

Special Issue Reprint

Advances in Fuel Energy

Edited by
Leszek Chybowski

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Advances in Fuel Energy

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Guest Editor

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Guest Editor

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This is a reprint of the Special Issue, published open access by the journal *Energies* (ISSN 1996-1073), freely accessible at: https://www.mdpi.com/journal/energies/special_issues/2G24AAE826.

For citation purposes, cite each article independently as indicated on the article page online and as indicated below:

Lastname, A.A.; Lastname, B.B. Article Title. <i>Journal Name</i> Year , Volume Number, Page Range.
--

ISBN 978-3-7258-8441-4 (Hbk)

ISBN 978-3-7258-8442-1 (PDF)

<https://doi.org/10.3390/books978-3-7258-8442-1>

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About the Editor

Leszek Chybowski

Leszek Chybowski is a Polish academic and researcher who has been affiliated with the Maritime University of Szczecin for over two decades. His scientific output includes more than 300 publications, 12 monographs, and numerous inventions and technical solutions, several of which are protected by patents. He is a researcher specializing in mechanical engineering, reliability and maintenance of technical systems, and the development and implementation of innovative engineering solutions, particularly in maritime and industrial applications. Prof. Chybowski is actively engaged in research and applied development projects funded by institutions such as the National Science Centre, the Polish Agency for Enterprise Development, and the Ministry of Science and Higher Education. The results of these projects include industrial implementations and the advancement of practical engineering technologies. His academic contributions have been recognized with several distinctions and awards, reflecting his impact on engineering science and academic development. Prof. Chybowski remains an active researcher and academic leader, contributing to the advancement of engineering research and the international visibility of his university.

Advances in Fuel Energy

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Ongoing climate change, the depletion of fossil fuel resources, and the continuously growing demand for energy have made the development and implementation of new types of fuels for energy systems one of the key challenges of modern engineering [1]. This is particularly relevant for internal combustion engines, boilers, and other thermal machines used in maritime, road, rail, and air transport, as well as in stationary power and heat generation systems. Alternative fuels such as biofuels, alcohols, synthetic fuels, gaseous fuels, ammonia, and hydrogen are increasingly being considered both as direct substitutes for conventional fuels and as additives to traditional fuels [2]. While their application may lead to significant environmental benefits, it also reveals complex technical and operational consequences.

The research results presented in this collection clearly demonstrate that even small shares of alternative fuels in fuel blends can substantially alter the combustion process. These changes include extended ignition delay, increased peak in-cylinder temperatures, and intensified pressure rise rates, which consequently lead to higher thermal and mechanical loads on the engine [3]. At the same time, it has been observed that increases in combustion temperature on the order of several tens of degrees Celsius may result in elevated nitrogen oxide emissions. This highlights the need for further research focused on optimizing injection strategies and combustion control when oxygenated fuels and their blends are used.

In parallel, this Special Issue presents research findings related to the evaluation of the physicochemical properties of alternative fuels, which directly affect the durability and reliability of fuel supply systems. The reported results indicate that alcohol fuels are characterized by low viscosity and very limited lubricity. The estimated lubricity values obtained suggest that, without appropriate additives or design modifications, long-term operation using such fuels may be problematic. At the same time, the development of models describing the temperature dependence of fuel viscosity and density presented in this collection represents an important step toward improved design and performance prediction of fuel supply systems.

Another important research direction addressed here involves emulsified fuels and fuels with modified physical structures, which enable substantial reductions in pollutant emissions without a radical deterioration in performance. Experimental results show that properly designed fuel emulsions can lead to nitrogen oxide emission reductions of nearly 50% and smoke reductions exceeding 80% at selected engine operating points. In addition, cases of improved thermal efficiency have been observed, indicating that these solutions may represent a viable alternative in the short- and medium-term energy transition [4].

From the perspective of practical implementation of alternative fuels, particularly significant are the results obtained from studies conducted on in-use engines and vehicles without introducing structural modifications. It has been demonstrated that low shares of biocomponents in gasoline fuels can lead to improvements in thermal efficiency on the order

of 1–2%, while simultaneously reducing hydrocarbon and nitrogen oxide emissions, even in older power units. At the same time, the increase in specific fuel consumption resulting from the lower heating value of the blends remains moderate, which is of particular importance for developing countries and regions with limited opportunities for fleet modernization.

The energy transition, however, extends beyond the combustion process itself and also involves the development of auxiliary systems and infrastructure. Research on new exhaust gas cooling systems indicates that replacing conventional water-based solutions with dry systems can improve safety, reduce fuel consumption by several percent, and lead to very significant reductions in CO, HC, NO_x, and CO₂ emissions. Equally important are issues related to the compatibility of alternative fuels with existing measurement and control systems, as exemplified by the dielectric properties of next-generation aviation fuels, which are critical for the proper operation of onboard fuel quantity indication systems.

In the long term, carbon-free fuels play a particularly important role, especially in the maritime and aviation sectors. Analyses of current market and regulatory trends indicate that transitional fuels such as LNG, LPG, and biofuels will not be sufficient to meet increasingly stringent requirements beyond 2030 [5]. As a result, growing interest is being directed toward ammonia and hydrogen, the implementation of which is associated with significant technological challenges, including storage safety, fuel flow control, purging processes, and control of combustion byproduct emissions. Research on optimizing fuel supply systems and control strategies shows that precise management of fuel and auxiliary gas flows can significantly reduce operational risks.

In light of the presented findings, it is evident that a key research gap remains the lack of an integrated approach to the assessment of alternative fuels that simultaneously considers emissions, efficiency, component durability, safety, and life-cycle costs. Future research should focus on the development of adaptive control systems for fuels with variable composition, further refinement of numerical models for combustion and mixing processes, and long-term operational studies conducted under real-world conditions. Equally important will be the integration of alternative fuels with hybrid technologies and energy recovery and storage systems.

It is hoped that this Special Issue constitutes a meaningful contribution to advancing knowledge on alternative fuels for thermal machines and helps define directions for further interdisciplinary research that will enable a safe, efficient, and economically viable energy transition in the decades ahead.

Acknowledgments: The Guest Editor would like to sincerely thank all authors for their outstanding contributions and all reviewers for their careful and constructive evaluations. In addition, I would like to thank the Special Issue Editor, for his administrative and technical support.

Conflicts of Interest: The author declares no conflicts of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

List of Contributions:

1. Górski, K.; Tziourtzioumis, D.; Smigins, R.; Longwic, R. Effects of Ethanol–Diesel Blends on Cylinder Pressure, Ignition Delay, and NO_x Emissions in a Diesel Engine. *Energies* **2025**, *18*, 2392.
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Article

Performance Analysis Based on Fuel Valve Train Control Optimization of Ammonia-Fuel Ships

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Abstract: In order to reduce carbon emissions, which are currently a problem in the shipping and offshore plant sectors, the international community is strengthening regulations such as the Energy Efficiency Design Index (EEDI) and Energy Efficiency Existing Ship Index (EEXI). To cope with this, eco-friendly fuel propulsion technology is being developed, and the development of an ammonia fuel supply system is in progress. Among them, fuel valve train (FVT) technology was researched for the final supply and cutoff of fuel and purging through nitrogen for ammonia engines. In this paper, we analyzed the change in ammonia supply due to FVT opening and the change in nitrogen supply due to closure. In addition, a plan to minimize risk factors was presented by applying a control method to remove residual fuel in FVT. According to the presented FVT model, the difference in the flow rate of supplied fuel was as much as 17.8 kg/s. Additionally, by opening the gas bleed valve at intervals during the closing process and purging about 0.28 kg of nitrogen, the internal fuel could be completely discharged. This is expected to have an impact on improving the marine environment through the application of eco-friendly fuels and the development of fuel supply system technology.

Keywords: gas valve train; fuel valve train; fuel supply system; ammonia; nitrogen ventilation; main valve; bleed valve

1. Introduction

In response to escalating global concerns regarding maritime pollution, the International Maritime Organization (IMO) is actively discussing measures to enhance operational efficiency through energy policies. This has prompted shipbuilders worldwide to spearhead the development of vessels employing environmentally friendly fuels such as hydrogen, ammonia, and ethanol.

In particular, classification societies have conducted extensive research on various alternative fuels to propose optimal fuels aligned with IMO regulations. Det Norske Veritas·Germanischer Lloyd (DNVGL) (2018) published a guidance paper assessing alternative fuels and technology solutions to facilitate decision-making for ship investments. The paper encompasses an overview of not only selected alternative fuels such as LNG, LPG, methanol, biofuels, and hydrogen but also innovative technologies, including batteries, fuel cell systems, and wind propulsion devices [1].

Lloyd's Register (2020) assessed zero-carbon fuels from an economic perspective and technology perspective. The study proposed 21 zero-emission vessels utilizing fuels such as methanol, hydrogen, ammonia, electricity, diesel, and LNG, alongside production and propulsion methods for natural gas—capable of carbon capture and storage—biomass, and renewable energy [2,3].

Amidst these alternatives, ammonia has emerged as a solution for storage and transportation, finding diverse applications in agriculture, fishery, and refrigeration. MAN B&W aims to develop ammonia-powered vessels by 2024, with the first ship to be an ammonia carrier that facilitates the handling of ammonia [4]. Concurrently, Japanese maritime entities, including NYK Line, Nihon Shipyard, and ClassNK, are actively researching their

first utilization of ammonia as a fuel in ammonia transport ships. In addition, NK proposes applicable regulations concerning physical properties of ammonia that require special consideration in terms of flammability and toxicity [5,6].

A report by Smith et al. predicts a 50% reduction in greenhouse gas emissions by 2050 through the adoption of eco-friendly fuels like ammonia and hydrogen in shipping. In addition, DNV analyzed that more than 50% of ship fuel will be converted to LNG, ammonia, etc., by 2050. Figure 1 shows fuel changes by year until 2050 [7,8].

