increased, while CO and C_2H_2 emissions decreased. CO emissions were reduced by up to 29% in RCCI mode. Additionally, CH emissions increased by approximately 97% by RCCI compared to CDM, while the dissolution of R_p in the engine started to decrease[6].

2 Materials and Methods

The experimental setup is as shown in the figure 2. The engine is connected to the dynamometer for power and torque values. High reactivity fuel was provided by the engine's own pump and fuel consumption was measured with the help of a precision scale. An injector pump set is used for low reactivity fuel. The encoder for fuel injection timing and fuel quantity is connected to the engine crankshaft. Various thermocouples were installed to measure the temperatures of various region.

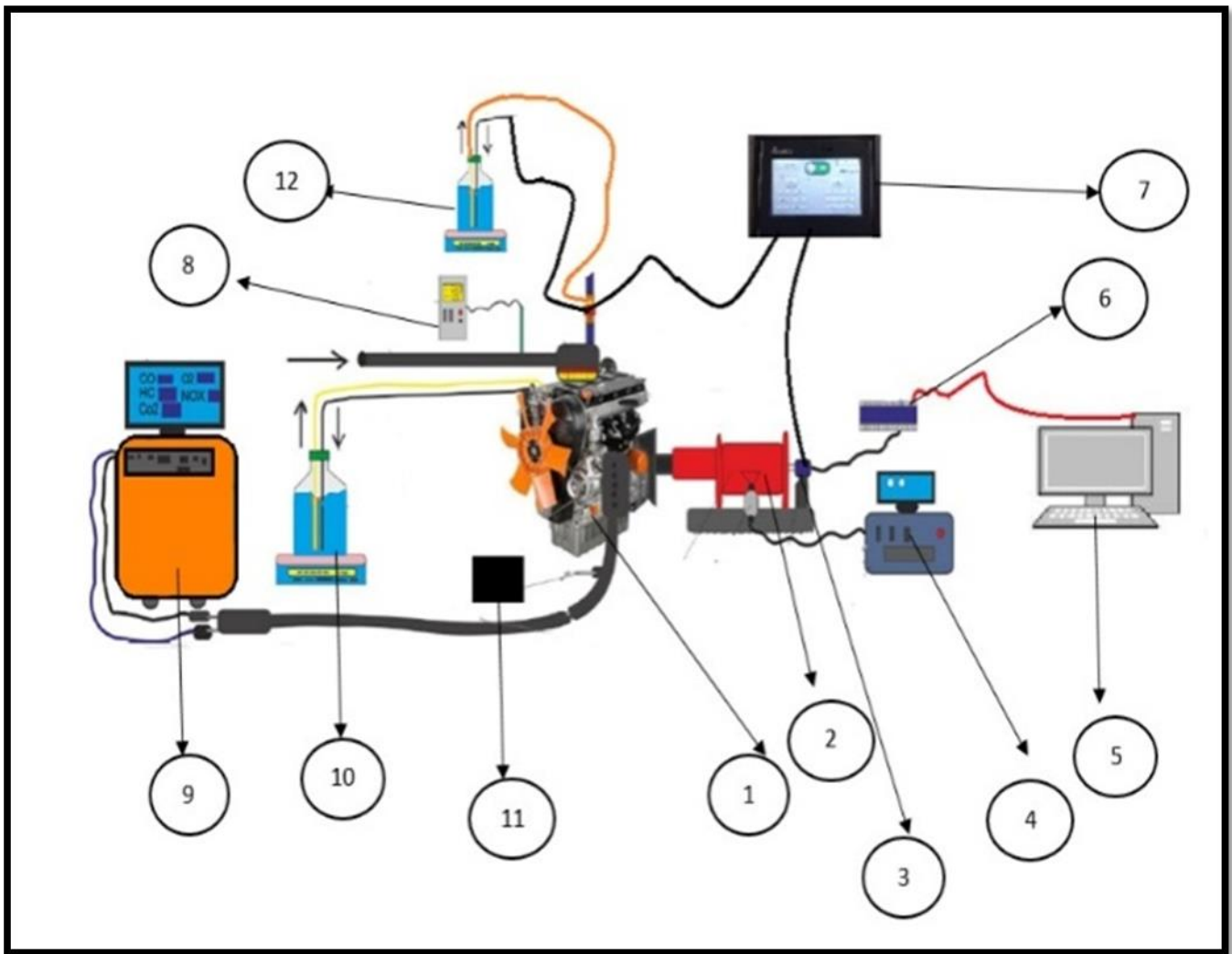


Figure 2: Experimental system

In figure 2, the experimental setup is presented schematically. The experimental setup as 1 number test engine, 2 number dynameters, 3 number encoder, 4 number dynameters control panel, 5 number dynameter results computer, 6 number dynameter processor, 7 number LRF fuel injection system, 8 number thermometer, 9 number emission device, 10 number scale for diesel fuel, 11 number thermometer for exhaust gas, 12 number scale for gasoline fuel

The experiments were carried out on a 3-cylinder, 1028 cm³ volume Lombardini LDW 1003 coded diesel engine. The engine has a maximum speed of 3600 rpm and a compression ratio of 22.8:1. cylinder diameter is 75 mm, stroke is 77.5 mm.

Table 1: Test engine properties

DEFINITION	UNIT	PROPERTY
Model		LDW 1003
Number of Cylinders		3
Total Cylinder Volume	cm ³	1028
Cylinder Bore-Stroke	mm-mm	75-77,5
Compression Ratio		22.8:1
Maximum speed		3600
Maximum Torque	Nm	67
Valve Timing	IVO/IVC	16 BTDC/36 ABDC
	EVO/EVC	36 BBDC/16 ATDC

In the studies, a Netfren brand dynamometer with a maximum speed of 6000 rpm, capable of measuring 150 KW power and 450 Nm torque was used. Emission measurements were measured with the Bosch brand BEA060 emission device, the features of which are given in Table 2.

While diesel fuel is injected directly into the cylinder, low activity fuels are injected from the intake manifold. LRF fuel is pumped to the injector with the help of a gasoline pump at 2 bar pressure. A PLC-based system has been developed that allows us to adjust the injector spray start and stop time as desired. The fuel

Table 2: Emission device

BEA 60			
Emission	MEASURING RANGE	UNIT	SENSIBILITY
CO	0-14	%	0.001
CO ₂	0-18	%	0.01
HC	0-9999	ppm	1
O ₂	0-25	%	0.01
λ	0,5-9,99	%	0.001
NO	0-5000	ppm	1

properties

injection control screen is shown in Figure 3. From this screen, both the fuel injection start timing can be determined according to the crank

angle and the injection duration can be determined. In this system, we can control 2 different injectors separately.



Figure 3: LRF injection system screen

The experiments were carried out at an altitude of 1000 meters above sea level. The tests were carried out at 1500, 2000, 2500 and 3000 rpm with the engine at full load. The low reactivity fuel injector was injected at 10, 20 and 30 degrees of open time depending on the crankshaft. The 10 degree definition describes the injector being kept open for a 10 degree crank angle. For example, it means that the injector is open between 340-350 crank angle.

3 Results and Discussion

As a result of the experiments, Power, Torque, Fuel Consumption, CO₂, CO, NO, HC emissions were compared for diesel and gasoline injection from the intake manifold at 10°, 20° and 30° crankshaft angles.

In terms of torque values, when the torque values at 1500, 2000, 2500 and 3000 rpm are compared with diesel fuel in 10°, 20° and 30° fuel injection situations, the values at 3000 rpm are very close to each other, and there is a decrease in torque values of approximately 1% at other speeds. Since power and torque values are dependent on each other, there is a decrease in torque values.

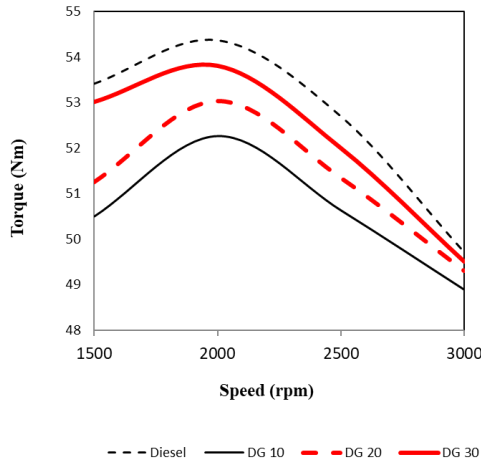


Figure 4: Torque diagram

In the specific fuel consumption values, when the fuel consumption values at 1500, 2000, 2500 and 3000 rpm are compared with diesel fuel in the 10°, 20° and 30° fuel injection situations, the average of all cycles decreases by 1% in the specific fuel consumption at 10° fuel injection, and the average of all cycles decreases by 4% at 20° reduction and, 30° resulted in a 6.4% reduction in fuel injection.

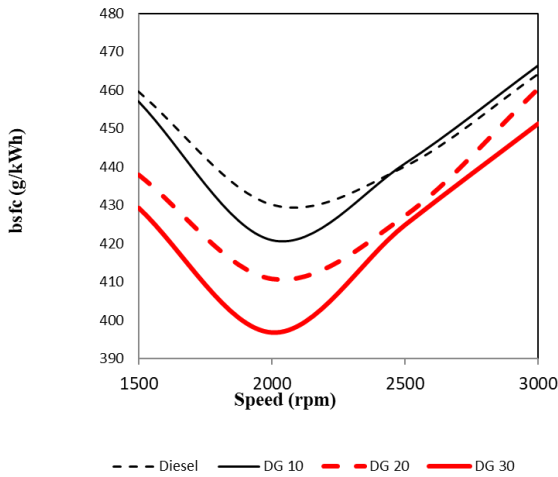


Figure 5: Fuel consumption diagram

CO₂ is a gas that causes global warming. Fuels with fewer or no carbon atoms are preferred in terms of CO₂ emissions. CO₂ emissions decrease by an average of 3% at 10°, 4% at 20° and 5% at 30°. As the amount of fuel decreases, CO₂ emissions also decrease.

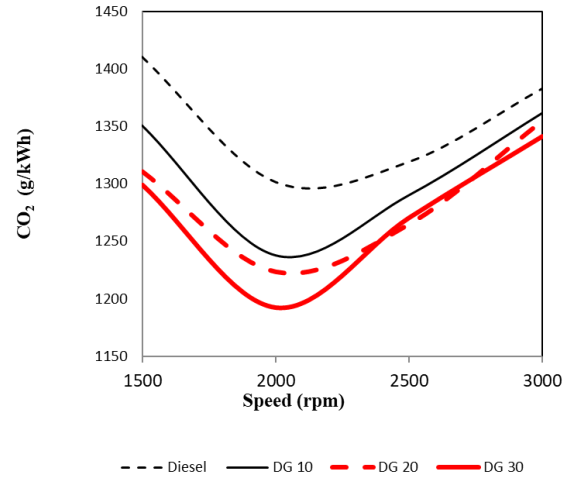


Figure 6: CO₂ emission diagram

Increasing the amount of fuel injection and increasing air velocity entering the cylinders will increase turbulence in the combustion chamber, resulting in a more homogeneous mixture. Since this will improve the combustion of fuel, a decrease in CO will be observed in high amounts. It is on average 12% more at 10°, 10% more at 20° and 9% more at 30°. Increasing the amount of fuel injection caused a decrease in CO emissions.

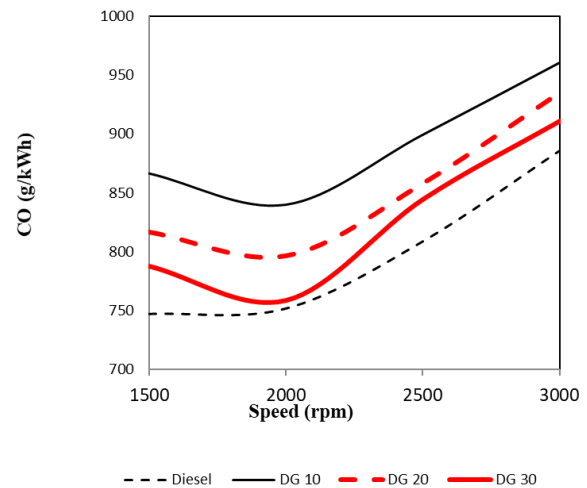


Figure 7: CO emission diagram

Hydrocarbon emissions are caused by fuel expelled from the exhaust without being burned. HC emissions increase as the amount of fuel injected increases. HC emissions increase by an average of 12% at 10°, 25% at 20° and 40% at 30°. Increasing low reactivity fuel amount causes flame extinction in areas close to the cylinder walls and HC emissions increase.

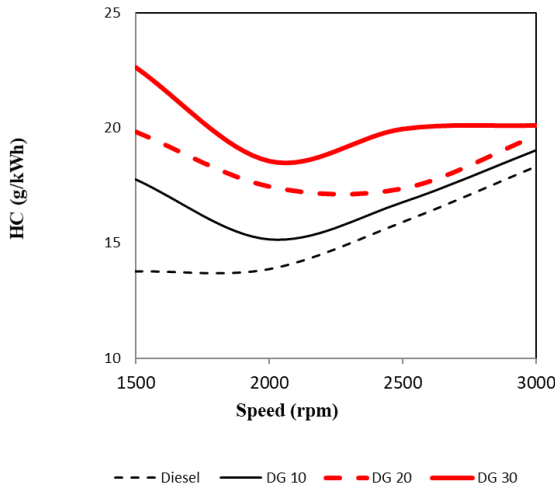


Figure 8: HC emission diagram

As seen in the figure 9, it can be seen that NO emissions decrease as the degree of gasoline injected increases. At maximum torque, the most filling is taken into the cylinder and temperatures increase. In-cylinder temperature determines NO emissions. It is highest in diesel fuel. With increasing spraying degree, a decrease of 5%, 10% and 15% occurred.

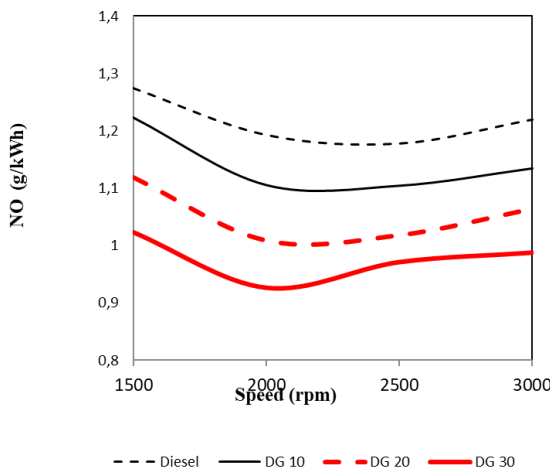


Figure 9: NO emission diagram

4. Conclusion

In this study, gasoline was injected into a diesel engine from the manifold at 1500, 2000, 2500 and 3000 rpm, at 10-20 and 30 degrees crankshaft angle. And in this study, power, torque, fuel consumption and emissions were examined;

- When the power and torque data were examined, not much of a decrease was observed. The decrease was due to the low

calorific value of the added fuel, and since the amount added was small, there was not much decrease.

- When CO₂ and CO emissions are examined, the increase in fuel amount in CO₂ emissions caused an increase in CO₂ emissions and a decrease in CO. In this way, combustion was improved.
- The increase in the amount of injection in HC emissions has caused an increase in HC emissions. Due to the easy evaporation of gasoline, it creates a cooling effect, which causes flame extinction in areas close to the cylinder walls. Fuel consumption adjustment, specific fuel consumption decreases with increasing fuel injection amount.
- High in-cylinder temperatures are the main reason for NO_x emissions. As the amount of fuel injected increases, the amount of NO_x decreases. Due to the easy evaporation of gasoline, it creates a cooling effect, which causes flame extinction in areas close to the cylinder walls.
- As a result of this study, although the use of RCCI did not have a significant impact on performance, it did have an impact on emissions.
- The increase in the amount of injection in HC emissions has caused an increase in HC emissions. Due to the easy evaporation of gasoline, it creates a cooling effect, which causes flame extinction in areas close to the cylinder walls. Fuel consumption adjustment, specific fuel consumption decreases with increasing fuel injection amount.
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THERMAL COUPLING OF PEM FUEL CELL STACK WITH METAL HYDRIDE HYDROGEN STORAGE SYSTEM: A COMPUTATIONAL STUDY

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Abstract

With the rising interest in hydrogen and Proton Exchange Membrane Fuel Cells (PEMFCs), selecting the most effective hydrogen storage technology is increasingly vital, particularly for transportation applications. Metal hydrides present notable advantages, including the capability for thermal coupling between storage and utilization systems. While PEMFCs necessitate heat removal for optimal performance, metal hydrides require heat to trigger hydrogen release reactions. This research examines the integration of PEMFCs with metal hydride storage systems, emphasizing their thermal coupling. The study investigates the potential of using cathode air to cool the fuel cell and supply the necessary heat for hydrogen desorption from a titanium-based storage system. Computational fluid dynamics (CFD) simulations are conducted to analyze the flow and heat transfer within a PEMFC stack section and the thermally coupled hydrogen storage system utilizing titanium as the storage medium. The findings offer valuable insights into efficient thermal management and integration strategies, aimed at enhancing the performance and efficiency of PEMFC and metal hydride systems.

Keywords: Hydrogen storage, PEMFC, Metal Hydrides, Computational fluid dynamics, Modelling

ADVANCEMENTS IN COMBUSTION TECHNOLOGY: THE ROLE OF NANOPARTICLE FUEL ADDITIVES, MECHANISMS AND THEORIES

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Abstract

This paper explores the transformative potential of nanoparticle fuel additives in combustion engineering, focusing on their unique properties and mechanisms that enhance fuel performance and reduce harmful emissions. Nanoparticles, classified as inert, catalytic, or reactive, exhibit exceptional physical, chemical, and thermal properties that significantly differ from bulk materials. These properties contribute to improved reactivity, catalytic activity, and combustion characteristics. The study examines various types of nanoparticles, including metal oxides and carbon-based materials, elucidating their roles in enhancing combustion processes. Key mechanisms such as secondary fuel atomization, micro-explosion, catalytic effects, reactivity participation, and thermal conductivity enhancement are discussed in detail. Nanoparticle additives address critical challenges in combustion technology, including improving fuel efficiency, reducing pollutant emissions, and enhancing overall engine performance. The paper highlights how these additives facilitate more complete combustion, lower emissions, and improve thermal efficiency through various mechanisms. Secondary atomization and micro-explosion phenomena enhance fuel-air mixing, while catalytic effects lower activation energies for combustion reactions. The research also explores the impact of nanoparticles on fuel physical properties, such as thermal conductivity and viscosity, which contribute to better atomization and more stable combustion processes. The paper concludes by emphasizing the significant potential of nanoparticle fuel additives in advancing combustion technology and developing more environmentally friendly fuel formulations, paving the way for cleaner and more sustainable energy solutions in the face of growing environmental concerns.

Keywords: Nanoparticles, Fuel Additives, Catalytic Activity, Secondary Atomization, Micro-Explosion, Thermal Conductivity of Nano Fuels,

4 INTRODUCTION

Nanoparticles have garnered significant attention in combustion engineering due to their exceptional properties and potential to enhance fuel performance. The substantial specific surface area they possess, coupled with the excess surface atom energy, gives rise to a plethora of unique physical, chemical, thermal, magnetic, electrical, and optical properties that exhibit marked disparities when compared to those found in bulk materials [4-6]. Such properties culminate in enhanced reactivity or catalytic activity, superparamagnetic tendencies, decreased melting points, and augmented theoretical densities in contrast to materials of micron-scale dimensions [3, 6]. Enhanced

reactivity and catalytic activity improve fuel economy and reduce pollutant emissions by facilitating more complete combustion. Superparamagnetic tendencies allow for better control and mixing of fuel within combustion chambers, while lower melting points promote better atomization and uniform combustion. Additionally, increased theoretical densities enhance the energy content of fuels, aiding the development of advanced, environmentally friendly fuel formulations. Overall, nanoparticles as fuel additives represent a significant advancement in combustion technology, promising cleaner and more efficient combustion systems.

Nanoparticles in combustion are classified into three categories: inert, catalytic, and reactive,

each playing a unique role in enhancing fuel efficiency and reducing emissions [3, 7]. Inert nanoparticles, such as aluminum oxide (Al_2O_3), though traditionally considered non-reactive, can exhibit catalytic effects under certain conditions, activation energy for exothermic reaction occurs [8]. Catalytic nanoparticles, such as cerium dioxide (CeO_2) and copper oxide (CuO), facilitate combustion reactions without being consumed, thereby lowering the activation energy required and reducing pollutants such as carbon monoxide (CO) and unburned hydrocarbons (HCs). Reactive nanoparticles, including carbon nanotubes (CNTs) and graphene, actively participate in exothermic reactions, contributing additional energy and improving combustion characteristics such as flame stability and heat release rates (HRR) [9, 10]. The diverse roles of these nanoparticles in combustion processes highlight their potential to enhance fuel performance and efficiency while minimizing environmental impact, promising significant advancements in combustion technology.

The application of nanoparticles in fuel additives aims to address several challenges in combustion processes. These challenges include improving the combustion efficiency of fossil fuels, reducing the formation of pollutants such as nitrogen oxides (NO_x) and particulate matter (PM), and enhancing the overall performance of engines. The incorporation of nanoparticles into fuels can lead to more complete combustion, lower emissions, and improved thermal efficiency, making them an attractive solution for both environmental and economic reasons.

In recent years, significant research efforts have focused on understanding the interactions between nanoparticles and fuel components during combustion. Studies have shown that nanoparticles can influence various aspects of the combustion process, such as ignition delay (ID), combustion duration, flame stability, and HRR [11-13]. For instance, alumina nanoparticles are known for their high reactivity with carbon, hydrogen, and nitrogen atoms, exhibiting a strong oxygen-supporting capability that enhances combustion efficiency [8]. The ignition-temperatures of aluminum nanoparticles, a role of particle size, are typically below 1000 K, aligning well with the operating temperatures of diesel engine combustion chambers [3, 6, 7].

Moreover, nanoparticles have the potential to enhance the fuel's physical properties. They can improve the thermal conductivity and kinematic viscosity of fuel blends, which can lead to better atomization and more efficient fuel-air mixing in the combustion chamber. This improvement in fuel properties contributes to a more uniform and stable combustion process, reducing the formation of soot and other particulate emissions [14-17].

The study of nanoparticle fuel additives encompasses a broad range of materials and mechanisms. Metal oxide nanoparticles, such as Al_2O_3 , CeO_2 , CuO , SiO_2 , TiO_2 , and ZnO , are widely researched for their catalytic properties in combustion reactions. These nanoparticles participate in intermediate catalytic reactions, lowering the activation energy required for chemical reactions and enhancing fuel reactivity and heat/mass transfer properties [16, 17]. Additionally, carbon-based nanoparticles such as CNTs and graphene have shown promising results in increasing the energy content and burning rates of fuels due to their exothermic reactions in oxygenated environments [9, 10].

Understanding the underlying mechanisms by which nanoparticles influence combustion processes is crucial for optimizing their application in fuel additives. Theories such as secondary fuel atomization and micro-explosion provide insights into how nanoparticles can enhance fuel-air mixing and combustion efficiency. Furthermore, the catalytic effects of nanoparticles, their participation in reactivity, and their impact on thermal conductivity are key factors that determine their effectiveness in improving combustion performance.

Overall, the integration of nanoparticles into fuel additives represents a significant advancement in combustion technology. By leveraging the unique properties of nanoparticles, it is possible to develop more efficient and environmentally friendly fuels that meet the growing demands for cleaner and more sustainable energy solutions.

5 NANOPARTICLES AS FUEL ADDITIVES

5.1 Energetic Nanoparticles

Carbon-based nanoparticles, such as CNTs and graphene, significantly enhance combustion processes by acting as reactants in exothermic reactions, thereby increasing the total energy released and improving fuel efficiency [9, 10].

Research shows that single-walled CNTs burn faster than multi-walled CNTs, leading to more efficient energy production [11]. Additionally, organic coatings on metal nanoparticles and carbon coatings on metal and metal oxide nanoparticles boost their reactivity and energy content, enhancing combustion efficiency [7, 12,13]. Aluminum nanoparticles are particularly effective due to their high reactivity and strong oxygen-supporting capability, aligning well with diesel engine combustion temperatures [8]. The ignition-temperatures of aluminum nanoparticles, a role of particle size, are typically below 1000 K, aligning well with the operating temperatures of diesel engine combustion chambers [3, 6, 7]. Overall, these nanoparticles contribute to increased energy release, improved fuel efficiency, and reduced emissions, highlighting their potential to revolutionize combustion technology and advance the development of fuel additives.

5.2 Non-energetic Nanoparticles

Metal oxide nanoparticles, such as Al_2O_3 , CeO_2 , CuO , SiO_2 , TiO_2 , and ZnO , play a crucial role in enhancing combustion processes despite not combusting within diesel engine chambers. Their primary function is to act as catalysts, facilitating intermediate reactions that lower activation energy and accelerate combustion, thereby improving fuel efficiency. These nanoparticles also reduce the oxidation temperature, enabling efficient combustion at lower temperatures, which benefits fuel economy and emission reduction [16, 17]. Additionally, metal oxides enhance fuel reactivity by improving the interaction between fuel droplets and air, ensuring complete combustion and minimizing pollutants. Furthermore, they improve heat and mass transfer properties within the combustion chamber, leading to more uniform and stable combustion [18]. Overall, the catalytic activity and thermal properties of metal oxide nanoparticles make them essential for advancing fuel additives and optimizing diesel engine performance.

5.3 Mechanisms and Theories

Secondary Fuel Atomization and Micro Explosion Theory

Secondary atomization, or micro-explosion, is a key process in combustion where larger fuel droplets fragment into smaller ones, enhancing fuel efficiency. This occurs due to heterogeneous nucleation on the droplet surface, facilitated by nanoparticles which degrade and alter the fuel's physical properties [14, 22-24]. The mechanism involves rapid vaporization within the droplet, creating pressure differentials that cause explosive fragmentation, producing ultra-fine droplets with a larger surface area-to-volume ratio, improving evaporation and fuel-air mixing [25]. Nanoparticles increase aerodynamic shear forces, aiding in droplet breakup, and their effectiveness depends on factors such as density, structure, porosity, and the base fuel's properties [26]. The process is influenced by the boiling points and volatilities of fuel components, with more volatile components driving micro-explosions that disrupt larger droplets [27]. This mechanism ensures efficient combustion by adequately atomizing and mixing fuel with air. Understanding these phenomena is crucial for optimizing fuel formulations and enhancing combustion performance in various applications. Basha et al. [30] explained the micro-explosion phenomenon in water-biodiesel emulsion fuel using alumina nanoparticles. This phenomenon occurs due to volatility differences between water and biodiesel. In a water-containing biodiesel emulsion with alumina nanoparticles, water droplets absorb heat rapidly due to water's lower boiling point, leading to micro-explosions. Consequently, a series of ultra-fine secondary fuel droplets form and evaporate rapidly. Thus, potential nanoparticles increase the fuel-air mixture in the combustion chamber by forming secondary droplets. Basha et al. [31] found that micro-explosion and secondary atomization phenomena in CNTs-modified biodiesel emulsion fuels significantly reduce exhaust gases and increase combustion rates compared to pure biodiesel. **Figure 1** shows schematic representation of secondary atomization (a) and micro-explosion (b) effect of modified fuels.

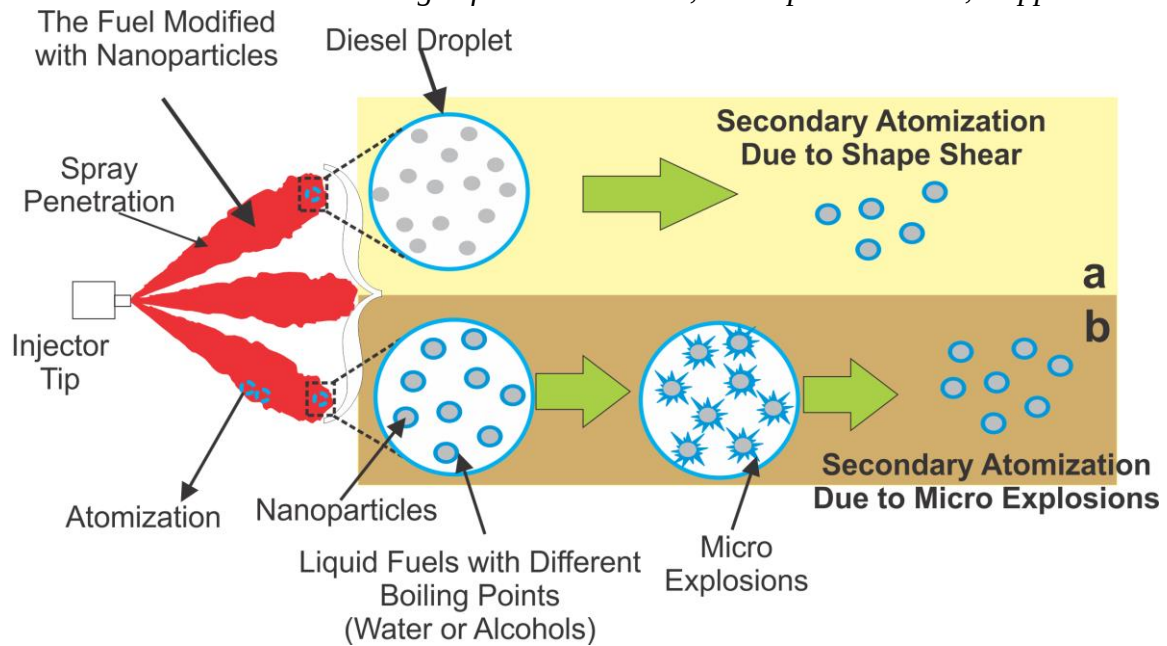


Figure 1: Schematic representation of secondary atomization (a) and micro-explosion (b) effect of modified fuel (modified from [3, 14, 15])

Catalyst Effect

Nanoparticle fuel additives play a crucial catalytic role in combustion processes and the treatment of combustion products by facilitating chemical reactions without being consumed [9]. This catalytic action significantly reduces the time and energy required to trigger these reactions, enhancing combustion efficiency, improving fuel utilization, and reducing emissions. Nanoparticles such as CeO_2 and CuO have shown exceptional catalytic properties, such as lowering soot ignition temperatures by approximately 300 °C at concentrations of 60 to 100 ppm, which improves combustion efficiency and minimizes harmful soot formation [33]. The catalytic activity of these nanoparticles is influenced by factors such as nanoparticle types, combustion temperatures, and specific surface areas, with smaller nanoparticles exhibiting

higher catalytic activity due to their larger surface areas providing more active sites for reactions [34]. Metal oxide nanoparticles engage in redox reactions during combustion, releasing oxygen that reacts with carbon monoxide, hydrocarbons, and soot, reducing exhaust emissions [3, 14, 15, 20]. This integration of nanoparticle fuel additives not only enhances fuel efficiency but also addresses environmental concerns by reducing harmful emissions, representing a significant advancement towards cleaner and more sustainable energy solutions. Thus, understanding the catalytic mechanisms of nanoparticle fuel additives is essential for developing more efficient and environmentally friendly fuels, highlighting their pivotal role in modern combustion technologies. **Figure 2** shows schematic representation of the catalytic effect of nanoparticles in modified fuel.

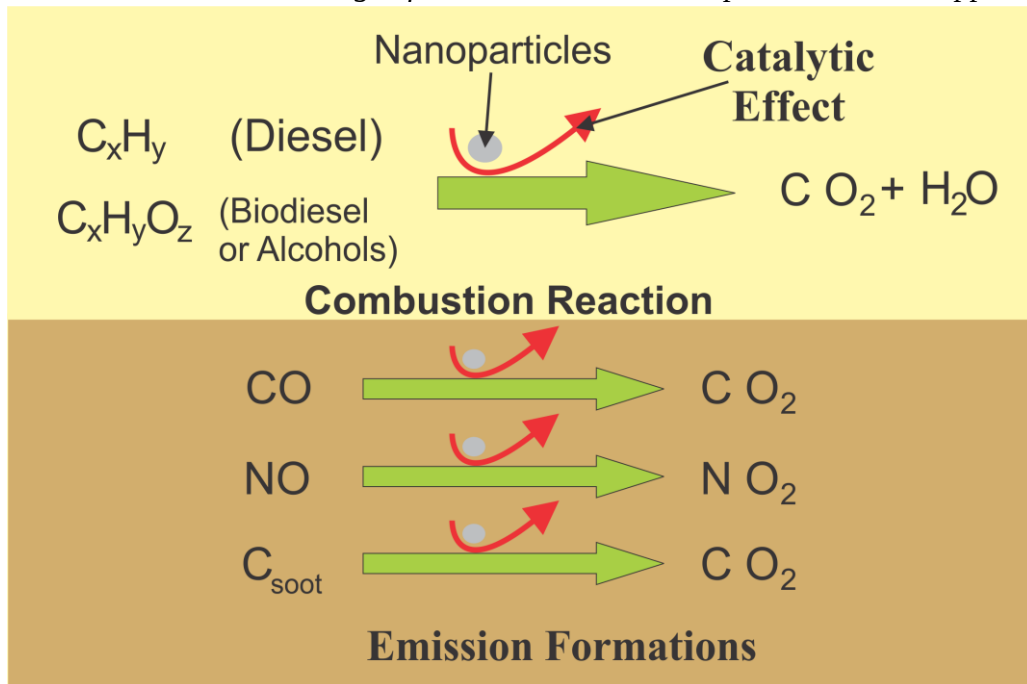


Figure 2: Schematic representation of the catalytic effect of nanoparticles in modified fuel (modified from [3, 14, 15])

Reactivity Participation

Energetic nanoparticles can participate in exothermic chemical reactions under specific conditions, burning in oxygen-rich environments and releasing heat [3, 9, 14, 15, 20]. The total heat released can be increased through exothermic metallic oxidation reactions [6]. Metal nanoparticles form metal oxide

nanoparticles during combustion, acting as active catalysts in subsequent reactions [7]. Additionally, metal nanoparticles can react with fuel components, especially when the base fuel contains water or alcohols, producing hydroxyl radicals that enhance soot oxidation [4, 7]. **Figure 3** shows Schematic representation of the reactivity effect of nanoparticles in modified fuel.

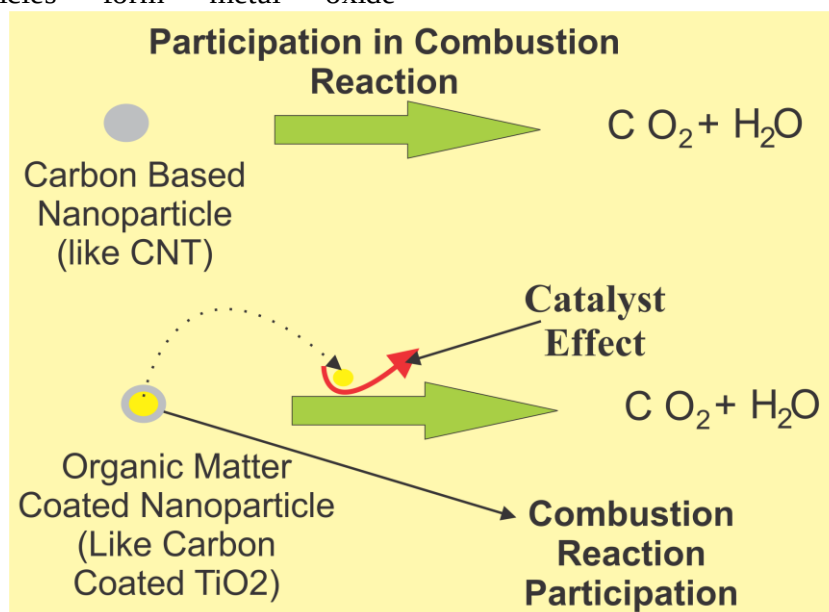


Figure 3: Schematic representation of the reactivity effect of nanoparticles in modified fuel (modified from [3, 14, 15])

Thermal Conductivity

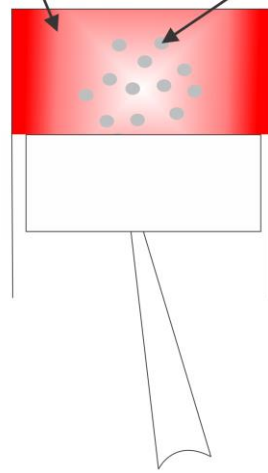
The effects of nanoparticles on the thermal conductivity of modified fuel depend on parameters such as nanoparticle size, shape, material, and base fuel type. Key mechanisms improving thermal conductivity include liquid layering around nanoparticles and Brownian motion of nanoparticles. Excessive clustering can adversely affect thermal conductivity due to sedimentation formation.

Hwang et al. [38] reported increased convective heat transfer coefficient and pressure drop in a circular tube with a constant heat flux when

Combustion

Chamber

Nanoparticles



Heat Absorption

Effect

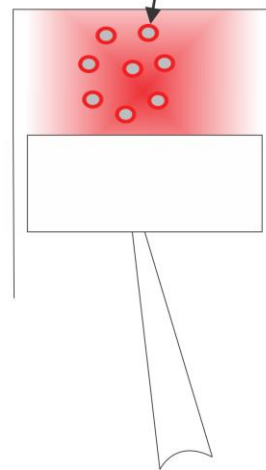


Figure 4: Schematic representation of the thermal conductivity effect of nanoparticles in modified fuel (modified from [3, 14, 15])

6 CONCLUSION

In conclusion, the integration of nanoparticle fuel additives into modified fuels significantly enhances their chemical and thermo-physical properties, optimizing combustion processes and contributing to cleaner energy solutions. These additives not only improve fuel properties, but also thermal conductivity, and calorific value, leading to better atomization, ignition characteristics, heat transfer, and energy output. Mechanisms such as micro-explosion improve fuel-air mixture quality, while catalytic interactions lower activation energy and enhance fuel reactivity, reducing emissions of nitrogen oxides (NO_x) and particulate matter (PM). Enhanced thermal conductivity from nanoparticles ensures stable and efficient combustion, minimizing soot and other pollutants. Overall, nanoparticle fuel additives

Al_2O_3 nanoparticles were added to water. Yu et al. [39] found that dissolving graphene nanoplates in ethylene glycol increased the fluid's thermal conductivity by 86% with a 5% volume concentration of graphene nanoparticles. The two-dimensional geometry, rigidity, and high aspect ratio of graphene and graphene oxide contribute to improved thermal conductivity and thermal transport properties of the mixture fluid. **Figure 4** shows schematic representation of the thermal conductivity effect of nanoparticles in modified fuel.

play a crucial role in advancing combustion technology, improving fuel efficiency, and addressing environmental challenges associated with fossil fuel use. The ongoing research and development in this field holds great promise for further optimizing the performance and environmental impact of internal combustion engines, paving the way for a more sustainable future in energy consumption and transportation.

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RESPONSIBLE GOVERNANCE, CSR PERFORMANCE AND FIRM VALUE CREATION

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Abstract

Corporate Social Responsibility (CSR) and firm value have sparked the interest of great deal literature. However, the relationship between these two areas of research remains completely misunderstood. With the aim of providing an accurate understanding and validating the proposed relationship, the current paper aims to investigate the moderation effect of “Responsible Governance” in the relationship between corporate social responsibility (CSR) and firm value creation, using a sample of 389 European companies listed in the STOXX Europe600 during 2008-2016. Our findings are consistent with our expectation that the integration of a strong system of responsible governance in the development of CSR strategy leads to generate both stakeholder and shareholder value. Moreover, this positive relation is conducted by the respect and application of Ethical and Community norms and codes of conduct that help company to enhance its reputation, to build and improve trust with its partners and thus ameliorate the firm value creation.

Keywords: Responsible Governance, Business Ethics, Corporate social responsibility, shareholder value creation, stakeholder value creation, Green Governance, STOXX 600 Europe.

STATE-FLOW BASED ENERGY MANAGEMENT SYSTEM IN MICRO-GRID INCLUDING FUEL CELL

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ABSTRACT

The proposed State-Flow (SF) based Energy Management System aims to optimize energy-related decisions within the microgrid. This includes scheduling the operation of the fuel cell for managing energy storage and coordinating with other sources such as PV panels. State-flow modelling allows for dynamic control of the microgrid. The system can adapt to changing conditions, such as fluctuations in energy demand, variations in renewable energy generation, or the availability of fuel for the fuel cell. The proposed approach has been simulated using MATLAB based on the investigation of the potential of State-flow as a supervisory controller. The developed system undergoes testing under different conditions to assess its performance and verify the design. In this test, the PV system serves as the primary energy source, while the energy storage system acts as a backup. The energy management system prioritizes supplying load demand from either the PV system or the fuel cell, with load shedding during peak hours. The obtained test results encourage the proposed approach based on State-Flow for enhancing the energy management system's performance.

Keywords: Energy Management System (EMS), State-Flow (SF), Micro-Grid, Fuel Cell

INTRODUCTION

Microgrids are compact electricity distribution networks that can run separately or connected to the main power grid. They typically consist of Distributed Generation Resources (DER), Energy Storage Units (ESU) and various types of electrical loads [1], [2]. Microgrid appears as a single component with respect to the main grid which is governed by control signals. The DERs in the Microgrid may be micro turbines, fuel cells, solar cells, wind turbine, or any conventional or non-conventional power sources [3]. Microgrids may function in an islanded or grid-connected mode, which means they either are linked to or unlinked from the main grid [4], [1]. Due to their capacity to offer dependable and sustainable power, especially in isolated or off-grid places, they are growing in popularity.

An Enhanced Energy Management System (EMS) in a microgrid can provide valuable real-time data and enable more accurate

and effective control and management of the grid. Many ways have been developed for enhancing an EMS through the use grid optimization and control. The acquired data can be used to optimize the operation of the microgrid, improve energy efficiency, and maximize renewable energy utilization. The EMS can analyze the measurements data to determine optimal power dispatch strategies, manage energy storage systems, and optimize the integration of distributed energy resources (DERs) such as Photo-Voltaic (PV) panels or/and wind turbines [5].

ENERGY MANAGEMENT SYSTEM (EMS)

An Energy Management System (EMS) is a crucial component in microgrids, responsible for optimizing the generation, storage and consumption of energy. It ensures efficient utilization of available resources. It involves the proactive, structured, and systematic coordination of energy purchase, conversion, distribution,

and consumption to meet requirements while considering environmental and economic objectives. The term Energy Management System (EMS) refers to a suite of power network applications that includes generation control, scheduling, and monitoring functions. It is often implemented through a computer system designed for the automated control and monitoring of energy-intensive equipment in buildings, such as heating, ventilation, and lighting systems. There are several reasons why energy management plans and strategies are needed:

- ✓ They are effective in influencing daily operations and behavioural patterns.

- ✓ They have a low implementation cost.
- ✓ They can lead to significant energy and maintenance cost savings.
- ✓ They contribute to occupant satisfaction.
- ✓ They can be integrated into long-term and sustainable strategies.

MICRO-GRID USING FUEL CELL

A microgrid that is used in this study can operate independently or connect to the main grid. It typically includes distributed energy resources (DERs) such as solar panels, energy storage units such as a fuel cell. Figure 1 shows PV system powering AC loads. This system is connected to utility power supply and fuel cell as backup.

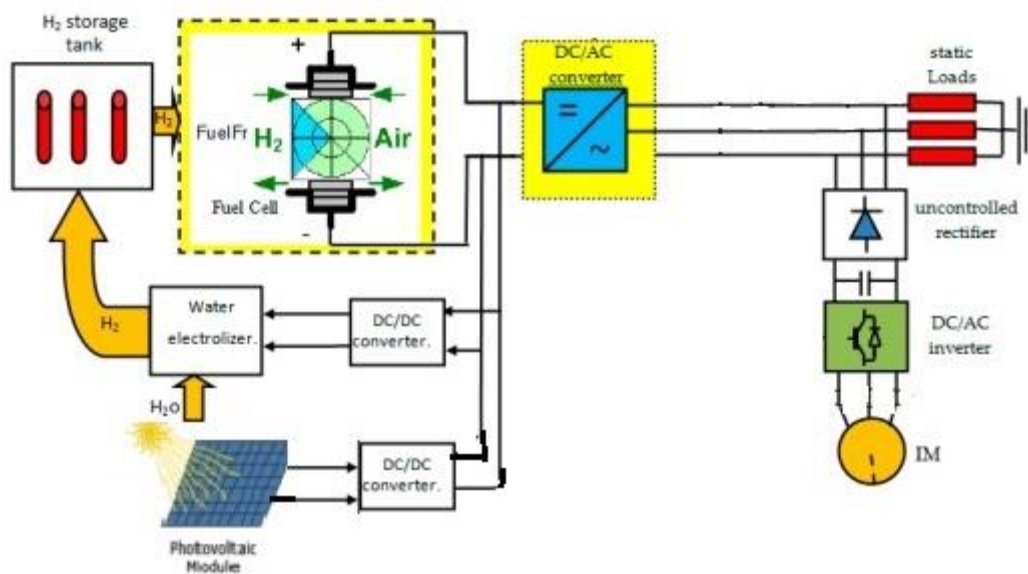


Fig. 1. Proposed Microgrid integrating PV panel and Fuel cell

Photovoltaic panel: Photovoltaic (PV) panels, commonly known as solar panels, are devices that convert sunlight into electricity through the photovoltaic effect. In the context of a smart grid, PV panels play a crucial role in integrating renewable energy into the electricity generation.

Fuel cell: A fuel cell is an electrochemical device that converts the chemical energy of a fuel directly into electrical energy through an electrochemical reaction. It is reversible fuel cell in our case; it can be used for energy storage. During periods of excess electricity generation, the fuel cell operates in electrolysis mode to

produce hydrogen, which can be stored for later use for power generation [6].

STATE FLOW

State-flow modelling is a graphical programming approach used for designing control logic. It represents the system's behaviour through states, transitions, and actions, providing a visual representation of the control strategy. State flow is particularly useful when the energy management system involves intricate logic and complex state transitions. To minimize reliance on backup sources, the supervisory control system using SF can follow

a set of rules and algorithms to prioritize power generation sources. The control system continuously monitors the energy generation and demand within the microgrid and makes decisions based on predefined criteria. It's important to note that the specific implementation details of supervisory control using State flow may vary depending on the micro-grid's configuration, available power sources, and desired performance objectives.

SYSTEM MODELLING AND SIMULATION

First condition to be verified is SOC of the fuel cell, and it yields to two different modes:

- Discharged mode: the SOC is less than or equal SOC min.
- Charged mode: the SOC is between SOC min and SOC max.

Second condition to be verified is P_{PV} compared to P_{Load} , and it yields depending on the ESU mode to other different modes:

- Charged mode: if P_{PV} is greater or equal to P_{Load} , it recognizes PV_connected mode. Otherwise, ESU mode is enabled.
- Discharged mode: if P_{PV} is greater or equal to P_{Load} , it recognizes PV_connected mode. Otherwise, Grid_connected mode is enabled.

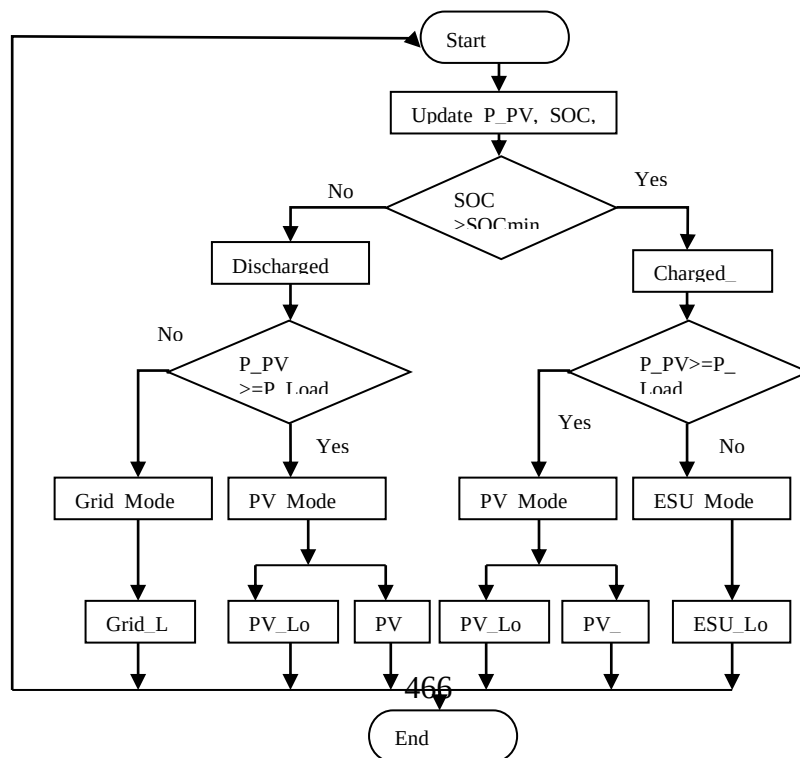
The supervisory control block is realized using State flow. To satisfy the Energy management of the overall system, algorithm is developed to ensure the well functionality of different components of the system, before going to more developed algorithms. It is comprised of PV system, energy storage unit, the power grid and the load. The flowchart of figure 2 shows the different paths and conditions of the energy management controller that has been developed and tested. The controller compares and analyzes different values and parameters: P_{PV} 'PV power', SOC 'State of Charge' of the ESU (Fuel cell) and P_{Load} 'Load power'.

To clarify more, each sub-mode can be described as follows:

- PV mode: The PV system is only connected to the load. Hence no ESU is charging.
- ESU mode: The Fuel cell is connected and discharged through the load.
- PV_connected mode: The PV system is connected to both ESU and load. Hence the load demand is supplied by the PV system and the excess power is used to charge the Fuel cell.
- Grid_connected mode: Because of their non-availability, neither PV system nor the Fuel cell are connected to the load. Hence, the grid is used to satisfy the load demand.

Fig.2. Flowchart of proposed Algorithm

To apply this protocol in SIMULINK, a series of measurements and comparison operations are performed. These operations result in Boolean control signals that are used to control ideal switches;



each switch connects a power source to the load (PV_Load, ESU_Load, Grid_Load) or a power source to another (PV_ESU). Table I defines the different controller inputs and outputs.

Table 1. inputs and outputs of state flow

Input	Description	Output	Description
P_PV	Power delivered from PV panel	PV_Load	Controller governs the connection between PV source and load
		PV_ESU	Controller governs the connection between the PV source and the fuel cell.
P_Load	Power demanded by the Load	ESU_Load	Controller governs the connection between the ESU and load
SOC	State of charge of the fuel cell	Grid_Load	Controller governs the connection between the grid source and load

RESULTS AND DISCUSSION

Now, after modelling using MATLAB/SIMULINK, application of SF minimizes the computational complexity of the problem solving and advantageously demonstrates the behaviour of the EMS. A variable load is connected to a 48V DC bus via DC to AC inverter. In order to pass through all possible cases and evaluate the proper work of state flow and the overall system, multiple scenarios can be realized and then tested. The irradiance and the load demand are adjusted to satisfy the following scenarios.

• **Scenario 1** [0 – 240 simulation time] (ESU discharge): The fuel cell SOC is greater than SOCmin, which yields the selection of

Charged_Mode initially. The power demand of the load is varying between 50W and 100W, which is not covered by the PV system that is provided with no irradiance input (for example during night hours). This makes the system follow ESU_mode, hence the use of the ESU and the discharge of the FC through the load.

• **Scenario 2** [240 – 300 simulation time] (Grid connection): The continuous discharge of the FC yields to reach the SOCmin, hence switch the mode into Discharged_Mode. The power demand now is around 300W, but the PV still not sufficient for the load demand. The system, in similar cases, prefer to supply the load demand from the grid instead of the ESU, which stands out the Grid_connected mode.

• **Scenario 3** [300 – 940 simulation time] (PV availability, sufficiency, and excess): The Photovoltaic panels are now exposed to sunlight with irradiance of 200kW/m² and MPP of about 212W, hence, 150W load demand can be easily satisfied selecting the PV_connected mode. The excess power is fed into the ESU, which raises the SOC above SOCmin and let the system go back to Charged_Mode.

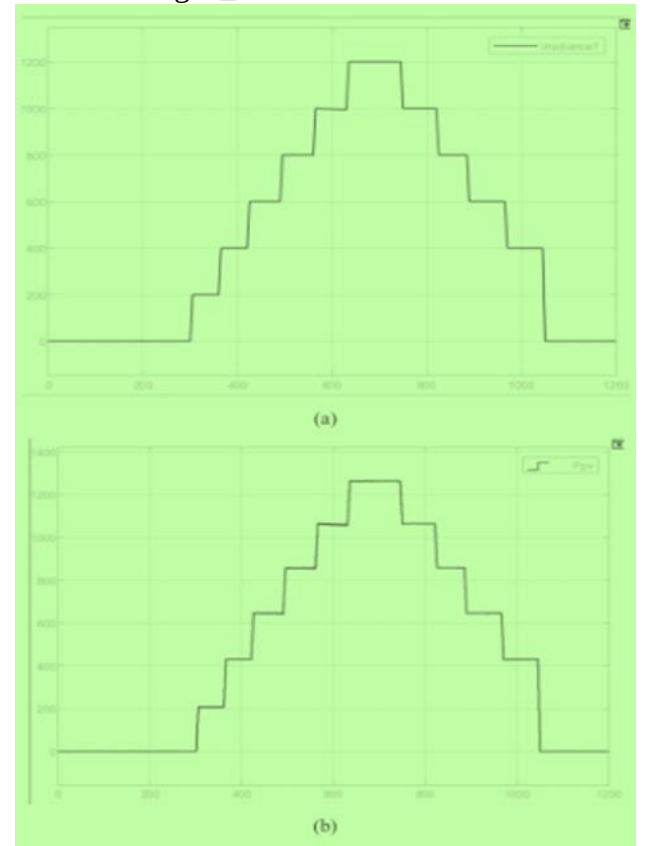


Fig. 3. Power flow scenarios: (a) Irradiance variation (b) PV power (c) SOC of the battery (d) Load power demand .