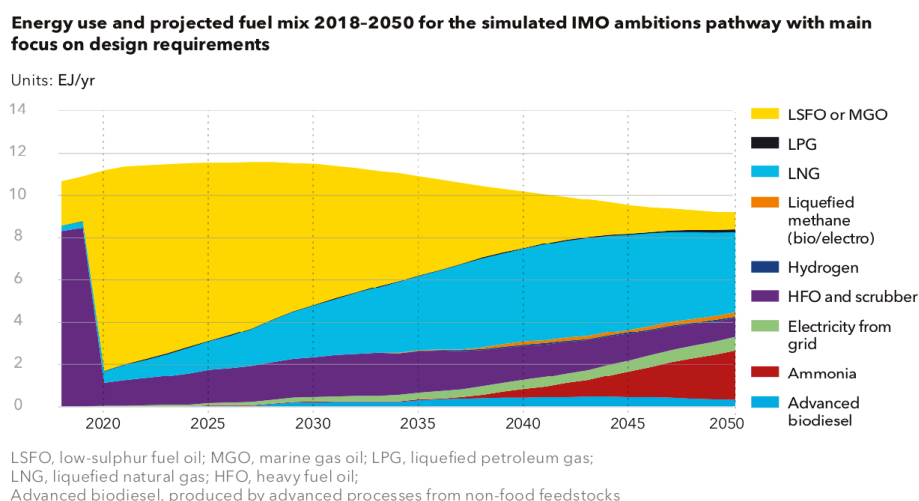


Figure 1. Energy use and projected fuel mix 2018–2050 for the simulated IMO ambitions pathway with main focus on design requirements (Source: DNV).

The International Maritime Organization (IMO) has set ambitious targets for reductions in GHG emissions. Total GHG emissions should fall by at least 50% and CO₂ emissions should fall by at least 70% below the 2008 figures by 2050 [9]. Consequently, DNV suggested that by 2050, at least 15% of long-distance ships should be fueled by ammonia or hydrogen [10].

Ongoing research is dedicated to engine systems utilizing ammonia fuel and related fuel supply systems. Studies on ammonia engines include dual-fuel applications with diesel engines [11,12] and analyses of fuel characteristics in single-fuel configurations [13]. Ammonia application in ships is evolving with a focus on classification [14], while universities and research institutes are conducting research for technology development [15].

In particular, Seo et al. evaluated the economic feasibility of ammonia-fuel carriers based on different fuel storage methods, shedding light on the influence of storage methods on cost variations. Additionally, Julia et al. suggested a high production potential for ammonia fuel, considering its technical, environmental, and economic viability in ship fuel applications [16,17].

As of 2024, over 90% of a vessel's fuel comprises fossil energy-based fuels such as heavy fuel oil (HFO) and marine diesel oil (MDO), with alternative fuels like LNG and biofuels. CO₂ emissions are thus inevitable [18]. To replace such fossil fuels with ammonia, it is essential to consider the heating value of the fuel required to maintain a vessel's propulsion capacity.

Also, ammonia, with its high density and relatively lower heating value, results in approximately 2.2 times higher fuel consumption compared to conventional fuels [19]. This necessitates substantial fuel storage facilities to accommodate the increased fuel consumption. According to the National Fire Protection Association (NFPA)'s hazard index table, ammonia is an extreme danger; level 3 in health hazard, and is a fluid with an ignition point at 200 F. Therefore, it is applied according to usage regulations, and typically in compliance with the regulations of ISO 23306:2020 [20]. These risks and low efficiency are obstacles to the application of ammonia engines despite their high environmental improvement rates.

In order to minimize the risk of ammonia, stabilization research is inevitable through the structure or control of the fuel supply system (FSS) and fuel valve train (FVT). Among them, FVT serves as the pivotal system connecting the fuel supply system and the final

connection valve system, providing fuel such as liquefied natural gas (LNG), liquefied petroleum gas (LPG), and ammonia to the engine in maritime vessels [21]. In engines utilizing gaseous fuels like LNG, the system is referred to as the gas valve train; however, for consistency in this paper, we adopt the unified term “FVT” to denote the concept of fuel. The FVT plays a crucial role in controlling the supply and shut-off of fuel, and performing nitrogen-assisted ventilation during the fuel shut-off process, thereby maintaining safe engine operation. Figure 2 illustrates the fuel supply system for a ship utilizing ammonia. Here, fuel is supplied from the high pressure (HP) pump in the FSS to the FVT, and upon valve opening, the fuel is delivered to the final engine. Nitrogen (N_2)-purging facilities are connected to both systems to prevent residual fuel, and pressurized N_2 inside the pipes is exhausted externally [22,23].

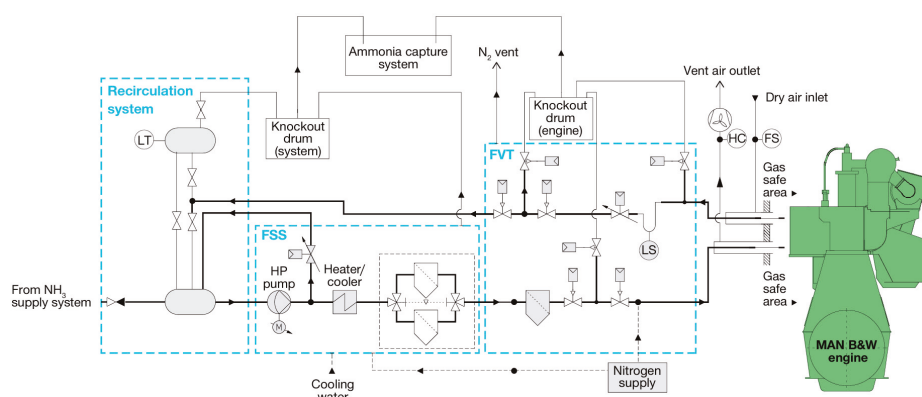


Figure 2. Principles of the ammonia supply system, showing main components (Source: Man B&W).

The primary function of the FVT is to supply and shut off fuel to the engine. Consequently, variations in fuel supply time occur depending on the opening time of the fuel supply valve during fuel supply.

Fuel shut-off requires distinct operating procedures due to differences between regular engine shutdown and emergency shutdown during fire or emergencies. In the case of a regular shutdown, fuel must be completely purged from the engine for long-term engine stoppage and maintenance reasons. Moreover, precautions must be taken to prevent potential hazards such as fuel leakage and fire after shutdown. During this process, fuel purging and internal ventilation are performed through bleed valves, utilizing N_2 gas to remove fuel from fuel supply devices and the engine inlet/outlet.

In contrast, emergency fuel shutdown arises in situations necessitating abrupt engine shutdown or engine damage. In such cases, the rapid closure of the fuel valve is essential. Similar to a regular shutdown, N_2 is employed to ventilate fuel supply devices and the engine inlet/outlet, concluding the final shutdown process swiftly and safely.

In the case of the currently commercialized GUV model of LNG fuel, a fully ex-proof encapsulated design is applied to completely block fuel emission to the outside. However, the area occupied by the external protection device is larger than that of the GUV, and a detection device for exposed fuel is essential. In addition, an increase in initial costs due to these structural changes and additional facilities is inevitable [24].

Holger Watter presented a gas valve unit (GVU) operation model according to load changes in LNG-fueled propulsion ships, and Lee studied fuel switching and gas leakage prevention through GVU stoppage in emergency situations while using gas fuel in a dual-fuel engine [25,26].

However, few studies exist on the operation of the fuel valve train (FVT) using ammonia fuel, responsible for overseeing the final fuel supply to the engine and purging residual fuel within the pipes via N_2 . This paper aims to fill this gap by establishing and analyzing the operation of FVT, a key component of emerging ammonia-powered vessels. Conventional and newly applied operation methods are compared to assess the resulting improvements.

2. FVT Analysis Conditions

2.1. Theory

2.1.1. Valve Size and Controller Selection

The coefficient of flow, denoted as C_v , represents the flow characteristics in valves and is commonly referred to as the flow coefficient. It is a numerical value used to calculate flow rates. C_v signifies the flow rate (in gallons per minute, GPM) through a valve under a pressure difference of 1 psi at 60 °F. The selected C_v maintains a pressure difference of less than 10 kPa between the main valve and bleed valve while satisfying the required flow for fuel supply. Equation (1) represents the calculation formula for determining C_v , where Q is the flow rate, SG is the specific gravity of ammonia fuel, and P is the pressure drop [27].

$$C_v = Q \sqrt{\frac{SG}{\Delta P}} \quad (1)$$

The valve mode defines the relationship between the desired actuator position and current actuator position. The desired actuator position can be set by a proportional–integral–differential (PID) controller. A controller's output (OP), for instance, is exported to the desired actuator position. Depending on the valve mode, the current actuator position can behave in one of the following three ways: (1) quick open mode, (2) equal percentage mode, or (3) linear mode [28].

For this simulation, linear mode was selected. The actuator can be modeled to move to the desired actuator position at a constant rate. The actuator moves according to Equation (2). The actuator position is converted sequentially until the final required point (Equation (3)), if the desired actuator position is above the current actuator position. The linear rate can be specified in the actuator linear rate. Typical stroke times (closure rates) are as follows: (1) electric–hydraulic actuators: approximately 12 inches/minute, (2) piston actuators (motor-driven): under 70 inches/minute [29].

$$Act\% = (Actuator\ Linear\ Rate)\Delta t + Act_o\% \quad (2)$$

$$until\ Act\% = Act_{Desired}\% \quad (3)$$

where Act is an abbreviation for Actuator position, t is time, and the subscript Act_o means initial actuator position.

2.1.2. Nitrogen Supply Selection

The nitrogen buffer capacity is the sum of the nitrogen volume required for ammonia-fuel engine operation and the additional nitrogen volume required for the low-flashpoint fuel supply system (LFSS) and other upstream systems that also connect to the nitrogen buffer (Equation (4)) [30].

$$V_{buffer} = V_{buffer, ME} + V_{buffer, LFSS} \quad (4)$$

It is the scope of the shipyard to determine the capacity of any additional nitrogen requirement, V_{buffer} of ME and LFSS. For purging purposes of the main engine with LPG fuel, the minimum required nitrogen volume capacity is calculated according to Equation (5).

$$V_{buffer, ME} = (10 \times P_{purge} \times V_{purge}) \times z / (P_{buffer} - P_{purge}) \quad (5)$$

In Equation (6), P_{purge} is the target pressure for pressurization during liquid freeing, which must be 700 kPa higher than the back pressure from the service tank or the nitrogen separator.

$$P_{purge} = P_{service\ tank} + 700(\text{kPa}) \quad (6)$$

V_{purge} is the total internal volume of piping going from the nitrogen supply line to the engine vent and comprises the following volumes:

- The LFF supply line going from the FVT to the engine;
- The internal LFF volume of the engine;
- The circulation line going from the engine to the vent connection.

Z represents a minimum number of times of purging the engine which should be immediately available. Assuming that on-board nitrogen production is available, engine makers recommend that z should be at least equal to 3 consecutive LFF starts. P_{buffer} is the storage pressure of the nitrogen, of which only the pressure exceeding P_{purge} is available for the purging of the engine. $P_{service\ tank}$ is the pressure of the service tank.