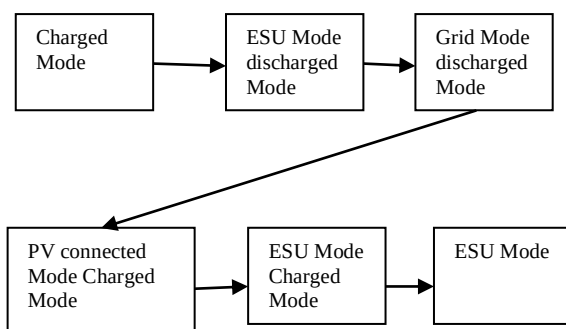
Fig. 4. State flow outputs (switches state)

During all this period within the Charged_Mode, the PV system is generating power greater than the demanded one; hence the load will be fully fed from it. For SOC less than SOCmax, the supervisory enables the charging process till the SOC reaches the limited upper value SOCmax. This can be achieved by the selection of PV_connected mode.

• **Scenario 4** [940s - 1040s] (PV availability and sufficiency, FC fully charged): The ongoing charging process of the FC makes it fully charged: SOC=SOCmax. The supervisory controller, consequently, stops it. On the other hand and due to the PV's sufficiency, the load continues to be supplied using the PV: PV_mode is enabled.

• **Scenario 5** [1040s – 1200s] (FC discharge) : The last discussed scenario is made to ensure the well connection between all supervisory' modes, it is preferable to switch the system backward to its initial mode, Charged_Mode.

So the charge collected during day hours has to be used during night to minimize the use of the power grid. With no irradiance input, the PV cannot supply the load, yields the discharge of the FC through the load. The supervisory passes through all primary and secondary



modes in the order as illustrated in figure 5.

Fig. 5. The order of the modes passed by the supervisory control

CONCLUSIONS

The proposed configuration can greatly satisfy the existing power demand, fed the fuel cell with the excess power and limit the use of conventional power generation during day hours and switch to the backup system (ESU) during night hours. The proposed system, hence, can save the fossil fuels from depletion, limit global warming and keep the environment clean and green, at the same time reduce the use of the grid by prioritizing the utilization of PV and ESU energy.

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THE EFFECT OF MACROECONOMIC VARIABLES ON ECOLOGICAL FOOTPRINT: PANEL DATA REVIEW ON OECD COUNTRIES

Sümeyye Rafia YILDIZ, Emrah GÜLAY

ABSTRACT

Ecological footprint, which is an environmental indicator, is defined as the impact on the environment as a result of human activities. Ecological footprint is seen as a useful tool to understand the environmental impacts of human activities and to determine areas where changes can be made to reduce this impact. At the same time, in order to target sustainable development, balance biological capacity, protect natural resources and leave a productive planet for future generations, it is necessary to measure the ecological footprint and reduce the ecological footprint according to these measurement values.

In this study, the relationship between the dependent variable ecological footprint and the independent variables gross domestic product per capita, renewable energy, trade openness, capital stock, carbon emissions, population, human development index, financial development index for 37 OECD countries between 1996-2022 is examined and interpreted with panel data analysis. There are significant relationships between the variables, expectations are met, and the results are included. The relevant study is intended to contribute to the literature.

Keywords: Ecological Footprint, Sustainability, Biological Capacity, Macroeconomic Variables, Environment, Energy Economy, Natural Resources

ROBUST FRAMEWORK FOR REAL-TIME TECHNO-ECONOMIC IN MICROGRIDS AMID CYBER-PHYSICAL ATTACKS UTILIZING SENSITIVITY ANALYSIS

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Abstract

In the contemporary landscape, managers and operators of power distribution systems found it challenging to rapidly respond online and in real-time to cyber-physical attacks in multi-microgrids. Therefore, this study proposes an innovative framework aimed at responding to cyber-attacks in real-time, focusing on techno-economic energy management across multiple microgrids. Large change sensitivity analysis was used to ensure a fast and effective response in determining the best energy management approach for cyber-physical threats, effectively solving computational problems in multiple microgrid scenarios. Moreover, in this context, the best choice of operational points in several microgrids was made by paying attention to technical, economic, and dependability constraints—an approach that was lacking in more recent work. A comparison of test results with those of current state-of-the-art methods revealed the capabilities and advantages of the proposed method. A comparison with current state-of-the-art methods demonstrates that the proposed framework significantly outperforms existing approaches, achieving up to 93.6% improvement in short-circuit levels (SCL), 87.1% in voltage deviation (VD), and 54.3% in expected energy not served (EENS). Moreover, it shows up to 28.6% better performance in losses and 32.7% in generation cost.

Keywords: Realtime, Multi Microgrids, Large Change Sensitivity Analysis, Cyber-Physical Attacks

1 INTRODUCTION

In a cyberattack, modern multi-microgrids (MMGs) could face significant economic and technical consequences [1]. Real-time self-healing mechanisms are crucial for securing them against cyber-physical attacks [2]. The major function of energy management systems (EMS) is to schedule and control the power flow within a microgrid at any given time, using real-time data to optimize energy resources, manage storage, and balance between the MG and the main grid [3, 4]. Integrating Network Reconfiguration (NR) into EMS will further enhance power transmission efficiency, reduce power losses, and provide cost savings for utilities and consumers [5, 6]. Dynamic reconfiguration in MGs involves modifying the grid's configuration during operation to maintain a stable and efficient power supply. It ensures operational stability and efficient power production by adjusting the grid's configuration as needed [7-9].

Prior related work has greatly contributed to understanding and addressing challenges in microgrid management. For example, [10] proposes an adaptive power management

approach specifically for MGs integrated with renewable energy sources, which reduces power oscillations and improves system stability. In contrast, [11] presents a dynamic MG construction approach to restore power distribution systems and enhance computational efficiency through adaptive models. This technique, tested on IEEE feeders, shows reduced complexity and a decrease in the average total load shed, making it more effective for managing mobile energy resources. Research in [12] evaluates the reliability of distribution systems and the impact of non-utility-owned distributed energy resources, employing strategies such as transactive reactive power management to improve voltage profiles and restore additional loads during faults. Meanwhile, [13] demonstrates methods to enhance power system resilience through adaptive decision-making strategies, while [14] proposes decentralized energy management techniques to achieve optimal microgrid performance. Finally, [15] addresses cyber-physical security in distribution networks, emphasizing that robust monitoring capabilities must be complemented by collaborative cybersecurity measures to counter emerging

threats. Table 1 contrasts the features of the suggested strategy with those of recent previous methods, highlighting the deficiencies in earlier studies.

Table 1. Identification of weaknesses in previous approaches

Factors	References					This Paper
	[13]	[14]	[16]	[17]	[18]	
Cyber-Physical Attacks	×	×	×	×	×	✓
Network Configuration	✓	✓	✓	✓	✓	✓
Energy Management	×	✓	×	✓	✓	✓
Power Loss	✓	✓	✓	✓	✓	✓
Voltage Profile	×	✓	✓	✓	×	✓
EENS	×	×	×	×	×	✓
Cost of Load	✓	✓	×	×	✓	✓

1.1 Contribution

This framework is designed to offer flexibility and effectiveness in optimizing and securing energy management systems by balancing conflicting objectives. It dynamically adapts to varying real-world conditions and manages differing goals, such as cost versus reliability. Key features of this framework include:

- **Technical Metrics and Protective Configurations:** This helps maintain stable operational settings by preventing changes in short-circuit levels (SCL). Technical metrics, such as fault current levels, are considered for safety and reliability.
- **Balancing Economic Objectives and Reliability:** This approach integrates cost objectives with reliability measures to find cost-effective solutions. It uses indicators like energy expected not served (EENS) to evaluate power delivery capability and employs voltage sensitivity indices (VSI) to understand how network changes impact voltage levels, which is crucial for both technical and economic reasons.
- **Factors Influencing Power Quality:** Stable voltage levels ensure high power quality to consumers. It is measured by Voltage deviation (VD). Reduction in distribution network losses improves economic efficiency as well as power quality. The loss sensitivity index identifies key network components, which have a major impact on

losses and thus aid in better placement decisions.

2 METHODOLOGY

The strategy is designed to determine the optimal generation plan for distributed generations (DGs) and the configuration of multi-microgrids in real time to ensure their best performance in response to cyber-attacks. It emphasizes both optimal and safe self-healing scheduling, with a focus on improving power quality and system reliability. To achieve this, the multi-objective mathematical function is optimized using a multi-objective optimization algorithm based on large change sensitivity, enabling quick and real-time decision-making. Figure 1 illustrates the graphical abstract of the proposed approach for real-time response to cyber-attacks on multi-microgrids. As shown, the hierarchical control structure allows data measurement systems to detect disturbances at any moment and rapidly apply corrective actions. The multi-objective function structure and sensitivity analysis-based recursive method address technical, economic, reliability, and resilience aspects.

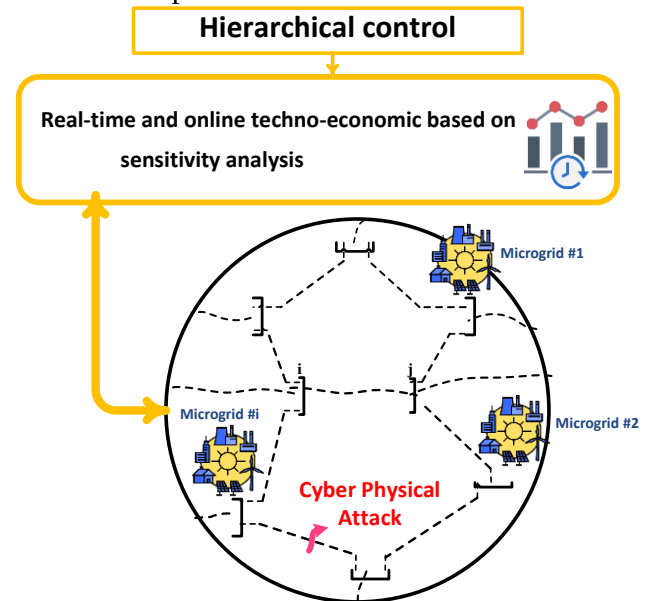


Figure 1. Strategic concept diagram for the suggested framework

As illustrated in Figure 1, interlaced power distribution lines connect different parts of the distribution network, including all the various MGs. The dynamic reconfiguration of the distribution network and the linked MGs is managed by controlling the opening and closing of switches within the grid. This setup allows the system to operate safely and efficiently in two modes: 1) connected to the main network and 2)

isolated from it in islanded mode. During the connected mode, energy is exchanged between the microgrid and the main network. Coupling switches within the network alter the power distribution path through their opening and closing actions. Equation (1) defines a binary formulation to model the open or closed state of each switch in the network, with 0 representing the open state and 1 representing the closed state.

$$Switch_i = \begin{cases} 1 & \text{when Switch is connected} \\ 0 & \text{when Switch is not connected} \end{cases} \quad (1)$$

To technical metrics and network reliability considerations, the cost functions of DGs and energy storage will be discussed.

2.1 Model of solar panels and wind turbines

The solar panel (PV) power generation can be calculated from the following equation:

$$P_{PV} = N_{PV} \times FF \times V \times I \quad (2)$$

Where N_{PV} is donate to number of solar panels and FF refer to fill factor.

The power generated by a wind turbine (WT) is a function of wind speed and the type of wind turbine, which is expressed by the following equation:

$$P_{WT} = \begin{cases} 0, & v(t) \leq v_{cut-in} \text{ or } v_{cut-out} \leq v(t) \\ P_r \left(\frac{v^3(t) - v_{cut-in}^3}{v^3 - v_{cut-in}^3} \right), & v_{cut-in} < v(t) < v_{cut-out} \\ P_r, & v_r < v(t) < v_{cut-out} \end{cases} \quad (3)$$

Where v_{cut-in} denotes the cut-in wind speed, indicating the lower threshold at which the wind turbine can generate power. Conversely, $v_{cut-out}$ represents the cut-out wind speed, signifying the upper limit beyond which the wind turbine stops generating power to prevent potential damage.

2.2 Model of demand response

Demand response (DR) model includes programs planned and implemented to reduce peak consumption and increase stability through voluntary reduction. The rewards for voluntary load reduction and interruptible/curtailable (I/C) load limitation are shown in equations (4) and (5), respectively.

$$Cost^{DR}(t) = \beta^{\frac{1}{c}} \times P^{DR}(t), t \in T \quad (4)$$

$$-\%10 \times \sum_{i=1}^n P^{Load}(t, i) \leq P^{DR} \leq \%10 \times \sum_{i=1}^n P^{Load} \quad (5)$$

where P^{DR} denotes voluntary load reduction in the DR program, $\beta^{\frac{1}{c}}$ illustrates the cost coefficient of interruptible load.

2.3 Model of cost

The formulation of cost models for photovoltaic, wind turbines, battery energy storage systems, diesel generators, microturbines, and the grid is expressed through equations (6) to (8) as detailed in references [19, 20].

The formulation of cost models for photovoltaic, wind turbines, battery energy storage systems, diesel generators, microturbines, and the grid is expressed through equations (6) to (8) as detailed in references [19, 20].

$$Cost^A(t) = \frac{Cost_{Cap}^A \times P_{Cap}^A \times AnR}{UL \times 365 \times 24 \times CF_A} + Cost_{O\&M}^A \times P^{PV}(t) \quad (6)$$

$$\forall t \in T, \forall A \in \{PV, WT\}$$

$$Cost^{ESS}(t) = \frac{Cost_{Cap}^{ESS} \times P_{Cap}^{ESS} \times AnR}{UL \times 365 \times 24 \times CF_{ESS}} + Cost_{O\&M}^{ESS} \times P^{ESS}(t) \quad (7)$$

$$\pm \beta^{TOU}(t) \times P^{ESS}(t) \quad \forall t \in T$$

$$\left\{ \begin{array}{l} Cost^A(t) = Cost_{O\&M}^A(t) + \frac{Cost_{O\&M}^A(t)}{Cost_{EMI}^A(t)} \Big|_{P_A^{max}} \times Cost_{EMI}^A(t) \\ Cost_{O\&M}^A(t) = c + b \times P_A(t) + a \times P_A^2(t) \\ Cost_{EMI}^A(t) = (C_{CO_2}^A + C_{SO_2}^A + C_{NO_x}^A) \times P_A(t) \end{array} \right. \quad (8)$$

$$\forall A \in \{DIGE, MT, Grid\}, \forall t \in T$$

equipment lifespan the units (UL), annual interest rate (AnR), and capacity factor (CF), which includes solar panels (PV), wind turbines (WT), and battery energy storage (ESS) are considered. The opposite occurs with variable costs, which concern expenses related to fuel for generators and maintenance. In addition, for the interruptible generators—that is, those that can be started and stopped, such as microturbines (MTs) and diesel generators ($DIGEs$)—costs also include the environmental impact due to the emission of gases like carbon dioxide CO_2 , sulfur dioxide SO_2 , and nitrogen oxides NO_x . The generation cost will depend on the actual power and specific cost coefficients a , b , c . [32].

2.4 Uncertainty of solar panels, wind turbine, and Load

The probability distribution of solar radiation is usually fitted by the beta Probability Distribution Function (PDF) to handle the uncertainty.

$$PDF(x) = \frac{\Gamma(a+\beta)}{\Gamma(a)\Gamma(\beta)} \times x^{a-1} \times (1-x)^{\beta-1} \quad (9)$$

where α and β are calculated from the mean value μ and the standard deviation by the equation (10).

$$\beta = (1-\mu) \times \left(\frac{\mu(1-\mu)}{\delta^2} - 1 \right), a = \frac{\mu \times \beta}{1-\mu} \quad (10)$$

The Weibull distribution function is typically used to describe the uncertain behavior of wind. More information about modelling and parameter selection can be found in.

$$PDF(v) = \frac{\kappa}{c} \left(\frac{v}{c} \right)^{\kappa-1} \exp\left(-\left(\frac{v}{c}\right)^\kappa\right) \quad (11)$$

$$\kappa = \left(\frac{\delta}{\mu} \right)^\kappa; c = \frac{\mu}{\Gamma\left(1 + \frac{1}{\kappa}\right)}$$

where κ and c indicate the shape and the scale parameters for the Weibull function, respectively. The uncertainty in the electrical load forecast is modelled by a normal PDF function. The modelling and related parameters are presented in [21].

$$f(x) = \frac{1}{\delta\sqrt{2\pi}} \exp\left(-\frac{(x-\mu)^2}{2\delta^2}\right) \quad (12)$$

3 OBJECTIVE FUNCTION FORMULATION

The research proposes a strategic model for the dynamic reconfiguration of power distribution networks with the aim of improving their security and efficiency. It is a model that represents technical, economic, and reliability aspects—unit commitment, cost minimization, and system security—all encapsulated in a mixed-integer nonlinear programming framework. It deals with the challenge of optimization in power distribution in the face of cyber-attacks among other risks. Any constraint-satisfying solution, according to the approach taken by the model, is optimal, which enables one to establish a flexible methodology surrounding hourly operation strategies. Equation (13) is a multi-objective optimization model for the general overall solution of reconfiguration problems under the dynamic and safe operation of distribution networks with conflicting priorities in a very complex energy landscape.

$$\text{Min} \rightarrow \{M(P_{DG_i}, Sstate_i, P_{DR_i})\} \quad (13)$$

Where, M represents the objective functions relevant to the planning problem discussed. The objective functions are depended on the independent variables P_{DG_i} (generation values), $Sstate_i$ (switch states) and P_{DR_i} (reduced demand).

- The equation (14) shows the economic objective function.

$$M_1(P_{DG_i}, Sstate_i, P_{DR_i}) = \left\{ \begin{aligned} &\text{Cost}^{PV}(t) + \text{Cost}^{WT}(t) + \text{Cost}^{BESS}(t) \\ &+ \text{Cost}^{DICE}(t) + \text{Cost}^{MT}(t) + \text{Cost}^{Grid}(t) + \text{Cost}^{dr}(t) \end{aligned} \right\} \quad (14)$$

- The technical objective function given by equation (15) taken into consideration is the loss, loss sensitivity factor (LSF), VD, and SCL.

$$M_2(P_{DG_i}, Sstate_i, P_{DR_i}) = \left\{ \{Losses + LSF\}_{Normalized} + \{VD\} + \{SCL\} \right\} \quad (15)$$

- The objective function for reliability and resiliency considered in this work includes the reliability and resiliency aspects of the power network, incorporating the EENS and voltage security margin (VSM) parameters. This objective is computed using equation (16).

$$M_3(P_{DG_i}, Sstate_i, P_{DR_i}) = \left\{ \{EENS\}_{Normalized} + \{VSM\}_{Normalized} \right\} \quad (16)$$

4 SIMULATION RESULTS AND ANALYSIS

This section introduces a new architecture designed to evaluate self-healing capabilities in real-time against cyber-physical attacks by incorporating dynamic reconfiguration and addressing advanced distribution network uncertainties, such as IEEE 69-bus systems and their subnetworks. The test is conducted over a 24-hour time profile. In these case studies, DGs, including PV panels, diesel generators, microturbines, and wind turbines, are used to supply power for the operation of the MGs. The 69-bus distribution network with interlinked MGs is used to validate this methodology. Data regarding all the loads and network lines can be obtained from the source shown in [22]. Moreover, the developed technique is compared with advanced techniques in comparative studies. In the IEEE 69-bus case study, the MGs are located at buses 27, 35, and 46, with dynamically coupled switches, as shown in Figure 2. An optimization algorithm based on the LCS technique will be developed and applied to optimize the mentioned functions, and the results will be benchmarked against other discussed optimization algorithms.

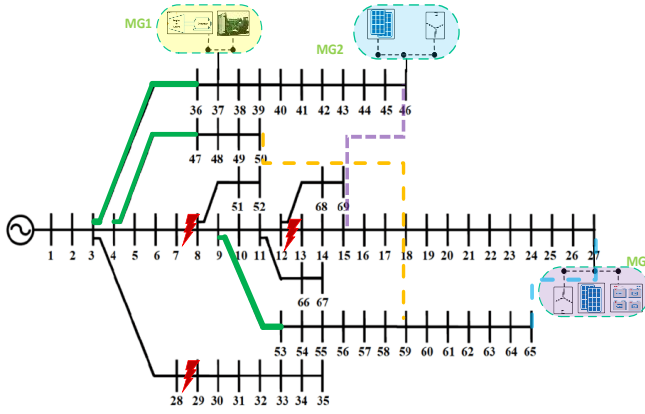


Figure 2. Dynamic switches of mgs to network and coupled switches between lines in IEEE 69 bus.

First, to assess the effectiveness of the proposed strategy in preventing cyber-physical attacks on the system, a sudden attack causing line outages between buses 28-29, 12-13, and 7-8 in the IEEE 69-bus network is simulated. As noted earlier, this evaluation considers both technical and economic parameters using the proposed strategy.

A multi-objective optimization algorithm was applied based on the implemented strategy to determine the optimal generation levels for each DG unit, as well as the dynamic switch states in the IEEE 69-bus systems, considering load variations. The goal was to improve both technical and economic aspects. Figure 3 shows the optimal DG power generation profiles for each unit while the load varies in the IEEE 69-bus systems. These plots provide valuable insights into the effective management of generated power and the optimization of power flows that optimal dynamic switching can achieve under different load conditions.

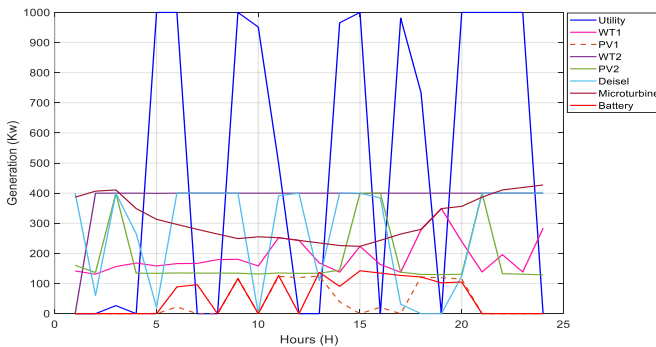


Figure 3. Distribution of optimal generation per units under different load factors in IEEE 69-bus systems.

Furthermore, the proposed strategy provides the optimal configurations of switching devices for the given line outages across different case studies. Figure 4 illustrates the scenarios of the interconnected switch breakers that are considered to achieve the best configuration for the initial distribution networks of IEEE 69 buses. From these illustrations, it is easy to identify the setup that maximizes both the performance and efficiency of the network.

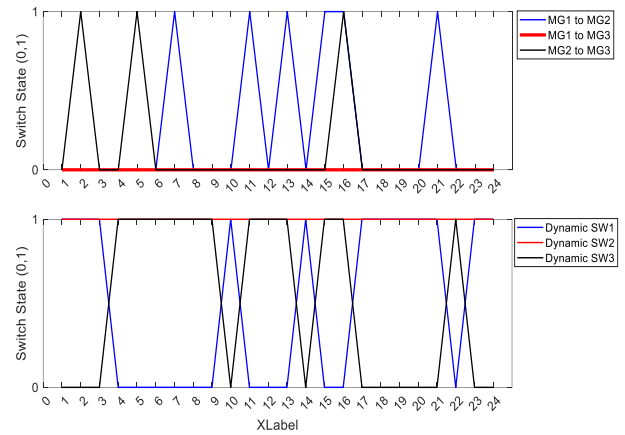


Figure 4. Optimal states of dynamically coupled switches in the ieee-69 bus network in response to varying load factors

Table 3 presents a detailed performance evaluation of the proposed strategy compared to various existing methods. This comparative analysis encompasses key metrics such as economic feasibility, power quality improvements, reliability enhancements, and network security considerations. All results from this evaluation are comprehensively documented in Table 3. Notably, the proposed method excels by integrating all economic and technical objectives into the total objective function during the optimization process, thanks to our innovative use of LCS analysis, which allows for near real-time optimization, completing in under 1 second for the IEEE 69-bus system.

Table 3. Evaluation of the suggested framework versus other advanced techniques for the IEEE 69 bus network.

Objectives Method	CPU-Time for Optimization (s)	Generation Cost (\$)	Losses (kW)	VD (pu)	EENS (kWh)	VSI (pu)	SCL (pu)
Suggested framework	0.92	1153.01	15.09	0.81	31.19	5.00	0.751
[23, 24]	6854.1	1712.31	16.32	6.31	38.54	1.24	10.24
[25, 26]	3765.7	1471.14	18.25	3.98	48.56	2.94	11.71

Additionally, the proposed approach effectively identifies optimal values for several independent system parameters, including generation levels and dynamic switch configurations, as illustrated in Figure 4. In contrast, most modern methods face extended optimization times, often in the order of minutes, which hampers their responsiveness for immediate decision-making. The technical and economic performance metrics in Table 6 clearly demonstrate that the proposed strategy consistently outperforms its competitors. A thorough analysis of the simulation results in Figure 4, along with the data in Table 3, provides strong evidence of the proposed method's effectiveness and superiority. This achievement is significant, especially considering that reliability and power quality indices were often neglected in previous studies. The new methodology enhances distributed generation control within the distribution network and smart microgrids by optimizing power flow and adjusting energy pathways through dynamic switching. According to Table 3, the proposed strategy shows significant improvements across various parameters compared to other methodologies. It achieves up to 93.6% better performance in SCL, up to 54.3% in EENS, and up to 87.1% in VD. Additionally, it performs up to 28.6% better in losses and up to 32.7% better in generation cost. Moreover, the strategy exhibits a remarkable 100% improvement in CPU processing time.

5 CONCLUSION

In the current complex energy landscape, managing real-time optimization for cost-effective distribution networks with multiple microgrids presents a significant challenge, particularly in ensuring self-healing capabilities against cyber-physical attacks. This paper

introduces a novel technique based on Large Change Sensitivity (LCS) analysis for strategic real-time self-healing, addressing both technical and economic aspects. The approach integrates dynamic reconfigurations, coordinated generation, and energy storage to optimize energy transfer and minimize risks through effective mitigation strategies. The proposed method shows significant performance enhancements, with improvements of up to 93.6% in short-circuit levels (SCL) and 87.1% in voltage deviation (VD). Additionally, it achieves a 54.3% improvement in energy expected not served (EENS), up to 28.6% better performance in losses, and up to 32.7% better in generation cost. Notably, the method also demonstrates a 100% improvement in CPU processing time compared to previous methods.

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EFFECT OF N₂ DILUTION ON DYNAMIC FLUCTUATION OF PROPANE-HYDROGEN FLAME

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Abstract

and energy efficiency have gained importance, different fuel mixtures and combustion methods are tested. In this study, burning Propane fuel as a mixture with Hydrogen and diluting it with Nitrogen is investigated. In the study conducted under lean combustion conditions ($\phi = 0.8$), 70% Propane - 30% Hydrogen was used as the fuel mixture. Additionally, a vortex generator with a vortex number of 0.4 was placed at the burner outlet. In all experiments, the thermal power was kept constant at 5 kW. The experiments were carried out by producing sound waves at different frequencies through speakers placed on the combustion chamber arms. The results showed that nitrogen dilution reduced the dynamic pressure oscillation amplitude of the flame by reducing thermo-acoustic combustion instabilities. On the other hand, when the N₂ dilution rate was increased, the flame approached the blowoff limit and experienced blowoff instability under the external acoustic forcing frequency.

Keywords: Propane, Hydrogen, Thermo-acoustic Instabilities

1 INTRODUCTION

Propane gas is an important gas currently used in burners around the world. It has an important place in balloon tourism, especially in the Cappadocia region. However, like other hydrocarbon fuels, it causes CO₂ and CO emissions and harms the environment. For this purpose, researchers continue their studies on burning propane gas by mixing it with different alternative fuels. Although low emission targets are considered in these studies, problems arise in terms of flame stability, especially when mixed with hydrogen.

There are many studies in the literature on the combustion characteristics of different gas fuel mixtures. İlbaş and Karyeyen [1] examined the

combustion characteristics of a hydrogen-containing synthesis gas mixture at different turbulator angle values. The study results showed that as the turbulator angle increases, the axial velocity values of the synthesis gas flame decrease towards the center of the combustion chamber. Wang et al. [2] investigated propane-air-CO₂ flames. In the study where CO₂ gas was used as a diluent, its effect on flame stability was examined. Study results showed that the addition of CO₂ reduced the hydrodynamic instability of the flame. Aguilar et al., [3] investigated the effect of hydrogen addition on methane flame stability. The study was carried out in a premixed burner. The results showed that as the

hydrogen content increased, the flame speed increased and therefore the flame length shortened. In another study, Bubnovich et al. [4] tested propane air combustion in a premixed perforated burner. The results obtained showed that the combustion temperature was between 1160 K and 1380 K. On the other hand, CO and NOx emissions were measured at very low levels.

When the literature is examined, it can be seen that the studies conducted on propane have a current field of study as a fuel. In addition, it is understood that there are still methods that need to be developed and these studies are important for industrial applications. In this study, flame dynamic instability data at different $O_2 / N_2 + O_2$ ratios were tested by adding 20% hydrogen to the propane flame. As a result of the experiments, the most ideal thermos-acoustic instability conditions were determined.

2 METHODOLOGY

The schematic representation of the system used in the experiments of diluting the propane/hydrogen mixture with nitrogen is presented in Figure 1. A premixed combustor was used in the experiments carried out in a model gas turbine combustion chamber. Fuel and diluents are pre-collected in a collector and mixed homogeneously with air in the pre-mixer stage. While the air required for combustion is provided by a compressor, the fuels are stored in steel tanks. The external acoustic forcing required to determine flame dynamic pressure oscillations is made through speakers. These speakers are located in the arms of the combustion chamber.

All experiments were carried out at 5 kW burning power. On the other hand, a low amount of excess air was used, although it was close to the stoichiometric ratio. For this purpose, the equivalence number was kept constant at 0.8. Additionally, a vortex generator is placed at the burner outlet. The vortex number of this vortex generator is kept constant at 0.4. By keeping these values constant, flame instability was detected at variable $O_2 / N_2 + O_2$ ratios. A constant 70% Propane / 30% Hydrogen mixture was used in the experiments.

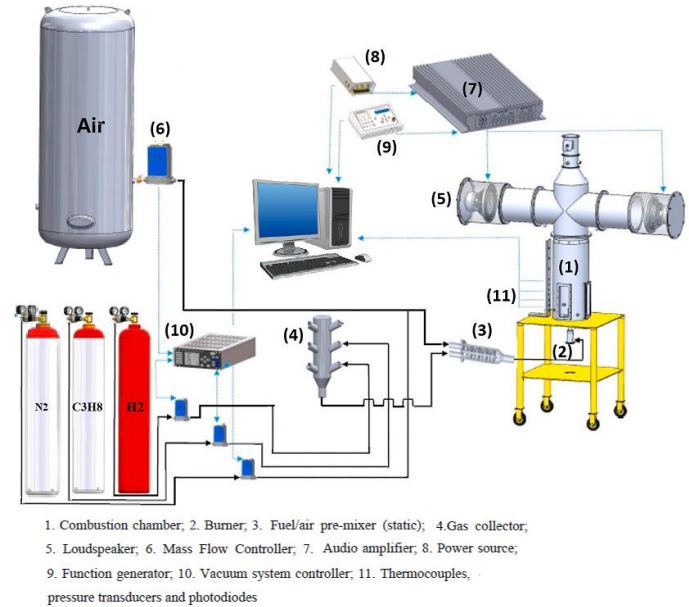


Figure 1. Schematic Design of Experimental System

3. RESULTS AND DISCUSSIONS

The H_2 ratio tested in this study is 30% by volume. Above this rate, up to 32% H_2 , flashback occurred without any acoustic strain. Thanks to this study, the maximum Hydrogen enrichment limit of propane gas at low swirl number (0.4) in a premixed burner was determined. According to previously measured values in the literature, in the case of Equivalence ratio (ϕ) = 1, the flame speed of propane gas is 39 cm/s, while that of hydrogen gas is 200 cm/s. Flame speed exceeding the limit values caused flashback instability [5]. In different hydrocarbon fuels, the addition of hydrogen has a critical value, after which the Markstein length decreases with the hydrogen ratio. This situation triggers thermal diffusive instabilities [6]. One of the most important problems encountered in hydrogen addition cases in the literature is flashback instability. Thanks to this study, it has been seen that N_2 addition has positive effects on hydrogen flames. The addition of hydrogen can shift the heat release amplitude of the flame towards higher frequencies [7]. As the dilution rate increased, the flame reached the blowoff limit and became unstable again. The data obtained in the experiments are explained as follows. In case of combustion with air under standard conditions, the flame rebounded with a dynamic pressure amplitude of 1387 Pa at a frequency of 90 Hz. Therefore, further acoustic forcing frequencies

were not tested. On the other hand, as a result of the addition of N₂, the dynamic amplitude value of the flame decreased and a value of 373 Pa was measured in the case of 20% O₂. While there was no significant change in 19% and 18% O₂ values after this value, when the O₂ rate was reduced to 17%, the dynamic pressure amplitude increased again and blowoff instability occurred in the flame.

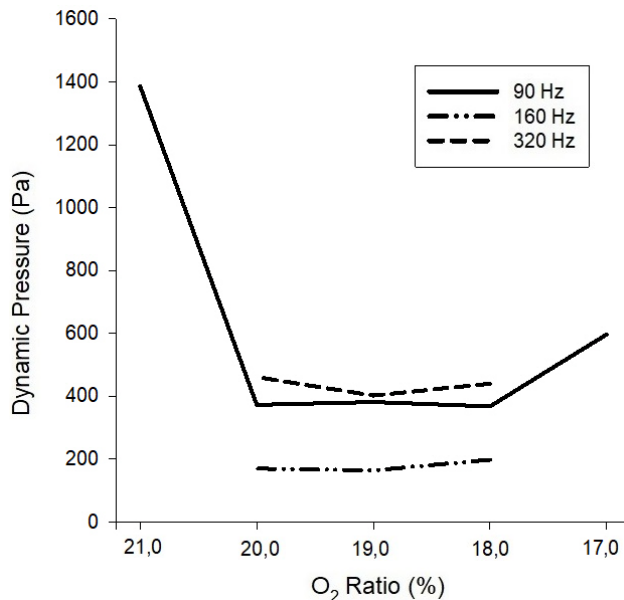


Figure 2. Effect of N₂ Dilution on Dynamic Fluctuation

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TECHNO-ECONOMIC INVESTIGATION ON SOLAR BASED ANAEROBIC CO-DIGESTION OF INDUSTRIAL SEWAGE SLUDGE AND MALT SPROUT WASTE FOR BIOHYDROGEN PRODUCTION

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Abstract

When sludge has been used as the substrate for the anaerobic digestion, it has not a high performance in the hydrogen production. Thus, anaerobic co-digestion with different by-products could assist to produce hydrogen (H₂) more efficiently. From this perspective, the effect of the addition of malt sprout which is a by-product of brewery industry on the anaerobic thermophilic digestion of sewage sludge has been investigated, in this study. The heat and electricity of the anaerobic reactor has been ensured from a solar panel. The inoculum was the waste activated sludge from a brewery industry wastewater treatment plant. Raw (Scenarios I, II, III) and dewatered sludge (Scenarios IV, V, VI) have been used as the substrate assisted with three different amounts of malt sprout. The malt sprout has been added in the amounts of 15 g/L, 25 g/L and 35 g/L. For all conditions, H₂ production yields (H₂y) and contents have been reported. The results revealed that the combination of raw sludge and 25 g/L of malt sprout (Scenario-II) has the maximum hydrogen production potential. The maximum H₂ production yield has been reported as 99 mL H₂/g-added malt sprout at Scenario-II. Also, maximum H₂ content has been observed as 68% in the same scenario. The optimum carbon/nitrogen (C/N) ratio and pH were 26.5 and in the range of 4.5-5.5, respectively for the highest H₂ production. Also, the operating costs of the system has been calculated in terms of energy consumption. Solar based biohydrogen production has decreased the overall costs approximately by 28%.

Keywords: Biohydrogen, Co-digestion, Industrial Sewage Sludge, Malt Sprout, Circular Economy.

1 INTRODUCTION

According to European (EU) Green Deal, the use of renewable energy resources has decreased the greenhouse gas (GHG) emissions [1,2]. Hydrogen (H₂) has been regarded as a key component for decarbonization of energy sector [1,3]. According to the EU Commission, the use of hydrogen energy is the best method as a cost-effective technology to generate the renewable electricity in order to ensure the GHG emissions reduction of minimum 50% by 2030 [2] in terms of carbon-neutrality aim. Also, biohydrogen production is a best alternative for a climate-neutral economy [4].

Biohydrogen production from biomass and wastes has a significant attention owing to recycling and reuse of wastes, recently [4,5,6]. Several policies and strategies have been developed for sewage sludge management in terms of circular economy approach [7]. The utilization of sewage sludge has many environmental benefits recently in terms of techno-economic perspective [7,8]. One of these utilization techniques is biohydrogen production

from sewage sludge. When sludge has been used as the substrate for the anaerobic digestion, it has not a higher performance for the hydrogen production [9,10]. Therefore, anaerobic co-digestion with various biomass wastes could assist to produce hydrogen more efficiently.

From this perspective, this study has aimed to determine the effect of the addition of malt sprout on the anaerobic thermophilic digestion of sewage sludge. The energy required for the heating process and electricity need have been ensured from a solar panel to produce biohydrogen. In the final stage of the study, a techno-economic performance assessment has been performed considering energy consumption for biohydrogen production to determine the benefit of solar panel use.

2 MATERIALS AND METHOD

In this study, the substrate is the industrial waste activated sludge in the result of brewery

wastewater treatment. The additive is the malt sprout is the by-product which generated in large amounts in the brewery industries.

The anaerobic reactor has a volume of 1 L. The temperature is 55 °C at the thermophilic conditions. The heating and electricity for pumping process of the co-digestion process has been ensured from a solar panel in this study. From this point of view, a renewable energy resource has been used for the biohydrogen production process. An economic amendment has been applied using solar energy. The operating costs of the system has been calculated in terms of energy consumption using solar energy.

Inoculum has been used as the raw sludge and dewatered (heated at 103°C for 15 minutes) sludge. The malt sprout has been added in the amounts of 15 g/L, 25 g/L and 35 g/L as the assisted by-product. The experimental scenarios related to this study has been given in Table 1, in detail.

Table 1. Experimental Design

Scenario	Inoculum	Additive
Scenario-I	Raw Sludge	15 g/L
Scenario-II	Raw Sludge	25 g/L
Scenario-III	Raw Sludge	35 g/L
Scenario-IV	Dewatered Sludge	15 g/L
Scenario-V	Dewatered Sludge	25 g/L
Scenario-VI	Dewatered Sludge	35 g/L

Volatile fatty acid (VFA) concentration, pH, also biogas amount and content have been analysed for 14 days. The biogas composition (H₂, carbon dioxide (CO₂) and methane (CH₄)) has been determined using Shimadzu 2010 gas chromatograph (GC) equipped with a thermal conductivity detector (TCD). Also, C/N has been measured every operation day.

The hydrogen production has been calculated according to Eq.1. In Eq.1., BHP (ml H₂/g-added malt sprout) is the hydrogen production, V₁ (ml) is the volume of daily hydrogen production potential from adding the malt sprout; V₂ (ml) is the volume of daily hydrogen production; M (g) is the added malt sprout.

$$\text{BHP} = (V_1 - V_2) / M \quad (1)$$

3 RESULTS AND DISCUSSION

The results revealed that the combination of raw sludge and 25 g/L of malt sprout has the maximum hydrogen production potential (Scenario-II). The maximum H₂ production yield has been reported as 99 mL H₂/g-added malt sprout at Scenario-II. Table 2 has showed the hydrogen production yields and H₂ content in terms of each scenario.

Table 2. Biohydrogen Production Potential

Scenario	H ₂ y (mL/g added malt sprout)	H ₂ Content (%)
Scenario-I	88	63
Scenario-II	99	68
Scenario-III	90.3	65.5
Scenario-IV	68	54
Scenario-V	79.5	59.6
Scenario-VI	74.5	56.3

The optimum carbon/nitrogen (C/N) ratio and pH were 26.5 and in the range of 4.5-5.5, respectively for the highest H₂ production and content (99 mL/g added malt sprout, 68%).

According to the findings, the operating costs of the system has been calculated in terms of energy consumption. Solar based biohydrogen production has decreased the overall costs for biohydrogen production approximately by 28%.

In the literature, Sillero et al. (2022) has investigated the anaerobic co-digestion of sewage sludge, wine vinasse and poultry manure for biohydrogen production. They reported that the addition of 10 g/L of poultry manure to the improves the hydrogen production potential of the co-digestion obtaining 88.00 mL H₂ [9]. From this result, it could be said that malt sprout has higher impact on biohydrogen production (99 mL H₂/ g-added malt sprout). A study by Kim et al. (2012), hydrogen production by anaerobic co-digestion of rice straw and sewage sludge has been investigated. They reported similarly raw sludge has higher hydrogen potential [10].

4 CONCLUSIONS

The results revealed that solar based biohydrogen production has reduced the overall costs approximately by 28%. This study has confirmed

that the addition of malt sprout which is a by-product of a brewery industry has improved the biohydrogen production potential of brewery industry waste activated sludge. Therefore, case studies, based on practical application of waste materials in full-scale industrial wastewater

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systems, for determining the dosage, particle size, and reuse of waste on improving biohydrogen production capacity should be highly investigated in future research.

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PREDICTING HIGHER HEATING VALUES OF PURE BIODIESELS: A MULTIPLE LINEAR REGRESSION APPROACH

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Abstract

Concerns over environmental impacts and the volatility of fossil fuel prices have recently led to an increase in interest in biodiesel. Assessing the compatibility of various biodiesels for the current transportation sector requires a detailed examination of their fuel properties under different conditions. Conventional methods for measuring fuel properties tend to be costly and time-consuming, leading to a move toward predictive models. Therefore, this study uses multiple linear regression to predict the higher heating value of pure biodiesels based on density, kinematic viscosity, and cetane number. According to the results, the obtained multiple linear regression has a maximum relative error of 4.9557%, a minimum relative error of 0.1777%, and an r^2 value of 0.9994, showing its strong ability to accurately fit the higher heating value data.

Keywords: Biodiesel, Higher heating value, Multiple linear regression

1 INTRODUCTION

Alternative biofuels, including biodiesel, alcohols, and vegetable oils, have shown great potential as alternatives to fossil fuels in the transport section [1]. Biodiesel is produced via transesterification wherein fatty acids in vegetable oils or animal fats react with short-chain alcohols (methanol or ethanol) using a suitable catalyst. This reaction produces glycerol and a mixture of fatty acid methyl or ethyl esters (biodiesel) [2]. Biodiesel has many benefits compared to diesel fuel. It can be produced from renewable sources. It is biodegradable, non-toxic, and free from aromatic compounds. On the other hand, it also has some disadvantages, such as lower heating value, higher viscosity, poor cold weather properties, and higher production costs [3-5].

Fuel properties are usually measured through analytical methods and the use of specialized equipment. This approach can be expensive and time-consuming for various fuel blends and operating conditions. To address these issues, this study seeks to develop a multiple linear regression model as functions of density, kinematic viscosity, and cetane number to predict the higher heating value of pure biodiesels.

2 MATERIALS AND METHODS

2.1 Collected fuel property data

For establishing a multiple linear correlation, data on density (at 15°C), kinematic viscosity (at 40°C), cetane number, and higher heating value collected from various articles in the literature are used for pure biodiesels produced under different conditions [6-14]. Table 1 presents the gathered data on fuel properties along with the relative errors between the measured data and calculated higher heating values by the multiple linear regression. All fuel properties were measured according to the relevant international standards by different authors [6-14].

2.2 Multiple linear regression

By using the multiple linear regression, the higher heating value (HHV, MJ/kg) is modelled as a function of density (DS, kg/m³), kinematic viscosity (KV, mm²/s), and cetane number (CN) as follows:

$$\text{HHV} = 0.0479230400242431 \cdot \text{DS} - 0.268785108341434 \cdot \text{KV} - 0.0183812522376531 \cdot \text{CN} \quad (1)$$

3 RESULTS AND DISCUSSION

This section presents and discusses a multiple linear correlation between density, kinematic viscosity, cetane number, and heating value, given that the fatty acid structure of biodiesel influences these properties.

Density impacts the engine performance and fuel injection characteristics, such as injection timing and injection pressure. Moreover, density is linked to other fuel properties like cetane number, heating value, and compressibility [8]. According to the EN 14214 and ASTM D6751 standards, the density standards at 15°C range of 860-900 kg/m³ and 870-890 kg/m³, respectively.

Viscosity affects the injection behaviour, atomization, air-fuel mixture quality, and spray characteristics [9]. High viscosity results in poor fuel atomization, while low viscosity leads to insufficient lubrication [10]. Therefore, EN 14214 and ASTM D6751 standards restrict the kinematic viscosity of biodiesel at 40°C to a range of 3.5-5 mm²/s and 1.9-6.0 mm²/s, respectively.

The cetane number defines the ignition quality of a fuel. Low cetane number causes prolonged ignition delays, while high cetane number promotes smoother engine performance [15]. EN 14214 and ASTM D6751 standards set minimum cetane number requirements of 51 and 47, respectively.

Higher heating value enables longer travel distances with a smaller fuel tank and provides higher engine power [16]. However, biodiesel has a lower heating value, compared to diesel fuel. That is why, a larger amount of biodiesel should be used to obtain the same amount of engine power, which generally increases the specific fuel consumption [17]. Specific regulations are not stated for the higher heating value of biodiesel in automotive applications in the EN 14214 and ASTM D6751 [17].

Based on Table 1, the relative errors range from 0.1777% to 4.9557%. The average relative error across 21 different biodiesels, as shown in Table 1, is calculated to be 1.9595%, with an r^2 value of 0.9994. Figure 1 shows the comparison between the measured higher heating data and those predicted by multiple linear regression.

The figure shows that the predicted values closely match the measured data in most cases.

Considering the regression results and Figure 1, the multiple linear regression model provides an accurate description of the higher heating value data in Table 1, both qualitatively and quantitatively. This is supported by the low relative errors and the high r^2 value.

4 CONCLUSION

In this study, a multiple linear correlation is obtained to predict the higher heating value of pure biodiesels as a function of density, kinematic viscosity, and cetane number. The obtained correlation has a maximum relative error of 4.9557%, minimum relative error of 0.1777%, and r^2 value of 0.9994, which shows its quantitative strong ability to closely fit the higher heating value data. Moreover, the correlation closely matches the higher heating value data, which shows its strong qualitative agreement, as shown in Figure 1.

Table 1. Measured data and relative errors

Biodiesel	DS	KV	CN	HHV	Error (%)
DAF sludge [6]	869.2	4.87	82.7	39.8	2.4483
Palm [7]	869.5	4.56	61	39.8	1.2006
Cumaru [8]	875.8	3.85	50.26	39.46	1.3997
Coconut [9]	860	2.352	66	38.329	2.7120
Chicken fat [10]	872.6	4.85	55.83	37.77	4.5481
Cotton seed [11]	886	4.6	54.6	39.5	1.8222
Linseed [12]	890	4.3	48	40.759	0.3571
Rapeseed [13]	879.6	4.42	48.3	40.32	0.6020
Sunflower [13]	878.6	4.55	51	40.42	1.1757
High oleic sunflower [13]	876.6	4.74	53.2	40.47	1.7608
Jatropha curca L. [13]	881.6	4.46	49.2	40.32	0.4320
Canola oil [14]	878	4.42	54	39.49	1.0276
Chlorella vulgaris	895	4.1	54.7	42.7	4.4879

[14]					
Corn [14]	878	4.42	56	39.93	0.1777
Mustard [14]	879	5.53	56	40.4	1.9589
Date seed oil [14]	878	4.85	57.1	41	3.1140
Kusum [14]	875	4.34	57.86	39.45	0.6403
Poppy seed [14]	896	4.58	55.5	39.99	1.7451
Sesame [14]	867	4.23	58.97	40.25	2.2898
Yellow oleander [14]	886	5.81	61.5	37.89	4.9557
Hazelnut [14]	896	4.81	63	39.58	2.2945

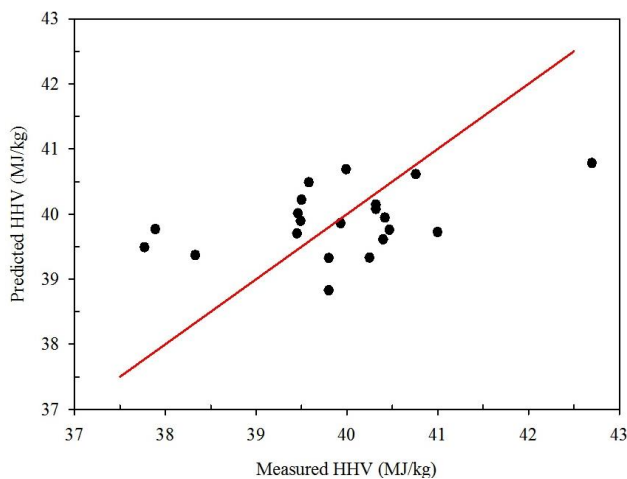


Figure 1. Comparison of measured data and calculated values

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TRENDS IN NaOH DECONSTRUCTION OF MAIZE STALK FRACTIONS IN THE PRODUCTION OF BIOETHANOL

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Abstract

In a bid to resolve the world's energy crisis and the numerous environmental and health concerns associated with the use of fossil fuels, production of energy from biomass has been identified as a suitable alternative. However, the presence of lignin in biomass, such as the maize stalk presents a recalcitrance which must be overcome to access cellulose fibres for conversion to biofuels. This study explores sodium hydroxide (NaOH) in the deconstruction of maize stalk whole and rind fractions for the production of ethanol. The experiment was done in a pulp digester operating at a set temperature of 120°C and 100kPa pressure for 60, 90 and 120 minutes respectively. The liquor to stalk ratio was 10:1 at 14, 16 and 18% NaOH concentrations. The resulting pulp was estimated for cellulose yield and residual lignin. The highest yield obtained was 46.8±2.9% for the whole stalk, and 50.0±0.2% for the rind fraction at 14% NaOH at 60 minutes. The lowest Residual Klason Lignin (RKL) was 4.0±0.01% for whole stalk and 4.7±0.01% for rind fraction at 120 minutes but 18% and 16% liquor concentrations, respectively. On the average, this means that more than 70% of the lignin is removed. Analysis of Variance reveals that at $\alpha_{0.05}$, there is no significant difference between the RKL values of the whole stalk and the rind fraction.

Keywords: Biomass deconstruction, Residual Lignin, Cellulose Yield, Pretreatment time.

1 INTRODUCTION

The need for sustainable feedstock for renewable energy production has become imperative due to the adverse effects of emission of greenhouse gas associated with the use of crude oil worldwide. Maize stalk makes an excellent feedstock for the synthesis of bioethanol in many ways. While numerous types of biomass materials can be utilised to produce bio-ethanol, such as wood shavings, solid waste from cities, and dedicated energy crops consisting of rapidly growing trees or grasses, one of the most abundant crop residues that is available is the stalk from maize production [1] [2]. The same areas where maize grain is grown also yield maize stalk, making it easily accessible to bio-ethanol plants that already make ethanol from maize starch. Maize can be grown all year, providing an unlimited

supply of raw material for the industry [3] [4]. These species can be harvested without requiring a large amount of manpower, energy, or machinery for collection and transportation.

However, maize stalk, like other lignocellulosic biomass, consists of cellulose, hemicellulose, and lignin. The presence of lignin which serves as a binder in the lignocellulose matrix creates a recalcitrance, preventing the access to cellulosic fibre for hydrolysis and fermentation [5]. This creates the need to overcome this recalcitrance using a variety of pretreatment methods. Thermal treatment such as steam explosion [6] uses high pressure steam, the sudden release of pressure causes rapid expansion and disruption of the cell wall. This method is efficient in deconstructing the biomass' cell wall although requires specialised equipment. Pyrolysis [7] [8] is another

energy intensive thermal pretreatment methods that enhances enzymatic accessibility but with complex by-products. Ionic liquids [9] [10], diluted acid pretreatment [11] [12], and ultrasound pretreatment [13] [14] are some other pretreatment techniques that have been researched. All of these techniques call for highly specialised equipment.

Since the morphology, chemical composition, and structural characteristics of biomass vary, each unique biomass must be treated with a pretreatment technique that is appropriate, appropriate, and economically viable. According to Jiang et al. [15] and Kolajo and Onilude [3], maize stalk is a heterogeneous mixture of pith and rind fractions with varying characteristics that may respond differently to similar delignification schedules. This study observes the delignification trends using sodium hydroxide as pretreatment for the whole and rind fraction in the production of bioethanol.

2 METHODOLOGY

The maize stalks, which were of the 3-month-maturing DMR-LSR-W seeds variety acquired from the Institute of Agricultural Research and Training (IAR&T), Ibadan, Nigeria, were harvested from a private farm in Iseyin, Oyo state. The leaves were removed from the stalks, and they were chipped into 2-3 mm chips. In certain chips, the rind—which is the tough outer layer of the stem—was separated from the pith. For this investigation, the entire stem and the rind fraction were utilised.

A chemical reactor built specifically for the purpose was used to pretreat the chips [16]. The pretreatment variables included a liquor to biomass ratio of 10:1 for both the whole maize stalk and the rind fraction, as well as active alkali (AA) charges of 14, 16, and 18% for periods of 60, 90, and 120 minutes at a predetermined temperature of 120°C and pressure of 100 kPa. Preliminary tests were used to determine

these schedules. The cellulose yield was obtained according to TAPPI T236 standards while Residual Klason lignin (RKL) was derived from the kappa number. These were determined as follows:

$$\text{Cellulose yield} = \frac{\text{Mass of pretreated fibres}}{\text{Mass of untreated biomass}} \times 100$$

$$\text{Kappa Number} = p \times \frac{f[1 + 0.13(25 - t)]}{w}$$

$$p = \frac{M(b-a)}{0.1} \quad (3)$$

Where,

f = factor of correction to a 50% permanganate consumption.

w = grams of moisture free pulp in the specimen

p = 0.1M permanganate consumed by the sample in cubic centimetres

b = thiosulphate consumed by the blank determination in cubic centimetres

a = thiosulphate consumed by the sample in cubic centimetres

M = molarity of the thiosulphate

t = actual reaction temperature in degree centigrade

$$\text{RKL} (\%) = 0.13 \times \text{Kappa number} \quad (4)$$

TAPPI T624 standards were followed in the analysis of waste liquor. The purpose of this was to ascertain whether or not there was sufficient active alkali in the waste liquor after pulping to justify the recovery of pulping chemicals.

$$\text{RAA} = X \times \frac{15.5g}{l} \text{ of AA as Na}_2\text{O} \quad (5)$$

3 RESULTS AND DISCUSSION

The findings from pretreating whole maize stalks and rind fractions are shown in Table 1. The pretreatment was started 60 minutes with an alkali concentration of 14%. While there were still some fibre bundles throughout the pulp, a higher proportion of the fibres were separated. The same was observed for pulp from the rind fraction which also contained a fair amount of fibre bundles in comparison to liberated fibres.

Table 1: Mean values for Cellulose Yield, Residual Active Alkali and RKL

S/N	AA (%)	FRACTION	TIME (mins)	pH	CY* (%)	DEGREE OF PULPING	KAPPA No	RAA** (g/l)	RKL*** (%)
C1	14	Whole	60	11.6	46.4±0.5	Fairly pulped	42.49	17.75	5.52±0.12
C2	14	Whole	90	11.6	45.6±0.8	Pulped	40.87	7.75	5.31±0.03
C3	14	Whole	120	11.6	45.6±0.8	Pulped	35.61	7.75	4.76±0.27
C4	16	Whole	60	11.6	44.8±0.2	Pulped	42.09	18.60	5.47±0.15
C5	16	Whole	90	11.5	44.4±0.4	Pulped	40.12	12.40	5.22±0.02
C6	16	Whole	120	11.5	41.6±0.9	Pulped	37.74	10.85	4.91±0.11
C7	18	Whole	60	11.5	39.7±0.9	Pulped	39.26	24.80	5.1±0.4
C8	18	Whole	90	11.7	39±0.58	Pulped	38.28	15.25	4.98±0.14
C9	18	Whole	120	11.5	36.7±1	Pulped	34.47	10.85	4.48±0.02
D1	14	Rind	60	11.6	45±0.5	Pulped	49.37	14.40	6.42±0.15
D2	14	Rind	90	11.7	42.7±0.5	Pulped	40.87	10.85	5.31±0.18
D3	14	Rind	120	11.5	41.7±0.4	Pulped	33.19	9.30	4.31±0.02
D4	16	Rind	60	11.6	44.7±0.5	Pulped	40.47	15.25	5.26±0.03
D5	16	Rind	90	11.7	41.7±0.1	Pulped	38.85	10.85	5.05±0.12
D6	16	Rind	120	11.9	41.3±0.7	Pulped	38.25	9.40	4.97±0.03
D7	18	Rind	60	11.8	43±0.5	Pulped	39.26	17.75	5.1±0.11
D8	18	Rind	90	11.8	41.7±0.5	Pulped	38.85	13.95	5.05±0.19
D9	18	Rind	120	11.8	39±0.5	Pulped	27.71	9.70	3.6±0.16

*Yield ± Standard Deviation **RAA- Residual Active Alkali ***RKL: Residual Klason Lignin± Standard Deviation

3.1 Cellulose Yield (CY)

The maximum cellulose yield recorded was 46.4±0.5% for the whole stalk at 14% concentration and 60 minutes, and 45.0±0.5% for the rind fraction at 14% concentration and 60 minutes. The cellulose yield ranged between 36.7% and 46.4% for the whole stalk and 39% to 45% for the rind fraction. These values are also comparable with a range of 40-45% for chemical pulp yields. The cellulose yield

gradually decreased as the pretreatment duration increased to 90 and 120 minutes at all concentrations of 14, 16 and 18%. The difference in cellulose yields between stalk and rind fraction is not statistically significant at 95% confidence level.

ANOVA of Cellulose Yield between Whole Stalk and Rind fractions

Anova: Single Factor

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.5	1	0.5	0.064334	0.803003	4.493998
Within Groups	124.3511	16	7.771944			
Total	124.8511	17				

3.2 Residual Klason Lignin (RKL) and Residual Active Alkali

For the whole stalk and the rind fraction, the pretreatment with the lowest RKL was $4.5 \pm 0.02\%$ and $3.6 \pm 0.16\%$, respectively. For the whole stalk and rind fractions, the RKL of the pre-treated biomass varied from 4.5% to 5.5% and 3.6% to 6.4%,

respectively. The black liquor's pH values, which varied from 11.9 to 11.5, showed that residual alkali was present. The residual active alkali yielded values ranging from 7.75g/l to 24.80g/l. ANOVA reports no significant difference between RKL values for whole stalk and rind fraction at $\alpha_{0.05}$.

ANOVA of RKL between Whole Stalk and Rind fractions

Anova: Single Factor

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.025689	1	0.025689	0.07404	0.789023	4.493998
Within Groups	5.551356	16	0.34696			
Total	5.577044	17				

3.3 Effects of Pretreatment variables on Cellulose Yield and RKL

Effect of Residence Time on Cellulose Yield

Figs. 1a and 1b illustrate how pre-treatment time affects the yield of pre-treated whole stalk and rind fractions. At constant temperature and alkali concentration, the cellulose yield generally decreased with increasing cooking time, attributed to the dissolution of the extractives and other non-fibrous components of the biomass material [17]. The biomass' potential for dissolution of its carbohydrate content will increase with

time, potentially affecting the pretreatment's yield. Two distinct phases are recognised in relation to the rate of dissolution as reported [18] [19].

Within the first half hour of pretreatment, there is an easily soluble phase that lasts for 30 minutes, and then there is a slower-moving second phase. The extractions dissolve in the first phase, and the amorphous fibrous component dissolves in the second phase. The fact that the cellulose yield for the whole stalk was lower than that of the rind fraction indicates that the non-fibrous pith components present in the whole stalk have disintegrated.

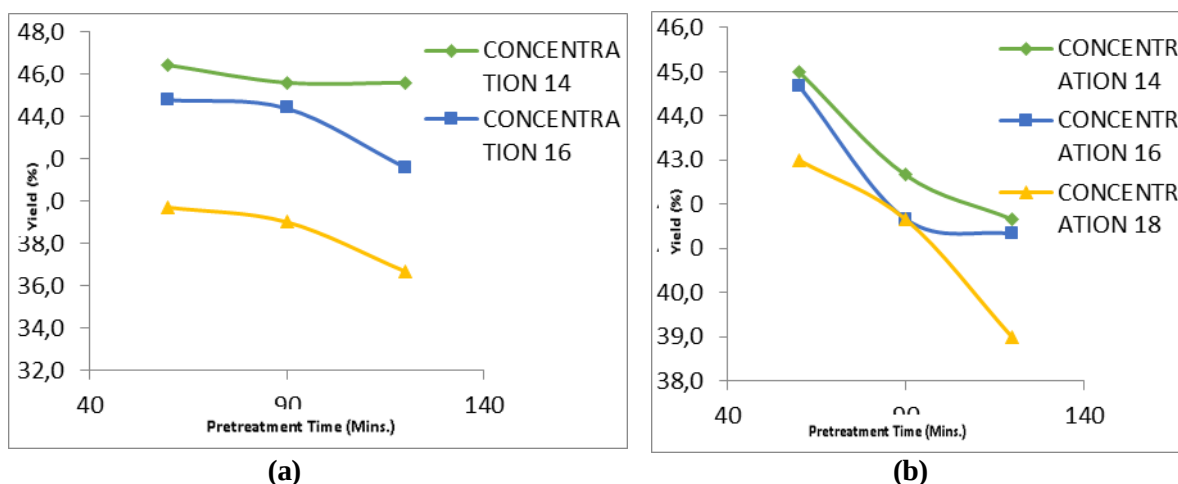


Fig. 1: Effect of Time on Yield of (a)Whole Stalk and (b) Rind Fraction

Effect of Liquor Concentration on Cellulose Yield

An increase in alkali charge resulted in a decrease in the amount of cellulose produced during pretreatment at constant temperature and time. This pattern is seen in both the rind fractions and the whole stalk (Figs. 2a and 2b). This might be the result of an increased chemical charge that sufficiently attacked the biomass's lignin and carbohydrate contents. The graphs

demonstrate that an increase in alkali charge led to a corresponding decrease in yields obtained, independent of the pretreatment time. These results are in line with numerous findings in the literature [20] [21] [22] [23], which state that peeling, chain cleavage, and the dissolution of amorphous regions of the carbohydrates as concentration increases, reduce pulp yield.

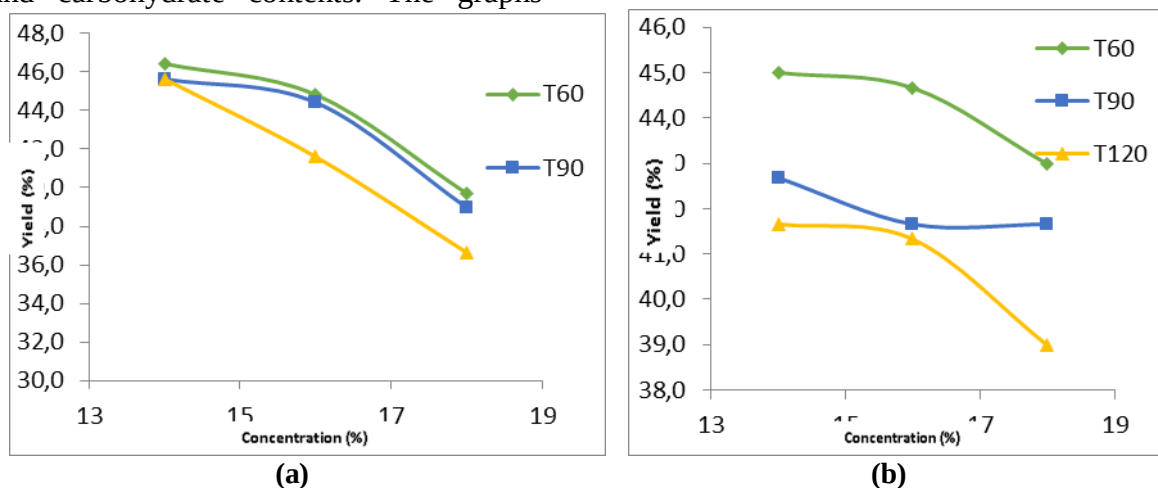


Fig. 2: Effect of Concentration on (a)Whole Stalk Yield (b) Rind fraction Yield

Effect of Time and Liquor concentration on RKL

Figs. 3a and 3b illustrate this effect. All liquor concentrations showed a corresponding decrease in RKL with an increasing time, with a linear relationship observed with 14% alkali charge. This indicates that a lower kappa number

results from more lignin being removed from the starting biomass as the pretreatment time is extended. On the other hand, the overall pattern agrees with findings from Shahzad [24] and Montagna et al. [25]. Each of them observed a drop in RKL with an increase in alkali charge or cooking time.

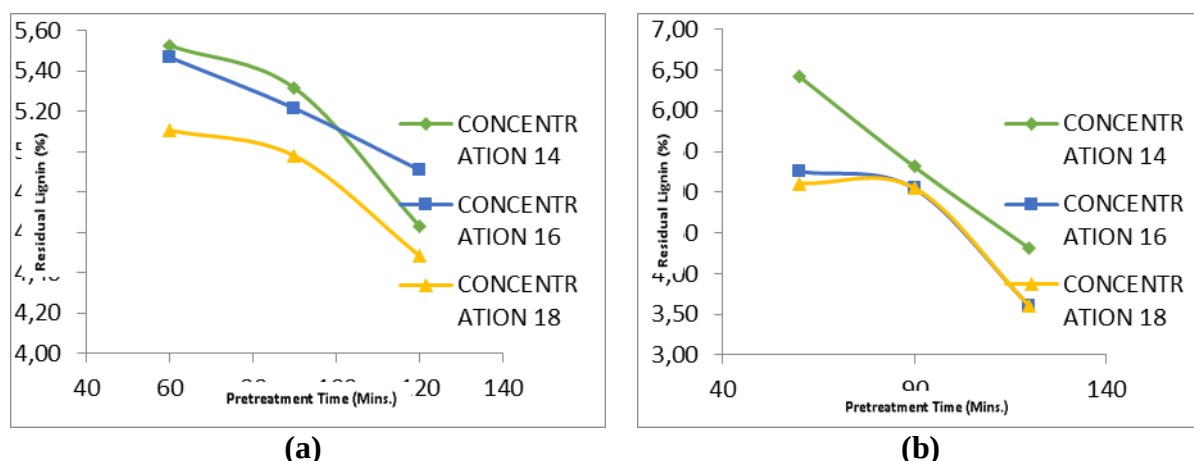


Fig. 3: Effect of Time on RKL on (a) Whole Stalk and (b) Rind fraction

According to Shahzad [24], longer cooking times can sometimes result in the cooking liquor's alkali being used up more completely, which causes the lignin to precipitate. When the lignin condenses, it stops being removed from the biomass further, which raises the kappa number and, in turn, the RKL reading. The absence of this phenomenon was noted with this pretreatment technique, indicating that NaOH is an adequate pretreatment for maize stalk fractions.

4 CONCLUSION

The longer the pretreatment time, the better the deconstruction. The RKL of the biomass decreases in proportion to increases in time and alkali charge. The cellulose yield is adversely affected by extended pretreatment times because the biomass's carbohydrate content begins to dissolve. Regardless of pulping duration, a higher alkali charge causes a lower cellulose yield. The amount of residual active alkali in the black liquor increases in tandem with an increase in alkali charge. The RKL and cellulose yield of the whole stalk and the rind fraction did not differ statistically significantly. Additionally, the rind makes better use of the liquor chemicals than the whole stalk, which required more pulping liquor due to their bulk. When applied commercially, this could result in some considerable savings.

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INVESTIGATION OF CULTIVATION CONDITIONS AND HARVESTING METHODS OF MICROALGAE SPECIES TO BE USED AS BIOMASS

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ABSTRACT

Microalgae, as a third-generation renewable energy source, has attracted great attention in recent years. Although microalgae are a promising option in the industrial production of food, fuel, medicine, and valuable biological-based products; it is important to consider parameters such as temperature, light, pH, mixing, CO₂ required for optimization of growing conditions and microalgae cultivation. The interaction between the complexity of the system structure and the usability of the system should be well evaluated in microalgae production where different growing systems, open and closed, are used. In this review article, growing environment used in microalgae cultivation, microalgae production systems, physicochemical parameters affecting microalgal growth and specific parameters required for optimum growth of various microalgae species are summarized. This article reviews these aspects in microalgae cultivation and includes further studies and discussion on improving the microalgae biomass to be obtained. Furthermore, the advantages and disadvantages of microalgae cultivation systems are examined and compared in detail. It is concluded that technology integration is inevitable for efficient extraction of microalgae biomass.

Keywords: microalgae, cultivation, biomass, biomass harvesting.

1. INTRODUCTION

Industrial-scale microalgae production with the biorefinery concept aims to reduce operating costs by obtaining valuable by-products in addition to biomass. The evolution of the microalgae market into different branches triggers the growth of the market share, which is projected to reach USD 3.08 billion in 2030. Although open ponds continue to dominate the global market due to low investment, operating and energy costs, developments in high quality industries such as pharmaceuticals, food, nutraceuticals and

cosmetics are expected to increase the use of photobioreactors [1]

The biorefinery concept, which enables the efficient utilization of microalgal biomass, is the process of obtaining multiple valuable bioproducts from one biomass. Microalgae are mostly considered as feedstock for biofuel production. However, besides biofuels, microalgae also possess a variety of valuable materials that can be processed or processed into high-value products [2]. Emissions from fossil fuels are largely responsible for the increase in global warming. Biorefinery concept is recognized as a promising

solution to reduce greenhouse gas emissions. Significant benefits, including bioeconomy, have been identified in microalgae-based biorefineries. The biorefinery concept also allows exploiting the full potential of microalgae and minimizes biomass waste accumulation. The main bottleneck of the microalgae biorefinery is the separation of different fractions into a single desired fraction. However, this can be overcome by process development in a cost-effective way using microalgae as promising candidates to produce high-value compounds in addition to biofuels [3]. Microalgae have advantages in terms of high growth rate, carbon reduction efficiency and elimination of food industry competition for biofuel production. Various microalgae are rich in different valuable compounds. In general, the important biofuel substrates derived from microalgae are lipids and carbohydrates. Other important microalgal fractions such as proteins, minerals and some alcohols are also used to produce chemicals, feeds or value-added products. By-products obtained during biofuel formation (e.g. glycerol from biodiesel production) can also be considered as value-added products. Residues from thermochemical conversion and other low-value carbohydrate and protein residues are utilized for combined heat and power (CHP) production. Apart from biofuels, promising by-products should be recovered from microalgal biomass and utilized through techno-economic designs that alleviate the pressure caused by high-cost processing [4].

In addition, microalgae can undergo genetic modifications to trigger the production of various compounds, including unnatural products. Microalgae such as *Chlorella*, *Dunaliella salina*, *Phaeodactylum*, *Chlamydomonas* and *Synechocystis* sp. have recently been widely used for genetic engineering due to the availability of a fully sequenced database. Several technological developments are available for microalgal cultivation, harvesting and extraction processes. Microalgae can be used to produce various products such as biofuels, food supplements, cosmetics, feed for aquaculture hatcheries, medicines and other valuable products [5]. Microalgae can be grown in open systems and photobioreactors in most applications. Open systems are difficult to control, which creates problems in large-scale production. Photobioreactors can overcome these problems with the sterile environment they provide. Light

source and light intensity are critical factors affecting the growth of microalgae. For efficient and cost-effective photo-bioreactor systems, artificial light source is used in photobioreactors. The division and photosynthesis kinetics of microalgae vary depending on many factors such as temperature, pH, light intensity and mixing. Experimental studies show that optimum growth conditions result in maximum biomass production. The optimization of the system and the presence of all the necessary nutrients for the microorganism such as nitrogen, oxygen, CO₂, etc. in the environment supports the activity of the cell biomass, the cellular metabolism pattern and the change in cell composition as well as the efficiency of photosynthesis [6]. *Chlorella Vulgaris* is an important source of biological products with high commercial value. In the studies conducted, maximum biomass production was obtained faster in red and white light than in blue, green and violet light at a light intensity of 100 $\mu\text{mol photons/m}^2\text{s}$; maximum biomass production at 30°C and maximum lipid production at 25°C; faster growth was observed at neutral pH (7.5-8.0) than in acidic (pH 3.0-6.2) and alkaline (pH 8.3-9.0) conditions. The maximum salt concentration to which *C. vulgaris* can adapt varies between 10 and 20 ppt. Aeration and mixing prevents sedimentation of microalgae, homogenizes the culture medium (e.g. temperature) and also facilitates gas exchange between the culture and air. Mixing with 0.5 vvm air promoted high biomass productivity in *Chlorella vulgaris* [7].

Spirulina platensis and other *Spirulina* species are frequently used in the food industry. Lighting, temperature, inoculation volume, mixing speed, pH, water quality and overall micronutrient enrichment are some of the environmental parameters that affect *Spirulina* production. Ideal temperatures for *Spirulina* range from 20 to 35 °C, with maximum biomass production observed at 30 °C. Low light intensity caused a decrease in growth in *Spirulina* species. In two different studies, it was observed that maximum biomass was produced at 6000 lux red light and 9000 lux white light, but different photoperiods such as 24 hours and 18 hours of light were also effective in growth. *Spirulina* species growing in alkaline waters had the highest dry weight, maximum protein production and highest antioxidant activity at the ideal pH range of 8.5 - 9.5. For *Spirulina*,

gentle mixing is an important point as the cell wall is more easily degradable than other microalgae species and the optimum level is 0.5 vvm [8].

Biomass productivity increased when *Nannochloropsis oculata* was illuminated, with the highest biomass rates recorded at 50, 160 and 300 $\mu\text{mol photons/m}^2\text{s}$. The optimum temperature for *Nannochloropsis oculata* was reported to be 20-25°C. The optimum pH range for *N. oculata* is 7.7 to 8.4. In *Nannochloropsis*, salinity of 20 ppt has been reported to favor biomass production; it is likely that cells are stressed at high salt concentrations. In addition, since *Nannochloropsis Oculata* is a microalgae species prone to biofilm formation, it is important to ensure continuous mixing and homogenization. The recommended mixing rates for *Nannochloropsis oculata* are between 0.5 and 0.75 vvm, and higher mixing speeds may cause cell deformation [9]. In scale-up studies, when the desired biomass concentration (g/L) is reached, instead of harvesting the entire culture volume, only part of the culture volume is harvested and the harvested volume is replaced with either fresh or recycled media. The bioreactor thus serves as inoculum for the next culture cycle. The proportion of culture harvested and the time interval between harvests is based on the growth rate (doubling time) and the lowest to highest cell density one wants to work with, in order to always keep the culture at optimal biomass concentration and exponential growth phase and thus maximize productivity [10].

2. DIMENSIONING

2.1 OPTIMIZATION

Optimization of photobioreactors focuses on increasing the efficiency, productivity and sustainability of processes involving photosynthetic microorganisms. The main reasons why photobioreactor optimization is important are as follows.

1. Increased Biomass Production: Optimizing parameters such as light intensity, carbon dioxide concentration and nutrient supply can significantly increase biomass yields. This is essential for applications in biofuel production, pharmaceuticals and food supplements.

2. Improved Metabolite Production: Many valuable compounds such as pigments, fatty acids and bioactive molecules are produced by photosynthetic organisms. Optimizing the

conditions inside the photobioreactor can maximize the production of these metabolites.

3. Energy Efficiency: Efficient use of light and other resources reduces energy consumption. By optimizing light distribution and minimizing energy losses, photobioreactors can become more cost-effective and environmentally friendly.

4. Cost Reduction: Improved growth rates and product yields lead to lower operating costs. This is especially important for commercial applications where profitability is a key concern.

5. Space Utilization: Optimized photobioreactors can deliver higher productivity per unit area, making them more suitable for large-scale production in limited spaces such as urban environments or industrial settings.

6. Environmental Impact: Improved efficiency in photobioreactors can reduce the environmental footprint of production processes. For example, optimized CO₂ use can help reduce greenhouse gas emissions and efficient nutrient use can minimize the risk of eutrophication.

7. Scalability: Optimization at small scales can inform the design and operation of larger, industrial-scale photobioreactors. This helps the smooth transition from laboratory to commercial production.

8. Process Stability and Consistency: Optimized systems are more likely to maintain stable and consistent production rates over time, which is crucial for the reliability of industrial processes.

9. Resource Management: Effective optimization ensures efficient use of resources such as water, nutrients and light, which is vital for sustainable operation.

10. Innovation and Research: Continuous optimization efforts lead to technological advances and innovations in photobioreactor design and operation, driving the field forward and opening new applications and markets.

In general, optimization of photobioreactors is essential to maximize the potential of photosynthetic microorganisms in various biotechnological applications, making the processes more efficient, cost-effective and environmentally sustainable [10]

2.2 CONTROLLED SCALE MAGNIFICATION

Scale-up in bioreactor systems aims to transfer laboratory-scale process performance to an industrial-scale system with higher total volume and capacity, and to determine reactor

design criteria accordingly. Although various types of photobioreactors have been developed to date, including bubble column, air-lift, stirred tank, tubular or other reactors, there is no standard design of the most suitable photobioreactor for the scale-up approach. Scale-up from laboratory scale to a commercial unit has bottlenecks due to difficulties in assessing various factors affecting the scale-up process during cultivation [11].

Most large-scale phototrophic cultivation yields lower than expected in the laboratory. Phototrophic microorganism growth mainly requires light, inorganic carbon dioxide, water and inorganic nutrients under favorable growth conditions related to pH and temperature. These are all closely interrelated and make the design of a photobioreactor more complex. Optimization of various factors such as light intensity, light-dark cycles, light distribution, hydrodynamics and environment (nutrients, pH and temperature) is necessary for the scalability of photobioreactors. Light availability for each cell can often be the most important factor for scale-up in photobioreactors. Photobioreactors must take into account light-specific factors in addition to the classical scale-up issues that also exist in heterotrophic reactor systems. In the cultivation of phototrophic microorganisms, scale-up challenges are often related to the availability of light in the reactor and production rates depend mainly on this [12].

2.3 PROCESS MODELLING

Microalgae are primary producers in the aquatic environment. Thanks to the pigments in their structure, they convert carbon dioxide and water into carbohydrates under the influence of light, thus increasing the nutrient value and dissolved oxygen ratio in the water environment. As a result, they form the first link of the food chain by providing their own development. The production of microalgae is limited by environmental factors. These are light, temperature and nutrients. When these limiting factors are improved, the production level increases. As a natural consequence of the increase in production exceeding a certain level, the environmental balance is disturbed and eutrophication occurs. In a eutrophic

environment, due to the excess of nutrient input (especially nitrogenous compounds and compounds that increase the growth of algae such as phosphate), turbidity increases with microalgae and bacterial activities and light is prevented from passing to the bottom of the water. Therefore, these factors are taken into account when designing systems for microalgae production [6].

In microalgae production, many small and large-scale systems are used, ranging from fully controlled tubular bioreactors to flat, dish reactors, bag systems, open ponds and greenhouse ponds. The biology of microalgae, land cost, labor, energy, water, nutrients, climate if production is open system, and the purpose of production are among the factors to be considered in culture selection. In addition, process modeling is also created based on all these scenarios. Various large-scale culture systems need to be compared in terms of their basic characteristics such as light utilization efficiency, ability to control temperature, hydrodynamic stress on microalgae, ability to provide unialgal and/or axenic culture and easy transition from laboratory-scale production to large-scale production. The type of microalgae to be produced and the purpose of production are the most important criteria for system selection. Factors such as climatic conditions, land and cost of water are also important in the selection of the system. Light, temperature and water quality are the main limiting factors in microalgae production. These factors also constitute an important part of the production cost [11].

It has been reported that the appropriate conditions required by the species to be produced in a microalgae culture under laboratory conditions should be provided. These conditions can be listed as follows;

Culture Stocks: Different volumes of erlenmeyers can be used according to the purpose. Stock cultures can be used in 200-250 ml flasks, 2 liter flasks can be used for medium cultures and photobioreactor system can be used for more intensive production.

- **Light** Light is the most important factor affecting culture density. LED lamps can be used for lighting. It is important to illuminate the culture environment for 12-18 hours with an average illumination of 500-1000 lux.

- **Temperature** Depending on the microalgae species, the appropriate ambient temperature should be set in the microalgae culture medium. Below the optimum temperature values suitable for the microalgae species, culture growth slows down, and if it exceeds it, it becomes difficult to control the density balance of the culture. For this purpose, the culture environment should be kept at a constant and desired temperature. It is useful to use a thermostat heating system for this purpose.

- **Aeration/Mixing:** It is often observed that microalgae cells settle to the bottom in culture vessels. To prevent this, the culture needs to be mixed. The environment is ventilated for mixing in the culture environment. In the laboratory environment, air is supplied to the culture vessels with the help of a compressor. In the photobioreactor, air should be supplied to the system with the help of a blower and diffuser system. The most important issue to be considered here is to filter the air supplied to the environment. In addition to providing the air mixture, it also provides inorganic carbon, which is an important element in the photosynthesis of cells, to the environment. Ventilation also plays a role in the homogeneous distribution of temperature and regulation of pH. It has been reported that it is beneficial to provide 1% CO₂ (carbon dioxide) to the environment with air. CO₂ accelerates the development of microalgae. The development time of the culture at this stage can vary between 4-7 days. Strong ventilation is recommended for the circulation of the culture environment. Incoming air should be filtered to minimize any risk of contamination from outside air [13].

As heterogeneity of light intensity and availability is a critical factor in microalgae production processes, the transfer of microalgae processes from the laboratory to largescale cultivation requires careful planning. Besides the important light supply, optimization of state variables such as pH, temperature, CO₂ supply and O₂ release, inoculum concentration and nutrient composition are also required before any scale-up is considered. Scaling factors should be considered from the beginning of the production system and equipment should be designed accordingly. Laboratory scale

experiments that take these state variables into account are essential for successful scale-up [14].

Laboratory-scale photobioreactors are usually made of transparent material, typically polyvinyl chloride or materials such as plexiglass and glass. If the lighting is internal, the photobioreactor can be made of non-transparent material due to the direct contact of the lamps with the cultivation. There are also different reactor sizes reported depending on which experiments are being performed. Common working volumes range from 1 to 30 L. In these systems, gas flow settings are individually adjustable, while temperature is controlled by transparent double jackets around the photobioreactor or a heat exchanger is used. For process control, temperature and pH measurements are made with sterilizable electrodes [15].

3. CONCLUSION

The photobioreactor scale-up procedure is the most challenging part of the implementation of biomass production technology on an industrial scale. It is clear that the scale-up mainly depends on the type and geometry of the reactor. In addition, the method of operation, such as batch or continuous, also seems to influence the scale-up. The difficulty of optimizing the process of generating a sufficient number of inoculum for largevolume open ponds or photobioreactors is one of the main challenges to be solved. The development of an automated station to inoculate a photobioreactor with inoculum has the potential to overcome this problem. However, it is clear that controlling the temperature and pH monitoring system, the mixing system and the LED lighting with systems such as Programmable logic controllers (PLCs) increases efficiency when scaling up bioprocesses and saves time by reducing labor, enabling quick detection and action on potential problems.

Biomass growth and secondary metabolite accumulation in microalgae production depends on various process parameters such as light intensity profile, mixing profile, aeration rate, nitrogen and carbon dioxide availability and temperature. It is seen that these factors

should be carefully taken into account and meticulously applied in the production model and photobioreactor design. Optimization of these parameters and the physiological state of the culture is necessary to achieve optimum results.

Modeling and optimization are valuable tools for scaling up and predicting photobioreactor behaviors, it has been clearly established in previous studies that they reduce the need for extensive laboratory experiments and save labor and resources. Design of experiments studies have emerged as a promising approach in this regard, exploring the relationships between explanatory variables and one or more response variables.

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A ROADMAP OF A TECHNO-ECONOMIC ANALYSIS AND BETTER USAGE OF BIOMASS FOR TECHNOLOGY INVESTORS ON BIOMASS POWER INDUSTRY

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Abstract

This paper presents the conceptual model of a roadmap of techno-economic analysis and applicability to the sustainable economic model for the biomass power producing companies through the economic integration of related data from the literature reviewing. The objective of this paper is to discuss sustainability and techno-economic criteria to integrate into sustainable business models. Also the main goal of this study is to identify and assess the relationship between techno-economic analysis and sustainable development of biomass power plants. Cost data needed by engineering practitioners to conduct enterprise-level financial analyses of biomass are presented in the road map. As a result, the paper offers some new dimensions considering new strategies for sustainable biomass energy power companies.

Keywords: Biomass, techno economic analysis, Industrial biotechnology, supply chains, business plans Guide, Format, Figures, Tables

1 INTRODUCTION

Energy is vital for the internal and external security of a country and energy issues are at the core of social, environmental and economic security challenges. Biomass is the most renewable energy option as the fourth largest energy source after coal, oil and natural gas (Executive summary, SLU report, 2009).

Biomass is a plant material -renewable energy source -from living or recently living plant, wood and agricultural crop residues in fields, forestry residues, animal waste , algae, energy crops and includes also garden pruning residues in urban area, and municipal solid waste to produce electricity with steam (Aldawoud etal, 2022).

It is a renewable fuel that doesn't pollute the environment (i.e. clean burning), abundant, renewable and relatively low cost raw materials for the energy producing establishments. Energy from biomass-fired power plants is generally considered "carbon neutral" in contrast to coal-fired power production (Lewandowski, ed., 2018).

Business Planners define better use of biomass for energy as: production, transport, conversion and use of biomass for energy in such a way that it contributes more to the policy aims of governments.

The Biomass Energy Power Plant (BEPP) produces electricity by firing biomass, including agricultural residues/wastes, forestry residues/wastes, and solid waste. Biomass is burned in a boiler to produce highpressure steam. This steam flows over the turbine blades. The rotation of the turbine drives the generator, which produces electricity (Gebreegziabher et al., 2014). Although a very well-known technology, the biggest disadvantage is the low efficiency levels of this kind of establishments on average.

The objective of this study firstly, is to give a compilation from the literature to promote the sustainable production of biomass for local and national power plants /Industrial biotechnology, and then to search the possibilities of international supply chain efforts for crop and other forest residues....

2 ANALYSIS AND FINDINGS

It is important to emphasize that preparing a business plan as a first step for biomass power plant to produce energy (electricity or heat), is necessary for the best current understanding of the technology and translate it into economic value. This is the role of techno-economic analysis. Firstly there must be availability of biomass resources and also industrial

biotechnologies, then to enhance sustainable production of biomass is vital to create a business model. In power generation from agricultural biomass, it is necessary to pretreat the biomass in order to transport the biomass from agricultural fields to the power station and to store it agricultural biomass (Bahadıroğlu, et al., 2022).

Someone may notice that the Biomass Power industry has grown slowly in the World over the five years to 2019 (Biomass Power in the US - Industry Market Research Report). Some of the restraining or the negative factors for biomass recycling including supply chain disruptions (Aydın, etall, 2007), some government regulations, changing consumer preference are affecting the biomass power industry growth in the near future. Also economic uncertainties, market fluctuations, and geopolitical factors can impact investor confidence and influence investment decisions. In order to expand small businesses based on renewable energy sources and to encourage small-scale investments, some rules and regulations are necessary for entrepreneurs in dealing with BEPP.

The industrial biotechnology is a thriving sector of the economy of some countries. In the U.S., the industry generates power from more than 122 registered and licensed biomass power plants. The industry is responsible for the employment of over 1,397 people (Biomass Power Plant Business Plan [Sample Template] - Profitable Venture).

The biomass power industry (or industrial biotechnology) generates power from wood and wood waste, generates biomass-fueled power, generates power from liquid biofuel, and generates power from waste.

In this study, a sustainable roadmap of a techno-economic analysis for better use of biomass for technology investors on biomass power industry is summarized. (**author's not:** therefore legal sustainability criteria must be defined first by the advisory commission or decision makers of any related countries) .

To be able to develop a project, resource assessments can be used as first screening tool for identifying suitable areas and to get insight into new, not used to full advantage and opportunities yet. Availability of biomass

resources is vital for power industry, because there is a growing demand for biomass production with local markets and export markets, both coming from biomass importing and producing countries.

This highlights the importance of creating affordable, sustainable biomass resources over time. In the agriculture sector EU countries the sustainability criteria has a remarkable influence in the future wood available potential, +/- 40% by 2050 (Bosch ., et al, 2013); (Dam J., and Junginger M., 2011); (A.Nadiri, et al., 2024).

Obviously in the implementation phase it is necessary to have supply chain institutions for business models to run the biomass energy business in a sustainable manner (Yavuz, and Tümenbatur, 2022). The important point here is to create a supply chain for restoring and delivering crops - organic matter- to the plant at a cost effective price. For the feedstock selection criteria and sustainability requirements, how much biomass is realistically available on the ground must be determined. Policy makers can apply flexible approach in defining bioenergy targets for a country (volume and time) to adjust expectations for real outcomes, if the country largely rely on imported biomass. Obviously for the region's rural development and land use, how large amounts of sustainable and affordable biomass can be realized to meet future demand must be determined.

Business models and renewable energy supply chain systems are complex systems that consist of several things and together cause uncertainty including:

- (a) Yield and purchase price of biomass raw materials; Providing of original data for example to assess labour time (hour/year/ha) for pruning in permanent crops .(The manual removal of the lower branches of crop trees, to a predetermined height- is also important factor for business plans of biomass energy).
- (b) Efficiency of conversion technology for raw material biomass to bio electricity and / or biofuel.
- (c) Biomass power plants capacity that impacts electric power output;
- (d) Selling prices and demand for electricity and biofuels;
- (f) Government incentives for renewable energy products.

Companies in this industry operate “electricity-generating facilities” using biomass (e.g. agricultural byproducts) by means of efficient business management criterias (Figure 1).

Then the industry’s expansion may depends on state-propelled in some countries, using renewable energy tax credits that encourage the use of biomass power. Tax credits can make biomass-power projects more affordable for biomass-power generation enterprises to execute. Then business plans can be implemented properly and also promote government policies / plans. In other terms, contacting stakeholders to the greatest extent, provide preferential treatment for the public and some energy industries in terms of commodities and taxes (Zhou, et al, 2022).

If the need for a sustainable and resilient energy future arises, the energy / power industry in any country should undergo significant transformations driven by technological advancements, and environmental concerns (Şarman A.S.2023).

Therefore, some regulations may require local utilities to generate electricity from renewable biomass power as a percentage of their total energy portfolio.

Increased campaigning for green technology also influence industry performance by sparking interest in technologies that replace pollutant-generating energy sources, such as coal and gas. These factors encourage aspiring entrepreneurs and investors to venture into starting a biomass power plant business.

It is possible to start on a small scale producing and supplying power at a community level or to start on a large scale with distribution networks spread across key cities all around any country. As a key staff in this business sector, Biomass Power Plant Engineers/Operators are responsible for operating machines used in generating biomass-fueled power, from wood, liquid biofuel, and waste. Also, Biomass Power Plant Managers are responsible for the purchase of raw materials such as wood and agricultural products, solid waste, landfill waste, and wood chips, bark, and sawdust for biomass plants. Any power plant Co., may transfer the management and/or day-to-day execution of an entire business supply chain function to a third-party service provider, eg., outsourcing.

Managers in biomass power plant maintains a logbook of their driving activities to ensure compliance with local municipal regulations. Company’s transport and logistics manager or supply chain manager plans their route according to a distribution schedule, keeps a record of vehicle inspections and make sure the truck is equipped with safety equipment.

Some projects worked on gaining experience in certification; others focused on the valorisation of residues and waste streams, yet others through the use of degraded land for biomass production, or by working with smallholders (Pavanan, et al., 2013).

It is important to select a certification scheme at the start of a project, even at the design phase, to understand what type of data management system is needed to meet requirements, and to align this with day-to-day business... Certification and policy frameworks are together instrumental to safeguard sustainability impacts of biomass and bioenergy production (netherlands-sustainable-biomass.pdf (etipbioenergy.eu).

If the theoretical biomass potential of the crop residue in any country available, is calculated in tons, for further use in bioenergy facility planning, some technical assumptions should be considered about kWh of electric energy amounts along with kWh thermal power to be generated per ton of plant residue.. ([Waste to Energy \(WTE\) \(uwaterloo.ca\)](https://www.uwaterloo.ca/wte/) (Tanyi & Adaramola, 2023).

The agricultural biomass potential for any country can be estimated using some methods and several algorithms, depending on the environmental and climate data covering related years. The total amounts of biomass residues obtained from arable field crops and horticultural crops in Turkey were estimated as 54,036 kilotonne and 4,986 kilotonne dry mass respectively (Avcioğlu, et al, 2011).

Important step for business plan is to collect price data to be used for assessing price levels in plan in short: straw , and pruning costs, transport costs, to assess labour time (hour/year/ha) for pruning in permanent crops (ie: The manual removal of the lower branches of crop trees, to a predetermined height).

After involving the general public during the planning phase, decision-makers for the business must consider logistics costs, estimated using country-specific transportation costs per km/ton in their supply chains, including up- and off-loading cost of feedstock.

Managers must create a supply chain for restoring and delivering crops, - organic matter- to the plant at a cost effective price.

These cost levels are then multiplied with the average number of kilometres the biomass needs to be transported within a 30, 100 and 200 km circle around the plant location taking account of the average biomass availability per type per km² (J.W.K.Wahono, et al, 2020).

In some countries, potential crop residues contributes roughly 96% while municipal solid waste contributes the remaining 4% of the total bioenergy potential per year (Tanyi & Adaramola, 2023). It is important to select a certification scheme at the start of a project, even at the design phase, to understand what type of data management system is needed to meet requirements, and to align this with day-to-day business... Certification and policy frameworks are together instrumental to safeguard sustainability impacts of biomass and bioenergy production (netherlands-sustainable-biomass.pdf (etipbioenergy.eu)).

The bioeconomy in any country, can grow if entrepreneurs take the initiative to develop a validated business model for sustainable biomass power plants (Wahono, 2020).

Some recommendations also useful to the success of any biomass energy roadmap. It is necessary to work closely with a biomass equipment manufacturer or vendor to collaborate on building design and equipment requirements. Decision makers also coordinate building scheduling with the equipment delivery. For example, it is easier to deliver and install the equipment if a crane can access the installation site. After identifying a crop delivery route, ensure that trucks can reach the storage area easily and turn around, if necessary.

It is important to select a certification scheme at the start of a project, even at the design phase, to understand what type of data management system is needed to meet requirements, and to

align this with day-to-day business. Self-assessment tools are beneficial for projects during project development and implementation to enhance continuous improvement of better practices. Certification systems should therefore enhance their use in their standards. Integrating sustainability requirements in policy frameworks and law allows governments to have a mechanism in hand to regulate and enhance sustainability in economically viable chains. These policy frameworks should be carefully designed to avoid a tendency towards the use of recognized certification systems that guarantee only a lower level of assurance.

3 CONCLUSIONS

In this paper, transportation activities of a supply chain for restoring and delivering crops, - organic matter- to the plant at a cost effective price is analysed economically giving practical experiences in improving the sustainability of biomass chains.

Since biomass power plant investment share of any country is important, these evidences show that countries can get adequate benefit from crop residue biomass potential of their natural geographic advantage on it. Biomass electricity producers and logistics companies must develop, adopt and implement emerging Information and Communication Technologies (ICT) and their applications sufficiently.

In the frame of these references, five functional areas related with transportation activities can be determined to develop and implement emerging technologies. These areas are advanced relation management with field crop and garden pruning suppliers in urban area, crop residue fleet tracking and management, advanced vehicle routing, scheduling to allocate biomass resources to loads and inbound good movements tracking among facilities. For each of these areas, several ICT applications must be used in production electricity from biomass and logistics systems of power plants..

It is important to emphasize that preparing a business plan first step for biomass power plant to produce energy (electricity or heat), is necessary for the best current understanding of a

technology and translate it into economic value. This is the role of techno-economic analysis. Obviously in the implementation phase it is necessary to have supply chain institutions for business models to run the biomass energy business in a sustainable manner (Yavuz, and Tümenbatur, 2022). The important point here is to create a supply chain for restoring and delivering crops, - organic matter- to the plant at a cost effective price.

Companies in this industry must operate “electricity-generating facilities” using biomass (e.g. agricultural byproducts) by means of efficient business management criterias.

For the road map of biomass there are certain factors that determine the feasibility of a business case : enabling policy environment, presence of sustainable supply (competitiveness feedstock, availability supply), efficiency in logistics , productivity and efficiency in conversion, presence of markets (price, unexplored markets, flexibility to switch between markets) , strong project partnership and management and capital (investment needs, opportunities for funding). (Figure 1).

Then the industry’s expansion may depends on state-propelled in some countries, using renewable energy tax credits that encourage the use of biomass power. Tax credits can make biomass-power projects more affordable for biomass-power generation enterprises to execute. Afterward, business plans can be implemented properly and also promote government policies / plans.

In other terms, contacting stakeholders to the greatest extent, provide preferential treatment for the public and some energy industries in terms of commodities and taxes (Zhou, et al, 2022). For business plans it is important which regions planners should focus on agricultural waste to be collected in any country . This roadmap (Figure 2) can also contribute to all countries 's renewable energy policies and achieve its zeroemission target.

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THE EUROPEAN RENEWABLE ENERGY SECTOR: INNOVATIONS, CHALLENGES, AND FUTURE PROSPECTS

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Abstract

The European energy sector has seen a profound transformation in recent years. Driven by the need to fight the ever increasing challenges of climate change, the European Union has set the world's most ambitious goals for renewable energy adoption and greenhouse gas emission reduction. These goals include achieving climate neutrality by 2050, with intermediate targets to cut emissions by at least 55% by 2030 compared to 1990 levels. This shift is not only about reducing carbon footprints but also about enhancing energy security amidst rising geopolitical tensions in the region, promoting technological innovation, and creating sustainable economic growth. The implementation of policies such as the European Green Deal and investments in wind, solar, and other renewable energy sources are central to this ambitious strategy. As a result, the region has become a global leader in renewable energy capacity, integrating diverse renewable technologies and building a more resilient and sustainable energy infrastructure.

Despite the extraordinary progress, numerous challenges still remain. The long-touted "just transition" towards green energy has faced obstacles such as rising energy prices and the phenomenon of "greenlash," where public resistance grows against renewable initiatives due to economic pressures. The sharp rise in energy prices seen across the continent has left many wondering if fossil fuels are even replaceable. But despite all the challenges, the European Union seems determined to march ahead towards its ambitious goals. Green energy investments have been on a steady rise, as has the desire to phase out polluting fuels. Many countries across the continent have managed to "green" their energy sectors in recent years, and renewable energy has become more affordable than ever before, even managing to sideline coal, the most polluting fossil fuel of all, in some European countries.

MODELING AND OPTIMIZATION OF BIODIESEL PRODUCTION USING DICTYOTA DICHOTOMA SYNTHESIZED MAGNESIUM OXIDE NANO-CATALYST

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Abstract

Hot aqueous extract of the Egyptian plentiful brown seaweed *Dictyota dichotoma* has been used for the phyco-synthesis of magnesium oxide nanoparticles (MgONPs). The Raman, X-ray photoelectron spectroscopy (XPS), and X-Ray diffraction (XRD) assured the green fabrication of MgONPs. The dynamic light scattering (DLS) depicted average particles size, poly dispersive index (PDI), and zeta potential of 195.6 nm, 0.632, and -42.7 mV, proving its stability. The BET analysis proved a specific surface area of 0.9550 m²/g, pore volume and diameter of approximately 0.001786 cm³/g and 7.47849 nm, respectively. The Fourier transform infrared (FTIR) spectroscopy recognized the probable functional groups convoluted in the one-pot synthesis of MgONPs including reducing, capping and stabilization. The field emission scanning electron microscope (FESEM) and high-resolution transmission electron microscope (HRTEM) revealed monodispersed spherical shaped MgONPs with average particle size of 2.4±0.6 nm. response surface methodology (RSM), Artificial neural network (ANN), and simulated annealing algorithm (SAA) based on a face center composite design (FCCD) of experiments were employed to model and optimize the transesterification of waste cooking oil (WCO) into biodiesel using the phyco-synthesized MgONPs. Those predicted optimum operating conditions of 3.97% MgO concentration, 3 h, 55.51°C, 302.91 rpm, and 3:1 methanol:oil molar ratio, with a biodiesel yield and conversion percentage of 94 and 93%, respectively. The qualification of the produced biodiesel matched well with the international standards.

Keywords: *Dictyota dichotoma*, Phyco-synthesis, Statistical and computational optimization, Waste cooking oil transesterification, Biodiesel

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NATURAL RADIOACTIVITY LEVEL AND RADIOECOLOGICAL RISKS IN SURFACE SEDIMENTS FROM COASTAL ECOSYSTEMS OF THE REPUBLIC OF CONGO

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Abstract

This study presents the level of natural radionuclide concentrations in surface sediments and the potential human and biota radiological hazards in the coastal ecosystems of the Republic of Congo. The sediment samples from lagoons, rivers and marshes sites were collected and analyzed by high-resolution gamma spectrometry of the Centre National de l'Energie, des Sciences et des Techniques Nucléaires (CNESTEN) of Morocco for determination of activities of long-lived gamma-emitting radionuclides of Th-234(U-238), Bi-214(Ra-226), Bi-212(Th-228), Ac-228(Ra-228), Pb-210 and K-40. The radiological risk to human health from gamma radiation emitted by these radionuclides was assessed by calculating five radiological risk parameters, and the ERICA tool was also used to assess the risk to marine biota.

Keywords: Natural radioactivity, Surface sediment, Radioécologique hazard, ERICA tool, Coastal ecosystem, Republic of Congo.

1 INTRODUCTION

The primordial radioactive elements (U-238, U-235, Th-232, K-40, etc.) have been present in the earth's crust since the formation of the earth. Their transfer, distribution and reworking in environmental compartments (air, water, soils, sediments, biota) are linked to the natural processes such as weathering of outcropping rocks, leaching and dissolution of rocks by groundwater, and volcanic activities [1], and the anthropogenic activities such as mining (coal mining, nuclear fuel cycle, oil exploitation), agriculture, port activities, fishing, etc., which effectively contribute to the degradation of environmental quality [2-4].

The Republic of Congo's coast basin situated on the South Atlantic ocean (Figure1), between Gabon's SW and Angola's NE is rich in mineral resources such as oil, phosphate and potash mines, and port activities that have led to the

urban development of the region, where the population is growing and shoreline areas are being occupied by small fishing boat docks, generate numerous solid, liquid, gaseous and plastic wastes, as well as pollutants such as radioactive elements [5] and making these ecosystems vulnerable to environmental disasters such as the coastal flooding and erosion, disruption of coastal biodiversity, as well as reduced freshwater availability [6]. Environmental pollution in general, and of marine-coastal ecosystems in particular, is nowadays a major concern for global society. This survey focuses on the assessment of environmental quality, origin and effects of natural radionuclides recorded in surface sediments of the Republic of the Congo's coastline.

2. MATERIALS AND METHODS

2.1. Sampling and analytical techniques

The study methodology is based on three protocols: field sampling, sample processing and

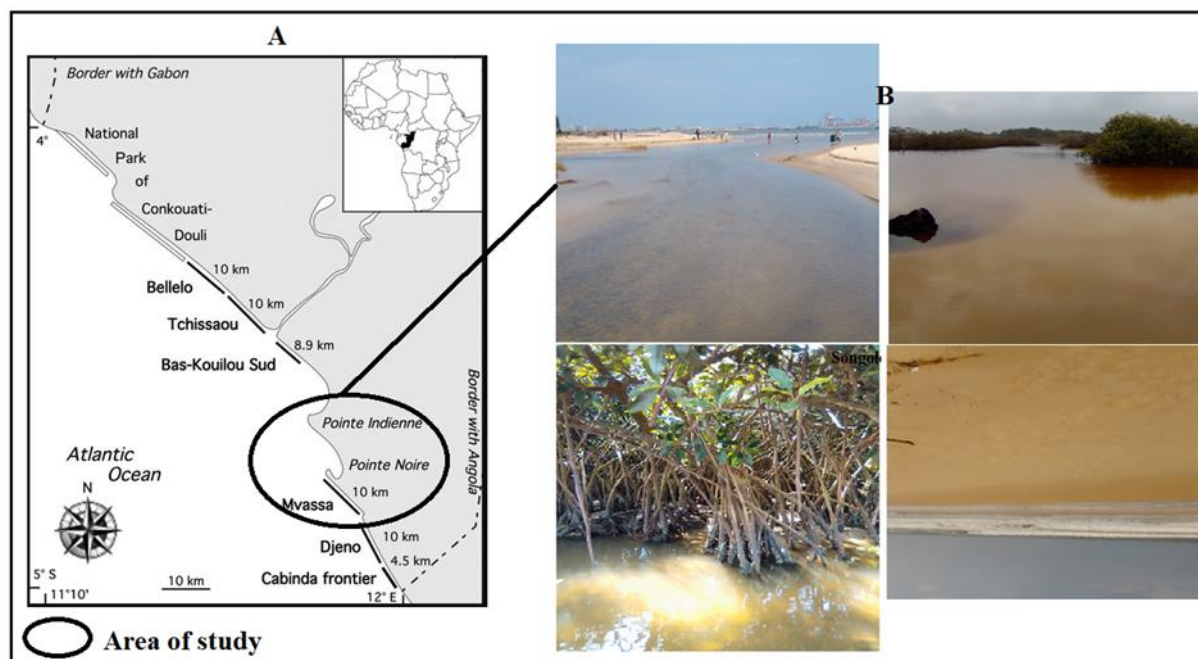
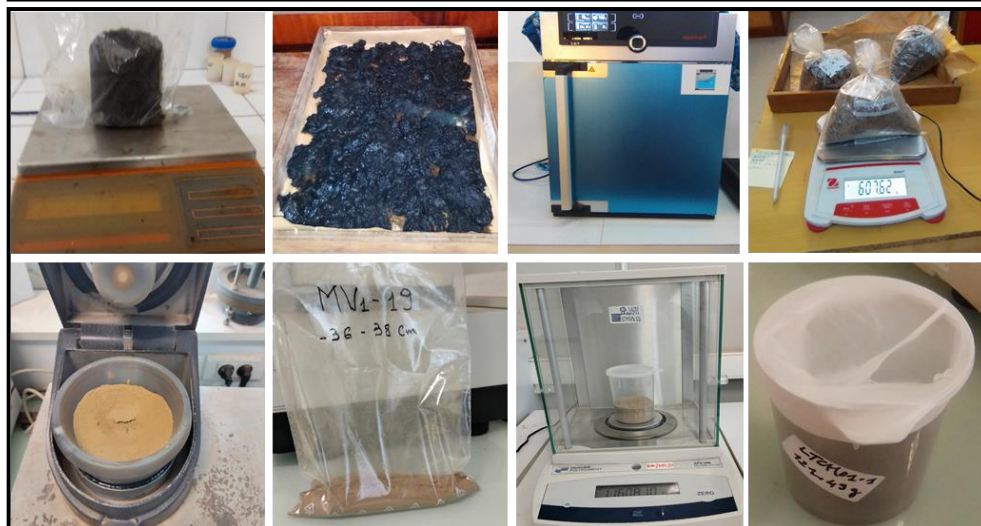


Figure 1: Map of the study area (A) [7]; Sampling sites (B).