2.2. System Design

2.2.1. Fuel Supply Module Design

To analyze the ammonia fuel consumption of ammonia-powered ships, a fuel supply system was designed. Ammonia fuel is stored in a service tank and supplied during vessel operation, with fuel injection conditions for engine supply controlled at a temperature of 35 °C or higher and a pressure of 8000 kPa through the fuel treatment system. The structure of the fuel supply system and FVT used Man B&W's ammonia supply system [4]. The performance table for each eco-friendly fuel is shown in Table 1.

Table 1. Comparison table for each eco-friendly fuel.

	Energy Content, LHV [MJ/kg]	Energy Density [MJ/L]	Supply Pressure [kPa]	CO ₂ Reduction Compared to HFO Tier II [%]
Ammonia (NH ₃)	18.6	10.6	8000	90
Methanol (CH ₃ OH)	19.9	14.9	8000	11
LPG	46.0	26.7	1000	13–18
LNG	50.0	21.2	5000	24
MGO	42.7	35.7	30,000	0
Hydrogen (H ₂)	120	8.5		

During this process, fuel distribution to the engine and the circulation of return fuel are controlled through the FVT. The vaporization and heating of liquid ammonia are achieved through heat exchange with steam or seawater using the glycol water system. In FVT, the two main valves are doubled for safety, and the engine is purged with nitrogen to remove internal ammonia.

The formula for calculating fuel consumption is provided in Equation (7). Vessel fuel consumption varies based on the type of fuel, engine size, and endurance, with different ammonia carriers having different consumption rates. Figure 3 illustrates the changes in ammonia fuel supply and return rate. Here, the fuel supply rate refers to the amount of fuel flowing into the engine per hour, and the recirculation percentage is the fuel return rate that remains and circulates without being supplied to the engine.

The fuel supply rate was calculated using the heating value of ammonia to achieve a capacity of 16,080 kW, enabling a supply of 5909 kg/h at maximum 100% load conditions. At this time, 5.5% of fuel circulates to the pump and tank. In the initial low-load condition of less than 10, about 115 kg/h of fuel is supplied to the engine and 82.7%, or 551 kg/h, is circulated. On the other hand, the amount of fuel circulated was the highest under the condition of 50% engine load, and this result is expected to indicate that the amount circulated is high compared to the amount flowing into the engine in the total fuel supply amount. Where LHV means lower heating value, and HFO means heavy fuel oil.

$$\text{Fuel consumption of Ammonia} = \text{Fuel consumption of HFO} \frac{\text{LHV of HFO}}{\text{LHV of Ammonia}} \quad (7)$$

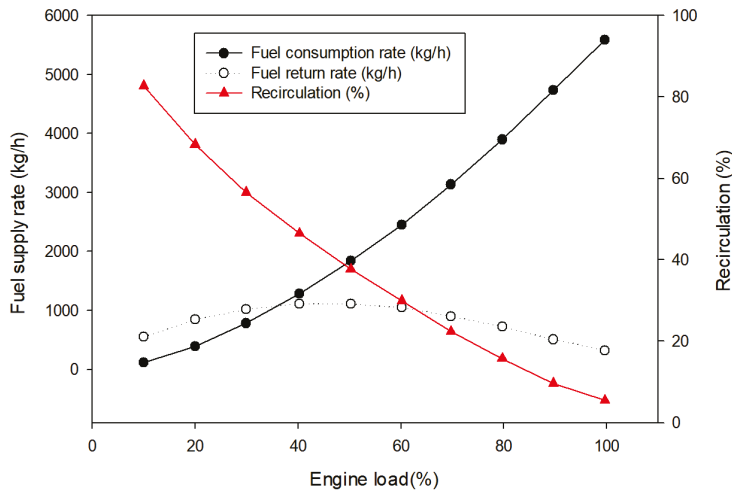


Figure 3. Fuel supply rate and recirculation according to engine load.

To analyze the fuel supply system and fuel valve train, the process design software AspenTech HYSYS (V12.1) was employed as the simulation and analysis tool. HYSYS has the advantage of accurately calculating state values necessary for thermodynamic cycle simulation, making it suitable for this study [31]. The thermodynamic and transport properties of the working fluid are used in conjunction based on the REFPROP database. Ammonia and nitrogen are used as the engine fuel and purging gas. The initial conditions are listed in Table 2 [32,33].

The ideal part of the fundamental equation is given by Equation (8).

$$\frac{a(\rho, T)}{RT} = \alpha(\delta, \tau) = \alpha^0(\delta, \tau) + \alpha^r(\delta, \tau) \quad (8)$$

where a is the Helmholtz energy, $\delta = p/p_c$, $\tau = T_c/T$, the superscript 0 refers to the ideal gas Helmholtz energy, and the superscript r refers to the residual Helmholtz energy. The subscript c refers to the critical value. p stands for pressure and T stands for temperature.

The ideal gas Helmholtz energy equation can then be expressed as Equation (9).

$$\alpha^0 = \ln \delta + 2.500571 \ln \tau - 12.76941 - 0.00813787\tau - 1.0150785 \times 10^{-7} \tau^{-7} \quad (9)$$

The residual Helmholtz energy contribution to the equation of state is given by Equation (10). Where M , I , and j are constants.

$$\alpha^r(\delta, \tau) = \sum_{k=1}^{10} M_k \delta^{I_k} \tau^{J_k} \quad (10)$$

2.2.2. FVT Design

The FVT receives ammonia fuel from the fuel supply system, distributes it to each cylinder, and recirculates some residual fuel to the fuel recirculating system. Liquid ammonia is supplied back to the inlet of the two-stage fuel pump in the fuel supply system.

The fuel flow is regulated based on engine load variations through the cylinder supply control valve. The ratio of recirculated fuel and the amount of fuel supplied by the fuel pump varies with engine load. Figure 4 illustrates the piping process delivering fuel to the six-cylinder engine through the FVT.

When converting a diesel-fueled vessel to ammonia, for a 6-cylinder engine, a maximum fuel consumption of 5909 kg/h (984.8 kg/h per cylinder) is required at full load. However, the recirculation is approximately 5.47%, resulting in 341 kg/h of fuel being returned by the FVT. The recirculation increases up to a maximum of 83% with load variations. Additionally, nitrogen gas is supplied to the main gas valve inlet and outlet of the

FVT, and the internal ammonia is vented into the atmosphere. The main gas valve and gas bleed valve operate according to the operation logic appropriate for each situation.

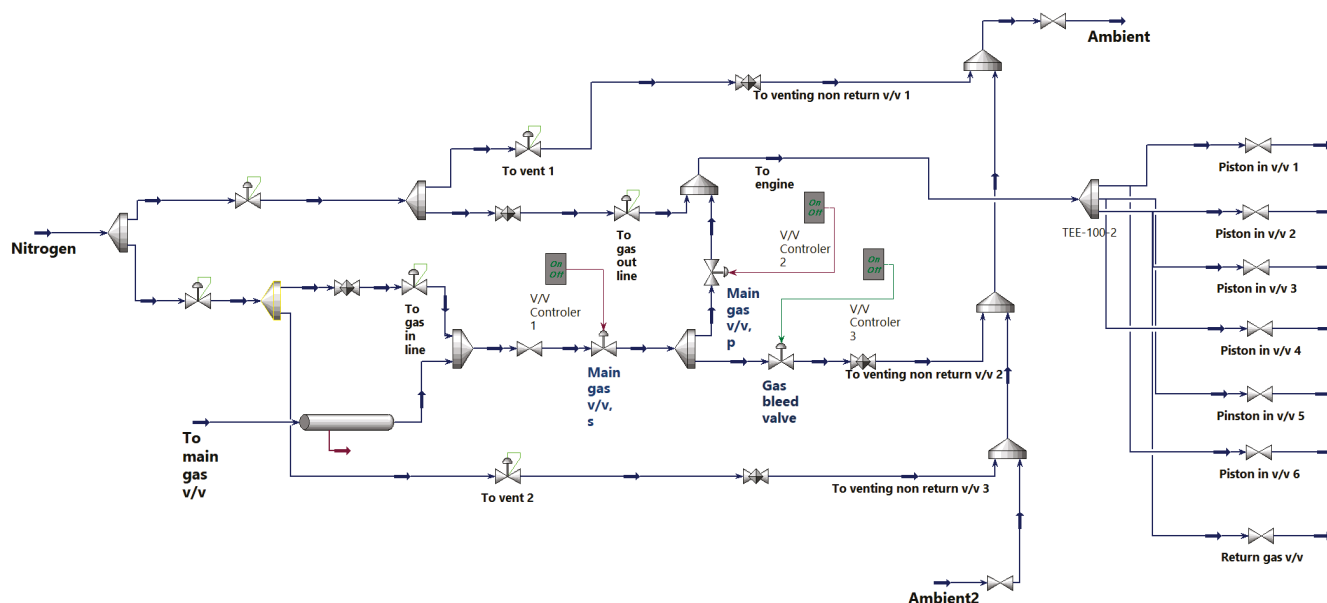


Figure 4. Piping process delivering fuel to the six-cylinder engine through the FVT.

At this time, ammonia was supplied through a high-pressure pump and heater, and a pressure of over 8000 kPa and a temperature of 35 °C were applied [4]. Additionally, in the case of nitrogen, a purging pressure of 30 °C and 800 kPa, similar to atmospheric temperature, was applied [30].

In this paper, FVT was designed during the start and stop process of an ammonia engine and its performance characteristics were analyzed. However, purging characteristics according to the structure of the ship and piping were not considered, and the performance characteristics according to the purging capacity commonly applied by engine companies were analyzed through simulation.

Table 2. Operating conditions of fuel and purging gas of FVT.