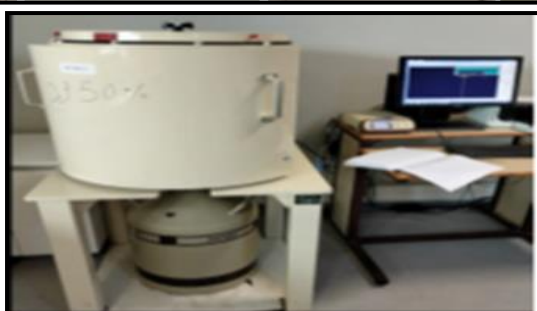
Sampling Process



Physical preparation



Gamma spectroscopy analysis



Gamma-ray spectrometry analysis. These three processes are shown in the diagram above.

The study area consists of rivers, lagoons and marshes distributed along the coastline, Figure 1. The coastline along the Congolese basin stretches 170 km from the southwest of Gabon to the northeast of Angola, and made up of various sediment deposits and have different geological characteristics.

The sampling campaign was performed over a period of 17 days in the low tide, between the end of the rainy season and the start of the dry season (May 15), from May 3 to May 21, 2022. Five hundred grams of surface sediment samples were obtained, using a scalpel and an auger, in depths between 0 and 5 cm.

Samples and study sites, physical preparation of sample and gamma-ray analysis equipment and protocol are described in our previous study [5].

2.2. Human radiological parameters assessment

Sediments are of vital importance, both in scientific research and in socio-economic terms. Their contamination by radioactive elements can expose people who use them for socio-economic purposes, such as construction, to harmful ionizing radiation. In order to understand the potential radioactive hazards presented by the marine sediments found in the Congolese coastal basin and the risks they pose to people who rely on them, five radiological parameters were evaluated, based on the activity concentrations of three natural radionuclides Ra-226, Ra-228(Th-232), and K-40 [8]:

- the total absorbed dose rate in air (D_{air}) [nGy/h] represents the gamma emission exposure rate in air 1.0m above the ground, and can be calculated using Equation (1).

$$D_{air} (nGy/h) = 0.462 A(^{226}Ra) + 0.604 A(^{232}Th) + 0.0417 A(^{40}K) \quad (1)$$

- the Radium Equivalent Activity (Ra_{eq}) [Bq/kg] is an index used to assess exposure to radiation.

$$Ra_{eq} (Bq/kg) = A(^{226}Ra) + 1.43 A(^{232}Th) + 0.077 A(^{40}K) \quad (2)$$

- The External Hazard Index (H_{ex}) [unitless] is caused by direct gamma radiation and is used to evaluate the safety of human health.

$$H_{ex} = 0.0027 A(^{226}Ra) + 0.0039 A(^{232}Th) + 0.0002 A(^{40}K) \quad (3)$$

- The Annual Gonadal Dose Equivalent (AGDE) [μ Sv/year] estimates the potential radiation dose that the gonads may receive from the three radionuclides ^{226}Ra , ^{232}Th and ^{40}K .

$$AGDE (\mu Sv/y) = 3.09 A(^{226}Ra) + 4.18 A(^{232}Th) + 0.314 A(^{40}K) \quad (4)$$

- The Annual Effective Dose Equivalent (AEDE) [μ Sv/year], was calculated using (Eq.5), with 8760 being the duration of one year of gamma radiation exposure, a 0.2 outdoor occupancy factor, and a 0.7 Sv/Gy conversion factor.

$$AEDE (\mu Sv/y) = D_{air} \times 8760 (h/y) \times 0.2 \times 0.7 (Sv/Gy) \times 10^{-3} \quad (5)$$

2.3. Biota radiological parameters assessment

The potential radiation dose received by six (06) animals and plants selected in the study area, was assessed for the first time, using the Environmental Risk from Ionizing Contaminants Assessment (ERICA) tool (version 2.0). Details about the potential of ERICA tool can be found in [5, 8].

3. Results and Discussion

Tables 1, 2 and 3 present the results of this study, respectively the levels of natural radionuclides concentrations of Th-234(U-238), Bi-214(Ra-226), Bi-212(Th-228), Ac-228(Ra-228), Pb-210 and K-40 from surface sediments of the coastal basin of the Republic of Congo, the radiological parameter risks of gamma radiation on human health and the potential radiation doses received by biota based on the ERICA tool on 6 selected reference organisms from the ecosystem studied.

The radiogenic activities of primordial radionuclides series shown levels, with a small exception for Th-232, within the worldwide

standards of the UNSCEAR, 35 Bq/kg, 30 Bq/kg and 400 Bq/kg defined for U-238, Th-232 and K-40, respectively [5, 9].

The risks of radiological parameters on human health were also in the same order of compliance with international limits [5, 9].

The radioecological assessment, based on the ERICA tool considering all radionuclides and 6 selected reference organisms (birds, crustaceans, molluscs-bivalves, pelagic fishes, reptiles and phytoplankton), indicated the calculated total dose rates below the screening dose rate of 10µGy/h, which matches to the risk quotient of 1, recommended in the ERICA tool. This suggests a low probability of radioecological risk in the study area. Pb-210 was found to be the most concentrated radionuclide, while Th-228 and Ra-226 were identified as the main pollutants. Phytoplankton was found to be the principal receptor, followed by pelagic fish, making them valuable bioindicators for monitoring radioactive pollution. These results are still in line with our previous study [5] and that of Ait Bouh et al, conducted in various coastal areas in Morocco [8] and Klubi et al, in Ghana [10].

4. Conclusion

The natural radioactivity levels, the human and biota radiation hazards were assessing for the first time in the coastal ecosystems in the Republic of Congo, and mark an inaugural study. The founded revealed the respect of international standards set by UNSCEAR for all radionuclides.

Radiological human health parameters and the radioecological parameters assessment for biota are in line with the global norms.

These studies are conducted as part of an environmental monitoring program in the marine and coastal environment, additional studies are underway on sediment cores taken from the same sites, to complete our information and also to track the vertical evolution of these radionuclides, and heavy metals pollutants, determine their absolute ages by Pb-210 or Cs-137 radiometric methods as well as trace their sources.

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ELECTRIC ENERGY CONVERTER FOR EXCITATION OF LOW-FREQUENCY MECHANICAL VIBRATIONS

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Abstract

Impact on the oil reservoir in various ways is a promising technology for increasing oil recovery, especially in conditions of depleted or hard-to-recover reserves, and this method consists mainly of physical impact to improve the permeability of the oil reservoir and increase the efficiency of oil production. Such a method may include various technologies, for example, the use of wave generators of mechanical vibrations, electromagnetic vibration exciters of mechanical vibrations, hydraulic vibration devices, etc.

Keywords: hard-to-recover reserves of deposits, vibrational exciters of mechanical vibrations, fluid, resonance

1 INTRODUCTION

For watered fields at a late stage of production, oil in the formations is retained mainly in the form of film oil in the walls of cracks and capillaries and in the form of residual reserves in terms of the size of oil clusters and geoblocks. It is known that a fluid-saturated reservoir consists of geoblocks and, due to Earth pressure, the geoblocks are separated by cracks filled with fluid and they are in a stressed state. Gas blocks have dominant (quasi-resonant) frequencies and when operating at the dominant frequency of the formation, the level of rock displacement ensures the maximum amplitude of vibrations of the geoblocks.

One of the promising methods of increasing oil recovery of the above-mentioned fields is the creation of low-frequency (1-20) Hz mechanical vibrations at the depth of the formation, which at the above frequency cause resonant vibrations of geoblocks. At this time, geoblocks are lapped and microcracks increase to macro-cracks, dividing blocks into sub-blocks [1].

2 PROBLEM STATEMENT

To create low-frequency (1-20) Hz mechanical vibrations at the depth of the formation, an electric energy converter is proposed, consisting of a three-phase electromagnetic exciter located at the depth of the formation [2]. Electromagnetic vibration exciters are the most advanced type of drive according to

their basic design. If in other types of drives electrical energy is converted through rotational motion into reciprocating motion, then in electromagnetic exciters the necessary reciprocating motion is obtained directly without any intermediate mechanisms.

Electromagnetic vibration exciters do not have nodes in which friction, sliding or rolling would take place, and they do not have bearings subject to high dynamic loads. To increase the specific power of the above converter, a three-rod traction electromagnet was used, the appearance of which is shown in Fig.1a. The converter has a movable armature supported on springs and identical windings on all three rods of a III - shaped magnetic circuit, which are connected to a star and connected to a three-phase standard power supply network through three identical series-connected capacitors (Fig.1b) [2,3].

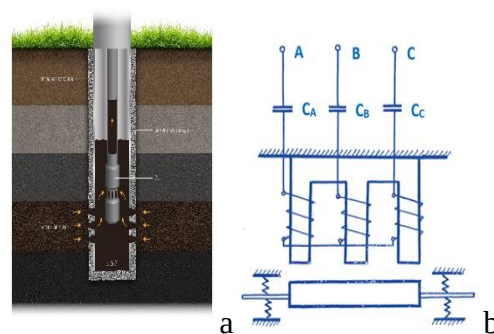


Figure.1 Vibration exciter

The anchor retracts due to the pulling force of the magnet, and falls off with the help of a spring,

which the anchor compresses when retracting. The retraction and fall-off of the anchor alternates periodically. In this case, the shape of the gap change curve in time is close to sinusoidal or may have a pronounced first harmonic component. The oscillations of the anchor have a stable and undamped character. The converter is a self-oscillating system, the processes in which, obeying the general laws of self-oscillating systems, have a number of features.

The valve regulating the energy supply to the system is a periodically occurring voltage resonance. All movements in the system are accompanied by redistributions between energy storage devices, which include: mass, spring, electromagnet winding and capacitance. The possibility of wasting the energy portions accumulated in them determines the ability of the system to perform work to overcome friction. In this case, energy enters the mechanical part from the electrical one, where energy exchange occurs both in terms of the frequency of the supply network and in terms of the frequency of mechanical vibrations, the intensity of which ultimately determines the operability of the system. The armature, making oscillatory movements, moves reciprocally and changes the value of the air gap δ in phase with all three rods. In this case, the three-phase exciter provides a symmetrical load of the phases of the three-phase circuit. The differential equations of the electrical and mechanical system of this converter are defined as

$$\begin{aligned} U_A &= i_A r_A + \frac{1}{C_A} \int i_A dt + W_A \frac{d}{dt}(\Phi_A) \\ U_B &= i_B r_B + \frac{1}{C_B} \int i_B dt + W_B \frac{d}{dt}(\Phi_B) \\ U_C &= i_C r_C + \frac{1}{C_C} \int i_C dt + W_C \frac{d}{dt}(\Phi_C) \end{aligned} \quad (1)$$

where $U_{A(B,C)}$ - are the phase voltages of phases A, B and C, respectively;

$r_A = r_B = r_C = r$ - active resistances of the windings of phases A, B and C;

$C_A = C_B = C_C = C$ - capacitance of capacitors in phases A, B and C;

$W_A = W_B = W_C = W$ - the number of turns of the phase windings of the exciter of low-frequency mechanical vibrations;

$\Phi_{A(B,C)}$ - magnetic fluxes in the rods of phases A, B and C

$$m \frac{d^2 x}{dt^2} + r_{mex} \frac{dx}{dt} + \frac{1}{\lambda} x = F_{\Sigma} \quad (2)$$

where m - is the reduced mass,

r_{mex} - friction resistance,

$\frac{1}{\lambda}$ - spring stiffness.

Given the symmetry of the load phases of a three-phase circuit, each of the equations (1) can be considered in isolation, taking into account that the magnetic fluxes Φ_A, Φ_B and Φ_C must have the same harmonic composition, each of the components of which has the same amplitudes with operators such as "sin" or "cos" of the same frequency, but the phase angles are different. The composition of magnetic fluxes must necessarily contain harmonic components (which, generally speaking, are dominant in comparison with other harmonic components), the frequency of which is determined by the frequency of the supply network.

Due to the fact that the power supply of the electromagnetic exciter in question is carried out from a three-phase network, where phase voltage shifts between each other at angles of 120° are determined, these phase shifts should also be contained in the arguments of the above-mentioned harmonic components of magnetic fluxes at the power frequency, which we will further denote $\omega(k)$. The retraction and falling off of the armature is periodic alternates (Fig.2).

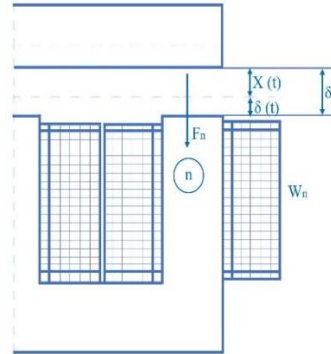


Figure 2. Cross-section of the device

In this case, the shape of the gap change curve in time is assumed to be close to sinusoidal or may have a pronounced first harmonic component, that the armature performs its oscillatory movements having some average air gap value δ_0 , relative to which it shifts in time by $x(t)$. Then

$$\begin{aligned} \delta(t) + x(t) &= \delta_0 \\ \delta(t) &= \delta_0 - x(t) \end{aligned} \quad (3)$$

At the same time, there are strict inequalities:

$$\begin{aligned} x(t) &< \delta_0 \\ \delta(t) &> 0 \end{aligned} \quad (4)$$

Note that the orientation of $x(t)$ is chosen to be positive in the case of attraction of the movable armature to the yoke, that is, according to the

conditionally positive direction of the traction force F_n of the n th rod with a winding. The pulling force of an electromagnetic exciter of low-frequency mechanical vibrations, as in any traction electromagnet, is related to the magnitude of the components of the magnetic flux in the magnetic system of these exciters. Establishing a connection between the harmonic compositions of the current $i(t)$ and the magnetic flux $\Phi(t)$ with a given change in the air gap $\delta(t)$ between the movable armature and any of the cores of the three-rod structure, we have:

$$i(t) = K \Phi(t) \delta(t) \quad (5)$$

where $K = \frac{1}{W\mu_0 S_\mu}$ is the constructive coefficient. Considering that the magnetic flux in each rod is generally described as

$$\Phi(t) = \sum_{g=1}^{\infty} \sum_{j=0}^{\infty} \Phi_{jm}^{(g)} \sin(\omega_j t + \alpha_j) \quad (6)$$

where is the internal amount $\sum_{g=1}^{\infty} \Phi_{jm}^{(g)} \sin(\omega_j t + \alpha_j)$ there is a Fourier series (summation by index j), and the outer sum (by index g) is the summation of Fourier series in which the fundamental frequencies (frequencies of their first harmonics) are correlated [2] as follows

$$nT_{(k)} = mT_{(k-1)} = \dots T_{o\delta\omega} \quad \text{or} \quad n \frac{2\pi}{\omega_{(k)}} = m \frac{2\pi}{\omega_{(k-1)}} = \dots = \frac{2\pi}{\omega_{o\delta\omega}} \quad (7)$$

in relation to $\Phi(t)$ in (6), for subsequent considerations, we will consider only the sum of the first lateral harmonics of $\Phi_{\Sigma}(t)$:

$$\begin{aligned} \Phi_{\Sigma}(t) = & \dots + \Phi_{(k-1)m} \sin(\omega_{(k-1)}t + \alpha_{(k-1)}) + \\ & \Phi_{(k)m} \sin(\omega_{(k)}t + \alpha_{(k)}) + \\ & + \Phi_{(k+1)m} \sin(\omega_{(k+1)}t + \alpha_{(k+1)}) + \dots \end{aligned} \quad (8)$$

However, special studies have made it possible to establish the presence of phase angles at $\frac{2\pi}{3}$ and in the harmonic components of magnetic fluxes at frequencies different from the frequency $\omega_{(k)}$. The main result of these studies is the following experimentally confirmed consideration. Since the modulation is carried out in windings located on all three rods of the magnetic circuit using a common armature (and, therefore, in phase, which is confirmed by voltage waveforms $U_L(t)$ on these windings (Fig.3), then if the shape of the envelopes for these three voltages coincides, a

shift of one of their $\frac{2\pi}{3}$ harmonic components in phase by entails the appearance of corresponding shifts in other harmonic components to preserve the invariance of the resulting shape of this package of harmonics.

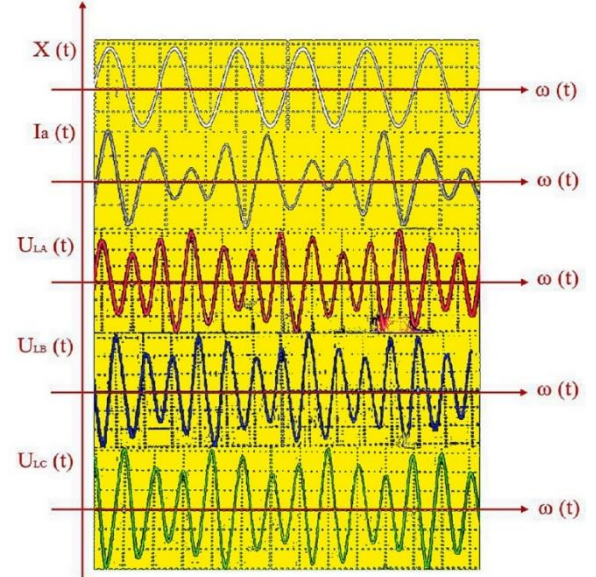


Figure 3. Oscillographs of the main parameters of the device

First of all, we note the following feature of the formation of conditional packets of magnetic fluxes of individual rods of a magnetic circuit. Let's imagine packages of magnetic fluxes in accordance with the connection of the windings creating them to the three-phase power supply in the form :

$$\begin{aligned} \Phi_{\Sigma A}(t) = & \Phi_{(k-1)m} \cdot \sin(\omega_{(k-1)}t + \alpha_{(k-1)}) + \\ & + \Phi_{(k)m} \cdot \sin(\omega_{(k)}t + \alpha_{(k)}) + \\ & + \Phi_{(k+1)m} \cdot \sin(\omega_{(k+1)}t + \alpha_{(k+1)}) \\ \Phi_{\Sigma B}(t) = & \Phi_{(k-1)m} \cdot \sin(\omega_{(k-1)}t + \alpha_{(k-1)} - 120^\circ) + \\ & + \Phi_{(k)m} \cdot \sin(\omega_{(k)}t + \alpha_{(k)} - 120^\circ) + \\ & + \Phi_{(k+1)m} \cdot \sin(\omega_{(k+1)}t + \alpha_{(k+1)} - 120^\circ) \\ \Phi_{\Sigma C}(t) = & \Phi_{(k-1)m} \cdot \sin(\omega_{(k-1)}t + \alpha_{(k-1)} - 240^\circ) + \\ & + \Phi_{(k)m} \cdot \sin(\omega_{(k)}t + \alpha_{(k)} - 240^\circ) + \\ & + \Phi_{(k+1)m} \cdot \sin(\omega_{(k+1)}t + \alpha_{(k+1)} - 240^\circ) \end{aligned} \quad (9)$$

These values in (9) show that when determining the symmetry of the parameters of the winding circuits of a three-phase electromagnetic exciter and its power supply system, symmetry is performed in the distribution of not only the parameters of the harmonic components of

magnetic fluxes at the supply frequency $\omega_{(k)}$, but also the parameters of the harmonic components of magnetic fluxes at the side frequencies $\omega_{(k-1)}$ and $\omega_{(k+1)}$.

Otherwise, it is executed

$$\Phi_{\Sigma A} + \Phi_{\Sigma B} + \Phi_{\Sigma C} = 0 \quad (10)$$

the condition and taking into account the presence in $\Phi_{\Sigma n}$ of the harmonic components $\omega_{(k-1)}$ and $\omega_{(k+1)}$. Note that this is consistent with the above-mentioned judgments, carried out on the basis of the above, regarding the appearance of phase shifts in the lateral harmonic components of individual phases while maintaining the shape of the envelope of packets of these harmonic components. However, in accordance with (2), the traction force of the converter, taking into account the above, is determined by summing the values of the magnetic fluxes, each of which is squared [2,3]. Therefore:

$$F_{\Sigma} = F_{\Sigma}(t) = h[\Phi_{\Sigma A}^2(t) + \Phi_{\Sigma B}^2(t) + \Phi_{\Sigma C}^2(t)] \quad (11)$$

For convenience, we rewrite (11) normalizing by h :

$$\frac{1}{h}F_{\Sigma}(t) = \Phi_{\Sigma A}^2(t) + \Phi_{\Sigma B}^2(t) + \Phi_{\Sigma C}^2(t) \quad (12)$$

Substituting (9) into (12) and performing certain transformations, we have that when squared, two types of combinational harmonic forms appear: total and difference.

In the case of total harmonic components, there is both an increase in their frequency (due to the summation of their frequencies) and an increase in phases. Since in the latter case, conditional

rotations of vectors at angles $n \frac{2\pi}{3}$ occur during summation, then there is a coincidence in phases and frequencies of components belonging to different harmonic components. With the symmetry of the parameters of individual circuits and mains power supply, the amplitude distribution of the harmonic components of the force is such that the above phase shifts lead to mutual compensation. The components of the total combination components completely compensate each other and, therefore, the resulting force on these components is zero.

Turning to the consideration of differential combinational harmonic components, we note that after transformations in (12), the following terms are preserved: the summation of constant

components and harmonic components at difference frequencies is carried out. The main harmonics can form such a system of components according to the distribution of their frequencies, in which the difference frequencies in the combinational harmonics of the force will be equal to the frequency ν , which is a given frequency of mechanical vibrations included in the frequency of the traction force, determining the frequency in its alternating component. The nature of the occurrence of $\omega_{(k+1)}$ and $\omega_{(k-1)}$ is explained by the movement of an electromagnet, in which the mechanical part is tuned to the frequency

$$\nu = \sqrt{\frac{1}{\lambda m}} \quad (13)$$

The following frequency composition is presented here:

$$\omega_{(k+1)} - \omega_{(k)} = \omega_{(k)} - \omega_{(k-1)} = \nu \quad (14)$$

and also

$$\alpha_{(k+1)} - \alpha_{(k)} = \alpha_{(k)} - \alpha_{(k-1)} = \theta \quad (15)$$

It follows that

$$\omega_{(k+1)} - \omega_{(k-1)} = 2\nu \quad \text{and} \quad (16)$$

$$\alpha_{(k+1)} - \alpha_{(k-1)} = 2\theta \quad (17)$$

Taking into account (14), (15), (16) and (17) these expressions (12) can also be represented in the form

$$F_r(t) = \frac{F_{\Sigma}(t)}{F_m} = \frac{1}{2}\gamma_{(k-1)}^2 + \frac{1}{2}\gamma_{(k)}^2 + \frac{1}{2}\gamma_{(k+1)}^2 + \gamma_{(k+1)}\gamma_{(k-1)} \cdot \cos(2\nu t + \theta) +$$

$$+\gamma_{(k)}(\gamma_{(k-1)} + \gamma_{(k+1)})\cos(\nu t + \theta) \quad (18)$$

where $F_m = 3 h \Phi_m^2$ - some normalizing value of the traction force of a three-phase electromagnetic exciter of low-frequency mechanical vibrations[2].

The traction force of the vibration exciter contains harmonic components forming a group of combinational harmonics, traction force. The frequency of these harmonics differs from the initial part of the total magnetic flux both in the direction of increasing frequency and in the direction of its significant decrease.

In addition, there are groups of force components that do not depend on time, and a group of components that have strictly doubled frequencies relative to the original ones. The main harmonics can form such a system of components according to the distribution of their frequencies, in which the difference frequencies in the combinational harmonics of the force will be equal to the frequency, which is a given frequency of

mechanical vibrations and thus included in the frequency of the traction force, determining the frequency in its alternating component[4,5].

The creation of vibration by this transducer in the bottom of an oil well contributes to the destruction of pore structures and an increase in channels through which oil can move. Vibration vibrations contribute to the removal of impurities and mechanical impurities, which improves the filtration properties of the formation. Vibration effects can temporarily reduce the viscosity of the oil, which facilitates its movement through the pores of the formation. The generation of vibration vibrations leads to an increase in pressure in a porous medium, which contributes to the displacement of oil from low-permeable zones to more permeable ones and further to producing wells[4,5,6].

The effective use of vibration exposure can significantly improve the economic performance of oil production and reduce the environmental impact.

3 CONCLUSION

1. The occurrence of the above processes in a productive formation serves to change the permeability of the formation and increase production. The creation of mechanical resonance phenomena in several wells located at a certain distance from each other at the same time led to an increase in oil production (by 10-12%) in most of the spent wells located in this area.

2. This method is used for the first time, since it is considered a method of physical impact on the productive reservoir.

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FOSSIL FUEL SUBSIDIES AND GREEN TECHNOLOGY IMPACT ON CARBON EMISSIONS: A STUDY ON ACHIEVING NET-ZERO POLICY

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Abstract

Reducing dependency on fossil fuels to mitigate carbon dioxide emissions is currently one of humanity's most urgent problems. However, government subsidies for fossil fuels encourage greater dependence on non-renewable energy sources rather than clean energy alternatives. Therefore, researchers and policymakers must focus on addressing the issues associated with fossil fuel subsidies and promoting the adoption of green technology. In this study, we investigate the relationship between increased fossil fuel subsidies, the adoption of green technologies, carbon storage in forests, and their combined impact on carbon emissions for the top twenty per capita carbon emitters between 2010 and 2022. Using bootstrapped quantile regression, our findings show that carbon stock in forests and renewable energy consumption negatively affect carbon emissions. However, the use of green technologies and fossil fuel subsidies is positively correlated with carbon emissions. An updated Granger causality analysis revealed unidirectional causality from fossil fuel subsidies, green technology, and carbon stock in forests to carbon emissions. Additionally, bidirectional causality was noted between renewable energy and carbon emissions.

Given these findings, it is suggested that governments create new energy policies aimed at increasing the share of non-fossil fuels in the energy mix instead of continuing with fossil fuel subsidy policies.

Keywords: fossil fuel subsidies; energy policy; green technology; eco-friendly technology

DEFORMATION BEHAVIOR OF DENSE AND POROUS MATERIALS AND REQUIREMENTS FOR THEIR USE IN SOFC DESIGN PRACTICE

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Abstract

The thermo-mechanical analytical model proposed for different solid oxide fuel cell (SOFC) designs addresses the deformation behavior and mechanical stability of SOFCs at various thermal stresses, specifically the creep resistance and the long-term endurance beyond the elastic limit.

The model considers the deformation of multi-layer SOFC in the temperature range of 600–800°C and presents the combination of the correlated parameters for SOFC performance evaluation, stability and long-term endurance under realistic operating conditions and temperature gradients. The numerical analysis of the thermo-mechanical properties of the SOFC materials is presented in terms of mechanical behavior at failure conditions and the influence of rheological and structural properties on SOFC long-term endurance. The SOFC thermal behavior, creep parameters of the SOFC materials and long-term stability are analyzed in terms of stresses, deformations and displacements.

Keywords: materials, performances, structure, operating temperature, modelling, design of compatibility.

1. INTRODUCTION

Conventional energy sources such as gasoline (diesel), coal and hydro source are the main sources for power generation. However, these conventional energy sources are being depleted, and are also unfriendly to the environment. Alternative energy sources such as renewable energy (RE) systems are becoming more popular in power generation applications. RE sources include solar energy, wind energy, photovoltaic (PV) cell energy, fuel cell etc. which are very effective in reducing the greenhouse gas emissions. In the near future, large portions of increase in electrical energy demand will be met through widespread installation of distributed generation (DG). Many advantages are considered for application of DG, i.e., increased service reliability, reduction of the need for grid reinforcement, generation expansion and power factor correction. Furthermore, it is possible to improve voltage regulation and local power quality more precisely using DGs in comparison to conventional centralized generators. DG sources comprise of direct energy conversion sources producing DC voltages or currents such as fuel cells and photovoltaic sources, high-

frequency sources such as micro turbines, and variable frequency sources such as wind energy. Power generation from solar energy sources and wind energy sources is unpredictable, because solar power depends on the availability of sun light and wind energy system depends on the wind. Since fuel cells have no geographical limitations, they are preferred for small scale power generation. Power generation in fuel cells depends on the hydrogen input which is available in abundance. Further, fuel cells are known for their low to zero emissions, high efficiency (35-60%) and high reliability because of the absence of moving parts.

There are six main types of fuel cell: alkaline fuel cell (AFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC), polymer electrolyte membrane fuel cell (PEMFC) and direct methanol fuel cell (DMFC), solid oxide fuel cell (SOFC).

Fuel cells are static energy conversion devices that partially convert the chemical energy of fuels directly into electrical energy and produces water as its byproduct.

Among different types and scale power generation systems, fuel cells have received more attention, because they can provide also

both heat and power. The successful utilization of materials requires that they satisfy a set of properties. These properties can be classified into thermal, optical, mechanical, physical, chemical, and nuclear, and they are intimately connected to the structure of materials. The structure, in its turn, is the result of synthesis and processing. A schematic framework that explains the complex relationships in the field of the mechanical behavior of materials, shown in Figure 1, is Thomas's iterative tetrahedron, which contains four principal elements: mechanical properties, characterization, theory and processing. Interrelationships among structure, properties, and processing methods, the most important theoretical approaches, and the most-used characterization techniques in materials science today.

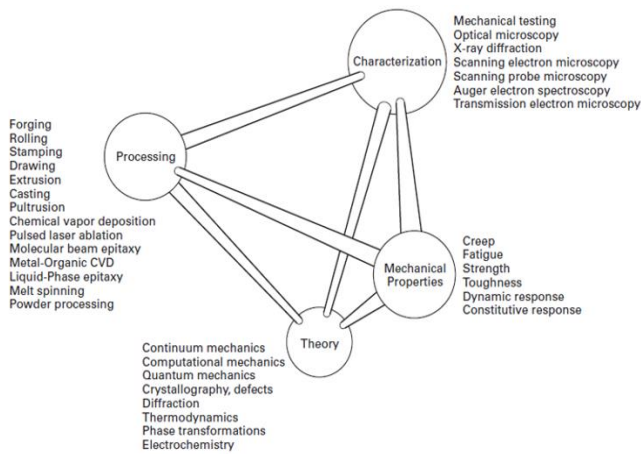


Figure 1. Tetrahedron, which contains four principal elements

According to the work is planned to study materials of different structural content exposed to operating temperature during the operation of the facility, namely (Figure 2):

1. Dense structure, based on zirconium (Zr);
2. Porous structure, based on titanium (Ti);
3. Materials based on transition metals, so-called MaxPhase in different chemical composition.

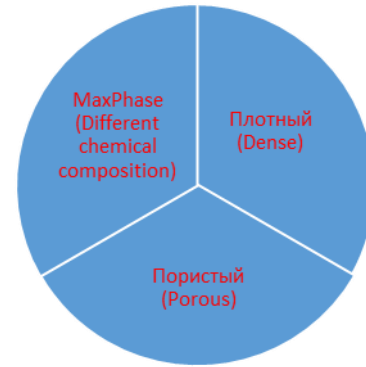


Figure 2. Materials with structure
Creation of materials with given and desired properties to ensure a higher consumer quality of devices by synthesizing compatible combinations of the indicated disciplining factors and structural properties of materials [7, 8]

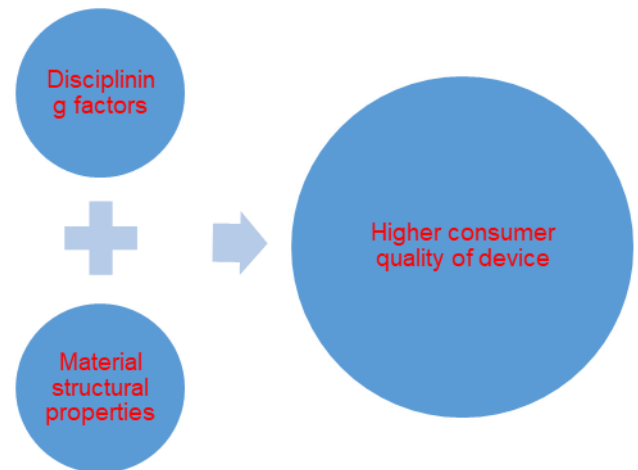


Figure 3. Creation of materials with given and desired properties

2. STATEMENT OF PROBLEM

2.1. The task for a dense structure synthesis based on zirconium

1. The thermomechanical analytical model is assumed for studying the deformation behavior of SOFC at various operational temperatures, in particular, provide the resistance of creep and long-term endurance outside the elastic limit.

2. The model takes into account the deformation of the multilayer SOFC in the temperature range of 600-800°C and is a decision on long-term endurance in the process of real operating conditions.

3. The numerical analysis of thermophysical properties of SOFC materials and their changes, depending on the mechanical behavior their destruction are estimated taking into

account the rheological and structural properties of materials for the long-term endurance of SOFC.

4. The results of modeling thermomechanical deformation behavior of SOFC allowed to develop an algorithm for a decision on synthesis of the materials properties and their characteristics outside the elasticity limit, which is significant for long - term operation of SOFC at elevated temperatures.

5. In the end, a technique has been developed for the synthesis of desired materials taking into account the operating temperature, topology surfaces, form, metric characteristics and thermophysical properties.

2.2. Solutions used for device design

The influence of the surfaces state on the deformation behavior of the device the constructive performance are considered for the irregularities range from C_0 to C_2 ($C_0 < C_2$). These results of poses have to make decisions according to the constructive characteristics and material support of the developed anode substrates - 1 - direction (Figure 4).

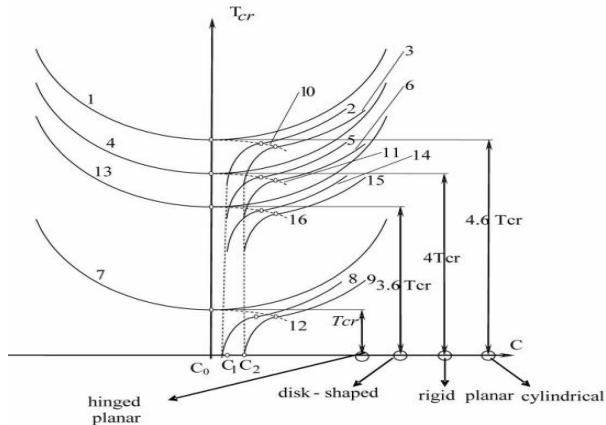


Figure 4. Critical temperature (T_{cr}) changes vs. surface irregularity for different SOFT design:

C_0, C_1, C_2 – Initial surface irregularities;
 T_{cr} – critical temperature for rigid planar design;
 $3.6 T_{cr}$ – critical temperature for disc shaped design;
 $4 T_{cr}$ – critical temperature for hinged planar design;
 $4.6 T_{cr}$ – critical temperature for cylindrical design;
 1 – SOFC cylindrical design with zero initial surface irregularity $C=0$;
 2 – SOFC cylindrical design with initial surface irregularity C_1 ;

3 – SOFC cylindrical design with initial surface irregularity C_2 ;
 4 – SOFC rigid planar design at initial surface irregularity $C=0$;
 5 – SOFC rigid planar design at initial surface irregularity C_1 ;
 6 – SOFC rigid planar design at initial surface irregularity C_2 ;
 7 – SOEC hinged planar design at initial surface irregularity $C=0$;
 8 – SOC hinged planar design at initial surface irregularity C_1 ;
 9 – SOFC hinged planar design at initial surface irregularity C_2 ;
 13 – SOFC disc shaped design with zero initial surface irregularity $C=0$;
 14 – SOFC disc shaped design with initial surface irregularity C_1 ;
 15 – SOFC disc shaped design with initial surface irregularity C_2 ;
 10, 11, 12, 16 – accordingly, surface irregularity characterizing the decrease of T_{cr} with approaching irregularity.

The application of the form, metric characteristics and material execution of dense elements are considered for various operational temperatures and are presented in the logarithmic coordinates (Figure 5).

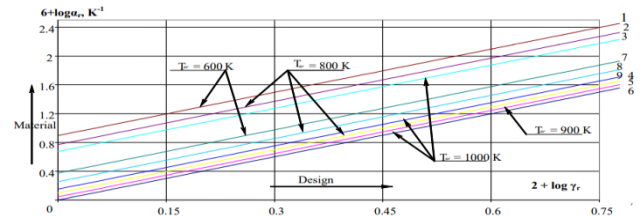


Figure 5. Materials properties vs. SOFC design:

1,2,3 – cylindrical\$ 4,5,6 – planar;
 7,8,9 – disk-shaped SOFC designs

The results obtained allow you to make decisions for the design of devices from dense materials with a different metric characteristic, form of execution and properties of material support.

Thus compatible combinations of these indicators for various operating temperatures might be determined.

2.3. Influence of the elements surface on the stability of the SOFC design

The third direction of work – to study of porous materials for use in the practice of designing a device as a whole and their elements. This issue has been discussed many times with project partners. With his great support and faith in the possibility of application in the practice of creating devices, the following task has been set and solved:

Development goal – the study of the deformation behavior of porous structure and the determination of an adequate deformation model for this behavior, taking into account mass transfer processes in a dynamic model for planning and effective implementation of various measures aimed at designing devices using of a similar material structure

Task content:

1. The problem of determining a mathematical model of deformation behavior and studying, on this basis, the stress-strain state of porous structure under quasi-static and dynamic loading is being solved.
2. The presence of mass transfer during loading, etc. the dynamism of porous structure distinguishes and is decisive for choosing their equations of state.

3. PROBLEM SOLUTION

The mathematical model of deformation behavior for studying the stress-strain state of any medium with a porous structure includes 21 equations, of which:

- 9 equations of the form $\varepsilon = \varepsilon(u)$ define geometric ratios;
- 9 equations of the form $\sigma = \sigma(\varepsilon)$ define physical ratios;
- 3 equilibrium equations (or equations of motion if dynamic loading is considered).

Source dependencies:

1. A porous structure is considered, including a solid phase from the skeleton of the structure and a phase of the filling pore.
2. Reduced modulus of elasticity porous structure is defined as [1]:

$$E_{pr} = \frac{m_s E_s + m_g E_g}{m} \quad (1)$$

where E_{pr} is the reduced modulus of elasticity; m , m_s , m_g are, respectively, the masses of the porous structure, the skeleton of the structure and medium fills the its pores; E_s and E_g – respectively, the Young's modulus of the skeleton and the medium that fills the pores

under compression.

During operation, the porous structure is also deformed under the influence of external factors. This contributes to the migration of the medium filling the pores in the direction of the pressure gradient - P in the pores, as a result of which the volume of the medium filling the pores changes, i.e. as a view from (1) E_{pr} is a function of time and therefore

$$E'_{pr} = \frac{m_s(E_g - E_s)}{(m_s - m_g)} m'_g \quad (2)$$

Under quasi-static loading, which provokes a slow change in the stress state of the porous structure due to displacement, the mass of the medium filling the pores m_g decreases (how many this is also question and must be defined!! This task is currently being studied)

Dependency analysis for E_{pr} :

1. It is assumed that only m_g changes with time, i.e. $m_g < 0$;
2. For most porous structures $E_g < E_s$;
3. Then from (2) due to the fact that $m_s(E_g - E_s) < 0$ and $m_g < 0$, then $E'_{pr} > 0$, which means that over time the reduced modulus of elasticity for a porous structure, containing a certain medium in the pores increases, t .e. the tension diagram between the normal stress " σ " and the relative strain ε for uniaxial tension in various modes (see Figure 1) will have the form (see Figure 2)

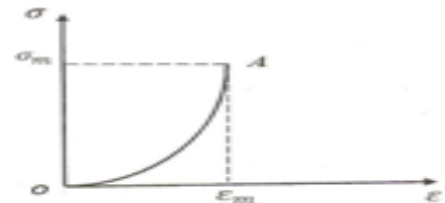


Figure 6. Tension diagram of a porous structure, the pores of which are filled with a medium, where σ_m , ε_m are the maximum values, respectively, of stress and strain

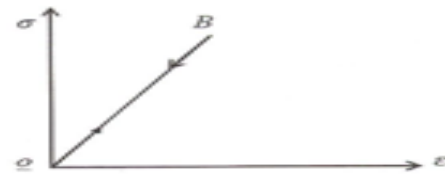


Figure 7. Tension diagram of a porous structure, the pores of which are filled with a medium (high-speed loading)

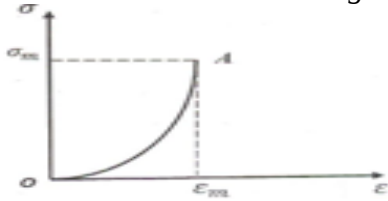


Figure 8. Tensile diagram for a non-porous elastic-plastic structure

Thus, we can conclude that when the stress-strain state of a porous structure is studied, depending on the loading rate, different equations of state should be used, i.e.:

1. With dynamic processes, i.e. under impulse loads, the dependence $\sigma = \sigma(\varepsilon)$ is represented by a straight curve, as a result of which the equation of state can be expressed by the Hook law.

2. Under quasi-static loading, i.e. for time-distributed loads, the application of the HUK law can lead to large inaccuracies (up to 80%). This is especially true for porous structures, in which the loading process is characterized by the presence of mass transfer and which have deformation characteristics that coincide with the characteristics for elastic-nonlinear bodies. Thus, the equation $\sigma = f(\varepsilon)$ of the load diagram branches can describe both plastic and nonlinear elastic deformation of a body with a porous structure.

Hence, to obtain the equation of state for porous body, the equation of state for structures with an elastic-plastic characteristic can be used.

Consequently, as a result of the analysis of the dependence that determines the change in one of the mechanical indicators - the reduced modulus of elasticity for the porous structure, two possible variants of its loading, different in terms of deformation behavior, have been established, namely:

1. Quasi-static (the reduced modulus of elasticity E_{pr} increases);
2. Speed loading (the reduced modulus of elasticity E_{pr} remains permanent).

As the initial equation, the functional dependence for elastic media in the form of the stress tensor σ_{ij} on the components of the strain tensor ε_{ij} , the components of the metric tensor g_{ij} and external disturbances (temperature, pressure and radiation dose) in various combinations is used, which is represented by the dependence below:

$$\sigma_{ij} = f_{ij}(\varepsilon_{\alpha\beta}, g_{\alpha\beta}, T - M, D),$$

To determine the equation of state for elastic and elastic-plastic structures in a general form, the method of expansion in a Taylor series of the original above equation was used to study the functional dependence σ_{ij} and ε_{ij} at $T, P = \text{constants}, D = 0$, which is presented both for stresses and for deformations:

$$\begin{aligned} \sigma_{ij} &= P g_{ij} + Q \varepsilon_{ij} + R \varepsilon_{ik} \varepsilon_{kj}, \quad i, j = 1, 2, 3 \\ \varepsilon_{ij} &= A g_{ij} + B \sigma_{ij} + C \sigma_{ik} \sigma_{kj} \end{aligned}$$

where P, Q, R are functions of the invariants of the strain tensor and the stress tensor. In a particular case, it is assumed that $P = lq, Q = 2m, R = 0, l, m$ – Lamé coefficients; $q = e_{ij} g_{ij}$ – relative volume change or the first strain invariant

To describe the deformation behavior of elastic-plastic structure, an analogy was used between the deformation characteristics of elastic and plastic structures in the processes of loading and unloading, which is based on the assumption that there are no constant values of the elastic modulus and yield strength for deformable porous structures.

After carrying out a number of mathematical calculations, the equations of state of porous structures were obtained for the variants of their loading, respectively, by quasi static (a) and dynamic loads (b):

$$\varepsilon_{ij} = (1 - k_0) \left(\frac{1 + \nu}{E_{sek}} \sigma_{ij} - \frac{\nu I_1}{E_{sek}} g_{ij} \right) \quad (a)$$

$$\varepsilon_{ij} = \frac{1 + \nu}{E_{pr}} \sigma_{ij} - \frac{3\nu}{E_{pr}} \sigma_{ij} \quad (b)$$

Conclusions and recommendations

1. An algorithm has been developed for the synthesis of dense structure materials based on zirconium with properties that are compatible combinations with the operating temperature, shape and metric characteristics of devices from these materials;
2. It has been proven that porous structures are characterized by nonlinear elastic behavior under quasi-static loadings developing in time;
3. The equations of state are obtained and a mathematical model of the deformation behavior of porous structures is formulated to study their stress-strain state, taking into account the corresponding loading modes
4. It has been established that when Hooke's law is used as an equation of state to describe the deformation behavior of porous structures

under quasi-static, i.e. loads distributed in time can contribute to 80% distortion of their stress-strain state.

5. The expansion in Taylor series of the original functional dependence was used, which determines the physical and geometric relationships in deformation behavior and, as a result, equations of state were obtained in general form for structure with elastic, elastic-plastic and nonlinear-elastic deformation character rustics.

6. The obtained dependences allow us to investigate various problems of studying the stress-strain state of porous structures under various loadings, determined taking into account the implemented technological measures in the process of generating electricity by fuel cells on an anode substrate.

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INFLUENCE OF CONTROLLED PARAMETERS ON CRYSTALLIZATION AND PROPERTIES OF HIGH QUALITY PIG IRON OBTAINED BY MODERN METHODS OF SMELTING

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Abstract

The study of the influence of silicon and carbon ratio on the parameters of high quality pig iron obtained by controlled melting method, on the crystallization process and properties is one of the current scientific tasks. It is found that when silicon is added to the melt after carbonization of synthetic cast iron, a number of values are obtained and the physical state of the alloy is of greater importance for obtaining high quality cast iron. It is confirmed that melting the metal does not change its electronic state, but it does change the void concentration. That is, the long-range interatomic order is broken, while the close-range order is preserved. It is shown that it is very advantageous to reduce the amount of silicon in the slag and then add the missing silicon to the alloy during the modification process. This allows the carbon to dissolve and the silica retention time to be maintained. The results of the study show that there is still no consensus on how the silicon to carbon ratio affects the structure and properties of synthetic cast iron. Therefore, the study of the influence of the silicon-carbon ratio on the structure and properties of cast iron as a function of the amount of silicon in the charge and the amount of silicon added in the future is still an urgent problem.

Keywords: controlled melting, high quality synthetic pig iron, crystallization process, silicon to carbon ratio, volume precipitation, mechanical properties.

1. INTRODUCTION

One of the main factors in obtaining widely used high quality cast iron is the purity of the charge material from the content of various additives that affect the physical and chemical state of the alloy and cause changes in its structure and properties. Therefore, for the production of high quality synthetic cast iron, it is necessary to use steel turnings, which are much purer than additives. One of the most important processes in the production of synthetic cast iron is the carbonisation of molten metal.

It has been established that the process of carbon dissolution in liquid iron consists of several stages: first, the packets of its basic levels are separated from the surface of solid carbon particles and dissolved in the liquid, and

then carbon atoms diffuse into the solution [1, 3].

Obviously, the dissolution of carbon in iron takes place between the base planes of the iron atoms. The further dissolution of carbon depends on temperature and time: the higher the temperature of the metal, the greater the dispersibility of the carburising agent and the faster the carbonisation.

For carbonisation to take place, the metal temperature must be above 1673K. When melting synthetic cast iron, there must be a certain relationship between chemical composition, high temperature and storage time at this temperature (heat treatment). Experimental results show that each percentage of silicon in the composition of the synthetic cast iron alloy reduces the solubility of carbon by 4-5%. It is therefore necessary to add silicon

to the alloy after carbonisation of synthetic cast iron.

As the liquid iron crystallises in the mould and cools to room temperature, the volume and linear dimensions of the casting change. Depending on the stage of cooling, these dimensions either decrease (settling) or increase (expansion). Depending on the state of the unit, settling consists of the precipitation of the liquid alloy during and after solidification. The most complex of these is the settling of cast iron in the solid-liquid state. Thermal factors, phase transformations, degassing, graphitisation, etc. are all involved.

The effect of silicon and carbon on the properties of cast iron is considered to be a function of either carbon equivalent or eutecticity [4, 5]. It has been found that one of the important parameters of synthetic cast iron is the value of the silicon to carbon ratio in the alloy with the same degree of eutecticity. The results of these works show that in cast irons with the degree of eutecticity 0.7...1.0 the value of the silicon-carbon ratio plays a really important role. It is found that the mechanical properties improve as the silicon-carbon ratio increases, but only to a certain extent. It is suggested that the value of this ratio should be in the range of 0.9-1.1. It is also noted that the maximum value of cast iron strength corresponds to the value of eutectic degree 0.8, where this coefficient is approximately equal to one [6, 7]. Analysis of the studies carried out has shown that there is still no consensus as to how the silicon/carbon ratio affects the structure and properties of synthetic cast iron. The study of the influence of the silicon/carbon ratio on the structure and properties of cast iron as a function of the amount of silicon in the charge and the amount of silicon added in the future remains relevant.

2. Problem statement

The main purpose of the controlled smelting is to develop a technological method for the production of high quality synthetic pig iron, providing 50% of the silicon content required in pig iron depending on its grade and 50% of its modification at 1673K, as well as to control the process of synthetic pig iron production itself, taking into account the many factors influencing the carbonisation process, as well

as when and how much silicon should be added to the alloy.

Determination of chemical composition, physico-mechanical, techno-logical properties and structure of eutectic cast irons, correct choice of methods and experimental equipment, their implementation increase the quality indicators. Experimental melting was carried out in induction furnaces IDP-1.0 and electric arc furnaces EDP-0.5 in ship repair and other foundries. The slag material consisted of steel scrap and industrial waste, ferroalloys (FS75, FMn75).

3. Problem solution

A graphitised electrode of the brand GK-O, ground to the size of (50x10) mm, was used for carbonisation of the alloy. The chemical permittivity was determined using an optical pyrometer to raise the temperature of the molten iron in the An-7529 and Quantovax-31000 devices.

When melted in an induction furnace, 50% of the slag material was liquid pig iron, and when melted in an electric arc furnace, the amount of silicon in the slag material was 50% of the required amount. In the furnace, the liquid alloy was heat treated at a temperature of 1723-1733K for 10 minutes.

Melting parameters monitored included degree of eutecticity (SEvt), silicon to carbon ratio (Si/C), silicon in the slag material and the amount of silicon added during chemical composition.

Standard specimens (d=30 mm and l=600 mm) were cast from each alloy to investigate the mechanical properties and microstructure of the synthetic cast iron. The strength properties were determined by standard methods and the structure of the cast iron before and after modification was studied using a NEOPHOT-21 microscope. The results of the chemical analysis, the properties of the cast iron and the control parameters are given in Table 1.

The table shows that the properties of cast irons with the same degree of eutecticity have different values. This is due to the variety of control parameters.

The values of density and strength properties increased depending on when, at what temperature and in what amount silicon, Si/C ratio

values and manganese excess of 0.1-0.2% were introduced.

The precipitation coefficient in cast iron alloys is equal to the sum of the precipitation coefficients of the individual stages:

$$E_{\text{general}} = (E_{p.p.f} - E_{\text{exp}}) + (E_{s.e.t.} - E_{\gamma \rightarrow \alpha}), \quad (1)$$

where E_{exp} - preset expansion; $E_{p.p.f}$ - pearlite fit; - expansion on eutectoid transformation;

$E_{s.e.t.}$ - stabilisation after eutectoid transformation.

Experimental results show that these parameters for synthetic cast iron are within the following limits

$$E_{\text{exp}} = (0,14-0,15)\%; E_{p.p.f} = (0,5-0,81)\%;$$

$$E_{\gamma \rightarrow \alpha} = (0,031-0,033)\%; E_{s.e.t.} = (1,33-1,35)\%.$$

Table 1. Chemical composition, properties and controlled parameters of synthetic cast iron alloys

Alloys №	Chemical composition			Parameters				Density ρ , g/sm ³	Hardness, HB	Durability σ_{mch} , MPa	Volumetric α %
	C	Mn	Si	S_{evt}	Si/C	Si (in charge)	Si (in the additive)				
Conventional	3,01	0,72	2,10	0,80	0,63	1,95	0,15	7,0	150	200	0,7
Cast Iron	3,00	0,70	2,05	0,80	0,63	1,80	0,25	7,10	180	250	0,8
1	2,88	0,95	2,20	0,80	0,70	1,10	1,10	7,30	240	300	–
2	2,85	0,92	2,00	0,80	0,70	1,00	1,00	7,32	240	300	–
3	2,88	0,90	1,80	0,81	0,61	0,90	0,90	7,31	240	300	–
4	2,92	0,91	2,05	0,80	0,70	1,00	1,00	7,30	240	300	–
5	3,02	0,85	1,79	0,80	0,60	1,04	0,90	7,32	240	300	–
6	2,40	0,95	2,08	0,69	0,81	1,01	1,04	7,35	250	350	0,2
7	2,69	0,85	2,03	0,75	0,78	1,10	1,02	7,35	245	320	–
8	2,70	0,74	2,20	0,74	0,80	1,05	1,10	7,35	245	320	–
9	2,44	0,78	2,10	0,69	0,85	1,95	1,05	7,34	250	350	–

A general linear design factor $E_{\text{linear}} = 1.18 \div 1.2$ is assumed.

The silicon content ratio must also be taken into account:

$$K = \frac{Si_{\text{charge}}}{Si_{\text{delivery}}} \quad (2)$$

here K – delivery rate; Si_{charge} – silicon content of oil shale, %; Si_{delivery} – the amount of silicon added to the composition, %.

The density of synthetic cast iron alloy in the temperature range of 1293-1863K was investigated by means of gamma radiation on the "Paraboid-3" device of NPO "UNIITMASH" and the following results were obtained.

The object of the study was grey cast iron with plastic graphite with eutectic degree 0.7-1.0. Experimental alloys were produced on the 'Paraboid-3' machine.

3. RESULTS AND DISCUSSION

It has been found that the most important factors affecting the settling of liquid pig iron are the release of gases during solidification and the release of carbon in the form of graphite. These factors can both reduce and increase the volume of the cast iron. The value of the settling factors varies with the type of cast iron. For example, the value of the linear settling factor for grey cast iron is (0.9 - 1.0) %, for white cast iron it is (1.6 - 2.3) % and so on.