Simulation Data		Reference
Fuel Condition		
Fuel Inlet Temperature [°C]	35	[4]
Fuel Inlet Pressure [kPa]	8000	[4,30]
Mass Density [kg/m³]	594.58	[31]
Mass Heat Capacity [kJ/kg-°C]	4.78	[31]
Thermal Conductivity [W/m-°C]	0.462	[31]
Viscosity [cP]	0.121	[31]
Purging gas condition		
Purging Gas Inlet Temperature [°C]	30	
Purging Gas Inlet Pressure [kPa]	800	[26,34]
Mass Density [kg/m³]	8.90	[32]
Mass Heat Capacity [kJ/kg-°C]	1.05	[32]
Thermal Conductivity [W/m-°C]	0.026	[32]
Viscosity [cP]	0.018	[32]

2.2.3. Selection of Valve Size and Nitrogen Supply

The valves controlled by the FVT include one master valve, two main valves, and an intermediate bleed valve for ammonia discharge. The valve sizes are selected with a C_v

value of 50 to minimize pressure drop at the maximum flow rate, thereby minimizing valve size and lowering the budget. The pressure change with respect to C_v variation is depicted in Figure 5a. The selected C_v value ensures that the pressure drop, measured as 2.9 kPa, for ammonia fuel passing through the main valve does not exceed 3 kPa.

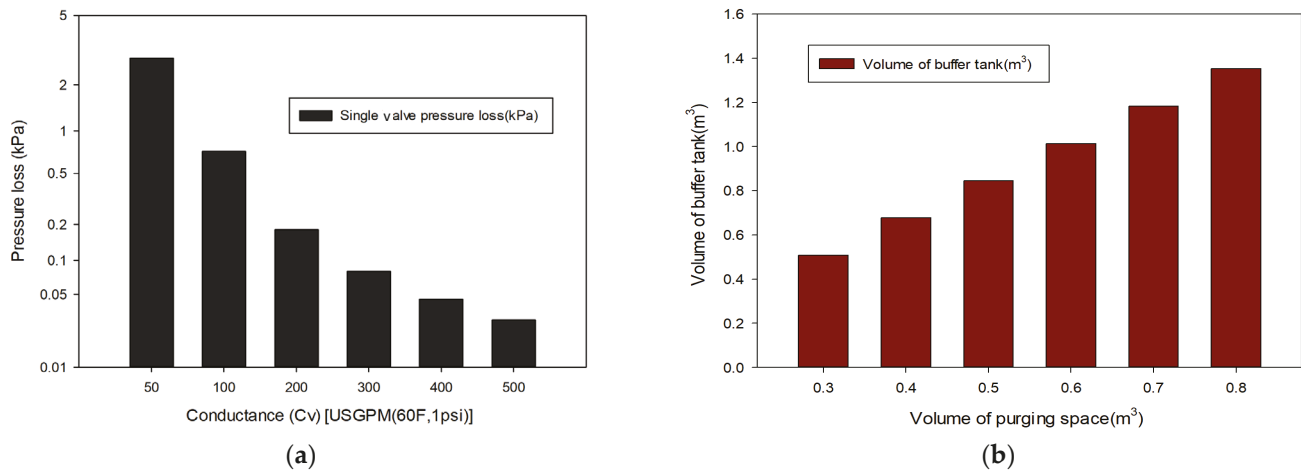


Figure 5. (a) Pressure change according to C_v change; (b) volume of buffer tank in relation to volume of purging space.

To analyze the nitrogen supply, the total nitrogen storage capacity was estimated for a 15,000 kPa high-pressure storage tank, assuming that pipe areas from the fuel supply system (FSS) to the nitrogen discharge valve at the engine ranges from 0.3 to 0.8 m³.

Figure 5b illustrates the buffer tank's capacity based on the purging space. Assuming that the purging space is 0.5 m³, approximately 0.845 m³ is required for ammonia storage. These results will be compared with the nitrogen capacity consumed in simulation models.

Additionally, according to the purging design for ship engines worldwide, nitrogen pressure operates between approximately 800 kPa and a maximum of 1500 kPa [33–35]. In the FVT-based ship fuel supply system, variations in pressure lead to differences in the rate and time of residual ammonia discharge from the engine. Table 3 presents the purging pressure variations for current dual-fuel engines or gas-fuel engines in ships.

Table 3. Purging pressure of a dual-fuel engine or gas-fuel engine.

Engine Producer	Wärtsilä [33]	MAN B&W [26]	HiMSSEN Diesel Engine [34]	Win GD [35]
Name of model	16V50DF	G60ME-C9.2-GI-TII	H54DFV	X92DF
Engine capacity [kW]	15,600	21,440	25,200	63,840
Reference pressure [kPa]	1500	700~900	850~1050	1000~1500

3. Analysis of Control Application Characteristics

3.1. FVT Startup during Engine Operation

3.1.1. Logic for Startup

The startup of the ammonia engine occurs when the final engine supply valve opens, securing fuel supply from the moment the initial fuel supply pump and the ammonia heating system are active. As the load increases, the fuel supply valves of each cylinder progressively open, leading to an increase in the fuel supply rate. Figure 6 illustrates the simplified startup logic of the ammonia engine.

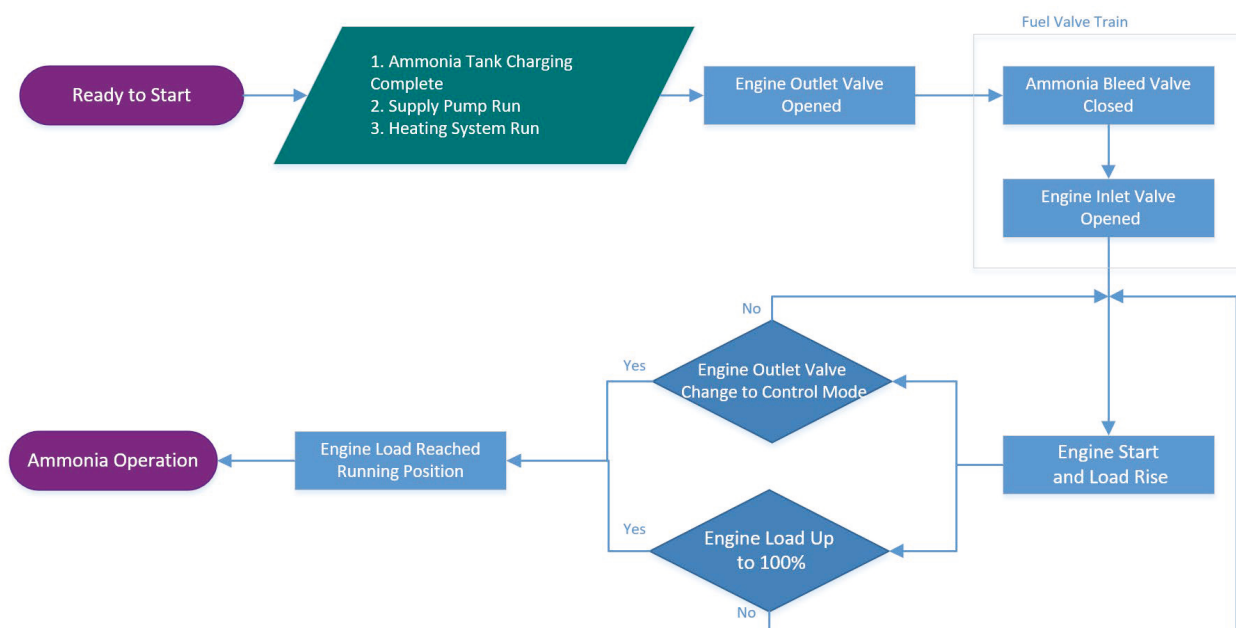


Figure 6. Simplified startup logic of ammonia engine.

During the operational procedure, the FVT starts when the bleed valve closes, simultaneously with the opening of the two main valves, supplying fuel to the engine. Each valve operates based on the actuator's opening time, and in the case of conventional LPG vessels, each valve has a maximum operating range of 10 s. However, during the startup process, the bleed valve closes, and the main valves open. Afterwards, the engine is operated manually and the maximum load is reached by raising the telegraph by the operator. At this time, the system is converted to normal running mode only when the final load condition is reached and the engine outlet valve is completely converted to control mode.

The operation begins only after completely venting the internal N_2 and securing liquid ammonia. Therefore, there are no risks related to opening time. However, the time to reach the appropriate flow rate and nitrogen composition are factors that delay the time until engine start. In addition, to verify the fuel transition within the pipes, engine performance was compared in consideration of the actuator's opening time.

In this study, the actuator's operating range was determined to be 2–10 s [30]. Comparative analysis was performed for the flow rate and ammonia and nitrogen composition of the fuel supplied to the engine in relation to the opening and closing of the bleed and main valves. Through dynamic simulation, the FVT opening rate with rapid increase in flow rate and rapid change in ammonia composition was derived.

3.1.2. Control Application Characteristics for Startup

During the engine startup, the main gas valve opens, and nitrogen in the pipes is bypassed to the knockout drum and circulated until all N_2 is completely removed. This leaves only the liquid ammonia to circulate. To achieve maximum ammonia supply in a short time while ensuring the complete removal of FVT's N_2 gas, the opening time of the main valve was analyzed. Regardless of the main valve's opening time, approximately 131.9 s were required to reach the maximum flow of 746 kg/h. On the other hand, the time to reach 50% of the maximum flow was 20.3 s after the main valves were opened, and depending on the valve opening rate, a flow difference of 4.78% (17.8 kg/h) occurred at a 30%/s opening rate. However, at the 80% point of the maximum flow at 47.4 s after the main valves were opened, the difference due to the valve opening rate showed only a minor increase of 0.56% (3.4 kg/h), indicating a diminishing impact of the valve opening rate on flow increase. The fuel flow rate and ammonia composition for the FVT's main valve with a 10% opening rate are depicted in Figure 7. Furthermore, the ammonia conversion rate

based on valve control conditions showed that the ammonia conversion reached 98.0% in the engine return pipe 67.8 s after the main valves were opened. After 200 s, the ammonia conversion rate reached 999,926.1 ppm (99.99%). On the other hand, residual nitrogen is expected to cause NOX generation during the combustion process along with air. Therefore, it is expected that engine startup will be necessary after the ammonia composition inside the system has been converted to 99.99% [36].