Thus, it can be seen that as the amount of coefficient also increases and approaches the

Type of cast iron	Chemical composition			Controlled Parameters		Charges	Si	Graphitisation Coefficient, %	Density, ρ_{3g}/sm^3	Твёрдость МПа	Линейные ступени, %				
	C	Mn	Si	S _m	Si/c						Expansion, E _{exp}	Pre-pearlite fit, E _{p.p.f}	Linear fit, E _{f.l.f}	Eutectoid transformation expansion, E _{exp}	Delivered fit, E
Prima-ry con-venti-onal cast iron	3,01	0,72	2,10	0,8	0,63	1,95	0,15	5,65	7,0	200	0,25	0,43	1,09	0,07	0,84
Prima-ry syn-thetic cast iron	3,0	0,7	2,05	0,8	0,63	1,8	0,25	5,04	7,1	250	0,12	0,35	1,13	0,03	0,90
Expe-rimen-tal cast irons:															
3.1	2,88	0,95	2,2	0,8	0,7	1,1	1,1	4,6	7,3	300	0,35	0,36	0,86	0,01	0,85
3.2	2,85	0,92	2,0	0,8	0,7	1,0	1,0	4,5	7,32	300	0,32	0,32	0,80	0,02	0,82
3.3	2,8	0,9	1,8	0,81	0,61	0,9	0,9	4,6	7,31	300	0,31	0,30	0,87	0,009	0,87
3.4	2,92	0,91	2,05	0,8	0,7	1,0	1,0	4,2	7,30	300	0,32	0,33	0,85	0,008	0,85
3.5	3,02	0,85	1,79	0,8	0,6	1,04	0,9	4,3	7,32	300	0,31	0,34	0,86	0,005	0,81
3.6	2,4	0,95	2,08	0,69	0,81	1,01	1,04	4,4	7,35	300	0,30	0,35	0,92	0,003	0,90
3.7	2,69	0,85	2,03	0,75	0,78	1,1	1,02	4,4	7,35	320	0,34	0,36	0,82	0,007	0,80

chemical bonding of carbon and iron in the structure increases, the value of the design

coefficient of steel.

Table 2. High quality cast iron steps

Typically, an increase in the draft coefficient requires the foundry to include the characteristic additions in the design of the casting. This avoids a gap in the fit of the casting. However, the use of additives leads to an irrational consumption of 10-15% of liquid metal. From this point of view, the study of

It turns out that in a liquid metal, the volume of the seat decreases as the volumetric expansion increases. The volumetric calculation is also affected by parameters such as metal composition, temperature, eutectic degree, carbon equivalent, silicon to carbon ratio and when and how much silicon is added to the metal. As a result, the seat in the casting can either increase or decrease to zero [8].

It should be noted that the influence of metal fluidity, temperature and the time and amount of silicon addition on the volume of the seat cavity is generally poorly understood. What is

measures to eliminate the fit gap in cast iron castings is one of the most urgent tasks.

It is well known that the fit gap in castings is formed during the crystallization of the liquid alloy (in the solid-liquid phase). By controlling the graphitization process at this stage, precipitation due to expansion can be reduced to zero.

known is that the volume of the seat cavity increases with increasing cast iron grade and decreasing carbon equivalent.

Research results show that synthetic cast iron grades with the same degree of eutectic obtained by controlled melting differ by several levels [9]. These cast irons obtained by controlled melting reduced the volume precipitation from (0.7-0.8)% to 0.2% and even to zero. Their density ranged from 7.3 to 7.35 g/cm³ (Table 2).

By reducing the seat volume to zero in the design of castings for heavy internal

combustion engine parts (mass 300-800 kg, wall thickness up to 20-60 mm), there is no need for finishing. This means that the consumption of useless liquid metal is reduced to zero. In addition, the cost of conventional linear seats has also been reduced (from 1.33% to 0.65%). This has reduced the cost of linear seating during mould preparation and reduced the consumption of molten metal.

In the actual crystallisation process, the solvent influence on the structure and properties of the cast iron is due to the graphite additives in the liquid. By dispersing graphite additives in the liquid alloy, they are absorbed by the growing crystals during the crystallisation process, resulting in increased intergranular contact, which in turn increases the strength and other properties of the cast iron.

The parameter that most strongly influences the structure and properties of iron-carbon alloys is high temperature and storage time at that temperature. From the above, it is clear that the study of the liquid state of synthetic cast iron is still an urgent problem and requires study.

When smelting synthetic pig iron, obtained as a result of the application of metal-saving technologies, it is subjected to a heat treatment to obtain a homogeneous alloy. This changes the liquid state of the alloy, reduces the size of the graphite additions and increases the dispersion of pearlite. Controlled melting also has a positive effect on the microstructure of the cast iron. The main core of the metal consists of dispersed pearlite and isolated compact graphite. Pearlite dispersion increased from 0.8 mkmm to 0.1-0.2 μm . The size of the graphite additives decreased to 20-30 mkmm (Figure 1).

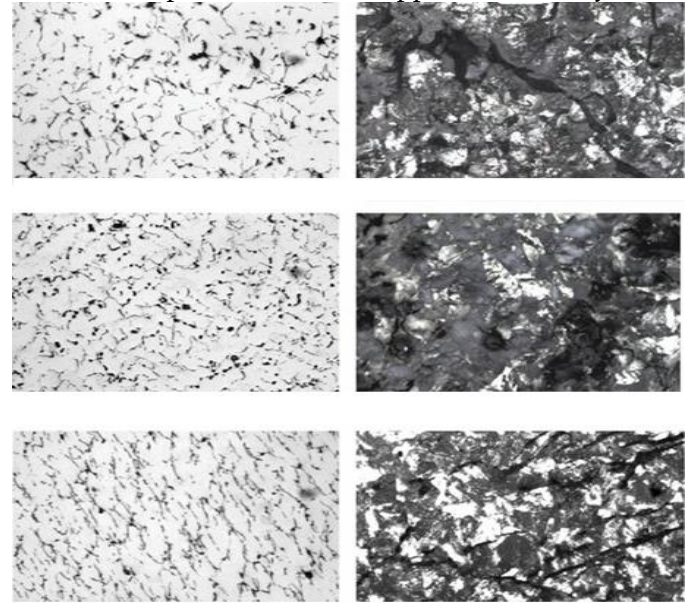


Figure 1. Microstructures of cast irons of one eutectic grade, $\times 100$

To achieve such results, it is suggested to reduce the amount of silicon in the charge and then add the missing silicon to the alloy during modification. This is due to the fact that the carbon is allowed to dissolve and the silica holding time is maintained. In this case the heat treatment is carried out at 1773-1753K for 15 minutes. However, it is necessary to study the effect of silica on the density of the alloy.

During melting, γ -irradiation was used. The results of the study are summarised in Table 3. Analysis of these results shows that silicon and carbon have a major influence on the density and hardness of synthetic cast iron. In this case, the amount of silicon in the slag played the most important role as the main influencing factor, followed by the amount of ferri-silicon introduced during modification and the value of the silicon to carbon ratio in the alloy.

The plot of the density of synthetic cast iron as a function of the degree of eutecticity and the silicon to carbon ratio is shown in Figure 2.

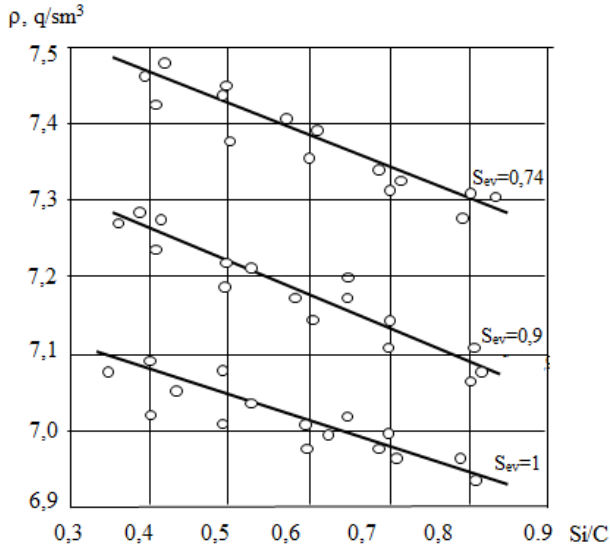


Figure 2. Graph of the dependence of the eutectic density of synthetic cast iron on the ratio of silicon to carbon

The figure shows that as the value of the silicon/carbon ratio increases and the degree of eutectic increases, the density decreases. Analysis of the microstructure of these cast irons shows that as the value of this ratio decreases from 0.8 to 0.4, the amount and size of graphite in the structure decreases. This

shows that the density of the cast iron increases, i.e. it reaches 7.3-7.5 g/sm³ (Table 3).

The subsequent increase in silicon leads to the formation of silicoferrite, which increases hardness and strength. This phenomenon occurs when the silicon content exceeds 3%. In our case, the silicon content increases from 1.5% to 2.5%. Therefore, the increase in silicon

leads to a decrease in the hardness of silicoferrite.

The point is that for the same eutectic grade and the same silicon to carbon ratio, different silicon to carbon ratios will give different pig iron densities. For example, cast iron with a eutectic grade of 0.74 and a silicon to carbon ratio of 0.7 (14÷17 alloys) has the same density as cast iron with a eutectic grade of 0.92 and a ratio of 0.4 to 0.7.

Table 3. Melting mode and parameters

Alloy	Composition of charge %							Preheating temperature, °C	Shelf life, min	Modification FC45 at 1400°C %	Density, q/sm ³	Hardness, HB	Degree of eutectic S _{ek}	Si/C
	Steel scrap	Recycled cast	Cast iron	Electrode crap	ΦMn75	ΦC45								
13Γ	60	40	–	1,1	0,5	2,2	1580	5	0,8	7,28	210	0,74	0,7	
14Γ	60	40	–	1,1	0,5	2,2	1467	15	0,8	7,38	207	0,74	0,7	
15 Γ	60	40	–	1,1	0,5	1,1	1470	15	1,6	7,35	197	0,74	0,6	
16 Γ	60	40	–	1,1	0,5	1,1	1580	5	1,6	7,37	207	0,74	0,6	
17 Γ	60	40	–	1,1	0,5	0,55	1560	5	0,8	7,45	217	0,74	0,53	
18 Γ	60	40	–	1,1	0,5	0,55	1470	15	0,8	7,58	207	0,74	0,53	
19 Γ	60	40	–	1,1	0,5	–	1560	5	1,6	7,51	207	0,74	0,41	
20 Γ	60	40	–	1,1	0,5	–	1470	15	1,6	7,54	207	0,73	0,41	
21 Γ	60	40	–	1,1	0,5	–	1560	5	0,8	7,40	229	0,73	0,41	
22 Γ	60	20	20	1,6	0,6	0,9	1470	15	0,8	7,36	197	0,75	0,53	
23 Γ	60	20	20	1,6	0,6	0,9	1560	5	0,8	7,31	197	0,75	0,53	
24 Γ	60	20	20	1,8	0,6	–	1470	5	1,5	7,25	187	0,92	0,4	
25 Γ	60	20	20	1,8	0,6	–	1560	15	1,5	7,25	187	0,92	0,4	

3. RESULTS AND DISCUSSION

In cast irons with the same degree of eutecticity and coefficient $K < 1$ (alloys 15 and 21), the amount of silicon added exceeds the amount in the charge at density value 0.4 and coefficient value 0.4. The proportion of ferrite in the structure increases, graphite grains are obtained between the dendrites and the density value increases. In this case it is advisable to increase the silicon/carbon ratio from 0.4 (0.6 - 0.7) (alloys 15 - 17). The microstructure improves but the density decreases slightly. On the other hand, when $K > 1$, the amount of silicon added decreases.

Graphite precipitates in the form of large plates, graphite flakes are formed in the microstructure and the density decreases. In such cases it is necessary to reduce the silicon/carbon ratio to 0.5-0.4.

However, at the limit $K = 0.8 \div 1.2$, the metallic base of the cast iron consists only of highly dispersed pearlite. In such cases it is advisable to maintain the silicon/carbon ratio (0.6 - 0.7).

Thus, to obtain high quality synthetic pig iron, the value of the coefficient "K" should be in the range (0.8 - 1.2), the level of eutectic should be in the range (0.74 - 0.8) and the ratio of silicon to carbon content (0.6 - 0.7) should remain within the norm. According to the research results, the designed technological mode and properties of the same eutectic pig iron with controlled melting managed to improve its structure and it was applied in production.

4. CONCLUSION

1. It has been established that the pre-casting processes and the zones of influence on the composition of the ingot material, the melting of the material, the heat treatment and modification of the liquid alloy, the crystallisation process of the physical state of the alloy, the structure and properties of these processes contribute to the production of high quality synthetic cast iron.

2. It is found that the amount of silicon in the slag, the amount of ferrosilicon added during modification and the price of the silicon to

carbon ratio in the alloy play an important role as the main influencing factors.

3. In order to obtain high density pig iron, to limit the amount of silicon in the ingot and to bring it to the composition, to give it an alloy during modification and to obtain a homogeneous composition, the alloy is heated to 1703-1703°C in 15 min. 1723K for 15 minutes. The thermo-temporal treatment is determined.

4 The dependence of the density of synthetic cast iron on the degree of eutecticity and the silicon/carbon ratio is studied and it is found that the density decreases as the silicon/carbon ratio increases. At the same time, the density decreases as the degree of eutectic increases.

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PREDICTIVE OPTIMIZATION STUDIES OF PRODUCTION VALUES OF SOLAR ENERGY SYSTEMS BASED ON ENVIRONMENTAL CONDITIONS WITH THE HELP OF MACHINE LEARNING ALGORITHMS

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Abstract

Solar energy systems, along with their significant advantages, also have disadvantages such as variable sunshine duration and radiation levels dependent on weather conditions, panel pollution over time, and lower energy efficiency compared to other sources. This situation introduces an immeasurable uncertainty that threatens the reliability and stability of energy systems, especially when considering the large-scale integration of renewable energy. To reduce this uncertainty, it is crucial to predict the system's production values in the short and long term based on environmental conditions, thereby increasing the system's predictability for energy distribution planning. The purpose of this study is to perform efficiency analyses on a rational solar energy system model with the help of machine learning, to make optimal energy production estimates according to the structure of the system and the environmental conditions, to apply machine algorithms according to short and long-term data groups and to compare their performances. Thus, as result of the studies, it is aimed to increase the predictability of the systems by proposing an smart estimation methodology that can be applied to real systems.

Keywords: Solar Energy, Machine Learning, Energy Forecast

1. INTRODUCTION

World's installed solar energy capacity was approximately 849 GW, and 55% of the world's installed renewable energy capacity consists of wind and solar energy as of the end of 2018 [1]. Thus energy production forecasting is becoming more important and studies in this fields are increasing.

In this study, to contribute to this field, experimental prediction works have been conducted to determine the machine learning algorithm suitable for the system's characteristics using the prepared data sets to offer an alternative solution for energy production forecasting of solar systems. The performance of the algorithms has been observed based on the data, and improvements have been made on the deemed appropriate prediction algorithm [2-4].

2. MATERIAL and METHODS

In this work, machine learning algorithms that can perform forecasting studies have been identified by the literature researches, hourly humidity, cloudiness, radiation and temperature data from various locations have been collected; and environmental characteristic analyses of these

locations have been conducted based on this data. Simultaneously, energy production values of real or theoretical systems established at selected locations have been monitored, and data sets have been created to integrate with environmental data over short and long periods.

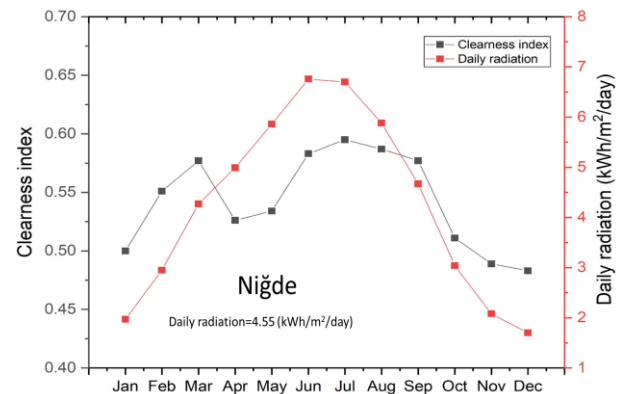


Figure 1. Yearly Data of A Selected Location

ANN, LASSO, SVM, KNN and xGBoost Algorithm are used as forecasting algorithms and multiple tests are run on collected data over long and short time periods. ANN algorithm is built on MATLAB in C+ language, other algorithms are developed in phyton and run on Colab software.

Dataset for different locations are collected from different sources such as General Directorate of Meteorology of Turkey and commissioned real systems in Turkey.

```
[121] score = np.sqrt(mean_squared_error(test['Power'], test['prediction']))
      print(f'RMSE Score on Test set: {score:0.2f}')

RMSE Score on Test set: 15163.08

[125] from sklearn.metrics import r2_score
      print('New R2 score',r2_score(test['Power'], test['prediction']))

New R2 score 0.7726966884104361
```

Figure 2. Xgboost Algorithm in Phyton – Colab screen view

3. MODEL DESCRIPTION

ANN algorithm was used on the input and output variables and as a result, the prediction model was obtained. For the validation and testing stages of the ANN model, the model was trained using 3 months of data and the trained model was tested on 22 days of data.

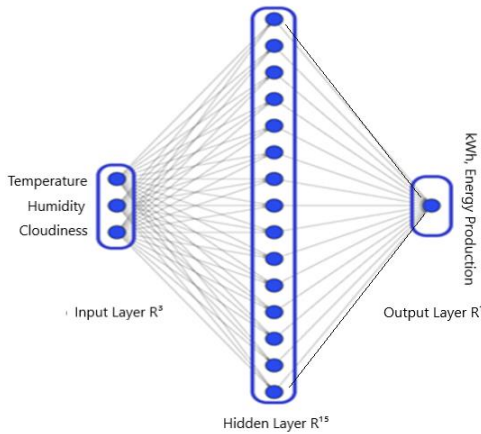


Figure 2. Modelling of ANN Algorithm

XGBoost, Lasso, SVM and kNN algorithms were developed in the python language and training was done using the same data as ANN. Power generation values were included in the algorithm as time series and estimation was performed as in Figure 3, real data and estimation data were compared.

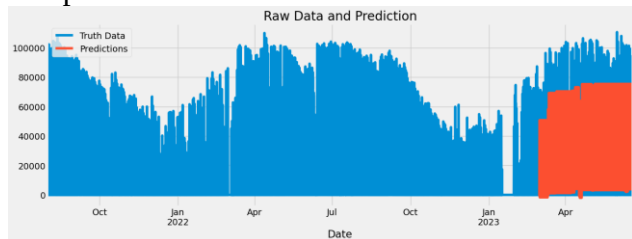


Figure 3. XGBoost train and test data comparison

The trained algorithms were tested with long-term data sets, and the algorithms were trained for short and long terms. Thanks to the training, the

stability of the algorithms was ensured and they became usable in tests. Thus, a prediction methodology that can work according to data sets of any different locations was created.

Algorithm Bias Formulas

Some weight/bias formulas used for algorithms:

ANN Bias:

$$net = \sum_{i=1}^m X_i \times W_i + b \quad (1)$$

SVM Formula:

$$\hat{y} = \begin{cases} 0 & \text{if } \mathbf{w}^T \cdot \mathbf{x} + b < 0, \\ 1 & \text{if } \mathbf{w}^T \cdot \mathbf{x} + b \geq 0 \end{cases} \quad (2)$$

Lasso Formula:

$$L_{lasso}(\beta) = \sum_{i=1}^n (y_i - x_i^T \beta)^2 + \lambda \sum_{j=1}^m |\beta_j| \quad (3)$$

XGBoost works on the black tree hierarchy while kNN works on the clustering methodology.

4. CONCLUSIONS

As a result of the studies, As a result of the studies, it was understood that the ANN algorithm was effective for wind energy predictions in both short and long time intervals (<1%), while the kNN and XGBoost algorithms were effective only in long time intervals (<1%). However, despite giving better results than their performances on short-term data, both SVM and Lasso algorithms could not give the desired results with error rates of 56% and 39%, respectively.

An ANN algorithm capable of predicting the system's future energy production values in the short and long term has been proposed, achieving a forecasting ability with an error margin below 8% in the short term and 1% in the long term, sufficient for planning energy usage based on the expected energy values produced by the system.

Figure 4. ANN performance for short (left) and long (right) period datasets

Figure 4. ANN performance for short (left) and long (right) period datasets

Figure 4. ANN performance for short (left) and long (right) period datasets

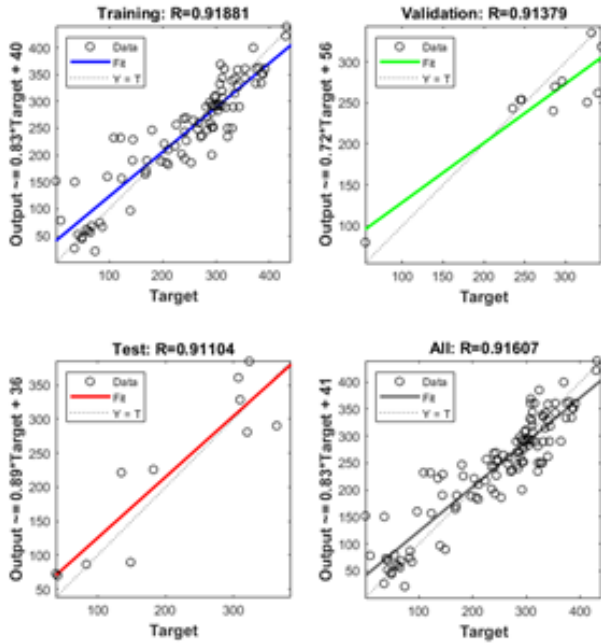


Figure 4. ANN performance for short (left) and long (right) period datasets

The solar energy characteristics of the locations whose data were used in the estimation studies were examined. When the characteristics were compared, the predictability of the solar energy potentials and solar radiation values of the location was examined. As a result of the examinations, it was observed that the hourly data gave approximately 3 times more accurate results than the daily data, proving how important it is for the algorithm stability to obtain the data more frequently.

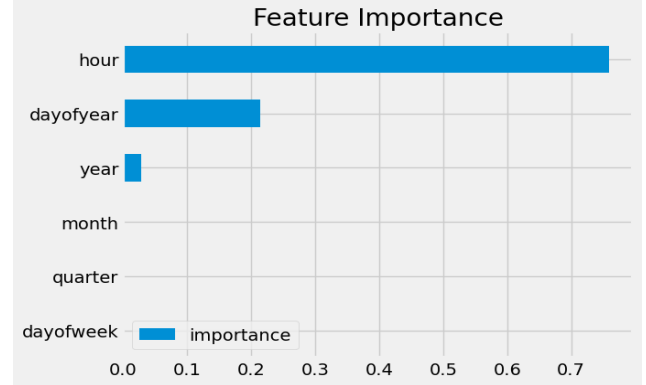


Figure 5. Importance rate of data frequencies

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BACTERIAL AND ARCHAEAL COMMUNITIES OF INITIAL PHASE OF A POTENTIAL MUD VOLCANO IN DÜZCE

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Abstract

The current state of knowledge regarding the microorganisms involved in anaerobic methane oxidation is based on studies of methane leaking environments, where high concentrations of methane and sulphate favour the high activity of archaea and bacteria syntrophic associations. In order to ascertain a more comprehensive understanding of the microbial diversity present in mud and water, we conducted molecular biological studies that target 16S rRNA conserved gene regions. The data of presented study enable the generation of a more detailed microbial diversity profile. According to this, mud and water samples were collected from the initial phase of potential mud volcano in Düzce. The abundance of bacteria, archaea, ANME1, MCRA, SRB2, DSS and DBB was determined by real-time PCR. The highest abundance of bacteria ($1.52E+10$) was observed in the mud sample. The group with the lowest density was identified as *Desulfobulbus* ($2.49E+02$) in the water sample. In conclusion, the data could provide evidence of the development of potential mud volcano in terrestrial environments.

Keywords: Microbial Communities, Mud Volcano, Bacteria, Archaea

1 INTRODUCTION

The anaerobic methane oxidation process is carried out by microorganisms in the natural environment [1]. The majority of methane produced in subterranean reservoirs is consumed by anaerobic microorganisms. These microorganisms are present in sulphate-contacting mud layers before the methane reaches the surface [2]. The geochemical modelling studies have revealed that microbial respiration is dominated by sulphate reduction at the surface. This is largely due to anaerobic methane oxidation (AOM). This process is typically observed in areas where both methane and sulphate begin to dissipate. These areas are referred to as the 'sulphate-methane transition zone', where both compounds are consumed in equal molar amounts. It is anticipated that temporal and spatial variations in the structure and functioning of microbial communities of mud volcanoes could be observed as a consequence of gas/liquid leaks, eruptions and changes in gas hydrate structure [3]. The current state of knowledge regarding the microorganisms involved in anaerobic methane oxidation is based on studies of methane

leaking environments, where high concentrations of methane and sulphate favour the high activity of archaea and bacteria syntrophic associations. Consequently, only a small proportion of the microorganisms in such habitats could be identified by classical microbiological techniques. The researches indicate that only a small proportion of the total microbial population, ranging from 1 to 5%, could be successfully classified. However, to determine more microbial diversity in mud volcano sediments and water, a complete microbial diversity profile could be obtained by molecular biological studies that target 16S rRNA conserved gene regions. These gene regions are mostly specific to bacteria in ecological studies. The current study was conducted to investigate the microbial diversity present in the mud and water samples collected from the initial phase of potential mud volcano in Düzce.

2 MATERIAL AND METHOD

In order to research the microbiological parameters in the study; mud and water samples were collected from initial phase of a potential mud volcano in Düzce, where artesian gas and

water were observed in the sampling site. Falcon tubes were stored at +4°C and transported to the laboratory immediately after sampling. Figure 1 also show the sampling area.

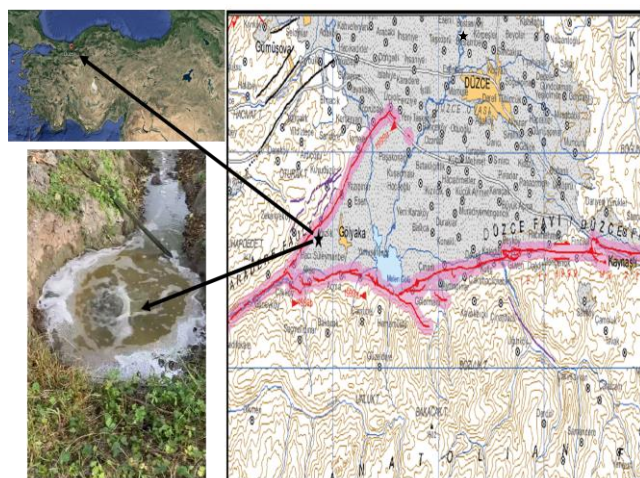


FIGURE 1. Map of the sampling area (In the event that a gaseous water outlet)

2.1 DNA Extraction

The microbial abundance in the samples from the study area was determined by real-time PCR (Roche LightCycler 96 instrument). The genomic DNA was extracted with DNeasy PowerSoil DNA Isolation (Qiagen) Kit. The procedure was optimised and applied with minor modifications for the purpose of DNA isolation.

2.2 Reaction of Real-Time PCR

The selection of group-specific primer sets were sourced from the literature [5-9] in order to ascertain the levels of bacteria (BAC), archaea (ARC), methanogens (MCRA), anaerobic methane-oxidising archaea (ANME1), sulphate-reducing bacteria (SRB2), *Desulfosarcinia* (DSS) and *Desulfobulbus* (DBB) (Table 1).

The Roche LightCycler FastStart DNA Master Sybr®Green I kit was utilised in accordance with the instructions for use in the aforementioned analyses.

Table 1. The group-specific primer sets

Group	Primer
ANME1	F: AGG TCC TAC GGG ACG CAT R: GGT CAG ACG CCT TCG CT
MCRA	F: 5-GGT GGT GTM GGD TTC ACM CAR TA-3 R: 5-CGT TCA TBG CGT AGT TVG GRT AGT-3
SRB2	F: ACT-TGA-GTA-CCG-GAG-AGG-GA R: CCT-AGT-GCC-CAT-CGT-TTA-GG
DSS	F: ACT-TGA-GTA-TGG-GAG-AGG-GAA-G R: ACC-TAG-TGT-TCA-CCG-TTT-ACT-GC
DBB	F: GCT-TGA-GTA-TGG-GAG-GGG-A R: CAC-CTA-GTT-CTC-ATC-GTT-TAC-AGC

BACT	F: CCG-TGA-ATA-CGT-TCY-CGG R: GGW-TAC-CTT-GTT-ACG-ACT-T
ARC	F: ATT-AGA-TAC-CCS-BGT-AGT-CC R: GCC-ATG-CAC-CWC-CTC-T

The protocol was optimised for each group with ANME1, MCRA, SRB2, DSS and DBB primers. The initial denaturation step was set at 1 cycle at 95°C for 5 minutes. Subsequently, the amplification step was performed at 95°C for 10 seconds, followed by amplification at 53°C for 15 seconds and elongation at 72°C for 15 seconds, for a total of 45 cycles. The protocol was concluded with a melting step. A single cycle was conducted, comprising a 5-second period at 95°C, with a rate of 65°C/second, followed by a 1-second period at 97°C for signal acquisition throughout the cycle. The final stage of the protocol is the cooling step. A single cycle was conducted at 40°C for a duration of 10 seconds.

The protocol for ARC and BACT involves an initial denaturation step, which is conducted at 95°C for 5 minutes. Subsequently, the amplification step was performed at 95°C for 10 seconds, followed by amplification at 50°C for 15 seconds and elongation at 72°C for 11 seconds, for a total of 45 cycles. The protocol was concluded with a melting step. A single cycle was conducted, comprising a 5-second period at 95°C, with a rate of 65°C/sec, followed by a 1-second period at 97°C for signal acquisition throughout the cycle. The final stage of the protocol is the cooling step. A single cycle was conducted at 40°C for a duration of 10 seconds.

Following quantification of all primers, the data were expressed as gene copy number per gram of mud and as gene copy number per millilitre.

3 RESULTS AND DISCUSSION

The results of the real-time PCR analysis revealed that the bacteria were more abundant than the archaea. The highest abundance of bacteria (1.52E+10) was observed in the mud sample. The group with the lowest density was identified as DSS (2.49E+02) in the water sample. The mud and water samples taken initial phase of potential mud volcano in Düzce indicate that methane, sulphur gases and related bacteria and archaea are present in the environment at significant levels (Table 2-3, Figure 2). In particular, the number of anaerobic methane oxidizing archaea (ANME1) group was in parallel with the findings of previous studies conducted in the literature on mud volcanoes.

Table 2. Gene copy numbers of bacteria and sulfate reducing bacteria groups (gene copies/ g of mud and gene copies/ ml of water)

Sample	BACT	SRB2	DSS	DBB
Mud	1.52E+10	5.98E+06	6.46E+07	4.81E+07
Water	2.75E+05	Nd*	1.89E+03	2.49E+02

*Nd: not detected

Table 3. Gene copy numbers of archaea, ANME and methanogen groups (gene copies/ g of mud and gene copies/ ml of water)

Sample	ARC	ANME-1	MCRA
Mud	4.50E+08	3.95E+05	3.54E+08
Water	1.62E+03	Nd*	Nd*

*Nd: not detected

The research conducted by Alain et al., 2006 reported that the microbial diversity analyses on mud volcanoes in the Carpathian Mountains in Romania had been detected similar our results. They found abundances of bacteria and archaea, as 3.4–5.1E+08 cells/g and 0.25–1.6E+06 cells/g dwt of mud, respectively.

It is frequently assumed that the rate of sulphate reduction within the sulphate-methane transition zone is directly proportional to anaerobic methane oxidation. The presented data could provide evidence of the development of potential mud volcano in terrestrial environments.

4 CONCLUSION

In generally, it has been demonstrated that different groups of sulphate-reducing bacteria and anaerobic methane-oxidising archaea (ANME) are involved in the anaerobic methane oxidation process in a terrestrial environments of methane seeps and mud volcanoes. Thus, the occurrence of this phenomenon in terrestrial environments could be indicative of initial phase of potential mud volcano development.

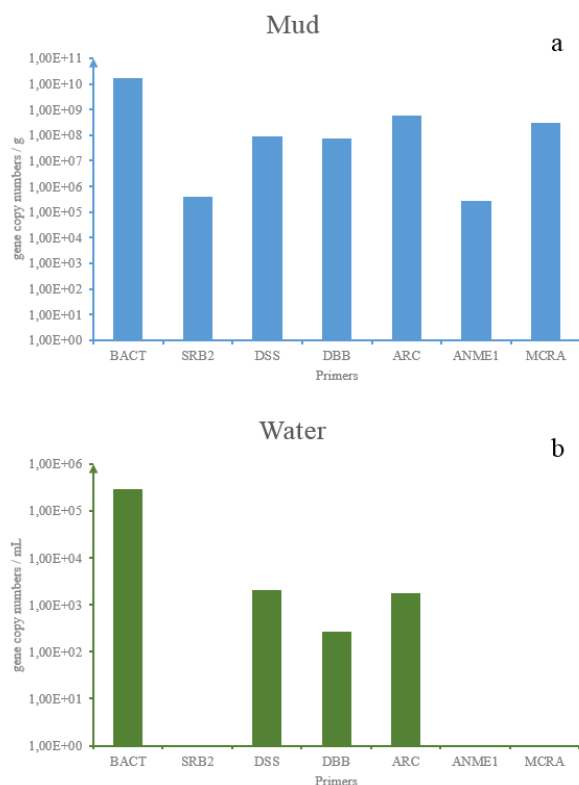


FIGURE 2. The results of the microbial community analysis of the mud (a) and water (b) samples using real-time PCR.

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Enhancing Cycling Stability of Lithium-Ion Battery Anodes through MoO₃ Nanoparticle Functionalization on Silicon Nanowire Arrays

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Abstract

The functionalization of molybdenum oxide (MoO₃) nanoparticles is introduced as a method to enhance the cycling stability of lithium-ion battery (LIB) anodes based on silicon nanowire (SiNW) arrays. In this study, MoO₃ nanoparticles are deposited onto SiNW arrays, fabricated through a metal-assisted chemical etching (MACE) process, using a drop-casting technique followed by thermal annealing. This results in a MoO₃@SiNW hybrid structure with improved structural stability, small particle size, and a porous configuration, which enhances electron and ion transport at the electrode-electrolyte interface. Electrochemical tests reveal that the MoO₃@SiNW hybrids outperform bare SiNWs, demonstrating better cycling stability and higher capacity, particularly under high current densities. The enhanced performance is attributed to the synergistic effects between MoO₃ nanoparticles and SiNW arrays, suggesting that this hybrid structure holds promise as a high-performance anode material for energy storage applications.

Keywords: Lithium-ion Battery; Silicon Nanowires; Molybdenum Oxides; Transition-Metal Oxides; Drop-Casting

1 INTRODUCTION

The rapid rise of electric vehicles and portable electronic devices has significantly increased the demand for lithium-ion (Li-ion) batteries due to their high energy density and cycling stability. Currently, most Li-ion batteries use graphite as the anode and LiCoO₂ as the cathode, yielding an energy density of around 150 Wh·kg⁻¹ [1-4]. However, this configuration is inadequate for the expanding needs of long-range electric vehicles, as it faces limitations in terms of areal capacity and energy density. As a result, alternative electrode materials with higher capacity and energy density must be explored. Silicon (Si), particularly in the form of silicon nanowires (SiNWs), has attracted attention due to its high theoretical capacity of 4200 mA·h·g⁻¹, nearly ten times greater than that of graphite [5-7]. SiNWs are especially promising as they offer one-

dimensional electron transport and a large surface area, and can be fabricated through the cost-effective and scalable metal-assisted chemical etching (MACE) method [8]. Recent interest in SiNW arrays produced via the MACE method stems from their applications in energy storage devices like Li-ion batteries, supercapacitors, solar cells, and sensors [9]. SiNWs, which grow directly on a silicon substrate, can function as both an electrode and current collector without the need for binders. Despite their potential, SiNWs face challenges such as low conductivity, large volume changes during cycling, and the formation of a solid electrolyte interface (SEI) film, which reduce their cycling lifespan. Various surface modification techniques, such as magnesiothermic reduction, electrospinning, spin-coating, and atomic layer deposition, have been explored to improve their electrochemical performance [5, 10-21]. Drop-casting, due to its simplicity and compatibility with large-scale processes, has

shown promise for enhancing electrode performance. In particular, molybdenum trioxide (MoO_3) has gained attention as an anode material due to its layered structure and capacity for high lithium-ion intercalation. This study focuses on using drop-casting to functionalize SiNWs with MoO_3 nanoparticles, aiming to improve SiNW-based electrodes for high-performance Li-ion batteries.

2 EXPERIMENT

2.1 Preparation of Metal-Assisted Etched SiNWs:

P-type boron-doped silicon wafers ($2.5 \times 2.5 \text{ cm}^2$) were cleaned using acetone, ethanol, and a boiling $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ solution. Silver nanoparticles (AgNPs) were deposited using a solution of 0.02 M AgNO_3 and 5 M HF, followed by etching in HF/ H_2O_2 to form SiNW arrays. Residual AgNPs were removed with HNO_3 and 2% HF, and the SiNWs were dried under inert gas.

2.2 Deposition of Mo Oxides on SiNWs via Drop-Casting:

O_2 plasma treatment was applied to enhance the SiNW surface hydrophilicity. A MoCl_5 solution was drop-cast onto the SiNW substrate, allowed to evaporate overnight, and then annealed at a temperature of 500°C in an oxygen atmosphere.

2.3 Characterization:

Samples were characterized using X-ray diffraction (XRD) with a PANalytical XPert PRO MPD Bragg-Brentano diffractometer, utilizing $\text{Co K}\alpha$ radiation ($\lambda = 1.789 \text{ \AA}$). Scans were performed across the 2θ range from 4° to 99° with a 0.17° step size and 200 seconds per step. Morphological analysis was conducted using field emission scanning electron microscopy (FE-SEM) on a JEOL JSM-7001F instrument. Energy-dispersive X-ray spectroscopy (EDX) was employed to determine the elemental composition of the samples.

2.4 Electrochemical Analyses:

Electrochemical measurements were carried out using an AutoLab PGSTAT30 potentiostat/galvanostat inside a nitrogen-filled glove box. A three-electrode setup was used, with 1 M LiClO_4 in a 1:1 ethylene carbonate and propylene carbonate solution as the electrolyte. Lithium rods were employed as both counter and reference electrodes, while SiNW arrays decorated

with Mo oxide nanoparticles served as the working electrode, with an active area of approximately 0.57 cm^2 . Cyclic voltammetry (CV) was performed over a voltage range of 0.0 to 2.0 V versus Li/Li^+ . Galvanostatic charge-discharge tests were conducted to assess long-term cycling stability at a current density of $100 \mu\text{A} \cdot \text{cm}^{-2}$ across a voltage range of 0.1 to 2.0 V.

3 RESULTS AND DISCUSSION:

The XRD pattern in the Fig. 1 compares the diffraction peaks of bare SiNW and silicon nanowires decorated with MoO_3 annealed at 500°C . The black curve represents the SiNW sample, where prominent peaks at $\sim 28.5^\circ$ and $\sim 69^\circ$ correspond to the (111) and (400) planes of crystalline silicon, respectively. In contrast, the red curve for the MoO_3/SiNW sample shows additional peaks, (marked by stars, which correspond to MoO_2 JCPDS #00-032-0671), with reflections observed at $\sim 26^\circ$, 35° , 46° , 48° , and 57° for the (040), (140), (002), (210), and (180) planes, respectively [22, 23]. These peaks indicate the successful formation of molybdenum oxide on the SiNW surface after annealing. The enhanced peak intensity and new reflections in the MoO_3/SiNW sample suggest a well-crystallized MoO_3 phase [4], confirming the structural integration of MoO_3 with the SiNWs. This crystalline structure is essential for improving the electrochemical properties of the hybrid material for lithium-ion battery applications.

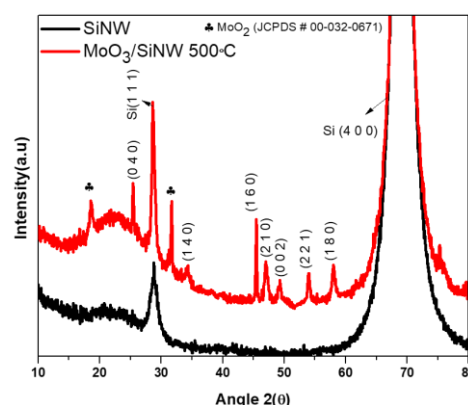


Figure 1. XRD patterns of as-synthesized SiNW arrays and SiNW arrays decorated with Mo Oxide nanoparticles annealed at 500°C for 15 min, in O_2 atmosphere.

Fig. 2 presents FE-SEM images comparing the morphology of bare and Mo oxide-decorated SiNW arrays. In Fig.2(a), the left image shows the

vertically aligned bare SiNW arrays at lower magnification, revealing smooth and well-defined structures. The corresponding higher magnification image on the right highlights the clean surfaces of the nanowires without any decoration. In Fig. 2(b), the SiNW arrays have been decorated with molybdenum oxide nanoparticles after being annealed at 500°C for 15 minutes in an oxygen atmosphere. The left image shows the decorated nanowires at low magnification, where the surface texture appears noticeably rougher than the bare nanowires. The higher magnification image on the right provides a closer look at the Mo oxide nanoparticles on the SiNW surfaces, illustrating the significant surface modification and roughness induced by the annealing and decoration process. Mo oxide nanoparticles are also clearly seen attached to the SiNWs, further emphasizing the successful decoration of the nanowires. This comparison highlights the morphological transformation of SiNW arrays before and after nanoparticle decoration.

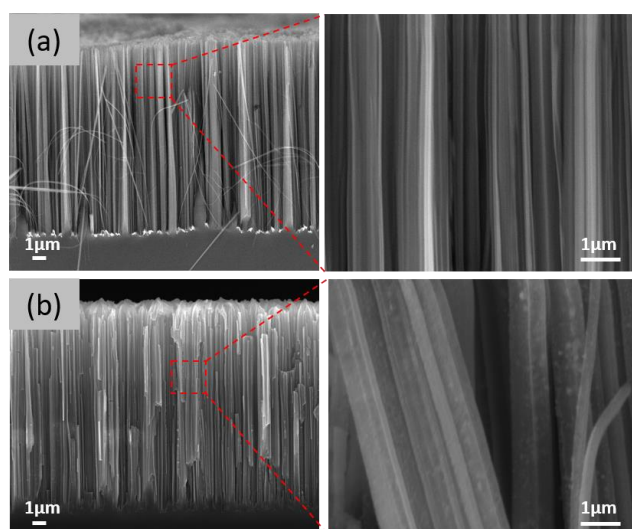


Figure 2. FE-SEM images of (a) bare SiNW arrays corresponding higher magnification (b) SiNW arrays decorated with Mo oxides nanoparticles with annealing temperature 500°C, for 15 min, in O₂ atmosphere corresponding higher magnification.

The Fig. 3 presents the FE-SEM image and corresponding energy dispersive X-ray spectroscopy (EDS) analysis of SiNW arrays decorated with molybdenum oxide nanoparticles. The SiNW arrays were subjected to an annealing process at 500°C for 15 minutes in an oxygen atmosphere to facilitate the deposition of Mo oxide. In the SEM image, the vertically aligned SiNW arrays are clearly visible, with the region marked as "Espectro 5" highlighting the area

analysed for elemental composition using EDS. The EDS spectrum provides insight into the chemical composition of this selected area, revealing a strong silicon (Si) peak, which corresponds to the bulk of the nanowire structure [7, 24-27]. Additionally, the spectrum displays a distinct oxygen (O) peak, indicative of the formation of oxide layers, likely due to the molybdenum oxide deposition and surface oxidation during the annealing process. Furthermore, the presence of multiple molybdenum (Mo) peaks confirms the successful decoration of the SiNW arrays with Mo oxide nanoparticles. The combination of this analysis demonstrates that the annealing process has effectively modified the surface of the SiNWs by incorporating molybdenum oxide, significantly altering the material's surface properties.

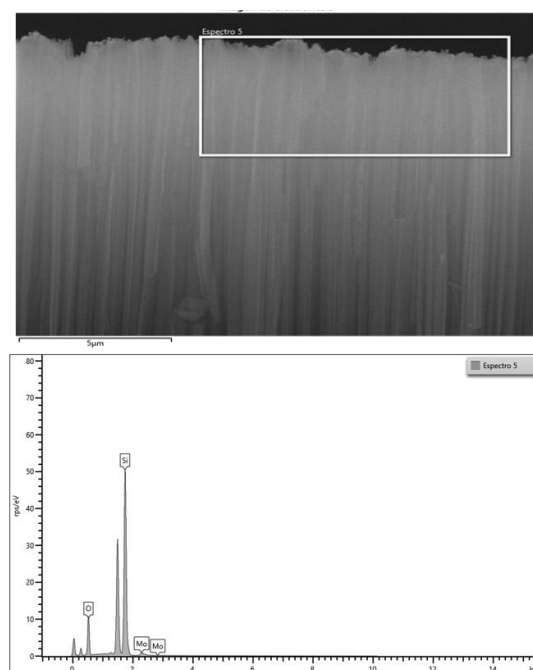


Figure 3. FE-SEM image and EDS spectrum of SiNW arrays decorated with molybdenum oxide nanoparticles after annealing at 500°C for 15 minutes in an oxygen atmosphere.

The electrochemical performance of Mo oxide nanoparticles decorated on SiNW arrays (annealed at 500°C in an oxygen atmosphere) was investigated using cyclic voltammetry (CV) and galvanostatic charge-discharge tests. Figures 4(a, c) present the CV profiles for the first ten cycles of bare SiNW arrays and MoO₃@SiNW hybrids. In Fig. 4(a), the voltage profile for the bare SiNW arrays exhibits a stable plateau during the initial charging phase, corresponding to the reaction between crystalline silicon and Li⁺ ions, leading to

the formation of amorphous Li_xSi , which aligns with previously reported behavior of silicon anodes. In contrast, Fig. 4(c) highlights significant differences in the CV profiles of $\text{MoO}_3@\text{SiNW}$ hybrids, showing two broad reduction peaks at 1.2 V and 0.4 V. The peak at 1.2 V in the first cycle is associated with lithium-ion insertion into the MoO_3 structure and the amorphousization of MoO_3 , while the 0.4 V peak corresponds to reversible conversion reactions [28]. These shifts in potential and peak current suggest enhanced lithiation and delithiation processes facilitated by the Mo oxide nanoparticles [29]. Figures 4(b, d) depict the first ten charge-discharge profiles of bare SiNW arrays and $\text{MoO}_3@\text{SiNW}$ hybrids at a current density of $100 \mu\text{A}\cdot\text{cm}^{-2}$. Fig. 4(b) shows that the bare SiNW arrays display a substantial initial discharge capacity, although there is an irreversible capacity loss likely due to the formation of a solid electrolyte interphase (SEI), with minimal capacity fading in subsequent cycles. In comparison, the $\text{MoO}_3@\text{SiNW}$ hybrids, shown in Fig. 4(d), demonstrate a significantly higher initial discharge capacity of $1.34 \text{ mAh}\cdot\text{cm}^{-2}$, compared to $0.35 \text{ mAh}\cdot\text{cm}^{-2}$ for the bare SiNW arrays. The presence of well-defined voltage plateaus, particularly at 1.5 V, indicates the contribution of Mo oxide nanoparticles in improving the electrochemical performance. The second cycle exhibits a capacity of $1.25 \text{ mAh}\cdot\text{cm}^{-2}$, which surpasses the second cycle capacity of the bare SiNW arrays. Additionally, the $\text{MoO}_3@\text{SiNW}$ hybrids exhibit minimal capacity fading, with nearly identical charge-discharge profiles for the 2nd and 10th cycles. The enhanced capacity and improved cycling stability of the $\text{MoO}_3@\text{SiNW}$ hybrids, compared to the bare SiNW arrays, emphasize the significant role of Mo oxide nanoparticle decoration in enhancing the electrochemical performance of SiNW-based anodes for lithium-ion batteries.

Figure. 5 compares the first discharge specific capacities from various studies to the results achieved in this work. The study by H. Ohtsuka et al. [30] used MoO_3 thin films fabricated via RF sputtering, achieving a specific capacity of $0.39 \text{ mA}\cdot\text{h}\cdot\text{cm}^{-2}$. K. Peng et al. [31] employed large-area SiNW arrays prepared by MACH as anode materials, with a first discharge capacity of $0.55 \text{ mA}\cdot\text{h}\cdot\text{cm}^{-2}$. H. Chen et al. attained a higher specific capacity of $1.70 \text{ mA}\cdot\text{h}\cdot\text{cm}^{-2}$ using Cu-coated SiNW arrays. While the Cu coating

enhances the capacity, it may compromise electrode stability due to copper's diffusivity and reactivity. In contrast, this work

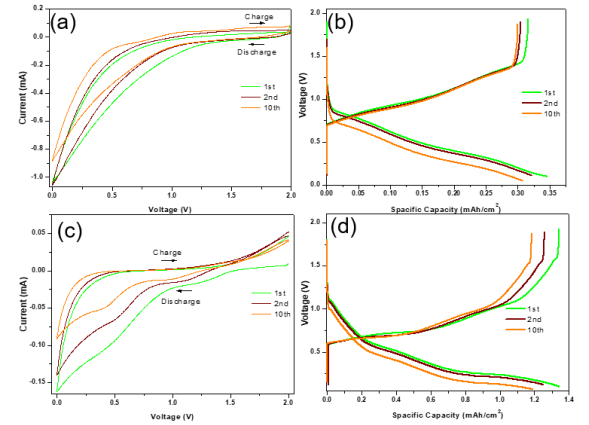


figure 4. Cyclic voltammograms and charge-discharge profiles for bare SiNW arrays and $\text{MoO}_3@\text{SiNW}$ hybrids annealed at 500°C . (a, c) CV profiles of bare SiNW arrays and $\text{MoO}_3@\text{SiNW}$ hybrids over the first 10 cycles at a scan rate of $0.1 \text{ mV}\cdot\text{s}^{-1}$, (b, d) Charge-discharge profiles of bare SiNW arrays and $\text{MoO}_3@\text{SiNW}$ hybrids at a current density of $100 \mu\text{A}\cdot\text{cm}^{-2}$.

achieves a first discharge specific capacity of $1.35 \text{ mA}\cdot\text{h}\cdot\text{cm}^{-2}$ by combining MoO_3 nanoparticles with SiNW arrays. Although this capacity is slightly lower than the Cu-coated SiNWs [32], the MoO_3 -based material offers better stability. The improved performance in this study is attributed to the increased active surface area of the MoO_3 nanoparticles on the SiNW arrays, which enhances lithium-ion insertion and extraction efficiency.

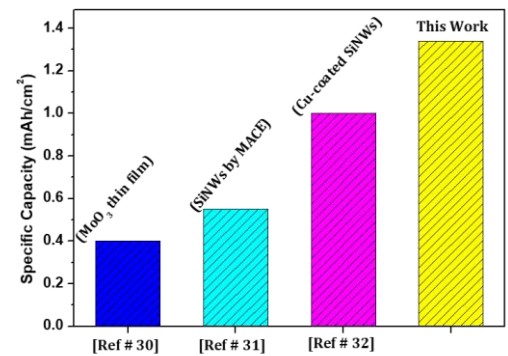


Figure 5. Comparative analysis of the first discharge specific capacities obtained in this work and from previous studies.

4 CONCLUSIONS

In this work, molybdenum oxide (MoO_3) nanoparticles were successfully deposited on silicon nanowire (SiNW) arrays through annealing at 500°C in an oxygen atmosphere. Structural characterization using FESEM, XRD, and EDS confirmed the uniform decoration of MoO_3 on SiNWs. Electrochemical testing, including cyclic voltammetry and charge-discharge analysis, demonstrated a significant improvement in the anode performance of the MoO_3 @SiNW hybrids compared to bare SiNWs. The MoO_3 @SiNW hybrids achieved a higher specific capacity of $1.34 \text{ mA} \cdot \text{h} \cdot \text{cm}^{-2}$, with stable cycling behavior over ten cycles. This enhanced performance can be attributed to the increased surface area and improved lithium-ion interaction provided by the MoO_3 nanoparticles. The results highlight the potential of MoO_3 @SiNW hybrids as promising anode materials for lithium-ion batteries.

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A NOVEL AND GREEN SYNTHESIS OF MIXED PHASE CoO@Co₃O₄@C ANODE MATERIAL FOR LITHIUM ION BATTERIES

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Abstract

CoO composite materials have garnered significant attention for their potential in lithium-ion batteries (LIBs). In this study, we present a novel and eco-friendly solution method to synthesize pristine Co₃O₄ and mixed-phase CoO@Co₃O₄@C composite anode materials for LIBs. These materials were characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The XRD analysis showed that the composite anode primarily consists of CoO, with minor amounts of cubic Co₃O₄ and traces of Co metal as impurities. SEM images revealed that CoO, Co₃O₄, and Co phases are dispersed within an amorphous carbon matrix. The electrochemical properties of the anode were examined through galvanostatic charge/discharge cycles and cyclic voltammetry. The composite anode demonstrated a reversible specific capacity of approximately 447±5 mAh g⁻¹ after 10 cycles at 100 mA g⁻¹ and 107±5 mAh g⁻¹ after 50 cycles at 500 mA g⁻¹, with enhanced cyclic stability and excellent rate capability. The improved electrochemical performance is attributed to the enhanced electrical contact between particles, better lithium-ion diffusion, and minimized volume changes in the anode.

Keywords: Lithium ion batteries, CoO, Anode materials, Capacity fade, Green synthesis, Electrochemical Performance.

1 INTRODUCTION

Designing electrode materials with high lithium storage capacity, rate capability, and long cycling life remains a significant challenge for developing high-performance lithium-ion batteries (LIBs). Graphite is the current anode material for commercial LIBs, but its limited capacity (372 mAh g⁻¹) and low potential (0.1 V vs. Li/Li⁺) necessitate alternatives with higher capacities and more positive insertion voltages to reduce the risk of lithium plating during fast recharges [1]. Transition metal oxides (MOs) are among the most promising anode materials, offering theoretical capacities 2-3 times higher than graphite, along with safer lithiation potentials [2]. However, MOs suffer from poor electronic conductivity and structural instability due to volume changes during cycling, which limits their performance [3]. Despite these challenges, MOs like CoO/Co₃O₄, MoO₃, SnO₂, NiO, ZnO, and NiFe₂O₄ have shown great potential due to their high theoretical capacities and natural abundance [4].

Cobalt monoxide (CoO) is particularly attractive, offering a high theoretical capacity of 715 mAh g⁻¹ [5]. However, its practical use is hindered by poor conductivity and cycling stability due to volume changes during lithium insertion/extraction [6]. To address these issues, carbon-based composites, such as CoO combined with graphene or carbon nanotubes, have been developed to enhance Li-ion storage capability and improve cycling performance [7].

In this study, we synthesized mixed-phase CoO@Co₃O₄@C using Punica granatum extract as both a reducing agent and carbon source. This method facilitates the production of mixed metal oxide particles with high crystallinity and submicron sizes. The extract's sugars such as fructose, glucose help control particle size and morphology, resulting in improved conductivity and promising electrochemical performance for LIB applications. This green synthesis method is

shown in Fig. 3a, c, the particle distribution in the composite material is heterogeneous, with three different particle morphologies, likely corresponding to CoO, Co₃O₄, and Co phases distributed in an amorphous carbon network. In contrast, the particle distribution of pristine Co₃O₄ (Fig. 3b, d) is homogeneous, with particles agglomerating and sizes ranging from 100 to 500 nm.

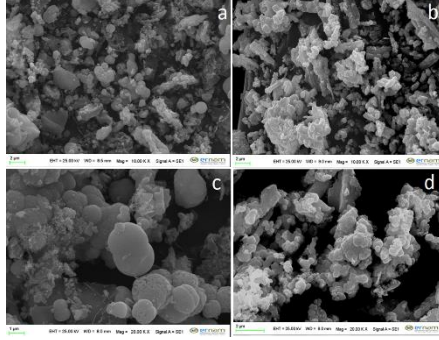


Figure 3. SEM Images of a, c CoO@Co₃O₄@C Composite and b, d Pristine Co₃O₄ (Low and High Magnification, Respectively).

To confirm the chemical composition, EDS analysis of the CoO@Co₃O₄@C composite was performed (Fig. 4). The EDS spectrum shows the presence of Co, O, and C, indicating the composite's phase purity. The content of Co, O, and C was calculated as 57.3, 29.1, and 13.5 wt%, respectively. The peaks for Au at 2.3 and 9.8 keV are due to the sputter coating process.

The resistance (R) was extracted from the I-V curve using Ohm's law, and resistivity (δ) was calculated using the equation $R = \delta L/A$, where A is the pellet area and L is its thickness. The dc electronic conductivity was determined as the inverse of δ . The electronic conductivities of pristine Co₃O₄ and the CoO@Co₃O₄@C composite were found to be 1.14E-6 S cm⁻¹ and 0.231 S cm⁻¹, respectively. These results show that the addition of amorphous carbon increased the electronic conductivity by a factor of 105.

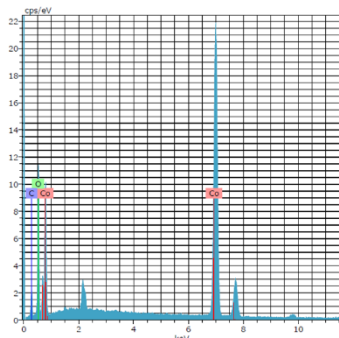


Figure 4. EDS Spectrum Result of CoO@Co₃O₄@C Composite

Figs. 5a and 5b show the CV curves of pristine Co₃O₄ and CoO@Co₃O₄@C composite anodes, used to assess the electrochemical reactions. For pristine Co₃O₄, a cathodic peak around 0.6 V in the first cycle is attributed to the irreversible formation of the solid electrolyte interface (SEI) film (Reaction 1) [10].

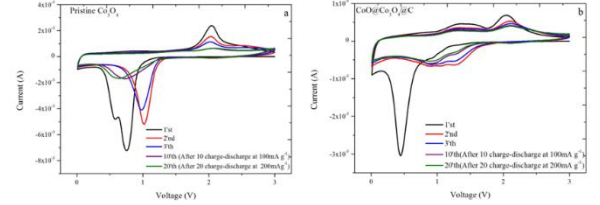
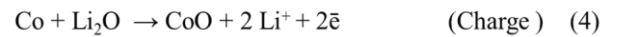
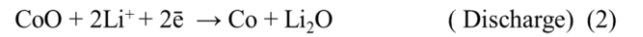
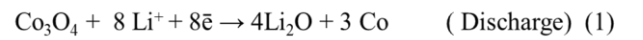


Figure 5. Cyclic Voltammograms a Pristine Co₃O₄ and b CoO@Co₃O₄@C Composite Anode. Scan Rate 0.1 mV s⁻¹

The cathodic peak at 0.8 V corresponds to the formation of Li₂O and Co by the reduction of CoO (Reaction 2). In subsequent cycles, the cathodic peak shifts to a lower potential. For the CoO@Co₃O₄@C composite, a cathodic peak at 0.47 V is observed in the first cycle (reactions 1 and 2). Both pristine Co₃O₄ and CoO@Co₃O₄@C composite anodes show an anodic peak at around 2.1 V in the first cycle, corresponding to the oxidation of CoO (Reactions 3 and 4), with slight shifts in the 2nd and 3rd cycles. After the 20th charge-discharge at 200 mA g⁻¹, the CV curves of the CoO@Co₃O₄@C composite in Fig. 5b show a slight shift, indicating reversible electrochemical reactions, while the pristine Co₃O₄ anode exhibits separated CV curves and decreased peak intensity due to high polarization.



Figs. 6a and 6b show the galvanostatic discharge-charge curves of pristine Co₃O₄ and CoO@Co₃O₄@C composite electrodes for the 1st, 2nd, and 10th cycles at 100 mA g⁻¹ between 0.01 V and 3.0 V. The curves align with the CV results, indicating typical characteristics of CoO and Co₃O₄ [11]. The pristine Co₃O₄ exhibits two voltage plateaus in discharge at 1.2 V and 0.8 V, while CoO@Co₃O₄@C shows a long sloping plateau at 1.2 V and 0.8 V, indicating some irreversible reactions due to amorphous metal

oxides. Reduction plateaus at around 1.0 V and 0.5 V correspond to Co_3O_4 reducing to CoO and then to Co .

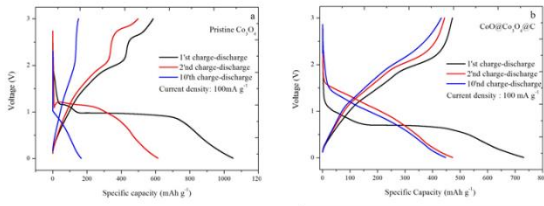


Figure 6. First Charge-Discharge Curves of Pristine Co_3O_4 and $\text{CoO}@\text{Co}_3\text{O}_4@\text{C}$ Composite Anodes in 0.01–3 V with EC–DEC 1:1/1 M LiPF_6 Solutions

The pristine Co_3O_4 electrode has initial discharge and charge capacities of $1052 \pm 5 \text{ mAh g}^{-1}$ and $586 \pm 5 \text{ mAh g}^{-1}$, respectively, with a Coulombic efficiency of 55.7%. After 10 cycles, the discharge capacity drops to $151 \pm 5 \text{ mAh g}^{-1}$, with a capacity fading ratio of 75.4% between the 2nd and 10th cycles. This loss is attributed to irreversible SEI film formation [12].

In contrast, the $\text{CoO}@\text{Co}_3\text{O}_4@\text{C}$ composite electrode shows initial discharge and charge capacities of $731 \pm 5 \text{ mAh g}^{-1}$ and $472 \pm 5 \text{ mAh g}^{-1}$, with a higher Coulombic efficiency of 64.5%. After 10 cycles, the composite retains a discharge capacity of $447 \pm 5 \text{ mAh g}^{-1}$, with a capacity fading ratio of only 5%, indicating better cycling stability.

To investigate rate capacity, both pristine Co_3O_4 and $\text{CoO}@\text{Co}_3\text{O}_4@\text{C}$ composite electrodes were cycled at current densities of 100, 200, and 500 mA g^{-1} , as shown in Fig. 7. Rate capability is crucial for lithium batteries. Fig. 7 demonstrates that both electrodes' capacities decreased with increasing rate, but the $\text{CoO}@\text{Co}_3\text{O}_4@\text{C}$ composite electrode maintained higher capacity at higher rates. Specifically, the $\text{CoO}@\text{Co}_3\text{O}_4@\text{C}$ composite delivered capacities of $473 \pm 5 \text{ mA h g}^{-1}$, $373 \pm 5 \text{ mA h g}^{-1}$, and $158 \pm 5 \text{ mA h g}^{-1}$ at 100, 200, and 500 mA g^{-1} , respectively, showing capacity retention of 93.9% (10th cycle), 76.4% (30th cycle), and 67.8% (50th cycle). When the current density returned to 100 mA g^{-1} , it restored a stable capacity of $\sim 318 \pm 5 \text{ mA h g}^{-1}$. In contrast, pristine Co_3O_4 exhibited capacities of $613 \pm 5 \text{ mA h g}^{-1}$, $121 \pm 5 \text{ mA h g}^{-1}$, and $50 \pm 5 \text{ mA h g}^{-1}$ at the same densities and did not recover its initial capacity upon returning to 100 mA g^{-1} , with only 13% ($\sim 80 \text{ mAh g}^{-1}$) recovery.

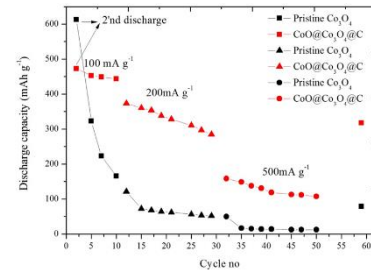


Figure 7. Rate Performance of Pristine Co_3O_4 and $\text{CoO}@\text{Co}_3\text{O}_4@\text{C}$ Anodes (0.01–3 V), Two-Electrode Swagelok Cells, EC–DEC 1:1/1 M LiPF_6 Solutions

The improved rate capability and cycle life of the $\text{CoO}@\text{Co}_3\text{O}_4@\text{C}$ composite electrode can be attributed to two main factors. First, the pristine Co_3O_4 electrode suffered from significant initial irreversible loss and poor rate capability due to poor electronic conductivity and large volume changes during lithiation/delithiation [13]. The composite electrode's 13.5% amorphous carbon enhances conductivity and buffers volume changes. Second, the formation of a solid-electrolyte interphase (SEI) contributes to initial irreversible capacity loss [14], with the SEI consuming Li ions and leading to high internal resistance and low Coulombic efficiency [15]. Amorphous carbon may influence SEI formation, potentially mitigating SEI thickening and reducing overvoltage [16]. Effective handling of SEI growth is crucial for materials with large volume changes [17]. The absence of stable solid electrolyte interface (SEI) film results in a rapid capacity fading due to continuous electrolyte decomposition [18]. The $\text{CoO}@\text{Co}_3\text{O}_4@\text{C}$ composite's enhanced Li-storage performance, particularly at higher rates, is due to the synergistic effect of the carbon coating layer.

4 CONCLUSIONS

We have demonstrated an innovative and eco-friendly synthesis approach for fabricating CoO composite anodes for lithium-ion batteries (LIBs). The $\text{CoO}@\text{Co}_3\text{O}_4@\text{C}$ composite anode exhibits superior specific capacity and cyclability compared to pristine Co_3O_4 . At a current density of 200 mA g^{-1} , the $\text{CoO}@\text{Co}_3\text{O}_4@\text{C}$ anode maintains a discharge capacity of $285 \pm 5 \text{ mAh g}^{-1}$ with 76.4% capacity retention after 30 cycles. At a higher current density of 500 mA g^{-1} , it retains a discharge capacity of $108 \pm 5 \text{ mAh g}^{-1}$ and demonstrates 97.4% coulombic efficiency after 50 cycles. This novel green method is both cost-effective and straightforward, making it suitable

for large-scale production. The impressive electrochemical performance of the CoO@Co₃O₄@C composite anode highlights its potential for use in high-performance LIBs.

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IMPROVING PEDIATRIC DOSE MEASUREMENTS WITH DEEP LEARNING MODELS FOR ACCURATE INTERNAL DOSIMETRY IN NUCLEAR MEDICINE

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Abstract

This study explores deep learning techniques for internal pediatric dosimetry in nuclear medicine, aiming to predict organ-specific absorbed doses before imaging. GATE Monte Carlo simulations were performed on 28 pediatric models (ages 2–17 years, both genders) to calculate specific absorbed dose rates (SADRs) for five radiopharmaceuticals. Deep learning models, including Keras, LSTM, and RNNs, were trained on this simulated dosimetry dataset. The models showed high accuracy in predicting dose rates for 30 organs, highlighting the importance of personalized anatomy and biodistribution. This approach offers promise for improving dose measurements in pediatric nuclear medicine.

Keywords: Internal dosimetry, Monte Carlo, pediatric dosimetry, deep learning

1 INTRODUCTION

Traditional dosimetry in nuclear medicine relies on Monte Carlo (MC) simulations, which are computationally demanding. Recent advancements in artificial intelligence (AI), particularly deep learning (DL), offer potential for more efficient and accurate dosimetry.

In pediatric nuclear medicine, personalized dosimetry is essential due to children's increased sensitivity to radiation.

MC simulations, combined with detailed digital models, are the gold standard for calculating absorbed doses.

This study explores DL techniques for predicting organ doses based on pediatric anatomy. By comparing DL predictions with MC simulations, we aim to improve dosimetry accuracy in pediatric patients.

Specific Absorbed Dose Rates (SADRs) are calculated using radiopharmaceutical biodistribution [1], [2], providing personalized dose assessments for better pediatric nuclear medicine out.

2 MATERIAL AND METHODS

2.1 Pediatric Phantoms And Radio-Pharmaceuticals

This study used an open-access dosimetry database developed with GATE MC simulations for five radiopharmaceuticals [1]: ^{99m}Tc -MDP, ^{123}I -MIBG, ^{131}I -INa, ^{131}I -MIBG, and ^{153}Sm -EDTMP. The simulations included 28 pediatric

phantoms of varying ages, genders, and anatomical features derived from 4D pediatric XCAT and IT'IS Family models.

2.2 DL Techniques

➤The Dense model includes a Dense_0 layer with 64 neurons, an input shape of (None, 9), and a ReLU activation function; a Dense_1 layer with 32 neurons and ReLU activation; and a Dense_2 layer with 1 neuron, using the Adam optimizer and Mean Squared Error loss.

➤The LSTM model features an LSTM layer with 64 neurons, an input shape of (1, 9), and a Tanh activation function, followed by a Dense_1 layer with 1 neuron, using the Adam optimizer and Mean Squared Error loss.

➤The RNN model comprises a SimpleRNN layer with 64 neurons, an input shape of (1, 9), and a Tanh activation function, and a Dense_1 layer with 1 neuron, using the Adam optimizer and Mean Squared Error loss.

3 MODEL DESCRIPTION

After developing Keras, RNN, and LSTM models, we compared their performance across radiopharmaceuticals and organs. Keras models generally outperformed the others, except for ^{99m}Tc -MDP, where LSTM and RNN performed comparably.

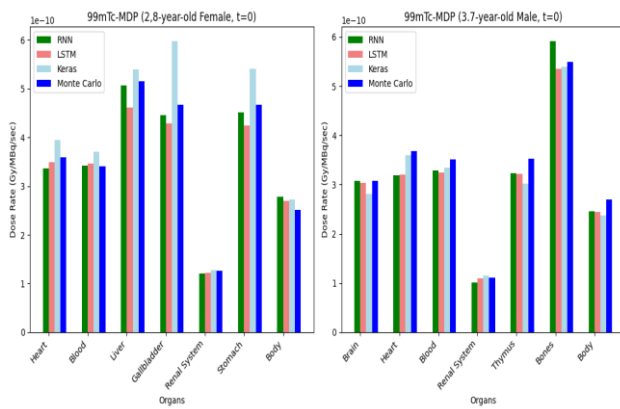


Figure 1: Comparison of predicted SADRs vs. Monte Carlo simulations for key organs using 99mTc-MDP, showing close alignment

For 123I-MIBG, the Mean Absolute Percentage Error (MAPE) ranged from 5.56% to 13.89%, the R-squared (R²) values ranged from 0.92 to 0.98.

For 99mTc-MDP, the MAPE ranged from 5.17% to 14.77%, and the R² values ranged from 0.93 to 0.98.

For 131I-INA, the MAPE ranged from 7.46% to 13.58%, and the R² values ranged from 0.91 to 0.97.

For 131I-MIBG, the MAPE ranged from 6.11% to 15.07%, and the R² values ranged from 0.91 to 0.98.

For 153Sm-EDTMP, the MAPE ranged from 6.71% to 18.49%, and the R² values ranged from 0.96 to 0.99.

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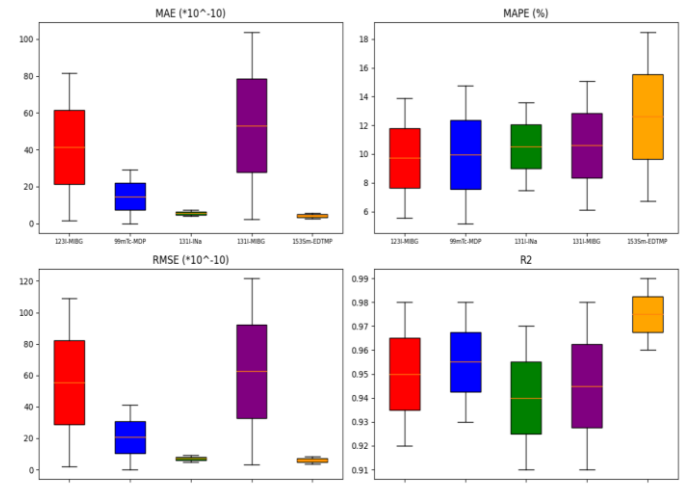


Figure 2: Boxplot of metric values of the best performing DL models for radiopharmaceuticals and features

4 CONCLUSION

This poster presents the methodology for developing an internal dosimetry prediction model for pediatric patients using Deep Learning and Artificial Intelligence techniques.

The Deep Learning regression models were trained on a simulated dosimetry database..

Although the results are within an acceptable error threshold, training with larger and more diverse simulated cohorts is necessary before clinical application.

Next steps include creating an online internal dosimetry prediction application for pediatric patients, incorporating the models developed in this study

THE AIR POLLUTANT REMOVAL CAPACITY OF *Chlorophytum comosum* AND *Sophora japonica*.

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Abstract

Air pollutants are categorized as indoor and outdoor pollutants. Indoor pollutants comprise volatile organic compounds (VOCs) derived from building materials, furniture, and consumer products such as benzene and formaldehyde. Outdoor pollutants include ozone, carbon monoxide, nitrogen oxides (NO_x), sulfur oxides (SO_x), particulate matter (PM), etc. Plants are real carbon dioxide consumers in the daytime. They also arrange the level of temperature and humidity in the air. They can catch particulate matter (PM) with their leaves. In this proceeding, we would like to underline the importance of plants for air-cleaning properties by mentioning *Chlorophytum comosum* and *Sophora japonica*.

Keywords: Air cleaning, Outdoor air quality, Indoor air quality, *Chlorophytum comosum*, *Sophora japonica*

1 INTRODUCTION

According to WHO, “Air pollution is the contamination of the indoor or outdoor environment by any chemical, physical or biological agent that modifies the natural characteristics of the atmosphere.” [1]

WHO has classified substances that impair air quality as outdoor and indoor air pollutants. Outdoor air pollutants determined by WHO are PM₁₀, PM_{2.5}, O₃, NO₂, SO₂ and CO. In addition, the WHO scanned the scientific studies on indoor air pollution and identified eight substances with definitive evidence that they are polluting and harmful as indoor air pollutants. These pollutants are benzene, CO, formaldehyde, naphthalene, NO₂, polycyclic aromatic hydrocarbons, radon, trichloroethylene, and tetrachlorethylene.

Air phytoremediation (AP) is an ecological remediation technology that utilizes green plants to eliminate pollutants from polluted air [2, 3]. Some plants can assimilate, degrade, or modify toxic contaminants in the air into less toxic ones, making it possible to remove airborne pollutants via AP technology [2,4].

After our literature research, we focused on the most studied plants: *Chlorophytum comosum* (Spider Plant) and *Sophora japonica*.

2 THE PLANT REMOVING THE INDOOR AIR POLLUTANTS: *Chlorophytum comosum* (Spider Plant)



Figure 1. The photo of *Chlorophytum comosum* [5]

The removal of benzene, toluene, cigarette smoke, xylene, formaldehyde, ethylbenzene, and the mixture of benzene, toluene, octane, and trichloroethylene, α -Pinene, particulate matter (PM), and CO₂ were investigated on *Chlorophytum comosum* (Figure 1). Sriprapat et al. [6] tested the removal capacity of toluene and ethylbenzene on the plants *Aloe vera*, *Sansevieria masoniana*, *Sansevieria trifasciata*, *Sansevieria hyacinthoides*, *Sansevieria ehrenbergii*, *Kalanchoe blossfeldiana*, *Dracaena deremensis*, *Codiaeum variegatum*, *Chlorophytum comosum*, *Dracaena sanderiana*, *Cordyline fruticosa*, *Aglaonema commutatum*. The highest removal values are for toluene, S.

trifasciata, ethylbenzene, *C. comosum*. Also *S. trifasciata* and *S. hyacinthoides* had a high value in the absorption of toluene and ethylbenzene. Torpy et al. [7] researched the removal of CO₂ of *Chlorophytum comosum* and *Epipremnum aureum* using green wall technology (Figure 3) [8]. Both plants were active in CO₂ elimination at densities higher than 50 µmol/m²s. When the intensity of the light was elevated, the green wall achieved meaningful reductions in high CO₂ concentrations within a sealed room environment.

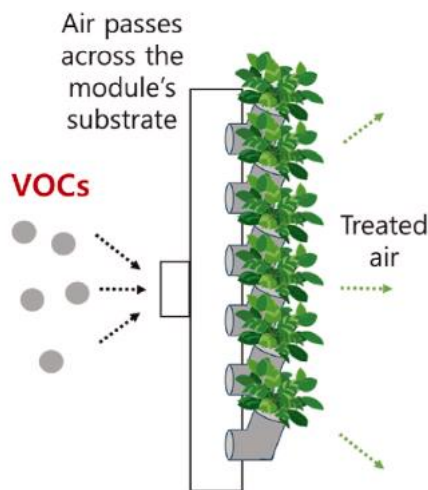


Figure 3. Active green wall system [8]

3 THE PLANT REMOVING THE OUTDOOR AIR POLLUTANTS: *Sophora japonica*

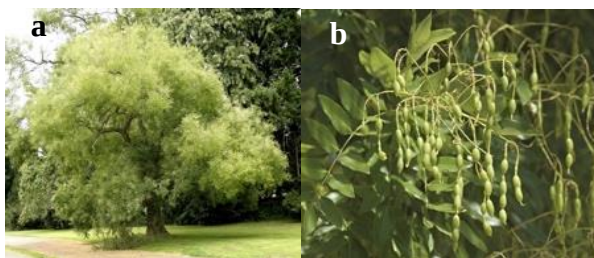


Figure 2. The photo of *Sophora japonica* [9-10]

Sophora japonica (Figure 2), the Japanese pagoda tree [11] (also called the Chinese scholar tree and pagoda tree; syn. *Styphnolobium japonicum*) is a species of lovely tree. Zhang et al. [12] selected nine plant species for their research from among the dominant roadside plant species: two shrubs (*Euonymus japonicus*,

Rosa chinensis), one climber species (*Parthenocissus quinquefolia*), and six tree species, including two conifers (*Pinus tabuliformis*, *Sabina chinensis*) and four broadleaved trees (*Sophora japonica*, *Ulmus pumila*, *Populus* sp., and *Ginkgo biloba*). *Sophora japonica* displayed the topmost PM capture capacity with its unique morphological characteristics, including significant trichomes, a dense network of grooves, and a complex cuticular wax layer [13]. *Sophora japonica* also showed the largest APTI (air pollution tolerance index) at both sites (traffic pollution and water reservoir). Combining the effect size of air pollution on membrane lipid peroxidation with APTI might better reflect plants' tolerance to air pollution. Shi et al. [14-15] reached the same result about *Sophora japonica* in their research.

4 CONCLUSIONS

Air-phytoremediation is a research field with a vast literature collection. The studies accelerate after the 2000s. As a result of our literature survey, we encountered the removal capacity of indoor pollutants on 140 plants. Among them, *Chlorophytum comosum* was tested against all types of VOCs, i.e., benzene, formaldehyde, ethylbenzene, octane, toluene, xylene, trichloroethylene, and α -Pinene. According to the literature data, benzene and formaldehyde removal levels are high.

Considering plants' capacity to remove outdoor pollutants, the research is concentrated on PM removal. Outdoor plants, trees, shrubs, meadows, and other plants have been studied. According to our literature survey, the PM retention capacity of 136 plants has been researched. *Sophora japonica* is the most potent PM_{1-2.5} catcher among them. Many local studies have been conducted on this plant's PM retention capacity. Additionally, the NO_x absorption capacity of this plant was studied and found to be high [16].

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DYNAMIC INVESTMENT DECISION-MAKING FOR PHOTOVOLTAIC HYDROGEN REFUELING STATIONS IN CHINA: A COMPOUND OPTION APPROACH

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Abstract

In order to achieve the "double carbon target" of carbon peaking by 2030 and carbon neutrality by 2060, it is necessary to enhance the proportion and efficiency of clean energy, develop new energy technologies and build a low-carbon, safe and efficient energy system. Hydrogen energy industry is a strategic emerging industry, and hydrogen refuelling station is the key infrastructure for its development. In this paper, for the differences in solar daily irradiation and hydrogen refuelling demand in different cities in China, the investment decision of photovoltaic hydrogen refuelling station and the influence of government guiding policy on investment behaviour are studied by using compound real options tools. Firstly, a techno-economic model of PV hydrogen refuelling station including PV power generation module, electrolyser, compressor, hydrogen storage tank, pre-cooling and refuelling device is constructed, and the profitability of PV hydrogen refuelling station under the combination of PV peak hours and designed daily refuelling capacity in different cities is analysed by the levelised cost analysis and the economic indicators. Secondly, for cities with unsatisfactory investment economics, a two-stage dynamic investment decision model is constructed based on the compound real options theory to calculate the probability distribution of the real option value and the optimal investment time point, and to analyse the impact of government policies.

Numerical simulation results show that: (1) the average value of levelised cost of hydrogen (LCOH) of urban PV hydrogen refuelling stations in China is 29.6CNY/kg under the full-load operation of daily hydrogen refuelling volume of 500 kg, with a significant cost advantage in the western region. (2) The annual peak hours and daily hydrogen refuelling volume are negatively correlated with LCOH, and increasing the annual peak hours and daily hydrogen refuelling volume can significantly reduce the LCOH; on the other hand, the daily hydrogen refuelling volume has a marginal decreasing effect on the LCOH of the PV hydrogen refuelling station. (3) The optimal investment point of the two-stage investment model in Nanjing is the 4th year, which increases the investment probability by 15% and the real option value by 5.61 million CNY. (4) Demand assurance policy on investment in PV hydrogen refuelling station promotes the biggest role, accelerated technology research and development policy can advance the optimal investment time point, the contract for difference and the introductory period subsidy policy on the initial investment has a promotion role, but the impact on the second stage of investment is not big, and increase the financial burden of the government.

Keywords: Photovoltaic hydrogen refuelling stations; Compound real options; Stochastic differential equations; Two-stage multiplicative Monte Carlo simulation; Dynamic investment decisions

1 INTRODUCTION

1.1 Background of the Study

In recent years, the concepts of "low-carbon life" and "transformation of energy structure" have gradually taken root in people's minds in the face of two key issues: climate anomalies caused by excessive global greenhouse gas emissions and the depletion of finite fossil resources. Since the "dual carbon target" was

proposed in 2020, China has been committed to promoting green and low-carbon development, addressing the challenges of climate change, and actively exploring the development path of the clean energy industry. As a strategic emerging industry, the hydrogen industry is crucial to accelerating the formation of new productivity, developing new kinetic energy and promoting clean energy transformation.

China, as the world's top hydrogen-producing country, jointly issued the Medium- and Long-Term Plan for the Development of Hydrogen Energy Industry (2021-2035) in March 2022 by the National Development and Reform Commission (NDRC) and the National Energy Administration (NEA). The plan puts forward the goal of establishing a complete hydrogen energy industry system by 2035, and plans to create a diverse ecosystem of hydrogen energy applications covering various fields such as transport, energy storage, industry, etc. Hydrogen energy will provide an important pathway for various industries to achieve decarbonisation. According to the China Hydrogen Energy Alliance, China's hydrogen production in 2022 will be 35.33 million tonnes, accounting for more than one-third of the total global hydrogen production. 2022 in the chemical industry accounted for 80.8% of the use of hydrogen, of which ammonia (11.07 million tonnes, 31.3%), methanol (9.25 million tonnes, 26.2%), and other petrochemicals (8.23 million tonnes, 23.3%); and in the construction, Power Generation and Transportation accounts for only 0.18%. Currently, the application of hydrogen energy is still in its early stages due to high cost and limited application scope. It is expected that by 2060, the demand for hydrogen in the industrial sector will decrease to 60%. Meanwhile, the demand for hydrogen in the transport sector will grow significantly, increasing its share to 31 per cent. In addition, the demand for hydrogen in the power and construction sectors will gradually increase, reaching 5 per cent and 4 per cent, respectively. It can be seen that the transport sector is of great significance in promoting the development of hydrogen energy. The construction and improvement of hydrogen refuelling stations, as the key infrastructure to ensure the supply of hydrogen energy and promote the development of the hydrogen industry, is crucial to promoting the application of hydrogen energy in the transport sector.

1.2 Overview of Related Studies

The importance of hydrogen energy in the global energy strategy is increasing day by day, and countries are actively introducing relevant policies to support the development of the hydrogen energy industry. They are actively exploring the technology path of the whole industrial chain covering all aspects of hydrogen

production, storage, transport and application in order to build a new hydrogen energy socio-economic system. Existing hydrogen production technology routes include hydrogen production from electrolysis of water, hydrogen production from fossil energy reforming, industrial by-production of hydrogen, and other technologies in the experimental and developmental stages, such as hydrogen production from biomass and hydrogen production from solar photocatalytic decomposition of water. Among them, the technological route of hydrogen production from water electrolysis is the use of renewable energy to produce hydrogen. Clean hydrogen is produced by utilising renewable energy sources such as wind, solar and hydropower as a power source. Its core advantage lies in sustainability. Through the process of electrolysis of water, these renewable energy sources are converted into electricity, which in turn breaks down the water into hydrogen and oxygen, and the whole process achieves zero carbon emission. Photovoltaic hydrogen production, as a renewable energy hydrogen production technology, is a sustainable path to produce clean hydrogen using solar energy, has become a research hotspot in recent years, and its cost-effectiveness study has received the attention of scholars from various countries. Touili et al^[1](2018) investigated the economics of photovoltaic hydrogen production in Morocco, selecting a photovoltaic-electrolysis system, and conducting 76 sites scattered across the country for electricity and hydrogen production were simulated, and an economic investigation of electricity and hydrogen production costs was carried out, concluding that Morocco has a high potential for hydrogen production development. Benalcazar et al^[2](2022) developed a Monte Carlo-based model to investigate potential economic and technological factors that may affect the success of the Green Hydrogen Strategy in Poland, and examined 17 Polish regions relying on wind or solar energy for the economic performance of large-scale The economic performance of PEM electrolyzers in 17 Polish regions was investigated, and the results showed that the most cost-effective geographical locations for the deployment of large-scale hydrogen production plants are the central and southern regions of the country. Chuanbo Xu et al^[3] (2023) conducted a detailed systematic analysis of the costs of off-grid PV

hydrogen production projects, focusing on three key factors: the acquisition cost of the power generation equipment, the efficiency of the electrolysis process, and the rate of technological advancement, for which a stress test was implemented. The study found that the levelised cost of hydrogen (LCOH) is 44.96 CNY/kg when evaluated in 2020 for a 100MW-scale power plant, with the largest cost component being the fixed cost of the power plant, which accounts for 30.39%. In addition, technological advances were found to have an extremely significant impact on the reduction of LCOH. In the study of the economics of PV hydrogen projects, the cost-effectiveness of PV hydrogen production and the potential of hydrogen production in the assessed region are mostly studied, while there is also consideration of the impact of uncertainties on the results of the study, and it is found that the rate of technological advancement has the greatest impact on the levelised cost of hydrogen production. Therefore, in this paper, the differences in regional irradiation are taken into account in the study of the economic benefits of PV hydrogen refuelling stations; at the same time, the impact of uncertainties (e.g., technological progress) on the decision-making is also introduced in the calculation of the timing of the investment in hydrogen refuelling stations.

Currently, many studies on hydrogen refuelling stations are based on case-specific examples, focusing on the sustainable operation of local hydrogen refuelling stations and the cost of hydrogen, which is instructive for their development planning. Zhao et al^[4] (2015) developed a dynamic system model of hydrogen refuelling stations with proton exchange membrane (PEM) electrolyzers and fuel cells. The dynamics of the hydrogen refuelling station was analysed using existing hydrogen refuelling and electricity demand data from public hydrogen refuelling stations. The results show that the cost of hydrogen can be as low as 6.71CNY/kg or 9.14CNY/kg when the hydrogen refuelling station is powered by a 200 kW wind turbine or 360 kW photovoltaic (PV) array, respectively. Dispenza et al^[5] (2019) discusses the estimation of the cost of hydrogen production for a PV hydrogen refuelling station in Sicily. Comparison of data related to the cost of hydrogen production by water electrolysis

derived from three different case studies was carried out to analyse the economic and environmental benefits. Toghiani et al^[6] (2021) investigated the system performance and the energy cost of hydrogen production of a PV hydrogenation system having an electrochemical hydrogen compressor and a PEM electrolyzer under different operating conditions, and arrived at the maximum energy and exergy efficiencies of the PV system 13.57% and 14.51%, respectively, and it was concluded that the exergy cost of hydrogen production at the parallel site with energy storage device is almost 30% higher than that at the off-site site. Most of the studies on the economic efficiency of PV hydrogen refuelling stations have used a techno-economic approach to analyse the cost of hydrogen production. Micena et al^[7] (2020) proposed a hydrogen refuelling station design powered by a PV power plant to supply a taxi fleet in a Brazilian city, and calculated the LCOH of the large-scale refuelling station to be about 8.96 dollar/kg, and that of the small-scale refuelling station to be 13.55 dollar/kg. Minutillo et al^[8] (2021) investigated the electricity demand and cost of a grid-connected PV hydrogen refuelling station using techno-economics methods such as LCOH analysis, and showed that the investment cost increases proportionally due to changes in the size of the PV plant and hydrogen refuelling station installations, and increases with the increase in the capacity of hydrogen production. Silvestri et al^[9] (2022) combined the WTW (Well-To-Wheel, abbreviated as WTW) analysis and Life-Cycle Costing (abbreviated as LCC) analysis together in order to calculate the equivalent CO₂ emissions avoided by the hydrogen route as an incentive strategy, and showed that the equivalent emissions avoided were 320 tonnes per year by considering a discounted payback period of 10 and 8 years, making the hydrogen levelised cost and profitability indices of 9.02 €/kg and 1.75 (10 years) and 7.86 €/kg and 2.12 (8 years) respectively.

Economic studies on hydrogen refuelling station projects have focused on operating costs and hydrogen production costs, and have used methods such as Net Present Value (NPV), LCOH and Internal Rate of Return (IRR) to assess their economic feasibility, but these methods usually assume that the project's cash flow is certain and do not take into account the

impact of future uncertainties. In addition, there are current studies that have analysed the dynamics of hydrogen refuelling stations and have found that hydrogen refuelling stations powered by renewable energy sources (such as wind turbines or photovoltaic arrays) can significantly reduce the cost of hydrogen, and have also found that grid-connected hydrogen refuelling stations have a higher cost of discharging energy than off-grid refuelling stations, but also have a much higher energy efficiency and efficiency of discharging energy. This is because the efficiency of the hydrogen refuelling station increases dramatically when the grid supplies power to the system. Therefore, in this paper, the dynamic investment decision of grid-connected PV hydrogenation station is investigated by the compound real options method based on the use of common methods such as NPV, IRR, and LCOH.

The Real Options Analysis (ROA) method, abbreviated as ROA, is an uncertainty study method for project investors to assess the feasibility of investment and to analyse investment decisions^[10]. With the Real Options Approach becoming more widely used, projects that can be delayed, expanded or abandoned based on future circumstances can be valued using the concept of Real Options in order to fully take into account the flexibility of the project and reduce the risk of change. The theory assumes that investment projects include three core characteristics^[11]: firstly, the project itself or some of its parts are irreversible, which means that the initial investment cost will not be fully recovered once the investment fails; secondly, the project faces uncertainty and may be affected by external factors such as policy changes, market fluctuations, and technological advances, which leads to the same uncertainty in the return on the investment; and finally, the timing of the investment has the flexibility and can be made at any point in time before the project deadline. Therefore, this method is suitable for projects with a long investment period and uncertain future profitability, and the above characteristics are basically consistent with the investment in the construction of PV hydrogen refuelling station projects in regions where the endowment of solar energy resources is not outstanding. Some scholars have already used the real option method to study the investment decision problem of hydrogen energy

projects in uncertain environments. Schmitz and Madlener^[12] (2015) used the binomial tree method to calculate the real option value of a wind hydrogen project, and applied Monte Carlo simulation to model the uncertainty of compressed air price, hydrogen price and storage cost. The results show that considering embedded options in the decision-making process does increase the investment value of the overall project. Li et al^[13] (2020) use a real options approach to evaluate the optimal investment strategy for hydrogen refuelling stations, integrating the generalised Bass model from technology diffusion theory into an N-stage compound real options framework and applying the combined model to a case study of a deployed hydrogen refuelling station in the Netherlands. The results show that the interaction between hydrogen refuelling station availability and adoption rate needs to be considered to avoid sub-optimal decisions. Van et al^[14] (2021) investigated decision making under uncertainty and value flexibility. Compound real options analysis is used to optimise expansion strategies when hydrogen pipeline networks are in place. The trade-off between early investment and missed gains from untimely investment determines the optimal expansion strategy. The study by Zhao et al^[32] (2024) analyses the investment strategy for hydrogen refuelling stations in China through a compound real options approach, considering both off-site and on-site HRS construction scenarios, and concludes that the demand growth and preferential policies are the main drivers for HRS investment, and shows that on-site HRS has cost-saving advantages.

In summary, it is found that existing studies on the economics of hydrogen production from PV generally use techno-economics methods such as LCOH analysis, sensitivity analysis, LCC analysis, and payback period to assess the cost and profitability of hydrogen production at hydrogen refuelling stations. In uncertainty studies for hydrogen projects, the main focus is on the uncertainty in power generation, electricity and hydrogen demand, and retail hydrogen prices. Although the existing literature has studied the value and investment issues of hydrogen projects using the real options approach, there is very little literature devoted to the investment issues of hydrogen refuelling stations, and the existing literature focuses more

on the storage and transportation of hydrogen in terms of hydrogen infrastructure investment. From the above literature review, it can be seen that there are two shortcomings in the current research on hydrogen refuelling stations. Firstly, hydrogen refuelling stations can be divided into on-site and off-site hydrogen refuelling stations, and different types of hydrogen refuelling station investments have different uncertainties, but the existing literature does not distinguish between their different investment characteristics. Second, the literature on the use of real options to study PV hydrogen refuelling station investments seldom provides a quantitative distinction between areas where investments are more suitable for the use of the real options approach and areas where traditional decision-making methods such as NPV are appropriate; and again, the existing literature mostly adopts the real options approach to conduct single-stage investment decision-making studies, and fails to consider the flexibility of adapting hydrogen refuelling station investments according to the future changes in the market and technological conditions, and thus multi-stage investment decisions are not studied.

Therefore, this paper will firstly construct a techno-economic model of PV hydrogen refuelling station, decompose PV hydrogen refuelling station into two parts: PV hydrogen production sub-system and external hydrogen refuelling station sub-system, and under the assumption of average working mass flow of hydrogen, establish an economic estimation model of PV hydrogen refuelling station that takes into account two factors: the annual peak hours and the daily refuelling capacity of the hydrogen refuelling station design, so as to help the investors to roughly judge the investment profitability of different refuelling stations with different refuelling capacity in different regions. The model is used to help investors to judge the investment profitability of hydrogen refuelling stations with different filling capacities in different regions. Afterwards, for regions with weak investment profitability, a two-stage dynamic investment decision model is constructed based on compound option theory, taking into account various uncertainties, and two-stage Monte Carlo simulation is used to assess the real option value of PV hydrogen stations. Finally, the impact of different

investment guidance policies on potential investors' decisions is analysed.

2 MATERIAL AND METHODS

2.1 Hydrogenation Capacity Analysis

The daily hydrogen refuelling demand of a PV hydrogen filling station is usually estimated based on the number of hydrogen fuel cell vehicles in the service area, the average daily mileage and the energy consumption per unit mileage energy consumption. Taking the 40 hydrogen-fuelled buses operating in Shuyang County, Jiangsu Province, on 8 January 2023 as an example, each bus travels 200km per day and consumes 6kgH₂ of hydrogen per 100km, which reduces CO₂ emissions by at least 48.75 tonnes of carbon dioxide per vehicle per year, compared to conventional fuel buses. In this study, a PV hydrogen refuelling station is planned to be constructed in Nanjing as an example, which is expected to serve 80 similar buses per day, and 40 buses are currently in service. Using the method of Riveros (2013), the daily hydrogen demand of the fleet is estimated by Equation (1)^[15].

$$D_{H_2} = N_v \times C_v \times K_v$$

Where D_{H_2} denotes the daily hydrogen demand of the fleet, kg/day; N_v is the number of vehicles to be refuelled per day, vehicles; C_v is the hydrogen consumption per vehicle per unit distance travelled, kg/km; and K_v is the average daily distance travelled by each vehicle, km.

2.2 System Structure of Photovoltaic Hydrogen Refuelling Station

Hydrogen refuelling stations can be classified into two types, 35MPa and 70MPa, based on the refuelling pressure. In China, most of the hydrogen refuelling stations currently provide mainly hydrogen at 35MPa pressure, while 70MPa pressure hydrogen refuelling stations are used as a supplement. Compared with the international development of hydrogen refuelling stations with 70MPa refuelling pressure, the construction of high-pressure hydrogen refuelling stations in China is still relatively lagging behind. Therefore, the research and design of this paper is a photovoltaic hydrogen refuelling station with a pressure of 70MPa hydrogen, and the main composition of the system is shown in Fig. 1, which is mainly composed of photovoltaic power generation module, electrolysis tank, compressor, hydrogen storage tank, pre-cooling

device and refuelling device.

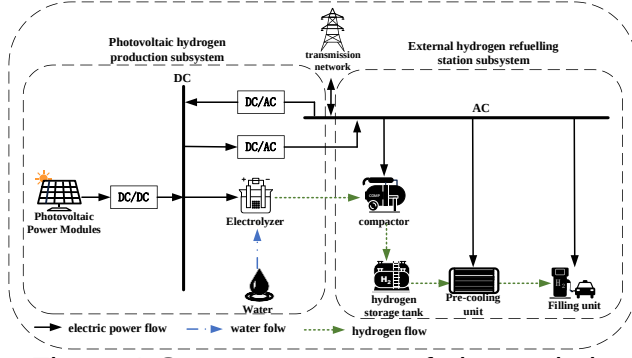


Figure 1 System structure of photovoltaic hydrogen refuelling station

Photovoltaic Power Modules

The photovoltaic module consists of a photovoltaic array, an inverter and a converter, which are responsible for converting solar energy into direct current. In this paper, the power demand for hydrogen production from electrolysis of water and hydrogen compression and cooling process is met by the grid-connected PV system. The grid acts as a virtual battery to balance the power supply and demand of the PV during peak and trough hours, and it is assumed that this charging and discharging process has no energy loss and cost. In practice, it is necessary to consider the price difference between the PV hydrogen refuelling station and the grid in terms of electricity sales and purchases. In order to simplify the model, it is assumed that the amount of electricity sold is equal to the amount of electricity purchased and its price, and the conversion losses are ignored due to the high energy efficiency of the converters and inverters, which reaches more than 90%.

The peak power P_{PV} of the grid-connected PV system is calculated using equation (2)^[16]:

$$P_{PV} = \frac{E_L}{\eta_V \cdot PSH}$$

Where E_L is the electrical energy consumed by the load during each day, kWh; η_V is the inverter efficiency, 0.9^[16]; and PSH is the number of peak hours of average daily irradiance, hours. Peak solar hours are the local solar radiation, converted to hours under standard test conditions (irradiance 1000 W/m²).

The power demand E_L of the PV hydrogenation station can be obtained from the sum of the load consumption generated by the electrolyser, compressor and pre-cooling unit therein and the hydrogenator, calculated by equation (3):

$$E_L = E_{ely} + E_{comp} + EC_{PCU} \times D_{H_2}$$

where E_{ely} and E_{comp} denote the daily power consumption of the electrolyser and compressor, kWh, respectively; EC_{PCU} is the energy consumption of the pre-cooling unit per unit of dispensed hydrogen, kWh/kgH₂; and D_{H_2} is the daily hydrogen demand, kg. In a two-stage investment problem, the daily energy consumption of the stage 1 externally-supplied hydrogen refuelling station subsystem is the sum of the energy consumption of the compressor and pre-cooling unit and the the sum of the energy consumption of the refuelling machine; while the daily energy consumption of the stage 2 PV hydrogen production subsystem is approximately equal to the daily energy consumption of the electrolyser.

Electrolyzer

Based on the type of electrolyser and operating temperature, electrolysers are classified into four main types: proton exchange membrane electrolyser (PEM), alkaline electrolyser (ALK), solid oxide electrolyser (SOEC) and anion exchange membrane electrolyser (AEM). The ALK electrolyzer was chosen for this study due to its long stack life, high production rate, low cost, easy maintenance and operation compared to other types. The efficiency of the ALK electrolyzer is usually 60-75%, which is taken as 70% in this paper for the convenience of the study calculations^[17] and based on the practice in the study of Micena (2020), it is assumed that the hydrogen gas leaves the electrolyser under a pressure of 1Mpa of pressure leaving the electrolyser^[7].

The electrolyzer efficiency is defined by the ratio of the available power in the form of hydrogen to the electrical input power to the electrolyzer and is calculated from equation (4)^[18]:

$$\eta_{ely} = \frac{\dot{m}_{H_2} \cdot LHV_{H_2}}{P_{ely}}$$

Where η_{ely} is the electrolysis efficiency of the electrolyser, 0.7; $\dot{m}_{H_2}$ is the mass flow rate of hydrogen produced by the electrolyser, kg/h; LHV_{H_2} is the low calorific value of hydrogen, 33.3 kWh/kg; and P_{ely} is the electrical power consumed by the electrolyser, kW. Considering that the electrolyser is continuously operating during the whole operation period of the PVH station, the hydrogen mass flow rate, $\dot{m}_{H_2}$ can be obtained from the daily hydrogen demand, D_{H_2} , divided by the daily operating time, t_{day} .

The daily energy consumption of the electrolyser is calculated by the electrical power it consumes and the daily running time, which is given by equation (5):

$$E_{ely} = P_{ely} \times t_{day}$$

Where, t_{day} is the daily operating hours of the electrolyser, hours. Referring to the research assumption of Micena (2020), this paper also assumes that the daily operating hours of the electrolyser is 18 hours/day^[7].

Compressor

Common types of hydrogen compressors are metal diaphragm, liquid-driven piston, mechanical piston, and ionic liquid compressors [19], which are used to increase the pressure of hydrogen under low-pressure hydrogen storage tanks to the required higher pressure level for storage, transport, or refuelling. Among them, metal diaphragm compressors are widely used in the hydrogen energy field and have the highest technological maturity, which are mainly suitable for on-site photovoltaic hydrogen refuelling stations and stationary hydrogen refuelling stations, and have the advantages of less sealing difficulty and high hydrogen quality, so metal diaphragm compressors are selected in this system. In addition, it is assumed that the inlet pressure of the diaphragm compressor is the same as the outlet pressure of the electrolyser, which is 1 MPa; and the outlet pressure is the maximum permissible pressure of the hydrogen refuelling station of 70 MPa class as stipulated in the Safety Technical Requirements of Hydrogen Storage Devices Used in Hydrogen Refuelling Stations of GB/T34583-2017, which is 90 MPa.

The most efficient way of compressing gases is through the adiabatic compression process. The rated shaft power of the compressor is calculated from equation (6) [7]:

$$W_{comp} = C_{comp} \cdot \frac{T_{in}}{\eta_{comp}} \left(\left(\frac{P_2}{P_1} \right)^{\frac{r-1}{r}} - 1 \right) \cdot \dot{m}_{comp}$$

Where W_{comp} is the compressor shaft power, kW; C_{comp} is the specific heat of hydrogen at constant pressure, 14.3 kJ/kg/K; T_{in} is the inlet hydrogen temperature of the compressor, 293 K; P_1 is the inlet pressure of the compressor, 1 MPa; P_2 is the outlet pressure of the compressor, 90 MPa; r is the specific heat capacity of hydrogen, 1.4; $\dot{m}_{comp}$ is the mass flow rate of the gas through the compressor is the gas mass flow

rate, kg/s; η_{comp} is the compressor mechanical efficiency, 0.7^[7].

Since the compressor shaft needs to be pushed by an electric motor, the efficiency of the motor needs to be taken into account when calculating the electrical energy consumed in the compression process. So the daily energy consumption of the compressor E_{comp} is calculated by equation (7)^[7]:

$$E_{comp} = \frac{W_{comp} \times t_{day}}{\eta_{ele}}$$

Where, t_{day} is the compressor daily operating hours, hours; η_{ele} is the motor efficiency, 0.9^[7].

In order to improve the economy of hydrogen storage and transport, it is necessary to compress hydrogen. It is known that the equipment investment cost of a hydrogen compressor for a volume flow rate of 300 m³/h is 320,000 dollar, and then the cost of hydrogen compression at other volume flow rates can be obtained from the power law given in equation (8).

$$C_c = 320000 \times \left(\frac{V_{H2}}{300} \right)^{0.6}$$

Where C_c is the initial investment cost of the hydrogen compressor, CNY; and V_{H2} denotes the hydrogen flow rate, m³/h.

Hydrogen Storage Tanks

Currently, internationally, two main pressure ratings, 35 MPa and 70 MPa, are used for on-board hydrogen storage cylinders. In order to be compatible with the on-board hydrogen storage system of the refuelling vehicle, the design pressure level of the hydrogen refuelling station must be matched. In addition to the use of a 20 MPa pressure long tube trailer as a mobile hydrogen storage solution, the maximum pressure of the fixed hydrogen storage system inside the hydrogen filling station is usually designed to be 45 MPa for 35 MPa pressure level hydrogen fuel cell vehicles, while the maximum fixed hydrogen storage pressure of the hydrogen filling station is usually designed to be 90 MPa for 70 MPa pressure level hydrogen fuel cell vehicles, while the photovoltaic hydrogen refilling studied in this paper station has a refilling pressure of 70 MPa, so the pressure of the hydrogen storage tank used in this system is 90 MPa.

The high-pressure tanks are sized to meet peak demand, supplying hydrogen during periods when their demand is higher than the daily average^[20]. For simplicity, the capacity of the hydrogen storage tank is considered in this

study to be the total mass of the average daily hydrogen refuelling multiplied by a safety factor, which is calculated through equation (9)^[7]:

$$M_s = m_{H_2} \times SF$$

Where M_s is the capacity of the hydrogen storage tank, kg; m_{H_2} is the average daily mass of hydrogen delivered, kg; and SF is the safety factor, 3. Here, it is assumed that the hydrogen storage tank can reserve 3 days of hydrogen demand^[21].

The cost of hydrogen storage tanks depends mainly on the capacity and applies to a minimum storage capacity of 10,000 kg of hydrogen and a maximum storage capacity of 10,800,000 kg of hydrogen. The formula for calculating the investment cost of hydrogen storage tank is shown in equation (10)^[1]:

$$C_s = UC_s \times Mass_s$$

Where C_s is the initial investment cost of the hydrogen storage tank, CNY; UC_s is the capital cost of medium-pressure hydrogen storage, which is set at 350CNY/kg^[1]; and $Mass_s$ denotes the mass of hydrogen in the tank, kg.

Pre-cooling Unit and Hydrogenator

In order to prevent overheating of the on-board hydrogen storage cylinder, the hydrogen refuelling rate is usually specified to be no more than 60 g/s. For the purpose of rapid hydrogen refuelling, when the terminal refuelling pressure is set to 35 MPa, the hydrogen is usually pre-cooled to 0-10°C; while when the refuelling pressure is 70 MPa, the hydrogen is usually pre-cooled to -40°C. In addition, the inlet end of the hydrogen dispenser needs to be equipped with a precision filter with a filtration accuracy of no more than 5µm to ensure the quality of the terminal hydrogen.

In addition, in order to control the hydrogen refuelling temperature to improve the hydrogen refuelling efficiency and safety, a pre-cooling unit is required in the hydrogen refuelling station, which can control the hydrogen temperature during the hydrogen refuelling process and solve the problem of temperature rise of the equipment so as to ensure the hydrogen refuelling efficiency and safety. The specific energy consumption per kg of hydrogen is a measure of the energy efficiency of the PCU, which can be calculated by equation (11)^[23]:

$$EC_{PCU} = \frac{0.3}{1.6 \times e^{(-0.018 \times T_{amb})}} + \left[\frac{25 \times \ln(T_{amb}) - 21}{D_{H_2}} \right]$$

Where EC_{PCU} is the energy consumption of the pre-cooling unit per unit of dispensed hydrogen, kWh/kgH₂; D_{H_2} is the amount of hydrogen dispensed per day, i.e., the daily hydrogen refuelling volume, kg; and T_{amb} is the ambient temperature, 25°C. The PCU needs to be connected to a dispenser fitted with a hydrogen refuelling hose, and according to the Reddi, Elgowainy, and Sutherland proposed assumptions^[24], this paper assumes that one single-hose hydrogen refueller is required for every 250kg of daily hydrogen demand.