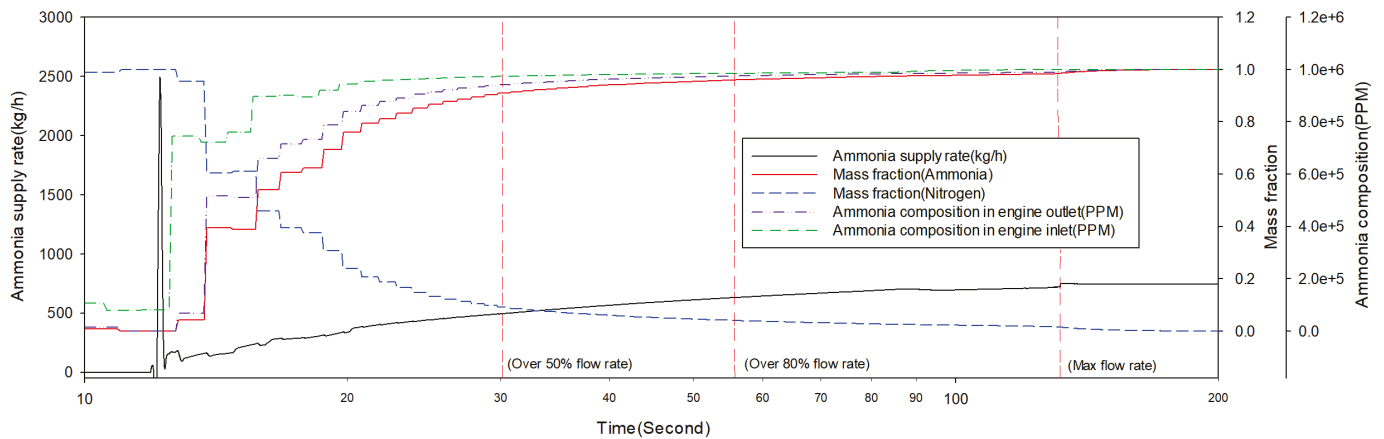


Figure 7. Fuel flow rate and ammonia composition due to the opening of the main valve of FVT with a 10% opening rate.

Figure 8a,b show the changes in fuel supply and ammonia composition in relation to valve opening rate. Under the condition of an opening rate of 20%/s, in Figure 8a,b, an increase in flow rate of 3.4 kg/h compared to the previous one was confirmed and the difference in ammonia conversion up to 98% in relation to valve opening rates was negligible, with less than 0.03% (245 ppm) variation.

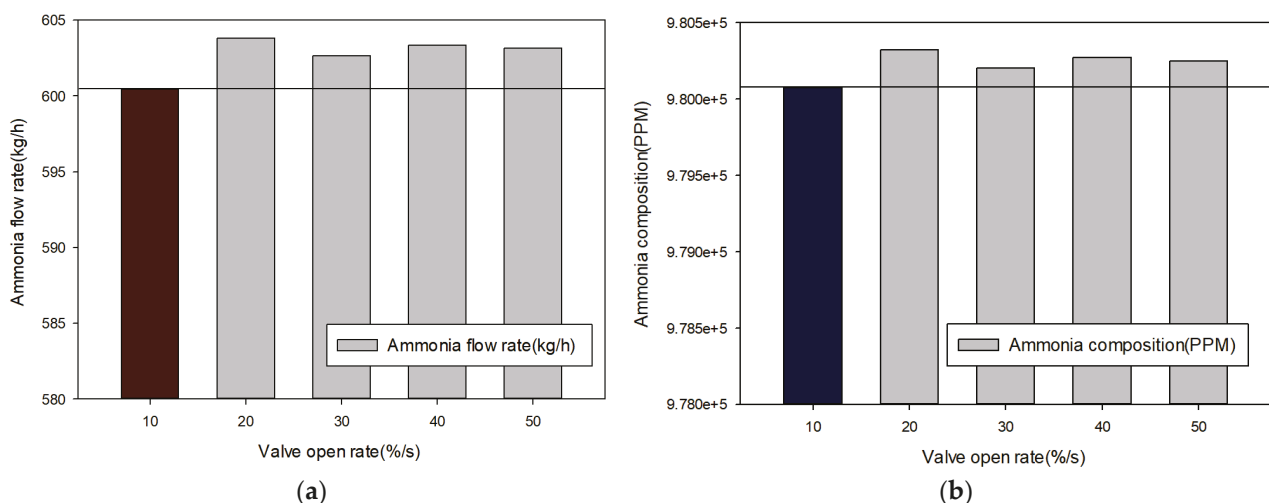


Figure 8. (a) Ammonia supply rate change in relation to valve opening rate; (b) ammonia composition change in relation to valve opening rate.

In the study proposed through experiments by Chun et al., by opening the GUV after starting the LNG fuel propulsion engine, a high flow rate increase of about 9 times the initial flow rate (20.5 times for this model) occurs. This phenomenon is expected to increase the flow rate due to changes in flow rate as high-pressure liquid ammonia flows into the pipe filled with low-pressure nitrogen gas after ventilation. In addition, the initial increase rate of flow rate is expected to vary depending on the supply pressure of 600 kPa and 8000 kPa for LNG and

ammonia. Afterwards, it was designed to gradually increase the flow rate with increasing load under low-load conditions [37]. Through comparison with this actual model, the operating accuracy of the proposed ammonia analysis model can be confirmed.

3.2. FVT Startup during Engine Shutdown

3.2.1. Logic for Shutdown

The ship's stopping methods include routine stops at ports or designated locations and emergency stops in urgent situations such as fire or collision. In a typical operational stop, the supply of fuel to the engine is cut off by closing the main valve, and any remaining ammonia fuel within the pipes is discharged through the bleed valve and the purging valve at the engine outlet via N₂ purging. This approach makes repair and maintenance more convenient and prevents potential fires due to pipe leaks.

In contrast, emergency stops prioritize the safety of the vessel and crew over engine maintenance. Risks are minimized by swiftly cutting off the fuel and purging any remaining fuel. Accordingly, it is essential to follow the existing shutdown logic, rapidly closing the main gas valve within two seconds and subsequently purging the residual fuel supplied to the engine via N₂ purging.

Figure 9a illustrates the conventional FVT operating logic during the shutdown process, without considering ordinary or emergency situations. In this scenario, the main valve is controlled with a two-second limit on the actuator, while the gas bleed valve is limited to a 10 s opening time. Afterwards, the fuel valve on the engine outlet side is blocked, and the bypass valve of the FVT is opened. Consequently, there is a segment where purging between the main gas valve and gas bleed valve fails, and residual ammonia may be present during maintenance or management.

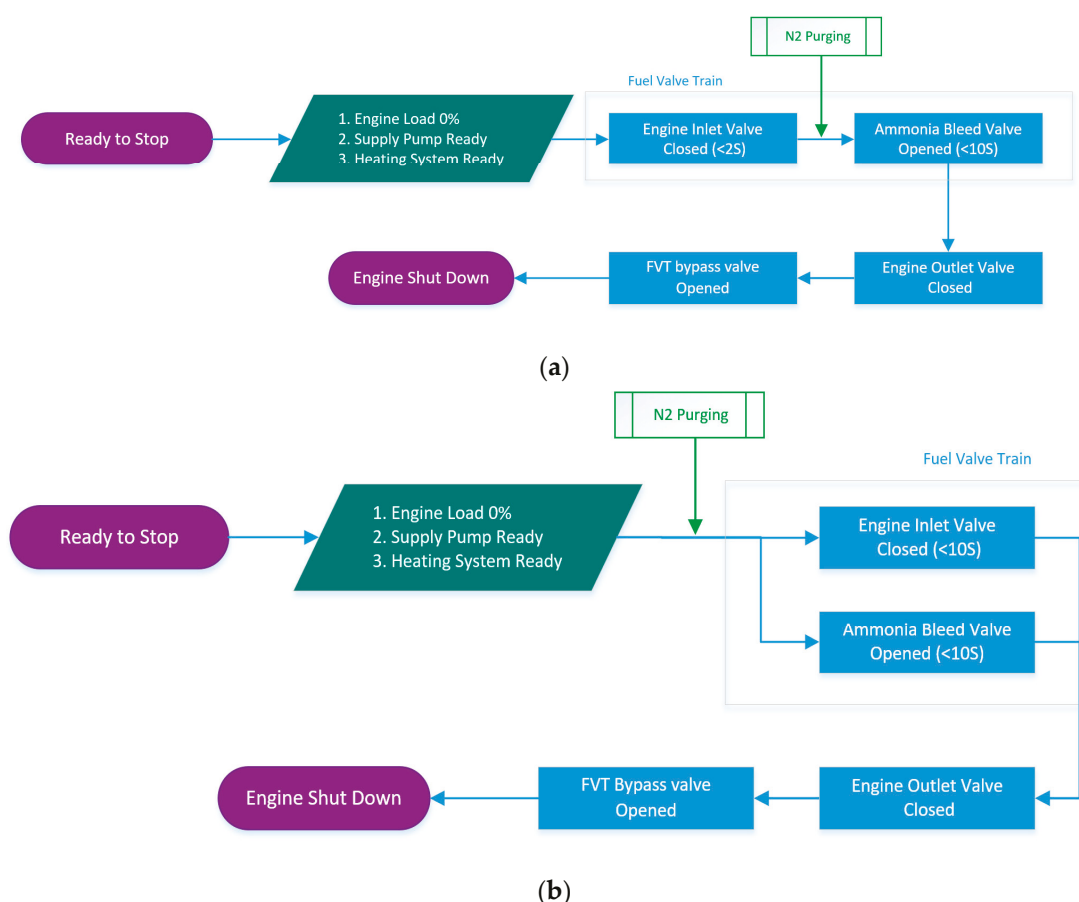


Figure 9. (a) FVT operating logic during engine shutdown of a ship; (b) newly proposed FVT operating logic.

Hence, in this simulation, for general shutdown processes in non-emergency conditions, the main valve is set up to completely purge ammonia through the bleed valve during the 2 to 10 s closing process. Figure 9b presents the N₂ purging logic behind the simulation [30]. At this time, the stop logic is constructed based on the state in which more than 99.995% of ammonia has been removed, and exposures to levels exceeding 50 ppm result in immediate irritation to the nose and throat. [38]

This operation method can be used to check operation performance by constructing valve opening and closing diagrams through the development of the actual FVT control model presented by Kang et al. [22].

3.2.2. Control Application Characteristics for Shutdown

In the conventional engine shutdown process, the main valve is locked, followed by the removal of ammonia from the pump side and engine inlet using nitrogen. After one second, the bleed valve opens. Figure 10 depicts the distribution of ammonia and the change in N₂ during the engine shutdown process. With an N₂ supply of 5148 kg/h, the ammonia distribution decreases to below 1 ppm after 294 s for the pump side and 305.5 s for the engine side. However, the ammonia concentration exceeds 600,000 ppm until about 278 s, and then tends to decrease rapidly. In this phenomenon, the liquid ammonia remaining inside the pipe is naturally vaporized, maintaining the ammonia composition, but it is expected to decrease rapidly after it is completely vaporized. Moreover, the numerical value of ammonia discharged through the bleed valve is 1,000,000 ppm (100% ammonia), confirming the presence of residual liquid ammonia within the FVT.

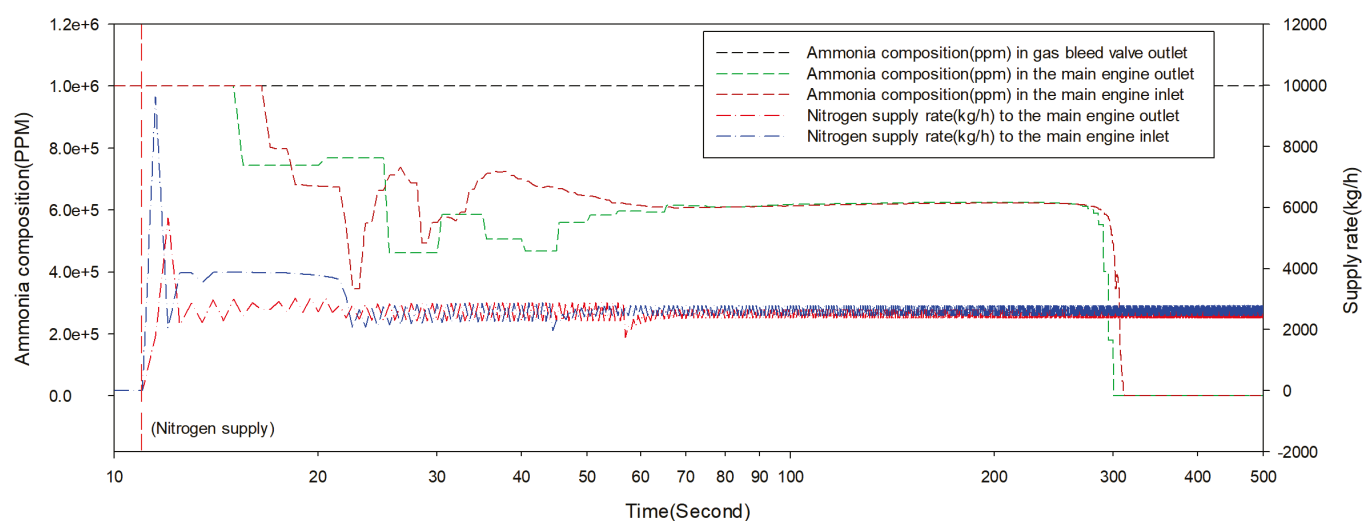


Figure 10. Ammonia composition and N₂ supply rate changes during engine shutdown.

Additionally, the analysis examined an increase in the purging pressure from 800 kPa to 1600 kPa. The time required for N₂ consumption and ammonia distribution to decrease below 1 ppm was investigated. Figure 11a,b illustrate the supply of N₂ entering each pump and engine, and the purging time. When supplying nitrogen at 1600 kPa, the engine and pump had minimum times of 149 s and 205.5 s, respectively. The N₂ consumption, relative to the supply flow over time, amounted to 1.25 m³ at 1200 kPa pressure for the engine and 1.42 m³ at 800 kPa for the pump.

The amount of N₂ required to purge the 0.5 m³ space provided by the engine manufacturer is 0.845 m³. However, this simulation required an additional supply of about 48.1% of N₂ from the pump side and about 81.3% of N₂ from the engine side to achieve an ammonia removal rate of over 99.995%.

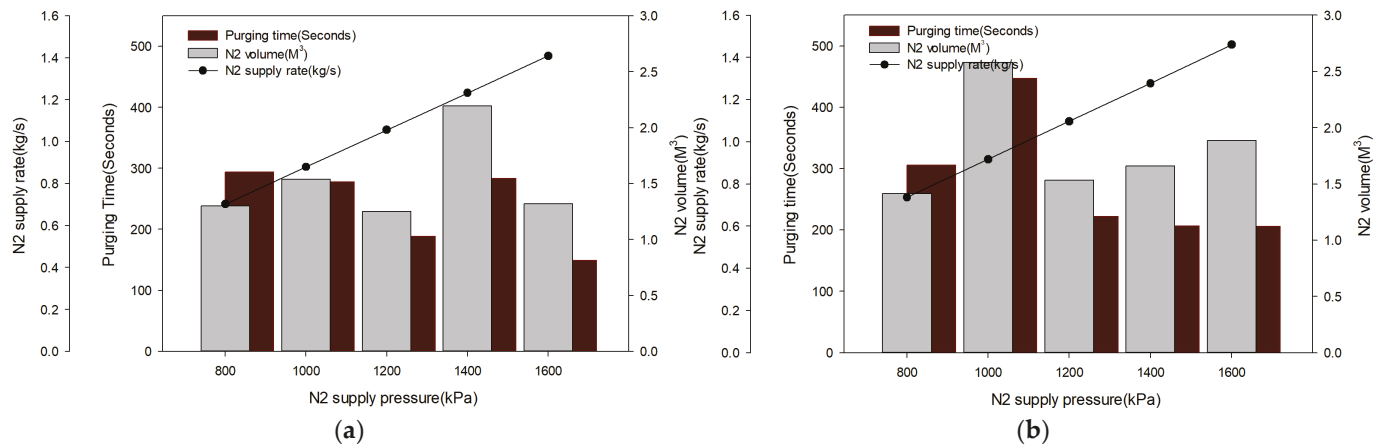


Figure 11. (a) N₂ flow rate and pump and purging time of the pump side; (b) N₂ flow rate and pump and purging time of the engine outlet side.

This study also compared the amount of nitrogen discharged and the time required for complete ammonia removal when applying valve opening variations that prevent residual ammonia in the FVT. Initially, changes in the opening of the main valve showed that complete ammonia removal occurred only at rates of 10–20%/s. If the fuel valve is shut off within five seconds, some ammonia remains in the FVT. A range of 10–30%/s was considered for the operation of the bleed valve with valve opening. Control times were selected at 10%/s for the gas bleed valve and 18%/s for the main gas valve to minimize nitrogen discharge through the bleed valve. In this case, the amount of N₂ supplied until complete ammonia removal was 0.28 kg. Maximum nitrogen consumption was achieved when the opening was 30%/s for the gas bleed valve and 10%/s for the main gas valve. The N₂ supply was 1.01 kg, representing a 360% increase compared to the minimum supply amount. Figure 12a illustrates the nitrogen consumption based on variations in the gas bleed valve and main gas valve opening.

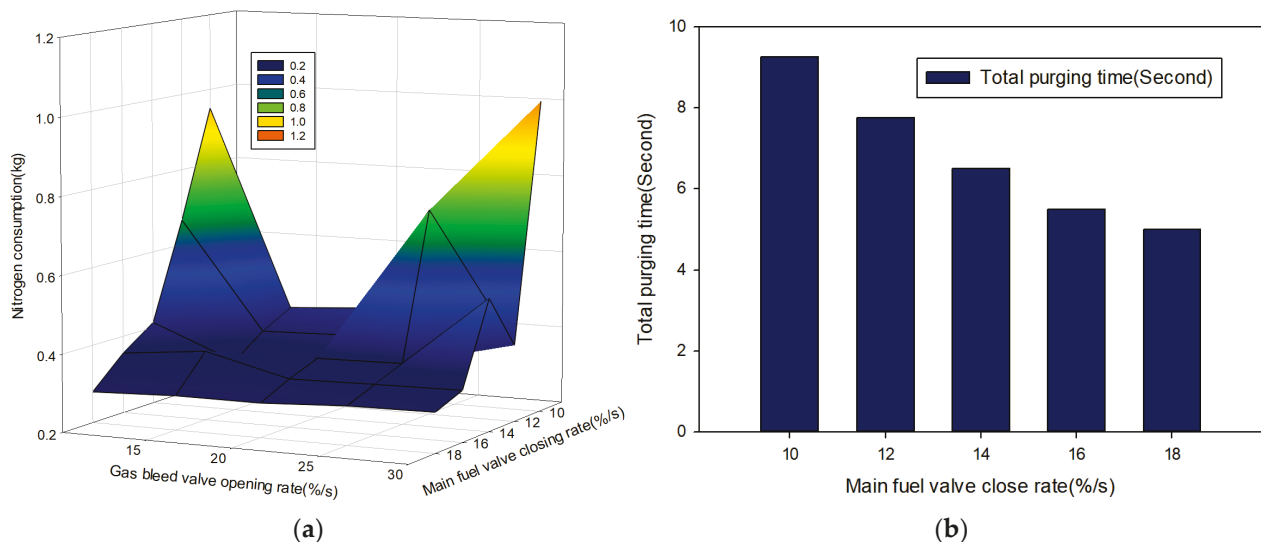


Figure 12. (a) Nitrogen consumption in relation to opening rates of gas bleed valve and to closing rates of main gas valve; (b) changes in purging time in relation to main gas valve closing rate.

On the other hand, the time required for the complete removal of ammonia by the FVT is influenced solely by the closing time of the main valve, independent of the opening time of the bleed valve. The minimum purging time was five seconds at a closing rate of 18%/s. Figure 12b depicts the variation in purging time in relation to the closing rate of

the main valve. Through the two results, it was confirmed that residual ammonia can be removed using a small amount of N_2 when optimized FVT control operation is applied.

4. Conclusions

The FVT for fuel supply and shutdown on ships showed improved performance under specific operational conditions during startup and shutdown.

Under startup conditions, the opening of the main valve influenced the time taken for the flow to increase. Up to a 50% flow increase, the maximum flow difference was observed to be 17.8 kg/h at an opening rate of 30%/s. However, the conversion rate of ammonia composition showed less than 1% difference in relation to valve opening rate. These results confirmed that flow rate improvement and ammonia conversion rate could be increased only through FVT control.

On the other hand, for the shutdown process of the engine, a model was proposed to sequentially lock the main valve and bleed valve during nitrogen purging, aiming to prevent residual ammonia within the FVT in typical port shutdown situations. Ammonia was completely removed after five seconds of nitrogen purging with a bleed valve opening rate of 10%/s and a main valve closing rate of 18%/s. At this time, the nitrogen consumption at the gas bleed valve was 0.28 kg.

In addition, variations in the nitrogen purging volume during the shutdown process were identified based on the purging pressure currently recommended for ships. The minimum supply volume was verified, with a total volume of 2.67 m³ required at 1200 kPa. The findings indicate that purging pressure should vary depending on factors such as engine size and pipe design.