2.3 Cost-effectiveness Modelling

Cost-benefit Analysis of a Photovoltaic Hydrogen Refuelling Station Without Considering Uncertainty

(1) Analysis of investment returns

The revenue sources for the operating period of the PV hydrogen refuelling station are hydrogen refuelling revenues and hydrogen refuelling subsidies, which are calculated through equation (12):

$$I = (P^h + B^h) \times Q^h$$

Where I is the annual revenue of the PV hydrogen refuelling station, CNY; P^h is the retail price of hydrogen refuelling, set at 35 CNY/kg^[25]; B^h is the operating subsidy for hydrogen sales, set at 40 CNY/kgH₂^[25]; and Q^h is the annual refuelling volume of the hydrogen refuelling station, kg.

(2) Analysis of investment costs

The Hydrogen Station Cost Model (HSCM) proposed by Weinert et al. (2007)^[26] has become a widely recognised method for calculating the cost of a hydrogen refuelling station. The model decomposes the cost into four main components: construction cost, operation cost, transport cost and feedstock cost, based on different hydrogen station design criteria. In addition, the time value of money and the salvage value of fixed assets are also considered in this study to influence the cost calculation.

Construction cost: the cost of the fixed assets required to build the station (cost of equipment), the cost of installation, and the cost of land and civil works required, equation (13) describes how the construction cost is calculated:

$$C_{inv} = C_{PV} + C_E + C_C + C_S + C_D + C_A$$

Where C_{inv} is the total construction cost of the PV hydrogen refuelling station, and C_{PV} , C_E , C_C , C_S , C_D and C_A are the initial investment costs of the PV power module, electrolyser, compressor, hydrogen storage tank, cooling and hydrogen refuelling machine, and safety and control system, respectively.

Operation and Maintenance (O&M) cost: here it refers to the cost that does not vary with the output during the operation period of the project, including the cost of maintenance, rent and insurance, etc., according to Micena (2020), the O&M cost, $C_{O\&M}$, is assumed to be 4 per cent of the cost of construction Calculated as shown in equation (14):

$$C_{O\&M} = C_{inv} \times 4\% \quad (14)$$

Feedstock cost: the annual purchase cost C_w of the water required for electrolytic hydrogen production, calculated as shown in equation (15):

$$C_w = P^w \times Q_w \times Q^h$$

Where P^w is the unit purchase price of water for hydrogen production, which is taken as 4.1CNY/m³^[27]; Q_w is the water consumption for hydrogen production, which is taken as 0.009 m³/kg^[27]; and Q^h is the annual refuelling volume of the hydrogen refuelling station, kg.

Electro-stack replacement cost: Among the existing studies, there are those that calculate the electro-stack replacement time according to the number of hours the electrolyzers work, and those that set the electro-stack replacement time according to the number of years, the latter is used in this paper. Assuming that the replacement cycle of the ALK electrolyser is ten years^[28], the electrostack will be replaced once in the project life cycle of 20 years. The replacement cost of the take-up stack is 15% of the initial investment cost of the electrolyser^[29]. The formula for calculating the present value of the replacement cost of the electrolyser to be replaced in year t_R is shown in equation (16):

$$C_R = C_E \times 15\% \times (1 + i)^{-t_R} \quad (16)$$

where C_R is the present value of electrolyzer replacement cost, CNY; i is the nominal discount rate; and t_R denotes the year in which the electrolyzer needs to be replaced, in years.

Fixed asset salvage value: the salvage value of the hydrogen refuelling station at the end of the

operating period is a return of 10% of the cost of the equipment^[21], and the salvage value of the fixed asset is the only value that is calculated as income into the cost of levelised hydrogen production, which reduces the value of the cost. It is calculated as equation (17):

$$S = 10\% \times C_{inv} \times (1 + i)^{-T} \quad (17)$$

where S is the present value of the salvage value, CNY; C_{inv} is the total construction cost of the hydrogen refuelling station, CNY; i is the nominal discount rate; and T is the project operating cycle of the PV hydrogen refuelling station, years.

In order to get the equal annual value of the construction cost of the hydrogen refuelling station it is necessary to calculate the capital recovery factor (CRF) according to equation (18) after calculating the equal annual value:

$$CRF = \frac{i(1+i)^T}{(1+i)^T - 1} \quad (18)$$

where i is the nominal discount rate; T is the project operating cycle of the PV hydrogen refuelling station in years. Therefore, the equal annual value of the construction cost is calculated as in equation (19):

$$C_{inv.a} = C_{inv} \times CRF$$

Similarly, the annual operating cost C_{OP} , which includes O&M cost $C_{O\&M}$ and labour cost C_P , and its equivalent annual value can be calculated using equation (20):

$$C_{OP} = C_{O\&M} + C_P$$

Where C_{OP} is the equivalent annual value of O&M and labour costs, CNY; $C_{O\&M}$ is the O&M cost, CNY; C_P is the labour cost, CNY. The annual per capita salary is set at 80,000 CNY per person^[30].

In this paper, the economics of PV hydrogen production is evaluated using levelised cost of hydrogen (LCOH) and net present value (NPV). LCOH is based on levelised cost of energy (LCOE), which is a methodology that can better evaluate the cost of power generation with different technologies and different production scales, and has been widely used in the field of renewable energy applications. LCOH is obtained by dividing the discounted value of the cost of each year of the life cycle of a PV hydrogen project by the discounted value of the annual hydrogen production during the life cycle. The formula for levelised cost of hydrogen LCOH can be simplified to equation (21) if the equal annual value method is used:

$$LCOH = \frac{C_{inv,a} + C_{OP} + C_w - S \times CRF}{T_a \times D_{H_2}}$$

Where T_a is the number of operating days per year, assumed to be 365 days; D_{H_2} is the daily hydrogen production, kg.

Net Present Value (NPV), as a core tool in project appraisal, is an analytical method based on Discounted Cash Flow (DCF). NPV is the difference between the cash inflows and outflows of an investment project, and an investment project is considered investable only if its benefits cover or exceed its costs, i.e., if NPV is at or above zero. In addition, NPV can also be understood as the net difference between the total discounted future cash flows of the project and the initial investment cost, which is reflected in the DCF analysis as the difference between the discounted value of the asset and the cost of constructing the project. Therefore, the NPV of the hydrogen refuelling station is calculated as shown in equation (22):

$$NPV = \frac{I - C_{OP} - C_w}{CRF} - C_{inv} - C_R + S$$

where NPV is the net present value, CNY; I is the annual revenue of the hydrogen refuelling station, CNY; C_{OP} is the annual operating cost, CNY; C_w is the annual purchase cost of feedstock water, CNY; C_{inv} is the construction cost of the project, CNY; C_R is the discounted value of the replacement cost of the electrolysis tank, CNY; and S is the discounted value of the residual value of the fixed assets, CNY.

Cost-benefit Analysis of a Photovoltaic Hydrogen Refuelling Station in an Uncertain Environment

When it is necessary to take into account the uncertainty of the price of hydrogen, the price of electricity and the demand for hydrogen over the life of the project, the annual cash flows are also a stochastic process, as these uncertainties vary as a result of stochastic processes. In this case, the equal annual value method will no longer be applicable, and it will be necessary to calculate the value of the cash flows for each year of the life of the investment and construction project in year t based on the point in time of the investment and construction, generally set as year t , and in turn calculate the sum of the discounted values of these cash flows discounted to year t , i.e., the current NPV of the investment project in year t . In the following, the PV hydrogen refuelling station is split into an externally supplied hydrogen refuelling station sub-system (HRSoff), which is considered to be

constructed in stage 1, and a photovoltaic hydrogen production sub-system (PVH2), which is considered to be constructed in stage 2, which in turn splits the cash flows of the two stages of the investment decision into two relatively independent cash flows. The cost-effectiveness of the two subsystems is decomposed and analysed for each year.

External hydrogen refuelling station subsystem

(1) Analysis of investment returns

The revenue from hydrogen sales at external hydrogen refuelling stations is calculated by equation (23):

$$I_t^h = P_t^h \cdot Q_t^h$$

Where, I_t^h is the annual revenue gained by selling hydrogen, CNY; P_t^h is the retail price per kg of hydrogen, CNY /kg H_2 ; and Q_t^h is the annual refuelling volume of the hydrogen refuelling station, kg.

In addition, externally supplied hydrogen refuelling stations are also entitled to an operating subsidy, with the annual operating subsidy calculated from equation (24):

$$I_t^B = B_t^h \cdot Q_t^h$$

Where, I_t^B is the annual operating subsidy given by the government to the hydrogen refuelling station in year t , CNY/kg H_2 ; B_t^h is the operating subsidy of the unit of hydrogen in year t , CNY/kg H_2 ; and Q_t^h is the annual refuelling volume of the hydrogen refuelling station, kg.

Since the operating subsidy is a short-term investment stimulus tool that is cancelled at the end of the industry's introductory period, it is assumed here that the subsidy is cancelled in year 5, and its change is calculated by equation (25):

$$B_t^h = B_0^h I(t < 5)$$

where B_0^h is the initial operating subsidy for hydrogen sales, which is set to be 40CNY/kg H_2 ^[25]; $I(-)$ is a schematic function, which takes the value of 1 when the conditional equation is valid, and 0 otherwise.

(2) Analysis of investment costs

The cost per unit of product decreases proportionally as its cumulative output increases. Models commonly used to describe this phenomenon are the learning curve model and the exponential cost decay model. The learning rate in the learning curve model indicates the

percentage reduction in the capital cost of a technology for each doubling of the cumulative value of a learning factor such as experience, while the exponential decay model simply describes the cost of capital as decreasing exponentially over time. Agaton et al^[31] (2021) argued that the construction cost decreases in a mature technology due to technological advances, and that the cost exponential decay function Eq. (26) to calculate the construction cost:

$$C_{0,t}^{off} = C_0^{off} \times e^{-\alpha t}$$

Where $C_{0,t}^{off}$ is the construction cost of investing in the construction of an external hydrogen refuelling station in year t, in dollars; C_0^{off} is the construction cost in year 0, in dollars; and α is the annual decreasing index of the construction cost.

In the formula, the construction cost C_0^{off} of the investment construction in year 0 includes the initial investment cost C_c of the compressor, the initial investment cost C_s of the hydrogen storage tank, the initial investment cost C_D of the cooling and hydrogenation machine, and the initial investment cost C_A of the safety and control system at the time of the investment construction in year 0. The formula for calculating the initial construction cost is shown in equation (27):

$$C_0^{off} = C_c + C_s + C_D + C_A$$

The operating cost in year t includes the O&M cost and labour cost in that year and the O&M cost is assumed to be 4% of the construction cost^[7], then the annual operating cost is calculated through equation (28):

$$C_{OP,t}^{off} = C_{O\&M,t}^{off} + C_{P,t}^{off}$$

Where $C_{OP,t}^{off}$ is the annual operating cost of the external hydrogen supply hydrogen refuelling station in year t, CNY; $C_{O\&M,t}^{off}$ is the annual operation and maintenance cost, CNY; and $C_{P,t}^{off}$ is the annual labour cost, CNY. It is assumed that the number of labourers at the external hydrogen supply and refuelling station is 6, and the annual per capita salary is 80,000 CNY per person^[30].

The feedstock cost of an externally supplied hydrogen refuelling station includes the cost of purchasing and transporting hydrogen, as well as

the cost of electricity consumption. The feedstock cost is calculated by equation (29):

$$C_t^f = (C_t^h + C_t^l) \cdot Q_t^h + (E_{comp,t} + EC_{PCU,t} \times D_{H_2,t}) \times T_a \times P_t^e$$

Where C_t^f is the feedstock cost in year t, CNY; C_t^h is the unit cost of purchasing hydrogen from an external centralised hydrogen plant, CNY/kg; C_t^l is the unit cost of transporting hydrogen, CNY/kg; $E_{comp,t}$ is the daily energy consumption of the compressor in year t, kWh; $EC_{PCU,t}$ is the energy consumption of the pre-cooling unit per unit of distributed hydrogen in year t, kWh/kgH₂; $D_{H_2,t}$ is the daily hydrogen demand in year t, kg; T_a is the number of days of operation per year, assumed to be 365; P_t^e is the price of electricity, CNY/kWh.

In addition, it is assumed that the residual return on fixed assets at the end of the hydrogen refuelling station's lifetime is 10% of the cost of the equipment^[21], which is calculated as an income into the NPV, which can reduce the system cost. Let T_1 be the investment period of whether or not to invest in the construction of the external hydrogen supply hydrogen refuelling station in stage 1, which is set to be 5 years; T_{hrs} is the lifetime of the hydrogen refuelling station, which is 20 years; T_w is the window period for assessing the economic value of the PV hydrogen refuelling station project, which is set to be 25 years; and t_s is the duration of the project from the investment and construction of the station in year t to the final cut-off year⁽²⁷⁾. The project lifetime and the residual value of fixed assets are calculated by equations (30) and (31):

$$t_s = \min(T_{hrs}, T_w + 1 - t) \quad (30)$$

$$S_t^{off} = 10\% \times C_{0,t}^{off} \times (1 + i)^{-t_s} \quad (31)$$

Where S_t^{off} is the residual value of fixed assets discounted to year t, CNY; $C_{0,t}^{off}$ is the construction cost of investing in an externally supplied hydrogen refuelling station in year t, CNY; and i is the nominal discount rate.

The net present value (NPV) of the project of investing and constructing the external hydrogen refuelling station in year t NPV_t^{off} , which is the discounted cash flow of each year of the whole project duration from investing and constructing the external hydrogen refuelling station in year t to the NPV of the project in year t. The income part includes the income from the sale of hydrogen and subsidy during the operation period as well as discounting the salvage value

at the end of the project, and the cost part includes the construction cost during the construction period, the operating cost during

$$NPV_t^{off} = \sum_{n=0}^{t-1} (I_{t+n}^h + I_{t+n}^s - C_{OP,t+n}^{off} - C_{t+n}^f) \times (1+i)^{-n} - C_{0,t}^{off} + S_t^{off} \quad (32)$$

Where I_{t+n}^h , I_{t+n}^s , $C_{OP,t+n}^{off}$, C_{t+n}^f are the revenue from hydrogen sales, subsidy revenue, annual operating cost, and annual feedstock cost of the hydrogen refuelling station that is externally supplied in year $t+n$, respectively, in CNY.

Photovoltaic hydrogen production subsystem

(1) Revenue from retrofitting on-site photovoltaic hydrogen refuelling stations

When an investor decides to retrofit an on-site PV hydrogen refuelling station by adding an on-site photovoltaic hydrogen production subsystem (PVH2), a corresponding cash flow will be generated during the retrofit process. Hydrogen for refuelling of the retrofitted on-site PV hydrogen refuelling station is produced by the PV hydrogen subsystem and the required electricity is also supplied by the PV system. Here, only the hydrogen produced by the PV hydrogen production subsystem is considered to be supplied to its own external hydrogen supply hydrogen refuelling station subsystem, and the sale of excess hydrogen to other organisations is not considered, so its revenue is to offset the feedstock costs of the original hydrogen refuelling station subsystem, including hydrogen procurement, transportation costs and electricity costs. The formula is shown in equation (33):

where I_t^{PVH2} is the revenue of the PV hydrogen production subsystem in year t , CNY; and C_t^f is the feedstock cost of the original external hydrogen refuelling station subsystem, CNY.

(2) Costs of photovoltaic hydrogen production subsystems

The construction cost of the photovoltaic hydrogen production subsystem in year t , $C_{0,t}^{PVH2}$, includes the construction cost of the photovoltaic power generation module, C_t^{PV} , and the construction cost of the electrolyser, C_t^E . It is calculated as shown in Equation (34):

$$C_{0,t}^{PVH2} = C_t^{PV} + C_t^E$$

The annual operating cost of the PV hydrogen sub-system in year t consists of the annual O&M

the operation period and the feedstock cost, which is calculated by equation (32). feedstock costs, which are calculated by equation (32):

cost and labour cost, and the annual O&M cost is assumed to be 4% of the construction cost, then the annual operating cost of the PV hydrogen sub-system is calculated by equation (35):

$$C_{OP,t}^{PVH2} = C_{0,t}^{PVH2} \times 4\% + C_{P,t}^{PVH2}$$

Where $C_{OP,t}^{PVH2}$ is the annual operating cost of the photovoltaic hydrogen production subsystem in year t , CNY; $C_{P,t}^{PVH2}$ is the annual labour cost, CNY. Let the additional PV hydrogen production sub-system requires 2 additional employees, at which time the total number of employees is 8, and the annual per capita salary is 80,000 CNY per person^[30].

The two key technological advances of photovoltaic power generation and hydrogen production in electrolysis tanks are important factors affecting the future cost of photovoltaic hydrogen production, which in turn will affect the economic efficiency of photovoltaic hydrogen refuelling stations. Therefore, this paper also constructs the exponentially decreasing models of PV power generation and electrolyser cost, which are calculated by Eq. (36) and Eq. (37), respectively:

$$C_t^{PV} = C_0^{PV} \cdot e^{-\beta t}$$

$$I_t^{PVH2} = C_t^f$$

$$C_t^E = C_0^E \cdot e^{-\gamma t} \quad (33)$$

Where C_t^{PV} is the construction cost of investing in the construction of the PV module in year t , CNY; C_0^{PV} is the initial cost of the PV system, CNY, and β is its decreasing exponent; C_t^E is the construction cost of investing in the construction of the electrolyser in year t , CNY; C_0^E is the initial cost of the electrolyser, CNY, and γ is its decreasing exponent.

The main feedstock for on-site PV hydrogen production technology is water (C_t^w) required for hydrogen production by electrolysis of water, with a procurement cost as shown in equation (38):

$$C_t^w = P_t^w \times Q_w \times Q_t^h$$

Where P_t^w is the unit purchase price of water for hydrogen production, taken as 4.1CNY/m³^[27]; Q_w is the amount of water

consumed to produce a unit kg of hydrogen, taken as $0.009 \text{ m}^3/\text{kg}^{[27]}$; and Q_t^h is the annual refuelling volume of the hydrogen refuelling station in year t , kg.

In addition, the retrofit of the on-site PV hydrogenation station requires the calculation of the residual value of the fixed assets and the replacement cost of the electrolyzers, where the discounted value of the residual value of the fixed assets is calculated according to equation (39):

$$S_t^{PVH2} = 10\% \times C_{0,t}^{PVH2} \times (1+i)^{-t_s} \quad (39)$$

Where S_t^{PVH2} is the discounted value of the residual value of the fixed assets invested in the construction of the photovoltaic hydrogen production subsystem in year t , CNY; $C_{0,t}^{PVH2}$ is the cost of construction of the photovoltaic hydrogen production subsystem in year t , CNY; i is the nominal discount rate; and t_s is the duration of the project, years.

From the assumptions in the economic benefit analysis of the PV hydrogenation station without considering uncertainty in Part I, it can be seen that the electrolyser replacement cost has an annual life of 10 years, and when the project duration is greater than the replacement life, the cost of replacing the electrolyser needs to be calculated; when the project duration is less than or equal to the replacement life, the cost of replacing the electrolyser does not need to be taken into account. The specific calculation formula is shown in equation (40):

$$C_R^{PVH2} = 0.1C_t^E[(1+i)^{-10}I(t_s \geq 10) + (1+i)^{-20}I(t_s \geq 20)] \quad (40)$$

Where C_R^{PVH2} is the discounted value of the replacement cost of the electrolytic tank of the PV hydrogen production subsystem, CNY; C_t^E is the cost of the electrolytic tank construction at the time of investment and construction in the t th year, CNY; and t_s is the duration of the PV hydrogen production subsystem project, in years. $I(\cdot)$ is a demonstrative function, with the value of 1 when the conditional equation holds, and 0 otherwise.

In summary, the NPV of the investment in the construction of the PV hydrogen sub-system in year t is the discounted cash flow of each year of the entire project duration from the investment in the construction of the PV hydrogen sub-system in year t to the NPV of the project in year t . The income part includes the income from the sale of hydrogen and electricity during the operation period as well as the discounted salvage value at the end of the project, and the

cost part includes the construction cost during the construction period of the sub-system, the operating cost during the operation period, the cost of the replacement of equipment and the cost of feedstock water, which is calculated by equation (41). feedstock water cost, calculated by equation (41):

$$NPV_t^{PVH2} = \sum_{n=0}^{t_s-1} (I_{t+n}^{PVH2} - C_{OP,t+n}^{PVH2} - C_{t+n}^W) \times (1+i)^{-n} - C_{0,t}^{PVH2} - C_R^{PVH2} + S_t^{PVH2} \quad (41)$$

Where I_{t+n}^{PVH2} , $C_{OP,t+n}^{PVH2}$, C_{t+n}^W are the revenues from hydrogen and electricity sales from the PV hydrogen production subsystem to the external hydrogen supply and hydrogen refuelling station subsystems, the annual operating costs, and the annual cost of feedstock water, in CNY in the $t+n$ th year, respectively.

2.4 Compound Real Options Model Construction and Solution

GBM Stochastic Process

Geometric Brownian motion (GBM) is a continuous-time stochastic process commonly used to describe the movement of stock or other asset prices over time. It is a special kind of Brownian motion that assumes that price movements are random but follow certain statistical laws, and is characterised by a normal distribution of the logarithm of the asset price, which means that the price itself follows a lognormal distribution, guaranteeing that the value of the random variable is always positive; secondly, the future value of the asset price does not only depend on the current value, but also has a path dependence; furthermore, it contains a random term dW_t that introduces uncertainty, reflecting the random fluctuations of real-world asset prices. Therefore, the GBM is often used to model security prices, interest rates, commodity prices, and other economic and financial variables that cannot take negative values. Assume that changes in asset prices contain both a deterministic growth trend, the expected rate of return (drift rate), which represents the average growth rate of the asset, and a stochastic fluctuation component, the standard deviation rate (volatility), which represents the magnitude of fluctuations in asset prices. The random variable S_t is then considered to follow the GBM when it satisfies the stochastic differential equation of equation (42):

$$dS_t = \mu S_t dt + \sigma S_t dW_t$$

Where S_t denotes the asset price at time t , μ is the expected return of the asset, σ is the

volatility of the asset's return, and dW_t is the increment of the Standard Brownian Motion, which represents the stochastic shocks. μ determines the long-run trend of the GBM, which is usually set to the historical average return of the asset, and σ determines the short-run volatility of the GBM, which is usually set to the historical standard deviation of the asset price. The estimates of μ and σ in the model require access to historical data on the assets and are dependent on the time period chosen, which may lead to different estimates for different time periods. Due to the availability of specific data and the content of this paper, the process of calculating the drift and volatility of the uncertainty parameters (retail price of hydrogen refuelling, electricity price, annual hydrogen refuelling volume) is not focused on showing the calculation of these parameters and instead the values used by Zhao and Liu (2024)^[32] are chosen.

The characteristics of GBM are briefly demonstrated by the following example. Assuming that S_t denotes the retail price of refilled hydrogen, the initial price is set to be 35CNY/kg, the time span of the simulation is one year, the number of paths is 10, and both μ and σ are set to be 0.2. As shown in Fig. 2, the horizontal axis represents the time, which is usually measured in terms of years, and the vertical axis is the 10 different paths of the retail price of hydrogen randomly generated according to the GBM, and each of the paths represents a possible scenario of the price change, which simulates the price change from the present to the next 25 years of price changes. The simulation allows for a rough prediction of the future trend of hydrogen prices.

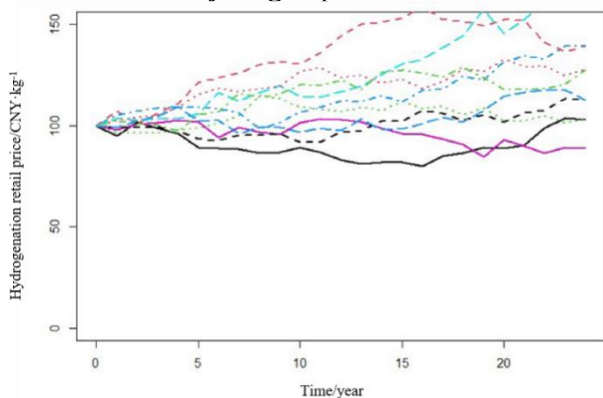


Figure 2 Fluctuating trends in retail hydrogenation prices obeying geometric Brownian motion

In practice, GBM can be used to simulate the volatility of asset prices over time and can be used to generate sample paths of prices to forecast future price movements through Monte Carlo simulation methods. Despite some errors, the accuracy of the simulation can be improved by increasing the sample size. This approach is applicable to a variety of scenarios such as financial analysis and option pricing. This suggests that GBM can be used as an effective tool to simulate and analyse stochastic fluctuations in asset prices. However, in specific studies, the simulation of the stochastic process of the underlying asset price generally requires a large sampling to be done in order to achieve a reasonable accuracy of the estimates, but this takes a lot of computational time. Therefore, in this paper, the Variance Reduction Procedure (VRP) is used to improve the accuracy of the estimates by reducing the variance of the random variables, so that more stable and reliable results can be obtained with the same number of simulations, and the computation time can be greatly reduced. The VRP includes the dyadic variable method, the control variable method, the focused sampling method, the interval sampling method, the moment matching method^[33], and the moment matching method^[34]. Among them, the dyadic variable method reduces the variance of the estimated quantity by generating a pair of negatively correlated price paths in Monte Carlo simulation, which has the advantages of easy implementation, wide applicability, and high computational efficiency compared with other variance reduction procedures. Therefore, in this paper, the pairwise variable method is used to improve the accuracy of the price paths of BGM simulations, which involves calculating two prices of the underlying asset at each simulation sample, one obtained by following the normal stochastic process and the other obtained by taking the inverse of the stochastic perturbation term. Of these two values, if one is higher than the true value, the other will be lower than the true value, and the resulting sampled value of the asset is calculated to be equal to the average of the two prices, thus improving the accuracy and stability of the simulation results.

Compound Real Options Modelling

compound real options reflect a new investment mindset and strategic thinking, which describes

a series of closely related rights before and after the investment decision in an uncertain environment, which are meant to make the decision-making choices more flexible, and thus the valuation method is advantageous in analysing multi-stage sequential decision-making problems. Since retail hydrogen price, electricity price and annual hydrogen refuelling volume are the main uncertainties in hydrogen station investments, these uncertainties play an important role in the valuation of hydrogen station projects. In this paper, the retail price of hydrogen is assumed to be P_t^h , following GBM^[34]. Similarly, the price of electricity P_t^e , which is the feedstock for on-site hydrogen production, follows GBM^[35]. The calculation equations are shown in equations (43) and (44):

$$dP_t^h = \mu^h P_t^h dt + \sigma^h P_t^h dz_t \quad (43)$$

$$dP_t^e = \mu^e P_t^e dt + \sigma^e P_t^e dz_t \quad (44)$$

Where μ^h and μ^e are the drift rates of hydrogen retail price and electricity price respectively, σ^h and σ^e are the volatility rates of hydrogen retail price and electricity price respectively, and dz_t is the standard Wiener process. In addition, the daily hydrogen refuelling volume at hydrogen refuelling stations represents the market demand, which is also uncertain. At the beginning of the development of hydrogen transport, there are not many hydrogen-fuelled vehicles, but over time, due to the increase in the number of hydrogen-fuelled vehicles and subsidies and tax incentives for hydrogen companies, the demand for hydrogen increases accordingly; whereas, if there is a shortage of hydrogen in a certain region, the demand for hydrogen may also show a decreasing trend. Based on Fan et al^[36] (2013), this paper assumes that the hydrogen demand, i.e., the daily hydrogen refuelling quantity Q_t^h , also follows GBM^[36], and sets μ^q as the hydrogen refuelling drift rate and σ^q as the hydrogen refuelling fluctuation rate, which are calculated by equation (45):

$$dQ_t^h = \mu^q Q_t^h dt + \sigma^q Q_t^h dz_t \quad (45)$$

Considering the investment flexibility that may result from a phased investment, this paper views the investment in a hydrogen refuelling station as a two-stage dynamic investment process. In stage 1, an external hydrogen refuelling station is built first. Then, depending

on subsequent market and technological developments, a decision can be made at any point in Phase 2 whether and when to add a PV hydrogen subsystem to convert the external hydrogen refuelling station into an on-site PV hydrogen refuelling station. As long as the external hydrogen refuelling station is invested in during Phase 1, the investor holds an expansion option during Phase 2 to choose whether or not to add an on-site PV hydrogen generation facility; if the investor chooses to defer the investment at any point in time, the decision-making process described above will be repeated for subsequent investment periods until the end of the period. Since the investment decision in stage 1 determines the retrofit decision in stage 2, the retrofit decision in stage 2 influences the investment decision in stage 1. Therefore, this two-stage decision-making is a sequential model, consistent with the nature of a compound real options^[37].

The risk-free rate is a key parameter in the Real Options Approach (ROA) model, where the pricing of derivatives is generally done by building a risk-free portfolio and then making the return on the portfolio equal to the risk-free rate, which represents the rate of return on theoretically risk-free investments (e.g., government bonds), and in this paper is taken to be 0.06^[33]. ROA treats investment in a capital investment project as an optimal stopping time problem, maximising the return on investment under potential stochastic uncertainty. Real Options Value (abbreviated as ROV_t) is the value of a capital investment project that takes into account the flexibility of the timing of the investment. Among all the stochastic paths that may characterise the future development scenarios, it can be divided into the paths that are chosen to be invested at a certain point in the simulated paths, which are called the investment paths, and the rest of the paths that are never invested due to their poor profitability, which are called the non-investment paths. The project value of the investment path is the present value of the investment profit discounted to period 0, and the project value of the non-investment path is 0. The current investment profit is the net present value of the investment discounted to the current period (NPV_t) in each simulation path. Waiting Options Value (abbreviated as WOV) is the option value of delayed initial investment, and its value is the difference between ROV and

NPV. The probability of investing within the project decision window T_w is the proportion of invested paths among all paths simulated to the total paths. The optimal investment point for each simulated path is the earliest time when investment is triggered.

According to the backward induction method of dynamic planning, the probability distribution of the optimal investment point in phase 2 is determined based on the cash flow generated by investing in the construction of the PV hydrogen generation sub-system in phase 2, and the option value, the NPV of the investment and the waiting value are calculated for each period starting from year 5, and then the cash flow from investing in the construction of the external hydrogen refuelling station sub-system and the superimposition of the option value of phase 2 are taken into consideration to determine the optimal investment point and the real option value of phase 1 in phase 1. The optimal investment point in Phase 1 and the real option value of the project will then be determined.

In order to calculate the probability distribution for obtaining the optimal investment time point for phase 2, the reverse forward iteration is started from the last phase of phase 2. Assume that T_{hrs} is the entire life cycle of the hydrogen refuelling station, which is set to 20 years. In the interval from year 5 to year 24, the investor chooses whether or not to invest in the PV hydrogen subsystem to retrofit the PV hydrogen refuelling station, assuming that the investment in the equipment generates cash flow immediately. In stage 2, the NPV of the current investment and the value of waiting for subsequent investment opportunities are calculated and compared for each period in each simulation path from the last period forward, respectively. The NPV of the investment in building the PV hydrogen subsystem in year t_2 of phase 2 is shown in equation (39). The option value of waiting for the last period is 0 because there is no income without investment, and the option value of the last period is the big value between the NPV of the current investment and 0 of the investment in the construction of PV hydrogen sub-system in that period, i.e., $\max(NPV_t^{PVH2}, 0)$, and then, in the j th simulation path, the value of waiting for the t th year, is the value of waiting for the subsequent investment opportunities. $WOV_{t,j}^{PVH2}$ is the discount of the option value in year $t+1$ to the

current period, and the waiting value is calculated as shown in equation (46):

$$WOV_{t,j}^{PVH2} = (1+i)^{-1} \cdot ROV_{t+1,j}^{PVH2}$$

Next, the decision is made by backward induction to stage 1, i.e., whether to invest in the construction of the initial external hydrogen refuelling station. It is assumed that the investment decision period for this stage is from year 0 to year $T_1 - 1$, a total of T_1 years. Still from the last year of the decision period, year $T_1 - 1$ backward induction calculates the option value for each year. The waiting value for the last year is 0. However, the value of the project investment in the current period includes not only the net present value of the investment in the construction of the external hydrogen refuelling station in that period, but also the discounted value of the option value in the year starting from phase 2 to that period. The greater of the investment value and the waiting value for that period is taken as the option value for that period. In general, it is assumed that whether to invest is considered in year t of the phase. The investment value $NPV_{t,j}^{hrs}$ of investing in the construction of an external hydrogen refuelling station in year t in the j th simulation path is shown in Equation (47):

$$NPV_{t,j}^{hrs} = NPV_{t,j}^{off} + ROV_{T_1}^{PVH2} \times (1+i)^{-(T_1-t)}$$

Because of the use of backward induction, the option value of the simulated path j is finally derived to be the project investment value of the simulated path ($ROV_{0,j}^{hrs}$) in year 0. Then the project investment value of each simulated path is averaged out to be the real option value of the PV hydrogen station, which is computed as shown in Eq. (48):

$$ROV = \frac{1}{N} \sum_{j=1}^N ROV_{0,j}^{hrs}$$

where $ROV_{0,j}^{hrs}$ is the option value in year 0 of simulated path j ; N is the number of simulated paths.

Compound Real Options Model Solution

In this paper, a two-stage Monte Carlo simulation method approach is used to solve the compound real options model, and the framework for solving this model includes the following four steps^[38].

(1) Simulate all random variables (hydrogen price, electricity price, and hydrogen refuelling

quantity) using a stochastic path with geometric Brownian motion;

(2) For each simulation path, calculate the current investment value NPV_t^{PVH2} and current waiting value $WOV_{t,j}^{PVH2}$ for the retrofitted photovoltaic hydrogen refuelling station in Eq. (41) and Eq. (46);

(3) The key of the second stage is whether to invest in retrofitting the PV hydrogenation station or not.

$$ROV_{t_2,j}^{PVH2} = \max(NPV_{t_2,j}^{PVH2}, WOV_{t_2,j}^{PVH2}) \quad (49)$$

$$\tau_{2,t_2,j} = \begin{cases} 1, & NPV_{t_2} \geq WOV_{t_2,j}^{PVH2} \\ 0, & NPV_{t_2} < WOV_{t_2,j}^{PVH2} \end{cases}$$

Where, $ROV_{t_2,j}^{PVH2}$ is the option value at decision point t_2 in simulation path j ; $NPV_{t_2,j}^{PVH2}$ is the investment value of investing in building PV hydrogen sub-systems at decision point t_2 ; and $\tau_{2,t_2,j}$ is the value of the investment decision at decision point t_2 in the second stage of simulation path j , which is responsible for recording the investment option at the time of backward recursion to the investment choice at decision point t_2 . When $NPV_{t_2,j}^{PVH2} \geq WOV_{t_2,j}^{PVH2}$, the investor will invest in the PV hydrogen sub-system immediately, $\tau_{2,t_2,j} = 1$. Otherwise, the investor will not invest in the PV hydrogen sub-system at the decision point t_2 , $\tau_{2,t_2,j} = 0$.

(4) For each simulated path, the option value for the first 1 period is extrapolated based on the option value for the second 1 period. For the one in $t_1 \in [0, T_1 - 1]$, the decision of whether to invest or not in that period depends on comparing the $NPV_{t_1,j}^{hrs}$ of immediate investment in transformation in the current period with the expected return $WOV_{t_1,j}^{hrs}$ on postponing the investment decision to the next 1 period. The decision rule is shown in equations (51) and (52):

$$ROV_{t_1,j}^{hrs} = \max(NPV_{t_1,j}^{hrs}, WOV_{t_1,j}^{hrs}) \quad (51)$$

$$\tau_{1,t_1,j} = \begin{cases} 1, & NPV_{t_1,j}^{hrs} \geq WOV_{t_1,j}^{hrs} \\ 0, & NPV_{t_1,j}^{hrs} < WOV_{t_1,j}^{hrs} \end{cases}$$

Where, $ROV_{t_1,j}^{hrs}$ denotes the option value of simulation path j at decision time point t_1 . $\tau_{1,t_1,j}$ is the recorded value of the investment decision of simulation path j at decision time point t_1 in phase 1, which is responsible for the recording of the investment choices in the reverse recursion to decision time point t_1 . Using $\tau_{1,t_1,j} = 1$ indicates that the investment in

The options held by the investor are American options that can be exercised at any time prior to the expiry of the hydrogen refuelling station. The backward recursion method is used, starting recursively from the final decision point in year $T_w - 1$, with the decision time point $t_2 \in [T_1, T_1 + T_{hrs} - 1]$ in stage 2. The decision rule for each path at this point is as in equations (49) and (50):

$$(50)$$

building a hydrogen refuelling station is chosen at decision time point t_1 , and $\tau_{1,t_1,j} = 0$ indicates that the investment will be postponed. The optimal decision time point and the corresponding revenue for each simulation path are obtained by the recursive comparison shown in Eq. (51) and Eq. (52). The optimal investment time points for stages 1 and 2 of each simulation path are the earliest time points corresponding to a value of 1 in the two sets $\tau_{1,t_1,j}$ and $\tau_{2,t_2,j}$, respectively. The flowchart of the two-stage Monte Carlo simulation method to find the compound real options is shown in Fig. 3.

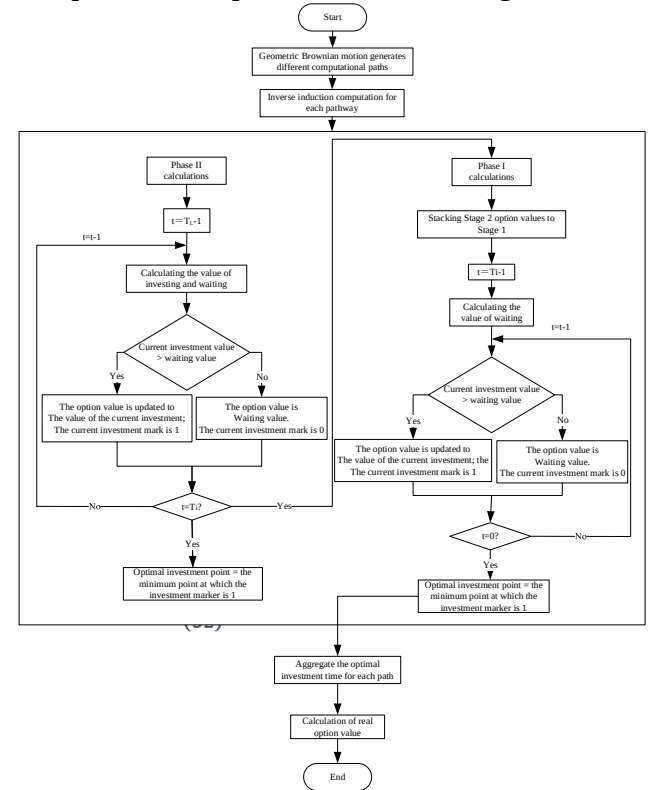


Figure 3 Flowchart of the two-stage Monte Carlo simulation method for finding compound real options

2.5 Research Hypothesis

Research Hypotheses of Chinese Photovoltaic Hydrogen Refuelling Stations in Deterministic Environments

To study the economics of a Chinese PV hydrogen refuelling station in a deterministic environment, this paper makes the following assumptions:

- (1) The PV hydrogen refuelling station with a design pressure of 70 MPa hydrogen mainly consists of PV modules, ALK electrolyzers, compressors, hydrogen storage tanks, pre-cooling devices and refuelling devices, and the power used for the electrolysis, compression and cooling operations is supplied by the grid-connected PV system.
- (2) The grid plays the role of a virtual battery, absorbing and "storing" excess PV hydrogen generation during peak PV hours, and then supplying power to the system as a virtual battery when PV hydrogen generation is insufficient to ensure continuous operation of the electrolysis hydrogen system. It is assumed that there is no energy loss or cost in the charging and discharging process.

(3) It is assumed that the amount of electricity provided to the grid by the PV system is the same as that purchased from it and the price is the same, and the energy loss during the conversion of electricity is not taken into account.

(4) The daily hydrogen refuelling volume is equal to the designed daily refuelling capacity, i.e. the utilisation rate of the designed refuelling capacity of the PV hydrogen refuelling station is 100%; the energy price, the initial investment cost of the equipment and the hydrogen refuelling demand remain unchanged.

(5) To simplify the analysis, it is assumed that the mass flow of hydrogen at the PV hydrogen refuelling station is constant at a constant rate under operating conditions.

(6) All amounts are based on the exchange rate in April 2024 (1 USD = 7.23 RMB).

Parameterisation and basic data

The parameter assumptions in the PV hydrogen production subsystem are divided into technical parameter assumptions and financial parameter assumptions, and the main technical parameter assumptions are shown in Table 1.

Table 1 Main technical parameters assumed in the PV to hydrogen project

Systems	Technical parameters	Data assumptions	Unit
photovoltaic power station	installed capacity	100	MW
	System life	20	year
	Inverter efficiency	90% ^[16]	%
	Photovoltaic annual degradation rate	0.5% ^[39]	%
ALK Electrolyser	Stack Replacement Cycle	10 ^[21]	year
	Electricity consumption for hydrogen production	55 ^[36]	kWh/kg
	Allowable load range	10%-110% ^[40]	%
	electrolytic efficiency	70% ^[18]	%

The financial parameter assumptions include parameter assumptions for calculating the initial investment cost, annual operating cost, and

electric reactor replacement cost. The specific financial parameters are shown in Table 2.

Table 2 Key initial investment cost parameter assumptions in PV hydrogen projects

System module	Cost classification	Niche	Unit cost	Unit
photovoltaic power generation	Initial investment cost	Procurement of equipment	2.38	CNY/W
		Installation	0.22	CNY /W
		civil engineering	0.41	CNY /W
		Other costs	0.16	CNY /W
		Subtotal	3.17	CNY /W
electrolysis for hydrogen production	Initial investment cost	ALK Electrolyser	2010 ^[21]	CNY /kW
		compactor	see below	/
		hydrogen storage tank	350 ^[41]	CNY/kgH ₂
	other	Stack Replacement	15% ^[29]	%
		water price	4.1 ^[27]	CNY /t

		Safety and control systems	see below	/
		Cooling and hydrogenation systems	170000 ^[42]	CNY/Unit

Compressor investment cost: In order to improve the economics of hydrogen storage and transport, it is necessary to compress hydrogen. It is known that the equipment investment cost of a hydrogen compressor for a volume flow rate of 300 m³/h of hydrogen is 320,000 CNY, and then the cost of hydrogen compression at other volume flow rates can be obtained according to the power law given in equation (8).

Safety and control system cost: according to Apostolou (2018)^[43], the safety and control system cost is $285\text{CNY} \times D_{H_2}$.

The main parameter dummy data involved in the cost-benefit analysis of the PV hydrogen refuelling station are shown in Table 3.

Table 3 Techno-economic parameters

Parameter	Clarification	Value
P^h	Hydrogenation retail price/CNY·kg ⁻¹	35 ^[25]
Q_w	Amount of water required to produce one kilogram of hydrogen/m ³ ·kg ⁻¹	0.009 ^[27]
γ	Electricity required to produce one kilogram of hydrogen/kg	3.9 ^[44]
i	discount rate	0.06 ^[32]
t_{day}	Daily hours of operation of the electrolyser/hour·day ⁻¹	18 ^[7]
T_a	Annual operating days/day	365

In addition to the parameter settings described above, the main underlying data for this example are the detailed data on latitude and longitude, average daily peak sunshine hours, and average annual power generation for major cities and counties in China, which are publicly available from NASA. The dataset covers the observation data of 897 cities and counties in 31 provinces, municipalities and autonomous regions in mainland China (Hong Kong and Macao, the two special administrative regions, are not included).

Research Hypotheses for Photovoltaic Hydrogen Refuelling Stations in Uncertain Environments

Due to the long lifecycle of PV hydrogenation station projects, which can generally reach 20 to 25 years, revenues and costs during the lifecycle are dynamically affected by multi-dimensional influencing factors such as market demand,

technological advances, and policy interventions, which makes the cash flow during the project lifecycle behave as a stochastic process with dynamic and complex changes. How to cope with the complexity and high risk of investing in PV hydrogenation stations in an uncertain environment is the core issue that investors need to face.

According to the arithmetic analysis in the deterministic environment which divides the region into recommended investment area, not recommended investment area and prudent investment area division, the annual peak hours of Nanjing is 1153 hours, and it is in the prudent investment area when the daily hydrogen refuelling volume is 500kg or 1000kg, in which case the direct investment in the PV hydrogen refuelling station does not have a significant return. Therefore, considering a two-stage PV hydrogen refuelling station investment in Nanjing in an uncertain environment, this section will remove the over-idealised assumption that the daily hydrogen refuelling volume is equal to the designed daily refuelling capacity in the initial estimation of the PV hydrogen refuelling station economics in a deterministic environment, as well as simplifying assumptions that the energy price and the initial investment cost of the equipment and the demand for hydrogen are constant, and consider the uncertainties of the retail price of hydrogen refuelling, the demand for hydrogen refuelling, the price of electricity purchased and other factors and the trend of decreasing equipment cost under technological progress and scale effect, the author's city Nanjing is chosen as a representative example city, and a specific scenario is designed to analyse the investment value of the project of dynamic investment in the construction of PV hydrogen refuelling stations in this city and the impact of policy guidance tools on the investment behaviour of rational investors. The following assumptions are made when investigating the dynamic investment decision of PV hydrogenation stations in China under uncertainty environment based on the assumptions of deterministic PV hydrogenation station systems:

(1) An investor is considering investing in an externally supplied hydrogen refuelling station and with a refuelling capacity of 1000 kg/day.

Upon completion, it will also consider converting it to a PV hydrogen refuelling station with a hydrogen production capacity of 1000 kg/day through on-site PV hydrogen production equipment.

(2) The investment consideration time for the external hydrogen refuelling station in phase 1 is 5 years, the lifetime of the PV hydrogen refuelling station in phase 2 is 20 years, and the decision window of the project is 25 years; it is assumed that the optimal investment point of time will be calculated from year 0 onwards.

(3) Using the above PV hydrogen refuelling station techno-economic model, the capacity of the main equipment is calculated based on the daily hydrogen refuelling demand.

(4) The Capacity Utilization Rate (CUR) of the current hydrogen refueling station, i.e., the percentage capacity utilisation rate of the daily hydrogen refueling volume to the daily design hydrogen refueling capacity; in the baseline scenario, it is assumed that the CUR is 50%, i.e., the daily design hydrogen refueling capacity is

1,000 kg/d but the actual daily hydrogen refueling capacity is only 500 kg/d.

(5) All amounts are based on the exchange rate in April 2024 (1 USD = 7.23 RMB).

Parameter setting

On the basis of the parameters and techno-economic assumptions of the PV hydrogen refuelling station system in a deterministic environment, the annual decreasing indices of the construction cost of the subsystem of the external hydrogen refuelling station, the cost of the PV power generation module, and the cost of the electrolyser are added, and the impact of uncertainty factors on the economics of the investment is also taken into account. The parameter assumptions involved in evaluating the investment in hydrogen refuelling stations using compound option theory at this point can be divided into techno-economic assumptions and uncertainty assumptions, and the data on the main technical assumptions related to hydrogen refuelling stations are shown in Table 4

Table 4 Techno-economic parameters

Parameter	Clarification	Value	Parameter	Clarification	Value
c_t^n	Procurement cost of hydrogen for centralised hydrogen production equipment/CNY·kg ⁻¹	15 ^[45]	c_t^l	Trailer transport cost of hydrogen from centralised hydrogen plant to external hydrogen refuelling station/CNY·kg ⁻¹	10 ^[46]
a	Annual decremental cost index for the construction of external hydrogen refuelling stations	0.06 ^[48]	B_t^n	Operating subsidy per unit of hydrogen in year t/CNY·kg ⁻¹	40 ^[32]
β	Photovoltaic cost degradation index	0.06 ^[21]	P_t^{no}	Price of hydrogen produced on-site and sold to nearby off-site hydrogen refuelling stations/ CNY·kg ⁻¹	22.5 ^[48]
γ	Decreasing cost index for electrolytic tanks	0.06 ^[21]	ζ	Annual decreasing rate of subsidies for the operation of hydrogen refuelling stations for external hydrogen supply	0.2 ^[49]
T_{hrs}	Life cycle of hydrogen refuelling station/year	20 ^[32]	T_1	Investment decision cycle/year	5 ^[32]

The compound real options model developed in this paper includes three state variables, which are the retail price of hydrogen refuelling, the price of electricity and the annual refuelling volume of hydrogen. The hydrogen refuelling price determines the revenue of the hydrogen refuelling station, and the retail market price of hydrogen as the final product is directly related to the profitability and return on investment of the project. Electricity price is one of the most important factors affecting the cost of hydrogen production, especially when using electrolysis of water for hydrogen production technology, the cost of electricity accounts for a considerable proportion of the total cost, so fluctuations in the price of electricity will also affect the economics

of the hydrogen refuelling station project. Hydrogen refuelling capacity represents the market demand for hydrogen energy, and the size of the market demand affects the size of the hydrogen refuelling station and the investment decision. These price and capacity uncertainties are key factors in the investment decision of a hydrogen refuelling station project, and they affect the risk and return of the investment. Incorporating these variables into a compound real options model allows for a more accurate assessment of the value and timing of the investment in a PV hydrogen refuelling station project. It is assumed that their volatility, drift and initial values are shown in Table 5.

Table 5 Uncertainty parameters

Parameter	Clarification	Initial value	Drift rate	Value	Volatilities	Value
P_t^n	Hydrogenation retail price /CNY·kg ⁻¹	35 ^[25]	μ^n	0 ^[34]	σ^n	0.15
P_t^e	Electricity price/ CNY·kg ⁻¹	0.6 ^[50]	μ^e	0.02 ^[35]	σ^e	0.02 ^[35]
Q_t^n	Annual refill/kg	182,500	μ^q	0.02 ^[36]	σ^q	0.02 ^[36]

3 SIMULATION CASE

3.1 Case Study of a Chinese Photovoltaic Hydrogen Refuelling Station in a Deterministic Environment

Economic Analysis of Photovoltaic Hydrogen Refuelling Stations in China Based on Two Factors

In this paper, using the above constructed techno-economic model for PV hydrogen refuelling stations and the peak sunshine hours data provided by NASA for major urban districts and counties in China, the impacts of different annual peak hours and refuelling capacity of hydrogen refuelling station design days on the economics are investigated. The economics of the hydrogen refuelling stations were evaluated through levelised cost of ownership (LCOH) to help investors judge the profitability of their investments in different regions and refuelling capacities.

According to NASA data, the highest annual peak hour is in Lhasa Shigatse (2128 hours), and the lowest is in Jishou City, Hunan Province (1099 hours), so the annual peak hour interval is set to be 500h ~ 2500h. GGII statistics show that as of October 2023, about 60% of China's hydrogen refuelling stations have a daily refuelling capacity of no more than 500kg, and 30% are between 500kg to 1000kg, with a maximum of 6400kg/d. Therefore, the daily hydrogen refuelling capacity interval is set to be 250kg/d ~ 6500kg/d. However, according to the public data of Hydrogen Energy Watch in January 2024, the 265 hydrogen refuelling stations currently in operation can refuel an average of 760kg of hydrogen per day, and in order to facilitate the comparison of the general situation in the whole country, this chapter will then make a comparison of the design of the daily hydrogen refuelling capacity interval of 250 kg/d ~ 1250 kg/d, this chapter will focus on calculating and analysing the economic indicators for PV hydrogen refuelling stations with a design range of 250 kg/d ~ 1250 kg/d.

The resulting levelised cost of hydrogen (LCOH) for the PV hydrogen refuelling station

project for different combinations of daily hydrogen refuelling capacity and annual peak hours of PV is obtained as shown in Figure 4. From Fig. 4(a), it can be seen that the combination of higher design daily hydrogen refuelling capacity and more annual peak hours of PV significantly reduces the LCOH. For comparison of the actual situation, the variation of LCOH under the combination of daily hydrogen refuelling capacity and annual peak hours of PV prevailing in the country is shown in Fig. 4(b). Under the conditions of low daily hydrogen addition (less than 500 kg/d) and low annual peak hours of PV (less than 1500 h), the LCOH is high and almost always higher than 35CNY/kg. however, when the daily hydrogen addition is increased to more than 1000 kg/d and the annual peak hours of PV reaches more than 2000 h, the LCOH decreases significantly to about 15CNY /kg to 20CNY/kg. Specifically, three cities, Nanjing (A), Beijing (B), and Lhasa (C), are shown as examples of LCOH values at 500 kg/d and 1000 kg/d of daily hydrogen addition, respectively. The annual peak hours of these three cities are 1153, 1577, and 2018, respectively. From the figure, it can be seen that Lhasa with higher annual peak hours has a LCOH of 21CNY/kg (C2) at 1000kg/d daily hydrogenation, while Nanjing with lower annual peak number has a LCOH of 31.3CNY/kg (A1) at 500kg/d daily hydrogenation. This suggests that there will be a significant cost advantage to build a PV hydrogen refuelling station in Lhasa, where both factors are advantageous. Meanwhile, comparing the three cities when the daily hydrogen refuelling rate is increased from 500kg/d to 1000kg/d and the hydrogen refuelling station is operating at full capacity, the LCOH decreases by about 1.7CNY/kg, which suggests that an increase in the daily hydrogen refuelling rate will drive the reduction of the LCOH, thus improving the economics of the project.