The above changes in shutdown conditions have been proposed as a means to completely remove ammonia within pipes, so as to minimize safety risks and enhance operational convenience. Through this control, the FVT itself is maintained below 50 ppm, eliminating the need for continuous monitoring and eliminating questions about leaks that occur during operation. In addition, it is possible to secure economic efficiency by applying an open design rather than using a fully ex-proof encapsulated design, which has a high initial cost.

For ships using gaseous fuels such as LPG and LNG, this analysis model is expected to be able to be utilized by applying fuel and nitrogen supply conditions and purging areas. In addition, safety can be secured through the proposed FVT control, and follow-up research on optimization methods according to fuel characteristics is expected to be necessary.

Author Contributions: Writing—Original draft, L.S.; Writing—Review and editing, L.S. and L.H.; Funding acquisition, S.Y. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by the Korea Institute of Marine Science & Technology Promotion (KIMST) funded by the Ministry of Oceans and Fisheries, Korea (20220634).

Data Availability Statement: Data are available on request due to restrictions, e.g., privacy or ethical.

Conflicts of Interest: The authors declare no conflicts of interest.

Nomenclature

N	Nitrogen
Act	Actuator position
Act ₀	Initial actuator position
Act _{Desired}	Desired actuator rate
C _v	Coefficient of variation
SG	Specific gravity
a	Helmholtz energy
a ⁰	Ideal gas Helmholtz energy
a ^r	Residual Helmholtz energy
Q	Flow rate

P	Pressure
P_{purge}	Purge pressure
$P_{service\ tank}$	Service tank pressure
t	Time
Act	Actuator
o	Output
V	Volume
V_{purge}	Purge volume
V_{buffer}	Buffer tank volume
ME	Main Engine
LFSS	Low-flashpoint fuel supply system
z	Minimum number of times of purging
LHV	Lower heating value
HFO	Heavy fuel oil
R	Gas constant
M, j, i	Constant
c	Critical
FVT	Fuel valve train
GVU	Gas valve unit
GWP	Global warming potential
PID	Proportional–integral–differential controller
OP	Output
IMO	International Maritime Organization
GHG	Greenhouse gas
LNG	Liquefied natural gas
LPG	Liquefied petroleum gas
MDO	Marine diesel oil
EEDI	Energy Efficiency Design Index
EEXI	Energy Efficiency Existing Ship Index
NFPA	National Fire Protection Association

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Article

Influence of In-Cylinder Turbulence Kinetic Energy on the Mixing Uniformity within Gaseous-Fuel Engines under Various Intake Pressure Conditions

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Abstract: To explore the potential for further enhancing the gas mixing uniformity of natural gas (NG) engines, this paper identifies turbulent kinetic energy (TKE), which has an essential impact on gas mixing, as the entry point of the research. After establishing a computational fluid dynamics (CFD) model for NG engines' direct injection and mixing processes, the inlet pressure is selected as the experimental variable to investigate the influence of TKE on gas mixing uniformity. In particular, by proposing the theoretical concept of the core mixing stage, the numerical variation rule between the best mixture concentration region (BMCR) percentage and the mean turbulent kinetic energy (MTKE) of the core mixing stage is analyzed under certain injection timing conditions. The results indicate that, with identical intake pressures, an advanced gas injection timing elevates the total turbulence kinetic energy (TTKE) during the core mixing stage, thereby amplifying the uniformity of the gas mixture at the ignition. In specific scenarios, as the intake pressure increases, the decreasing trend in the BMCR proportion closely resembles the diminishing trend in the MTKE during the core mixing stage. Scrutinizing the variation trend in either parameter allows for an approximate prediction of the variation trend in the other parameter. When the intake pressure is gradually raised from the naturally aspirated state, the adequacy of the gas jet development is progressively reduced by the increasing back pressure in the cylinder.

Keywords: natural gas engine; turbulent kinetic energy; mixing uniformity; inlet pressure; core mixing stage

1. Introduction

It is widely recognized that the internal combustion engine holds a pivotal position in the automotive industry [1,2]. Serving as a power source, it efficiently converts the thermal energy generated by the combustion of fossil fuels into mechanical energy to meet various transportation needs [3]. Nevertheless, in contradiction to this energy conversion process, the combustion of fossil fuels inevitably leads to the production of pollutant emissions such as CO, NO_x, HC, and PM, which have a certain degree of negative consequences on the ecological environment [4,5]. In pursuit of effectively diminishing the negative consequences and actively aligning with the energy conservation and environmental protection policies enacted by various national governments [6,7], exploring alternative fuels to decrease dependency on traditional fossil fuels has become a historical inevitability [8].

In the realm of energy, natural gas is commonly regarded as an ideal substitute for traditional fossil fuels (petrol, diesel) because of its numerous benefits, including affordability, ample reserves, and environmentally friendly combustion [9,10]. However, a distinguishing drawback of natural gas lies in its constrained energy density [11], which

inherently leads to a relatively slower rate of mixing with air than conventional fossil fuels. Especially in direct injection gas engines, the slower mixing rates and shorter mixing duration frequently result in suboptimal gas mixing within the cylinder precisely at the ignition [12], consequently lowering the engine's combustion efficiency.

To tackle this challenge, researchers worldwide have investigated the mixing characteristics of direct-injection gas engines based on factors such as the shape of the combustion chamber, the type of nozzle, and the injection position. By modifying the structure of the piston head, the effect of combustion chamber geometry on gas engine mixture formation was further explored by B. Yadollahi et al. [13]. The study's findings demonstrated that combustion chambers equipped with narrow-bowl piston heads yielded a more homogeneous air–fuel mixture and increased the production of the combustible mixture in proximity to the spark plug position. In the study conducted by Karri Keskinen et al. [14], the correlation between the mixture formation process and nozzle type in direct-injection gas engines was analyzed. It was found that the nozzle structure greatly influenced the in-cylinder mixture formation, and the optimum mixing performance could be obtained by using a hollow conical nozzle. Jinwen You et al. [15] investigated the impact of various injection positions on the homogeneity of gas blending within the cylinder at the ignition. The results of their analyses revealed that the gas mixing uniformity was further improved by adopting an earlier injection timing and selecting a vertically downward-facing gas injection. Although the scope of research on mixing characteristics has been enriched by the above research methods, there are still certain limitations in effectively improving gas mixing uniformity. This arises because all the aforementioned studies, which explore the variation rules of gas mixing uniformity by altering the structure of relevant components, lack a theoretical discussion of the intrinsic factors significantly affecting gas mixing uniformity. Additionally, modifications to the structure of relevant components also result in marked elevations in the experimental time cost.

Given the intimate association between the mixture formation process and turbulent kinetic energy (TKE) [16], this nexus is adopted as a point of departure for delving into the gas mixing laws, which can provide a reference to improve the gas mixing uniformity at the ignition moment. Typically, heightened TKE tends to facilitate the enhancement of gas mixing velocity [17], consequently exerting a positive influence on improving the uniformity of gas mixing [18,19]. With the objective of exploring this specific influence, the inlet pressure is designated as the experimental variable to delineate the impact of TKE on the gas mixing uniformity. Furthermore, with the proposal of the theoretical concept of the core mixing stage, an analysis was conducted to dissect the numerical variations rules between the mean turbulent kinetic energy (MTKE) and the best mixture concentration region (BMCR) proportion under specific injection timing conditions.

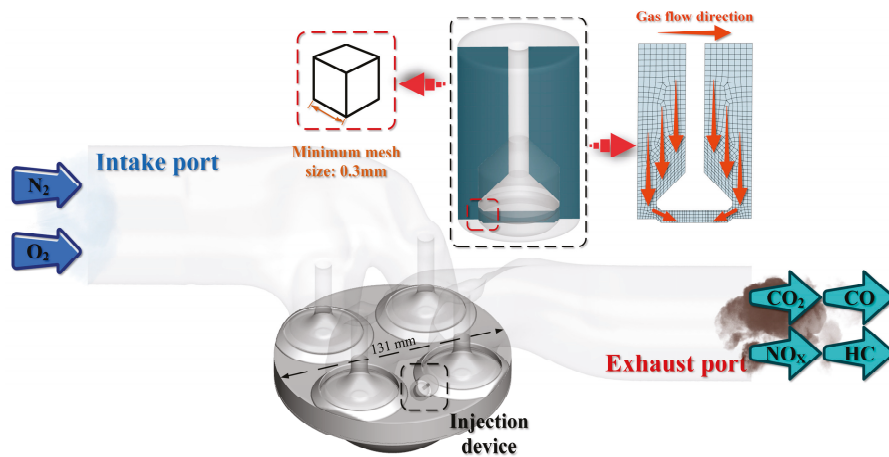
2. Model Validation and Scheme Design

2.1. CFD Model

The four-valve engine model was utilized in this experiment [20]. The main parameters of the engine and the computational fluid dynamics (CFD) model are depicted in Table 1 and Figure 1, respectively. The CFD model in Figure 1 corresponds to the intake valve opening timing (30° BTDC), as indicated in Table 1, at which time the exhaust valve was in an open state. Considering that the intake flow between the two intake valves often exhibits higher levels of TKE due to their interaction [21], the gas injection device was chosen to be installed on the cylinder head midway between the two exhaust valves at an angle of 45° to the horizontal. In this injection method, the gas jet could fully contact the intersecting intake flows, enhancing the mixing efficiency between the gas and air. The adopted injection device featured a pull-open valve with a valve diameter of 7 mm and a lift of 1.5 mm. The corresponding mesh division can be seen in Figure 1. Faster jet velocities and improved mixing efficiency are typically achieved by this type of valve opening [20,22]. The transition times for both valve opening and closing were set to 1 ms.

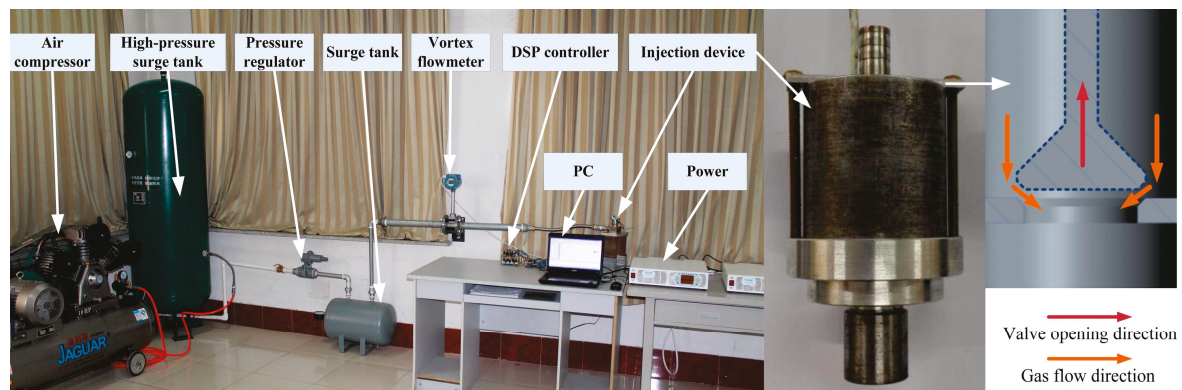
Table 1. Main parameters of the engine.