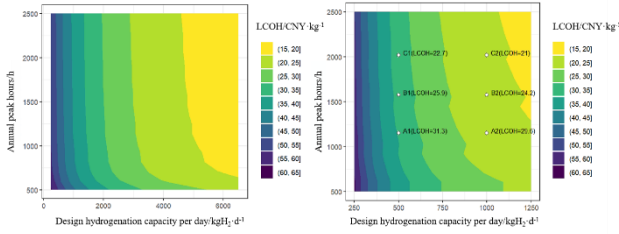


Figure 4 Two-factor contour plot of LCOH

As can be seen in Figure 4, the daily hydrogen refuelling volume and annual peak hours of PV should be maximised in order to achieve the best economics of the PV hydrogen refuelling station project. With the combination of high daily hydrogen addition and high annual peak hours of PV, the LCOH of the investment project is lower and the overall economics of the project is optimal. Therefore, the area with a combination of high daily hydrogen addition and high annual peak hours of PV with a daily hydrogen addition of 1000 kg/d or more and annual peak hours of PV of 2000 hours or more is classified as a recommended investment area; while the area with a combination of low daily hydrogen addition and low annual peak hours of PV with a daily hydrogen addition of less than 500 kg/d and annual peak hours of PV of less than 1,100 hours is classified as a region of no recommended investment areas; and areas with a combination of high daily hydrogen addition and low annual peak hours of PV or low daily hydrogen addition and high annual peak hours of PV are prudent investment areas.

The calculated LCOH results for the above three example cities when designing the daily hydrogen refuelling capacity of 500kg and 1000kg are shown in Table 6. Overall, investing in a PV hydrogen refuelling station in Nanjing is the least economically efficient, with an LCOH of 31.3CNY/kg for a daily hydrogen refuelling volume of 500 kg and 29.6CNY/kg for a daily hydrogen refuelling volume of 1000 kg. Although the economics are relatively increased, the difference in the results of the various economic indicators with those of Beijing and Lhasa is still very large. According to the above regional division, Nanjing is obviously located in the prudent investment area, in this case, direct investment in PV hydrogen refuelling station benefit is not considerable, therefore, we can consider a two-stage PV hydrogen refuelling station investment in Nanjing, firstly, invest in the external hydrogen refuelling station, and then increase the PV hydrogen sub-systems when the

subsequent appropriate time, and transform the original hydrogen refuelling station into a PV hydrogen refuelling station, this strategy can help the investor to reduce the risk of the initial investment, to This strategy can help the investor reduce the initial investment risk and obtain greater economic returns. Specific phased investment scenarios will be discussed under the uncertainty scenario.

Table 6 Results of the economics indicators for the sample cities

Daily hydrogen ation/kg	Cities	Annual peak hours/h	LCOH/CNY·kg ⁻¹
500	Nanjing	1153	31.3
	Beijing	1577	25.9
	Lhasa	2018	22.7
1000	Nanjing	1153	29.6
	Beijing	1577	24.2
	Lhasa	2018	21

LCOH Analysis of PV Hydrogen Refuelling Stations in Major Urban Districts and Counties in China

Based on the data of average daily peak sunshine hours in the NASA database, the LCOH of PV hydrogen refuelling stations can be obtained for a total of 897 cities and districts and counties in 31 provinces, municipalities directly under the central government and autonomous regions across the country, and the data can be statistically analysed at the level of the national cities and districts and counties, at the level of the four major regions in China, and at the level of the provinces.

Firstly, the statistical characteristics of LCOH of PV hydrogen refuelling stations at each location are analysed at the level of urban districts and counties across the country. When the daily hydrogen refuelling volume is 500kg, the frequency histogram of LCOH distribution of PV hydrogen refuelling stations across the country is shown in Fig. 5. As can be seen from the figure, the values of LCOH of PV hydrogen refuelling stations across the country range from 24 CNY/kg to 36CNY/kg, and the LCOH of PV hydrogen refuelling stations in most regions mainly focuses on the range from 28 CNY/kg to 32 CNY/kg. The overall distribution shows a right skewed distribution, indicating that the LCOH of PV hydrogen refuelling stations in a few regions is lower than the overall concentration range, while the slightly longer tail

on the right side indicates that there are a few regions where the LCOH of PV hydrogen refuelling stations is higher. The highest LCOH of PV hydrogen refuelling stations in the country is in Jishou City, Hunan Province, at 35.8CNY/kg; the lowest is in Rikaze City, Tibet Autonomous Region, at 23.7CNY/kg; and the average value of LCOH of PV hydrogen refuelling stations in the major urban districts and counties in the country is 29.6CNY/kg.

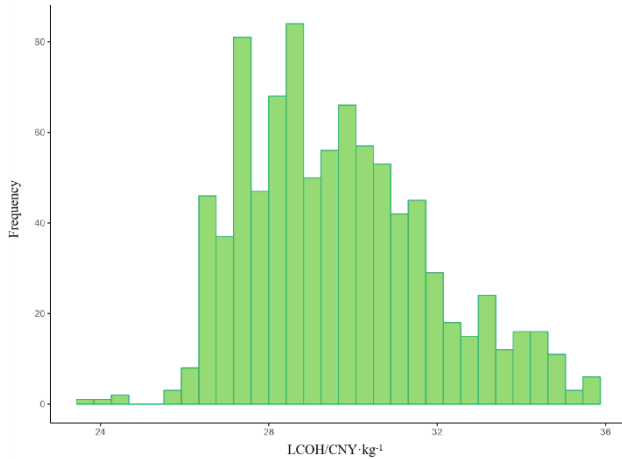


Figure 5 Histogram of the distribution of LCOH at PV hydrogen refuelling stations in various locations for a daily hydrogen refuelling volume of 500kg

Figure 6 shows the distribution and trend of LCOH cost across the country for different daily hydrogen addition levels when the daily hydrogen addition is 500kg, 1000kg, 1500kg and 2000kg, respectively. From Fig. 6, it is observed that the median LCOH gradually decreases as the daily hydrogenation demand increases. The median is 29.3CNY/kg for a daily hydrogenation rate of 500 kg, while the median is 26.7CNY/kg for a daily hydrogenation rate of 2000 kg. By comparing different daily hydrogenation rates, it can be seen that the LCOH tends to be concentrated and decreasing in each place as the daily hydrogenation demand increases, and although the cost varies in different hydrogenation rates, the overall trend is that the higher the daily hydrogenation rate, the lower the LCOH. In addition, it can be seen from the figure that the effect of daily hydrogen refuelling volume on the LCOH of PV hydrogen refuelling stations is marginal and decreasing, and the decrease of LCOH of PV hydrogen refuelling stations with an increase of daily hydrogen refuelling volume from 500kg to 1000kg is much larger than the decrease of LCOH of PV hydrogen refuelling stations with an increase of

daily hydrogen refuelling volume from 1500kg to 2000kg.

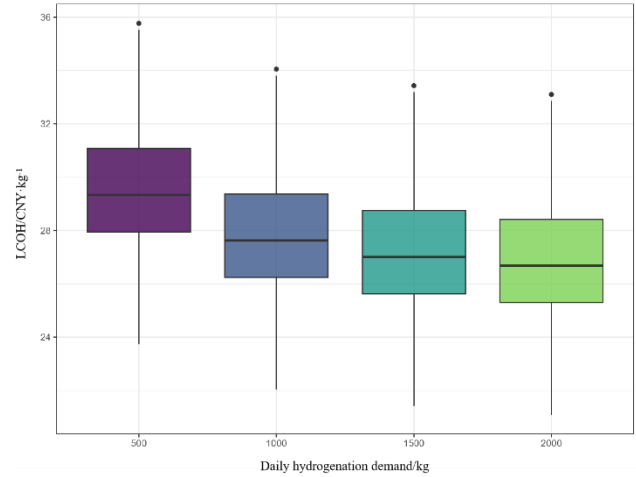


Figure 6 Grouped box plots of LCOH at PV hydrogen refuelling stations across locations for different daily hydrogen refuelling levels

Figure 7 demonstrates the relationship between annual peak hours, daily hydrogen refuelling levels and LCOH, and the data points in the scatterplot are shown in different colours and shapes to indicate different daily hydrogen demand levels (500 kg, 1000 kg, 1500 kg and 2000 kg), respectively. As can be seen in Fig. 7, the LCOH of the PV hydrogen refuelling station gradually decreases with the increase of the annual peak hours, and there is a negative correlation between the two. For the same number of annual peak hours, the higher the daily hydrogen demand, the lower the LCOH of the PV hydrogen refuelling station. At each daily hydrogen refuelling level, there are large fluctuations and some higher outliers in the PV hydrogen filling station LCOH at lower annual peak hours (below about 1250 hours). However, as the annual peak hours increase, the outlier points gradually decrease and the data distribution tends to be concentrated. So Figure 8 shows the negative correlation between annual peak hours, daily hydrogen refuelling grade and PV hydrogen station LCOH, increasing annual peak hours and daily hydrogen refuelling can significantly reduce PV hydrogen station LCOH, and the cost distribution is more concentrated and stable across the area at high annual peak hours.

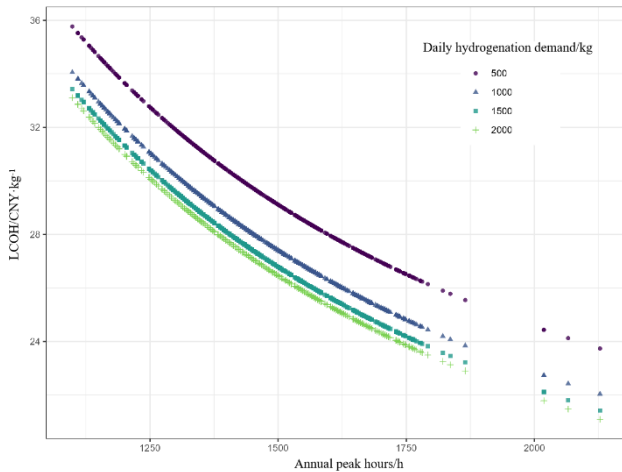


Figure 7 Scatter plot of annual peak hours, daily hydrogen refuelling rating and LCOH of PV hydrogen refuelling stations

Secondly, the economics of PV hydrogen refuelling stations are analysed in terms of the four major regions of China. According to the difference in geographical location, the 31 provinces (excluding Macau and Hong Kong) municipalities and autonomous regions in China are divided into four major regions: northeast, east, west and central. The northeast includes Liaoning, Jilin, and Heilongjiang provinces; the east includes Beijing, Tianjin, Hebei, Shanghai, Jiangsu, Zhejiang, Fujian, Shandong, Guangdong, and Hainan provinces; the west includes Inner Mongolia Autonomous Region, Guangxi Zhuang Autonomous Region, Chongqing Municipality, Sichuan, Guizhou, Yunnan, Shaanxi, Gansu, Qinghai, Ningxia Hui Autonomous Region, and Xinjiang Uygur Autonomous Region; Tibet Autonomous Region; Central China includes Shanxi, Anhui, Jiangxi, Henan, Hubei and Hunan Provinces. When the daily hydrogen demand is 500kg, the violin diagram of LCOH in the four regions is shown in Figure 8.

Figure 8 shows violin plots of the LCOH, distribution in the four major regions of China (Northeast, East, West, and Central). The violin plots combine the box-and-line and density plots to present in detail the distribution patterns, concentration trends, and variability of the data. The width of the violin plot represents the density of the data, i.e., the concentration of the data points in the interval; the white dots represent the median LCOH in each region; the upper and lower limits of the box line part indicate the first quartile (Q1, lower quartile) and the third quartile (Q3, upper quartile), respectively. As seen from the figure, the width

of the violin plot is larger in the northeastern region, then the distribution of LCOH values is more concentrated, and most of the data are concentrated near the median of 29.6CNY/kg; the distribution in the eastern region is relatively wider, and shows the characteristics of a bimodal distribution, which indicates that there are large geographical differences within the eastern region. The density curve in the western region is slimmer, showing a more concentrated distribution, but there are multiple high value outliers at the top, indicating an overall lower LCOH in the western region, with a median of 27.7CNY/kg, but a situation of higher costs in some areas. The density curve of the central region is smoother and relatively uniformly distributed, but there are some extreme values distributed on both sides, and its median value of LCOH is the highest, at 31.3CNY/kg. Overall, the western region has a lower and more concentrated distribution of LCOH, with the lowest median value, showing a strong cost advantage. The LCOH distributions in the Northeast and Central regions are closer, but the overall cost is higher in the Central. The eastern region has a bimodal distribution of LCOH, showing clear geographical differences, with the bimodal distribution reflecting significant imbalances within the region.

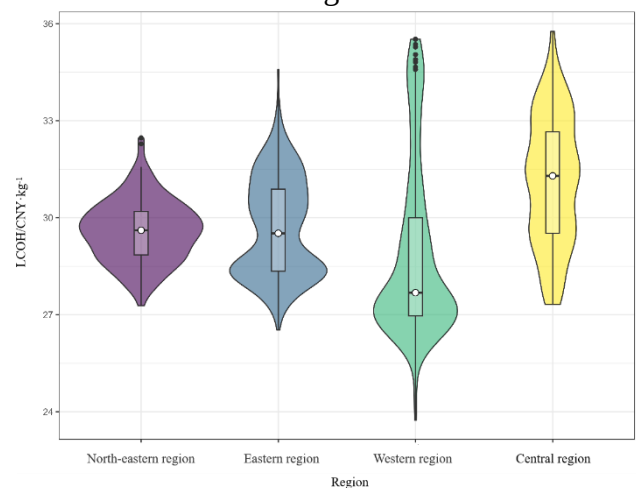


Figure 8 Violin diagram of LCOH of PV hydrogen refuelling stations in four regions

3.2 Analysis of the Results of a Dynamic Investment Benchmark Scenario for Photovoltaic Hydrogen Refuelling Stations in an Uncertain Environment

In a complex and volatile market environment, investment decisions for PV hydrogenation station projects face a number of uncertainties, including market demand, technological

advances, energy price fluctuations, and policy interventions. These uncertainties can have a significant impact on the costs and benefits of the project, making the investment evaluation and decision-making of PV hydrogen refuelling stations more complex and challenging. This part systematically analyses the dynamic investment decision of PV hydrogen refueling stations in uncertain environments by applying a compound real options model with a hypothetical scenario case in Nanjing. By setting up different market and industrial guiding policy scenarios to assess the impact of uncertain factors on investment timing and investment value, it aims to provide investors with scientific and reasonable decision-making basis and strategic recommendations.

Overall Investment Analysis of Photovoltaic Hydrogenation Station Projects

The investment decision of the PV hydrogen refuelling station in an uncertain environment is analysed based on the distribution of the optimal investment time points in each period and the real option value of the project among the many simulation paths. The optimal investment time point in the forecast period is determined by the mean, the plural and the median of the optimal investment time points in each simulation path. The mean is the average of the optimal investment points of all the simulated paths, reflecting the overall trend of the concentration of investment points, which can also be referred to as the "comprehensive investment points"; the plural is the most common optimal investment points, reflecting the specific year in which the most investment points are concentrated, which can also be referred to as the "high frequency investment points"; the median is the optimal investment point distribution and the real option value of the project during the forecast period. "The median is the value in the middle of the optimal investment points in descending order of magnitude, reflecting the 50 per cent of optimal investment points that are earlier than that point, and can also be referred to as "robust investment points".

The real option value (ROV) of an investment project is the mean value of the project value calculated for each simulated price path in period 0. The initial net present value (NPV0) is the mean value of the profit from the immediate investment in period 0; the waiting value (WOV) is the difference between the ROV and NPV0.

If the phased investment is not considered, and the dynamic decision-making of the overall investment in the PV hydrogen refuelling station is carried out directly in Nanjing, the time series of the value of the investment and the probability distribution of the optimal time point are shown in Fig. 9. In Fig. 9(a), the horizontal axis indicates the investment time point in years; the vertical axis indicates the current waiting value, the current option value and the current net present value of the investment in millions of yuan. The current waiting value is the option value of the delayed investment, discounted for the option value of the next period; the net present value of the current investment is the net present value of the investment discounted to the current period in each of the simulation paths; the value of the current option is the value of the capital investment project that takes into account the flexibility of the timing of the investment, and its value is the larger of the net present value of the current investment and the current waiting value.

Figure 9(b) shows the probability distribution of the optimal investment time for investing in a PV hydrogen station project in the Nanjing area under the hypothetical scenario. The horizontal axis shows the investment time point (in years), including a "no investment" option; the vertical axis shows the frequency. The data show an overall right-skewed distribution, with a higher probability of investing between years 7 and 12, with a probability of about 6 per cent for each time period, and the highest probability of not investing, at 32 per cent. The probability of investing is lower in the other time periods, especially in years 0 to 3 and 21 to 24, where there is almost no probability of investing. This suggests that investors tend to invest in the middle of the decision window (i.e., between years 7 and 12) and are less likely to choose to invest in the early or late stages of project initiation. Investors also have a higher likelihood of choosing not to invest. If an investor chooses to invest, the mean value of the optimal investment point calculated from period 0 is year 11, the plural is year 8, and the median is year 11. This indicates that investors should focus on the high frequency investment point in year 8 and make small exploratory investments to take advantage of high return opportunities that arise early on, while continuing to observe market movements in preparation for the main

investment in year 11. The ROV of the investment programme in Year 11 is 19.09 million CNY, NPV0 is -37.56 million CNY and WOV is 56.65 million CNY. This indicates that with the current mean value of investment net cash flow of -37.56 million, the economics of the investment project are very poor and investors are more likely to choose not to invest, while the higher ROV indicates that the value of the project can be significantly increased by flexibility in choosing the timing of the investment, as the incremental value due to the flexibility in choosing the timing of the investment, i.e., the waiting value, is as high as 56.65 million CNY.

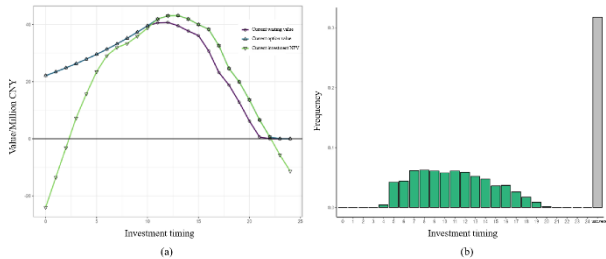


Figure 9 Probability distribution of the time series of values and optimal times for the investment in the Nanjing PV hydrogen refuelling station

Comparative Analysis of Single-phase and Two-phase Investments

If an investor considers investing only in a single-stage external hydrogen supply hydrogen refuelling station subsystem without considering the investment decision to convert it to a PV hydrogen refuelling station versus the probability distribution of the optimal investment time point for investing in a two-stage hydrogen refuelling station, as shown in Fig. 10. If the staged investment is not considered and only a single-stage external hydrogen refuelling station is constructed, it can be seen from Fig. 10(a) that the probability of investing in the order of 0 to 4 years increases sequentially, but is generally lower in the first 4 years, not exceeding 4%; and the probability of investing in the last year is higher, at 26%. In contrast, the probability of not investing is the highest at 67 per cent. This suggests that investors in this scenario are highly likely to choose not to invest. However, if the investor plans to invest, the optimal time to invest would be year 4, when the ROV of the investment project would be 10.93 million CNY, the NPV0 would be -16.01 million CNY, and the WOV would be 26.95 million CNY.

Figure 10(b) shows the probability distribution of the optimal investment time point for stage 1 when considering a two-stage dynamic investment decision for hydrogen refuelling stations. The so-called two-stage dynamic investment decision of hydrogen refuelling station is to choose to invest in the subsystem of external hydrogen refuelling station firstly in the investment decision period of 5 years from 0 to 4 years (Stage 1), and then to choose the appropriate investment time point to invest in the subsystem of photovoltaic hydrogen production in the retrofitting decision period of 20 years from 5 to 24 years (Stage 2) to retrofit the original external hydrogen refuelling station into a photovoltaic hydrogen refuelling station. As can be seen in Figure 10(b), the investment probability from 0 to 4 years increases sequentially from 0, where the first 4 years have a lower probability of no more than 5%, and the last year has a higher investment probability of 38%, which is 12% higher compared to investing in a single-phase externally supplied hydrogen refuelling station in the same year. The probability of not investing is 52 per cent, which is 15 per cent lower compared to a single-stage externally supplied hydrogen refuelling station. This indicates that investors are more inclined to invest in two-stage PV hydrogen refuelling stations. The probability of not investing is still greater than the probability of investing, and there is a high probability that the investor will also choose not to invest. However, if the investor plans to invest in years 0-4, the mean, plural and median of the optimal investment point is year 4, when the ROV of the investment project is 16.54 million CNY; NPV0 is -2.2 million CNY and WOV is 18.74 million CNY. It is the same optimal investment time point as investing in a single-stage hydrogen refuelling station, which is year 4, but at this point the ROV increases by 5.61 million CNY. Therefore, it is a better strategy to consider a two-stage investment in an external hydrogen refuelling station, i.e., investing in an external hydrogen refuelling station first during the 5-year investment decision period, and then choosing the appropriate point in time to add a photovoltaic hydrogen sub-system based on future changes in the market, technology, and energy prices, etc., to convert the existing external hydrogen refuelling station into a photovoltaic refuelling station, which could

significantly enhance the profitability possibilities.

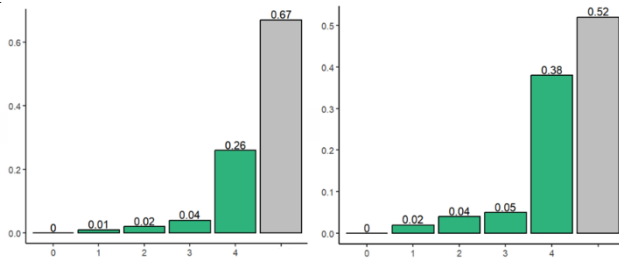


Figure 10 Probability distribution of optimal investment timing for single-phase and two-phase investments in Nanjing

Nanjing Two-phase Investment Analysis

The investor now chooses to make a two-stage investment decision for the PV hydrogen refuelling station in Nanjing, and from the above analysis, it can be seen that the optimal investment time point for investing in the externally supplied hydrogen refuelling station sub-system in Stage 1 is the 4th year, and the probability distribution of the optimal investment time point for investing in the PV hydrogen sub-system in Stage 2 is shown in the right-hand panel of Fig. 11. The horizontal axis indicates the investment time point in years from 5 to 24; the vertical axis indicates the frequency. The data show that in the baseline scenario, the probability of not investing is 0, and the probability of investing between 9 and 11 years is relatively high, with the highest probability of investing in the 10th year at 52%, and the mean, multitude, and median of the optimal investment time points are all in the 10th year. The probability of investment is lower in other time periods, especially in the 5 to 7 year and 13 to 24 year time periods, where there is almost no probability of investment. This suggests that the probability distribution of investment points in the baseline scenario is relatively concentrated, with investors tending to invest in the early to middle part of the decision window (i.e., between years 9 and 11), and less likely to choose to invest in the earliest or later part of the project's initiation period with no likelihood of not investing. An investor who chooses to invest in a PV hydrogen fueling station would have an ROV of 14.64 million CNY, an NPV0 of -21.55 million CNY, and a WOV of 36.19 million CNY for the retrofit project in Year 10, the optimal retrofit point calculated from Period 0. Therefore, in the baseline scenario, the optimal

investment time point for the two-stage hydrogen station investment in NJ is Year 4 for the Stage 1 externally supplied hydrogen station, and the optimal retrofit time point for the Stage 2 PV station is Year 10. Overall, under the current assumptions, the percentage of those who choose not to invest in stage 1 PV hydrogen refuelling stations in NJ reaches half, and therefore, the incentive to invest is weak. In order to change the investment behaviour of investors, it is necessary for the government to implement effective industrial guidance policies.

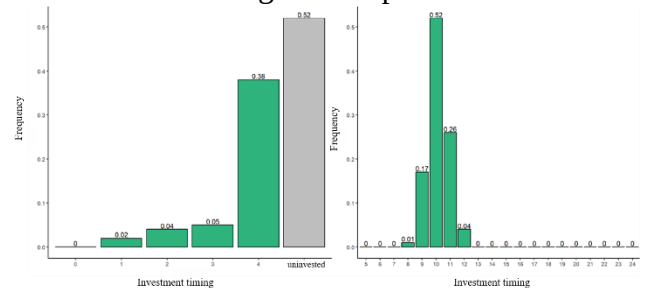


Figure 11 Probability distribution of optimal investment timing for two-stage investment in Nanjing

3.3 Analysis of Optimal Investment Timing Under Different Industrial Guidance Policies

In this paper, we will consider four commonly used government policies to guide the industry, including the policy of subsidising during the introductory period, the policy of accelerating technological research and development, the policy of applying contracts for difference, and the policy of demand assurance. These policies will have different impacts on the costs and benefits of PV hydrogen refuelling station projects. The introductory subsidy policy will increase the revenue of PV hydrogen stations in the form of subsidies during the introductory period; accelerated technology R&D will promote technological advancement and reduce the initial investment cost of PV hydrogen station equipment; the implementation of the contract for difference can guarantee the stability of the revenue of the PV hydrogen station project by fixing the price of the hydrogen refuelling contract; and the demand assurance policy can eliminate the uncertainty of the demand for hydrogen stations, thus enabling PV hydrogen stations to obtain stable revenue. In the next section, we will analyse the distribution of the optimal investment points for rational investors under each of these four policies.

Subsidy Policy for the Introductory Period

In the baseline scenario, the initial retail hydrogen refuelling price is set at 35CNY/kg, a price that matches the current price of other fossil fuels in China, which is considered a desirable target price and has also been adopted by hydrogen pilot cities in China to stimulate the demand for hydrogen consumption. However, in reality, the retail price of hydrogen should be between 70-80CNY/kg^[32], higher than the assumed target price, as the construction cost of hydrogen refuelling stations is still high and the related technology is still being optimised. In addition, there are government subsidies. According to the "Action Plan for Accelerating the Construction of Fuel Cell Vehicle Demonstration Cities in Guangdong Province (2022-2025)", during the 14th Five-Year Plan period, the government will provide a one-time construction subsidy of 2.5 million CNY per station for hydrogen production and refuelling stations that have been completed and formally operated and have a capacity to refuel at least 500kg of hydrogen per day. Therefore, in order to protect the profitability of enterprises, this paper further considers the subsidy policy during the introduction period, i.e., the government will increase the operation subsidy to 40CNY/kg for the first five years and cancel the policy after five years. This will make the actual hydrogen selling price of the enterprise reach 75CNY/kg, which is exactly within the reasonable price range of 70-80CNY/kg.

Figure 12 shows the probability distribution of the optimal investment time points for two stages of hydrogen refuelling stations after the implementation of the subsidy policy in the introductory period. The left panel shows the probability distribution of the optimal investment time point for investing in external hydrogen supply hydrogen refuelling stations in phase 1, from which it can be seen that the distribution of the optimal investment time point is more concentrated, with an overall right-skewed distribution, which is more favourable for investing earlier. The investment probability in year 0 is the highest, reaching 84%, while the probability of choosing not to invest is only 13%. In contrast, the probability of investing in years 1-4 is very low at around 1%. This suggests that investors in this scenario are highly likely to choose to invest in an externally supplied hydrogen refuelling station in Phase 0

in order to enjoy the dividends of the subsidy early on. The ROV of the investment project at this point is 33.13 million CNY, an increase of 16.59 million CNY or about a factor of 1 over the baseline scenario; the NPV0 is 31.93 million CNY, an increase of 34.13 million CNY; and the WOV is 1.2 million CNY. The figure on the right, on the other hand, demonstrates the optimal investment time-point probability distribution for converting the externally-supplied hydrogen refuelling station to a PV hydrogen refuelling station in Stage 1, which is the same as that of the baseline scenario, Stage 2, and the ROV, NPV0, and WOV of the investment project remain unchanged. This is due to the fact that in the modelling assumptions the revenue of the PV hydrogen station in stage 2 is the sum of the cost of offsetting the cost of electricity and the cost of purchasing and transporting hydrogen from the original externally supplied hydrogen refuelling station, and the addition of the operating subsidy for the first 5 years of hydrogen retailing does not change the revenue of the PV hydrogen station, and also does not have an impact on the cost of stage 2.

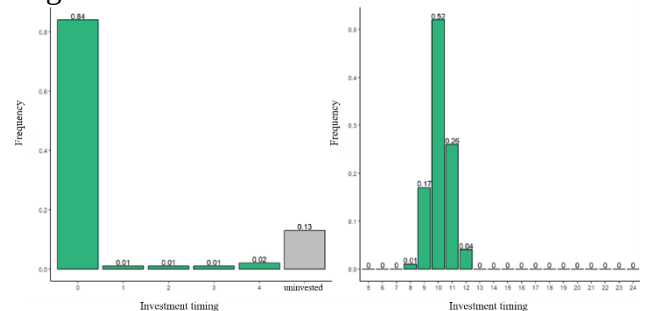


Figure 12 Probability distribution of the optimal investment time point for the subsidy policy in the introductory period

In summary, the adoption of an introductory subsidy policy in this scenario advances the optimal investment point in phase 1 to year 0 compared to the base scenario, significantly increasing the project investment probability by 39 per cent. Since the revenue of the externally supplied hydrogen refuelling station comes from the sale of hydrogen and the operating subsidy, the investment probability increases accordingly when the operating subsidy for the retail price of hydrogen increases. Meanwhile, the ROV of the investment project increases by 16.59 million CNY from the baseline scenario, expanding by about a factor of one, while the NPV0 is 31.93 million CNY, an increase of 34.13 million CNY.

Therefore, the introductory subsidy policy has a significant impact on the investment timing of the externally supplied hydrogen refuelling station in phase 1, significantly advancing the optimal investment timing to year 0 and greatly increasing the probability of investment. However, the policy does not change the revenues and investment costs of PV hydrogen refuelling stations, so the optimal retrofit time point and retrofit profitability of retrofitted PV hydrogen refuelling stations in phase 2 are hardly affected. This suggests that the incentive policy associated with retail hydrogen prices has a positive impact on investment in the construction of externally supplied hydrogen refuelling stations, but that it does not promote investment in retrofitting PV hydrogen refuelling stations in phase 2

Accelerated Technology Development

In the baseline scenario, it is assumed that the construction cost of the external hydrogen refuelling station, and the PV and electrolyzer costs of the PV refuelling station follow a decreasing exponential function, which describes the decrease in the cost of a mature technology due to technological advances and is taken to be 0.06. In the future, as the hydrogen technology develops, the design of the refuelling station is standardised and modularised, or the supply chain matures and becomes more efficient, the advantages of new equipment and processes that allow for a reduction in investment costs may be available. processes, simplified production processes, and lower component costs, which will lead to lower investment costs for hydrogen refuelling stations. This trend can be expressed by the adoption of policies to accelerate technological development, resulting in lower investment costs due to the increase in the decreasing index of the construction costs of hydrogen refuelling stations for external supply, and the investment costs of photovoltaic power generation and electrolyzers in photovoltaic hydrogen refuelling stations.

Therefore, in this scenario, assuming that the accelerated technology development increases the cost decreasing index to 0.08, the optimal investment time point probability distribution for the two-stage investment is shown in Figure 13. The left figure shows the optimal investment time point probability distribution for the investment in external hydrogen refuelling station in stage 1. Similar to the baseline

scenario, the figure shows a left-skewed distribution and the investment probability at each time point also shows a sequential upward trend, with the investment probability in the 0-3 year being lower, not exceeding 6%, and the investment in the later period being more favourable. The investment probability in year 4 is the highest at 45 per cent, slightly higher than the 44 per cent probability of not investing. The mean, the plural and the median of the optimal investment point are all in year 4, but investors also have a higher probability of choosing not to invest. If invested, the optimal investment time point is year 4, and the ROV of the invested project is 19.58 million CNY, an increase of 3.04 million CNY, or 18.4%, from the baseline scenario; the NPV0 is 2.49 million CNY, an increase of 4.69 million CNY; and the WOV is 1.79 million CNY. The right panel in Fig. 16, on the other hand, demonstrates the probability distribution of the optimal investment time point for the conversion to a PV hydrogenation station in phase 2. As seen in the figure, the investment probabilities are higher in years 9 and 10, at 43% and 49%, respectively. The investment probability is lower in year 8 and 11, which are only 2% and 6%, while the remaining years have almost no investment possibility. This suggests that investors tend to invest between years 9 and 11, which is slightly earlier than the investment interval of the baseline scenario (years 9-11), and are less likely to choose to invest at an earlier or later stage. The mean, plural and median of the optimal retrofit time point for this phase is year 10, and an investor who invests in a PV hydrogenation station will have an ROV of 19.61 million CNY for the retrofit project in year 10 of the optimal retrofit time point calculated from phase 0, which is an increase of 4.97 million CNY in value over the benchmark scenario retrofit, an increase of 33.9 per cent.

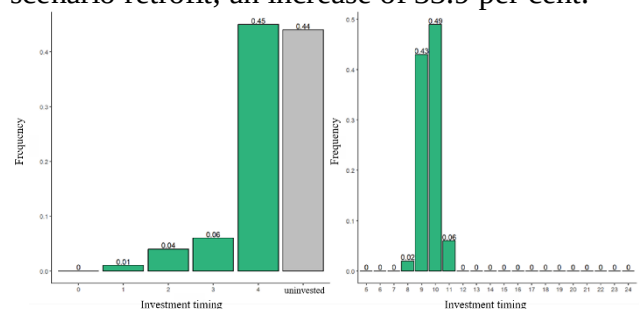


Figure 13 Probability distribution of optimal investment timing for accelerated technology development

In summary, accelerated technological research and development has led to a decrease in unit costs as the scale of production increases and experience is gained. When the annual decreasing index of the construction of external hydrogen refuelling station increases, its construction cost decreases accordingly, and thus the investment probability increases accordingly. In contrast, the decreasing indices of the PV and electrolyser investment costs lead to a decrease in the construction cost of the PV hydrogen refuelling station and thus an increase in the ROV of the retrofit investment. Therefore, a left-skewed distribution is presented compared to the baseline scenario, where later investment is more favourable. Accelerated technology development increases the probability of investment in stage 1 by 8%, with the optimal investment point being year 4. The ROV of the investment project increases by 3.04 million CNY, an improvement of 18.4%, and the NPV0 increases by 4.69 million CNY. Therefore, the policy has a facilitating effect on stage 1 investment decisions. It also makes the possible optimal time point for investing in the PV hydrogenation station in phase 2 tend to be earlier than the baseline scenario, but the optimal retrofit time point is still year 10, at which point the ROV for investing in the retrofit increases by 4.97 million CNY, which is an improvement of 33.9%.

Introduction of Contracts for Differences

A Contract for Difference (abbreviated CfD) is a financial derivative that is a contract between a buyer and a seller that allows both parties to settle their positions based on the price movement of the underlying asset at some point in the future. Specifically, CFDs allow traders to profit on the difference between the price of the underlying asset at the time of the contract and the actual price at the time of closing the position. In this study, CfD is a financial support mechanism between the government and the investors of hydrogen refuelling stations. It aims to encourage investment in hydrogen refuelling stations by reducing investment risk through a stable revenue stream. Under the CfD mechanism, the government or its designated organisation will sign a contract with the hydrogen station investor to set a fixed price for hydrogen refuelling, known as the "strike price". This price is usually higher than the average market price to ensure that the investor has sufficient revenue to repay its investment.

Assuming that the execution price of the set retail price of hydrogen refuelling is 60CNY/kg in this scenario, the probability distribution of the optimal investment time point is shown in Figure 14. As can be seen from the figure, if the contract for difference is signed to set the retail price of hydrogen refuelling at 60CNY/kg, the probability distribution of the optimal investment time point in stage 1 in the left figure is opposite to that of the benchmark scenario, with a right-skewed distribution, showing a decreasing trend from 0-4, with the probability of non-investment decreasing to 0, and the probability of investment being high in the years 0-3, with the probabilities of investment being 47%, 34%, and 14%, and the probability of investment in the remaining years being lower than 4%. At this time, the mean of the optimal investment time point is year 1, the plural is year 0, and the median is year 1. This indicates that most of the optimal investment points are concentrated in the initial two years of the project, and the investment decision should be concentrated before year 1, which is the high frequency of optimal investment points. The ROV of the investment project is 63.55 million CNY, an increase of 47.01 million CNY or nearly three times larger than the baseline scenario; the NPV0 is 63.41 million CNY, an increase of 65.61 million CNY; and the WOV is 140 thousand CNY. This suggests that the strategy is effective in facilitating the investment in external hydrogen refuelling stations in Stage 1, and that the ROV of the investment in this scenario is increased by 30.42 million CNY, or approximately one-fold, and the NPV0 is increased by 31.48 million CNY, or one-fold, compared to the scenario with the addition of an introductory period subsidy policy. In addition, similar to the effect of the scenario with the introductory period subsidy policy, the execution price of hydrogen price set by the CFD contract is 60CNY/kg, which also does not have an impact on the revenue and investment cost of the Stage 2 PV hydrogen station, so the probability distribution of the optimal investment timing and investment value of the Stage 2 PV hydrogen station in this scenario are the same as those in the baseline scenario.

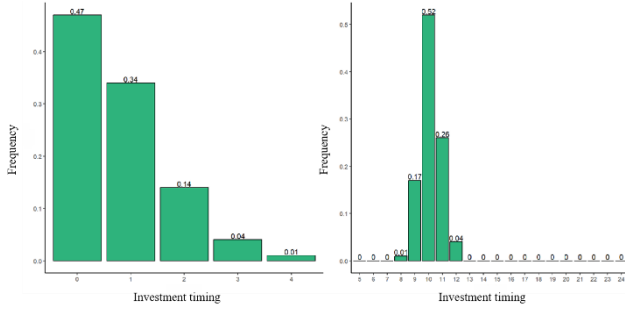


Figure 14 Probability distribution of the optimal investment point in time for the introduction of contracts for differences

In summary, compared with the baseline scenario, the optimal investment time point for each period in phase 1 is significantly earlier, with a right skewed distribution of probabilities in years 0-2. Earlier periods are more favourable for investment, and the project's investment probability is significantly increased by 52%. The optimal investment time point is concentrated in the first 2 years, and the investor should complete the main investment decision before the 1st year in order to seize the opportunity of high return in the early period. Since the revenue of the externally supplied hydrogen refuelling station comes from the sale of hydrogen and operating subsidies, the investment probability increases accordingly when the revenue from the sale of hydrogen is generated, but does not change the revenue and cost of the PV refuelling station in phase 2. Meanwhile, the ROV of the investment project is 63.55 million CNY, nearly three times larger than the baseline scenario; NPV0 increases by 65.61 million CNY. Compared to the introduction period subsidy policy scenario where the investment probability is high only in year 0, the investment probability in the first 3 periods (years 0-2) of this scenario is higher, and the ROV and NPV0 of the investment in year 0 are both expanded by about a factor of one. Therefore, the strategy of signing a retail hydrogen refuelling price in the CFD with an enforcement price of 60CNY/kg has a significant impact on the investment timing of the external hydrogen refuelling station in phase 1, bringing forward the investment timing by year 1 and diversifying the investment, while significantly increasing the probability of the investment, which is more profitable than in scenario 1 (subsidy policy in the introductory period). However, the optimal investment time point and investment profit of the retrofitted PV

hydrogenation station in stage 2 are not affected, and the optimal investment time point is still the 10th year. It can be seen that the incentivising effect of the introduction of the contract for difference policy on investment only manifests itself in an increase in investor investment in the external hydrogen refuelling station, and has no effect on the later stages of the retrofit.

Demand Assurance Policy

Factors influencing the sale of hydrogen fuel from hydrogen refuelling stations to consumers include geographic location, the number of hydrogen-fuelled vehicles, and consumer purchasing behaviour. In the short term, the logistics and transport sectors are the main consumers of hydrogen fuelled at hydrogen filling stations. Since hydrogen refuelling stations are mainly used to serve commercial hydrogen fuel cell vehicles with fixed driving routes, they are not suitable for passenger hydrogen fuel cell vehicles with more variable driving routes. In addition, since China has not yet officially defined hydrogen as an energy source rather than a hazardous chemical, consumer concerns about the potential explosion risk of hydrogen will be difficult to dispel in the short term. In addition, the high cost and the "mileage anxiety" caused by the insufficient supply of hydrogen refuelling stations still prevent consumers from purchasing hydrogen-fuelled vehicles^[52]. As a result, the function of hydrogen refuelling stations has not been fully utilised. In the future, with the development of the hydrogen industry, the retail price of hydrogen is expected to be competitive with other fuels. Meanwhile, China has instituted a series of measures to promote the popularity of hydrogen-fuelled vehicles, including providing purchase subsidies for heavy-duty hydrogen-fuelled vehicles^[53] and exempting them from vehicle purchase tax^[54]. These policies may increase the willingness of end-users to purchase hydrogen-fuelled vehicles, which will increase hydrogen demand and lead to an increase in the capacity utilisation rate (CUR) of hydrogen filling stations, i.e., the daily hydrogen refuelling volume as a percentage of the daily design hydrogen refuelling capacity capacity capacity utilisation rate. In the baseline scenario the CUR is set to be 50%, i.e. the daily design hydrogen refuelling capacity is 1000kg/d and the actual daily hydrogen refuelling capacity is only 500kg/d. The future hydrogen demand at the

hydrogen refuelling station will increase can be expressed as an increase in the CUR.

In this context, it is assumed that the government adopts a assured demand policy so that $CUR = 100\%$, i.e., the daily hydrogen refuelling capacity is equal to the daily design refuelling capacity, which is 1000 kg/d, which is considered ideal for the operation of hydrogen refuelling stations. Therefore, it is assumed that the refuelling capacity of the hydrogen refuelling station is increased to 1000 kg/d. The probability distribution of the optimal investment time point for the two stages is shown in Fig. 15, and the data on the left shows that the investment probability in year 0 is 13%, and the investment probability decreases in the next three years, with the highest investment probability of 39% in year 4; while the probability of choosing not to invest is 22%. The integrated investment point is in year 3, and the high-frequency investment point and the robust investment point are in year 4. The optimal investment time point is concentrated in year 4 for most paths, while fewer paths have an optimal investment time point in year 3 or earlier. At this point, investors should make tentative investments in year 3, but focus primarily on investment opportunities in year 4. The optimal investment time point of this scenario has an earlier trend than the benchmark scenario, and the project investment probability increases by 30%, and the ROV of the investment project is 46.24 million CNY, which is 29.7 million CNY more than that of the benchmark scenario, expanding by nearly two times; the NPV0 is 36.45 million CNY, which is an increase of 38.65 million CNY; and the WOV is 9.79 million CNY. The right panel in Fig. 15 shows that in stage 2, the optimal investment time points for each period for investing in the PV hydrogen refuelling station are clustered into year 5, with the highest probability of investing in retrofitting in year 5 at 100%, and the probability of investing in the other time points at 0. The mean, the plurality, and the median of the optimal retrofitting time points for this stage are all in year 5, which means that an investor's investment in stage 2 can be determined to have occurred in year 5. This means that once an investment is made in an externally supplied hydrogen refuelling station in stage 2 it will inevitably be invested in the construction of a PV hydrogen subsystem, which is an effect that cannot be achieved by other policies. Compared

to the optimal investment point (year 10) for the baseline scenario Stage 2, which is 5 years earlier, the ROV for investing in the retrofit project is 42.99 million CNY, which is 28.35 million CNY more than the ROV for the baseline scenario retrofit, or about a twofold enlargement, and the NPV0 is 32.26 million CNY, which is an increase of 52.81 million CNY.

The results show that the probability distribution of the optimal investment time point for an externally supplied hydrogen refuelling station in phase 1 is more dispersed in the scenario with a demand assurance policy, but the probability of investment increases in the early years. Investors should make tentative investments in year 3, but focus mainly on investment opportunities in year 4. At this point, the probability of not investing is lower at 22 per cent, a 30 per cent reduction from the probability of not investing in the base case. The ROV of the Phase 1 investment projects increased by 29.7 million CNY and NPV0 by 38.65 million CNY from the baseline scenario, which was effective in facilitating Phase 1 investments. The probability distribution of the optimal investment point for each phase of stage 2 retrofitting to a PV hydrogen station is all advanced and concentrated in year 5, when the probability of investment is 100 per cent, which is significantly different from the baseline scenario, indicating that the demand assurance policy has a very strong effect on the probability of investment in stage 2 retrofitting to a PV hydrogen station.

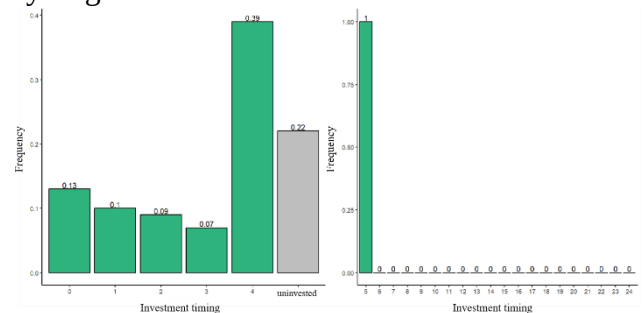


Figure 15 Probability distribution of the optimal investment time point for demand assurance policies

As hydrogen-fuelled vehicles are still in the early stages of development, their small number leads to insufficient demand for hydrogen refuelling stations, i.e. low capacity utilisation, which creates a high investment risk for investors. The above results show that boosting the demand for hydrogen, i.e. increasing the capacity utilisation

rate, has a positive effect on facilitating investors to invest in the construction of externally supplied hydrogen refuelling stations and is a determining factor influencing the conversion of externally supplied hydrogen refuelling stations into PV hydrogen refuelling stations. This is due to the fact that an increase in the number of consumers using the hydrogen refuelling station not only increases the revenue from hydrogen sales to consumers of hydrogen fuel cell vehicles, but also increases the sales of hydrogen to nearby external hydrogen refuelling stations when the external hydrogen refuelling station is

converted to an on-site photovoltaic hydrogen refuelling station. In addition, in the case of increased hydrogen demand, the on-site PV hydrogen refuelling station can save a significant amount of hydrogen storage and transportation costs compared to an externally supplied hydrogen refuelling station. The optimal investment time points, ROV, NPV0, WOV, and their standard error values for the baseline scenario and the above four hypothetical scenarios for stages 1 and 2 are shown in Tables 7 and 8, respectively.

Table 7 Results of economic performance indicators in the scenarios of phase 1

Scenario	Phase I						
	Optimal investment point/year	ROV/ Million	ROV standard error/million	NPV0/ million	NPV0 standard error/million	WOV/ million	WOV standard error/million
Base scenario	3.6	1654	41	-220	46	1874	18
Subsidy policy for the introductory period	0.1	3313	45	3193	46	120	5
Accelerated technology development	3.7	1958	44	249	46	1709	16
Contract for differences policy	0.8	6355	9	6341	9	14	0.3
Demand assurance policy	2.7	4624	74	3645	73	979	16

Table 8 Results of economic performance indicators in the scenarios of phase 2

Scenario	Phase II						
	Optimal investment point/year	ROV/ Million	ROV standard error/million	NPV0/ million	NPV0 standard error/million	WOV/ million	WOV standard error/million
Base scenario	10.2	1464	4	-2155	5	3619	2
Subsidy policy for the introductory period	10.2	1464	4	-2155	5	3619	2
Accelerated technology development	9.6	1961	5	-2155	5	4116	2
Contract for differences policy	10.2	1464	4	-2155	5	3619	2
Demand assurance policy	5	4299	1	3126	1	1173	0.3

Of the four two-stage investment incentives for PV hydrogen refuelling stations in uncertain environments, demand assurance policies, i.e. increasing hydrogen demand, have the best effect on retrofitting externally supplied hydrogen refuelling stations to PV hydrogen refuelling stations in Stage 2 (with a probability of investing in retrofitting of 100%); accelerated technological research and development, i.e. lowering the cost of the initial investment in the two-stage process, has an effect in facilitating retrofitting PV hydrogen refuelling stations in Stage 2 (with a tendency for the optimal investment timing to be advanced). In contrast, the implementation of a contract for difference

(CFD) and an introductory subsidy policy, i.e., the implementation of a retail hydrogen price incentive policy, has a positive impact on the investment in hydrogen refuelling stations for external hydrogen supply, but does not contribute to the investment in the conversion of PV stations to PV stations in phase 2. In particular, the implementation of the Contract for Difference policy has a better effect on Stage 1 than the introductory subsidy policy. Therefore, among the four policy instruments, the one that most promotes the construction of PV hydrogen refuelling stations is the demand assurance policy, followed by the policy of accelerating technological research and

development, whereas the introduction of the contract for difference and the introductory subsidy policy have no effect on the conversion to PV hydrogen refuelling stations in stage 2. This is in line with Zhao et al^[32] (2024), who argue that the most favourable policy is the policy to enhance consumer demand for hydrogen, followed by tax incentives and stronger operating subsidy policies; and with Xu et al^[55] (2020), who argue that the imperfect operating subsidy policy is not a major obstacle affecting the development of hydrogen refuelling stations in China; and with Meng et al^[56] (2021), that the subsidy policy does not have a lasting driving force for the development of hydrogen refuelling stations.

However, this result differs from Ren et al^[57] (2023), which argues that government subsidies and tax incentives are more important than expanding hydrogen demand in driving the development of China's hydrogen economy. Nonetheless, this scholar looks at the macro development of China's hydrogen economy, whereas this paper focuses on the specific case of hydrogen refuelling station investment and combines case studies with data from a specific region (Nanjing). It is therefore logical that different perspectives lead to different understandings and emphases on policy priorities, and hence different results.

4 CONCLUSION

Hydrogen refuelling stations can be divided into two categories: external hydrogen refuelling stations and on-site hydrogen refuelling stations, and the number of the former is much larger than the latter. External hydrogen refuelling stations rely on the external supply chain to obtain the hydrogen supply, which requires more energy and resources to transport the hydrogen, which may involve high hydrogen storage and transportation costs and greater risks, and may also have a certain impact on the environment. Therefore, this paper assesses the value of the initial investment and renovation investment of the external hydrogen supply and refuelling station through the analysis methods of cash flow analysis, levelised cost of hydrogen (LCOH) analysis, internal rate of return (IRR), dynamic payback period (DPBP) and real options (ROA). Firstly, the techno-economic model of the PV hydrogen refuelling station is constructed, and the PV hydrogen refuelling station is decomposed into two parts: the

external hydrogen refuelling station subsystem and the PV hydrogen production subsystem. The relationship between the annual peak hours and the design daily refilling capacity of hydrogen refueling stations and the economic indicators of hydrogen refueling stations is explored to help investors roughly judge the investment profitability possibilities of hydrogen refueling stations with different refilling capacities in different regions, and the LCOH of PV hydrogen refueling stations in a total of 897 cities and districts and counties of municipalities and autonomous regions in 31 provinces (excluding Macao and Hong Kong) across the country is analysed. Then, the city of Nanjing, which is in the prudent investment zone classified according to the two-factor analysis, is selected to use the flexibility of investment to enhance the profitability and risk resistance of investment in the region. Based on the compound real options theory, a two-stage dynamic investment decision model is constructed and the compound real options is priced using backward induction and two-stage Monte Carlo simulation to analyse the impacts of uncertainties in retail hydrogen price, hydrogen quantity and electricity price on the investment decision, with the aim of determining the optimal timing of the investment and retrofitting strategy for PV hydrogen station projects in China. Based on the findings of this paper, the following conclusions are drawn:

(1) In a two-factor analysis of the economics of PV hydrogenation stations, it was found that the overall economics of the project is best for a combination of high daily hydrogen refuelling (>1000 kg/d) and high annual peak hours (>2000 hours), and investment is recommended. For regions with high daily hydrogen addition and low annual peak hours or low daily hydrogen addition and high annual peak hours, investment should be cautious, while for regions with both low daily hydrogen addition and annual peak hours (daily hydrogen addition <500 kg/d and annual peak hours <1100 hours) investment is not recommended.

(2) The LCOH of PV hydrogen refuelling stations across the country is mainly concentrated in the range of 28CNY/kg to 32CNY/kg, with an overall right skewed distribution; increasing the annual peak hours and daily hydrogen refuelling volume can significantly reduce the LCOH, but there is a marginal diminishing effect of daily hydrogen

refuelling volume on the LCOH. At the regional level, the western region has the most concentrated LCOH distribution and the lowest median, showing a strong cost advantage; while the eastern region has a bimodal distribution of LCOH, with significant geographical differences.

(3) In this paper, assuming Nanjing as the construction site of the PV hydrogen refuelling station, and assuming a scenario in which the current daily hydrogen refuelling capacity is only half of the designed daily hydrogen refuelling capacity, an arithmetical analysis of investment choices over the next 25 years is carried out. The probability distribution of the optimal investment time for investing in the overall PV hydrogen refuelling station project is first analysed, and it is found that under the hypothetical scenario investors in Nanjing tend to invest in the middle of the decision window (i.e. between years 7 and 12), but there is also a 32% probability that they do not invest. Investing in a PV hydrogen station project in two phases results in a significant increase in NPV0 of 35.36 million CNY compared to investing in the overall PV hydrogen station project during the decision window between years 0 and 24. By comparing the probability distribution of the optimal investment time point for investing in a single-phase hydrogenation station versus investing in a two-phase hydrogenation station, it was found that both were more favourable to invest at a later stage. However, the investment probability of a two-stage investment project is 15% higher than that of a single-stage project and the ROV is 5.61 million CNY higher, so the overall economics of investing in a two-stage hydrogen station project is higher than investing in only a single externally supplied hydrogen refuelling station.

(4) Among the four industry-led policies in this paper, the demand assurance policy provides the greatest impetus for investing in PV hydrogen refuelling stations, and the policy of accelerating technological research and development can also be transformed somewhat in advance into the optimal investment time point for PV hydrogen refuelling stations. While the implementation of the contract for difference and introductory subsidy policies have an obvious promotion effect on the investment in external hydrogen refuelling station subsystems in phase 1, they have no effect on the investment in retrofitting

PV hydrogen refuelling stations in phase 2. In addition, both CFDs and introductory subsidies impose heavy fiscal costs on the government, and the advantages and disadvantages need to be considered in a comprehensive manner.

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