Parameter	Value
Bore (mm) $\times$ Stroke (mm)	131 $\times$ 155
Number of cylinders	6
Displacement volume (L)	12.53
Compression ratio	11.5
Rated power (kW)/speed (rpm)	257/2000
Intake valve open/close (CA)	30° BTDC/45° ABDC
Exhaust valve open/close (CA)	78° BBDC/30° ATDC

**Figure 1.** CFD model of the engine.

2.2. Model Validation

The mesh-independence verification of the CFD model has been completed in previous work [23]. Here, the transient flow rate of this model was verified to ensure that the experimental results met the accuracy requirements, and the experimental platform is shown in Figure 2. In the figure, the digital signal processor (DSP) served as the primary device governing the injection duration. The pressure regulator was responsible for adjusting the pressure from the upstream high-pressure surge tank to the injection pressure required for the experiment, with its downstream connected to the surge tank. The main function of the surge tank was to provide a constant and stable injection pressure to the injector. Only under stable injection pressure conditions could the cumulative flow rate measured by the vortex flowmeter be regarded as a valid experimental data sample.

**Figure 2.** Flow measurement platform of gaseous-fuel injection device.

Limited by the spatial distance between the flowmeter and the injection apparatus, an accurate determination of the transient flow during a single operational cycle of the

injection device was unachievable. Therefore, opting to dynamically inject for a period of time through the injection apparatus to accumulate flow, followed by a subsequent conversion, obtained the transient flow rate during a single operational cycle. In consideration of experimental safety, air was chosen as the medium for the experiments instead of natural gas. Similarly, the medium in the CFD simulation was also set to air to ensure the reliability of the validation results. To exclude the effect of cumulative injection time on the experimental outcomes, comparisons were made between the results at 5 min and 12 h of dynamic injection. The gas injection pressures were set at 1.0, 1.2, 1.4, 1.6, 1.8, and 2.0 bar. The injection durations were set at 40, 60, and 120 ms, corresponding to engine speeds of 3000, 2000, and 1000 rpm, respectively. The injection pulse width was set to one-quarter of the injection duration.

The comparison of experimental and CFD numerical results under a single working cycle is shown in Figure 3. It was determined that the transient flow rate achieved from the long-term conversion (lasting 12 h) deviated less from the CFD numerical results than that obtained from the short-term conversion (lasting 5 min), aligning well with the expectations. It was necessary to explain that one of the reasons for the significant error observed under the 5 min dynamic injection condition was that within the short injection duration, the impact of upstream pressure, data collection, and other random factors on the experimental results was more pronounced. Another noteworthy reason was that during the 5 min dynamic injection period, the wear on the injection device was relatively unstable, causing fluctuations in the effective lift of the valve, which, in turn, affected the experimental results. By analyzing the errors between the experimental and CFD results for single operating cycles at various pressures shown in Figure 3, it was observed that the upstream pressure had minimal impact on the errors. The maximum error occurred at 1000 rpm and an inlet pressure of 1.0 bar. In conclusion, based on the transient flow rates measured during individual cycles, the flow characteristics of the transient injection simulation model for the gas fuel injector were validated.

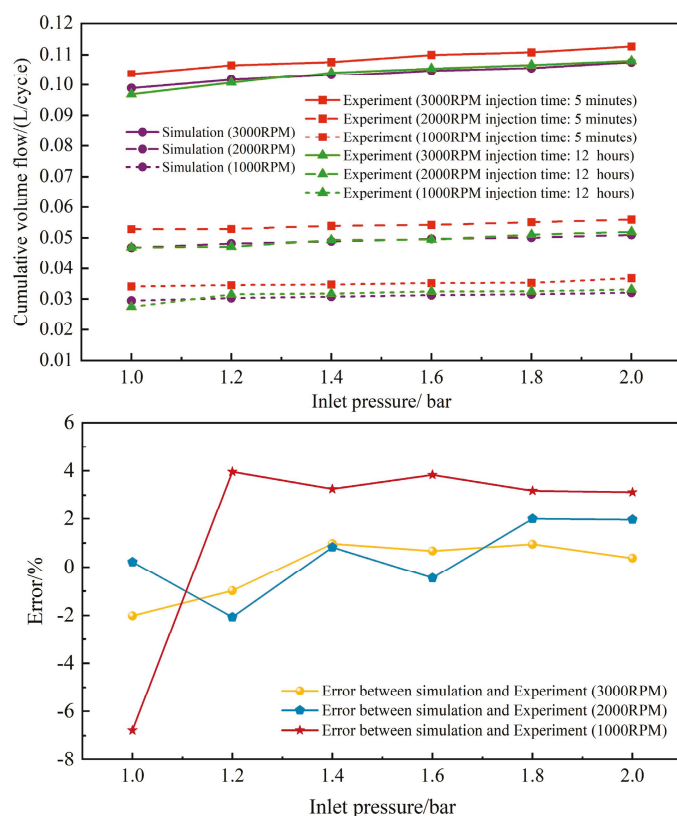


Figure 3. Comparison of experimental with CFD numerical results.

2.3. Scheme Design

Five different intake pressures of 1.0 bar, 1.5 bar, 2.0 bar, 2.5 bar, and 3.0 bar were selected as experimental variables to investigate the influence of TKE on the gas mixing uniformity. Given the generally higher levels of TKE during the intake valve opening phase, an earlier start of injection (SOI) could be employed to fully harness the TKE generated by the intake flow to enhance the gas mixing within the cylinder. To minimize excessive gas spillage caused by scavenging processes, the SOI corresponding to these five groups of intake pressure was set as the exhaust valve closing time (CA 390). Furthermore, five additional schemes were configured with CA 635 as the end of injection (EOI). This time selection could be adequately contrasted with the scheme using CA 390 as the SOI, as the intake valves were already closed at that time, and the TKE level within the cylinder was relatively low. Notably, the back pressure within the cylinder at that time point coincided with the inlet pressure of the injection device [20], ensuring the supersonic development of the gas jet at the nozzle throat throughout the injection process. To facilitate an effective comparison of the mixing effects of different schemes at the ignition timing, it was stipulated that all scenarios maintained a consistent air–fuel ratio within the cylinder. Details of the specific schemes are shown in Table 2.

Table 2. Numerical simulation schemes.

CASE	Intake Pressure, Mpa	SOI, ° CA	EOI, ° CA
1	1.0	390.0	427.0
2		597.0	635.0
3	1.5	390.0	434.4
4		589.3	635.0
5	2.0	390.0	442.0
6		584.0	635.0
7	2.5	390.0	449.7
8		571.7	635.0
9	3.0	390.0	457.0
10		561.8	635.0

Subsequently, the CFD numerical calculation was carried out for the specific scheme developed above, and the corresponding CFD calculation software was FLUENT 2022. Considering that the effects of various turbulence models on the jet penetration distance and the related wall functions on the computational accuracy have been analyzed in previous research [24], the RNG k - ϵ two-equation turbulence model and the non-equilibrium wall functions were selected for the CFD numerical calculations in this study. The numerical convergence limit for the energy equation was set to 10^{-6} , while those for other equations were set to 10^{-4} . The turbulent Schmidt number was specified as 0.7. Assuming the initial computational domain to be at rest, its initial velocity was set to 0. The inlet pressures for the intake port and the injection device were set to 2 bar and 10 bar, respectively, with corresponding temperatures of 353 K and 300 K. The outlet pressure of the exhaust port was set to 1.8 bar, and the temperature was 773 K. The initial pressure and temperature of the combustion chamber were the same as those of the exhaust port. Since the jet tended to reach supersonic within the throat region of the injection device, the mesh size here was minimized to 0.3 mm, as shown in Figure 1. With the goal of reducing computational costs, the mesh size away from the throat region was gradually enlarged, with a maximum size not exceeding 3 mm. For simplicity, the natural gas in the CFD numerical calculations was assumed to be 100% methane. Given that combustion was not covered in this study, the CFD numerical calculations spanned from the moment of intake valve opening (CA 330) to the timing of ignition (CA 700).

3. Results and Discussion

Since all scenarios shared a consistent air–fuel ratio at the time of ignition, the average mass fraction of gas at the ignition was calculated to be between 2.5% and 3.0%, based on the total mass of air and gas in the cylinder after intake valve closure (IVC). Here, this interval was defined as the BMCR. Correspondingly, concentration regions of 0–2%, 2–2.5%, 3–3.5%, and greater than 3.5% were assigned as the thinnest, thinner, thicker, and thickest intervals, respectively. Among them, the BMCR percentage (the volumetric proportion of the stoichiometric mixture in the cylinder at the ignition) served as the primary benchmark for evaluating gas mixing uniformity in this study.

The proportion of gas in each concentration interval of CASES 1–10 was extracted, as depicted in Figure 4. It was evident that CASES 1, 3, 5, 7, and 9 with CA 390 as the starting time of injection (SOI) had a significantly higher BMCR percentage at the ignition than CASES 2, 4, 6, 8, and 10. The occurrence of this phenomenon was attributed to the earlier SOI of the former, which increased the mixing time of the gas. Concurrently, the TKE generated by the intake flow during the opening of the intake valve could effectively be utilized by the gas injected earlier into the cylinder to accelerate the gas mixing. It was noteworthy that, with the increase in intake pressure, the BMCR proportion for CASES 1, 3, 5, 7, and 9 exhibited an initial upward trend followed by a subsequent decline, whereas the BMCR percentage for CASES 2, 4, 6, 8, and 10 tended to converge. At an intake pressure of 1.5 bar, CASE 3 achieved the highest BMCR proportion, reaching a notable 82.47%. In order to better elucidate the phenomena described above and to clarify the influence of TKE on gas mixing uniformity, detailed analyses were conducted on CASES 1, 3, 5, 7, and 9, which presented higher overall BMCR proportions. In particular, the analysis process was unfolded primarily in accordance with the stages of gas jet development and gas core mixing.

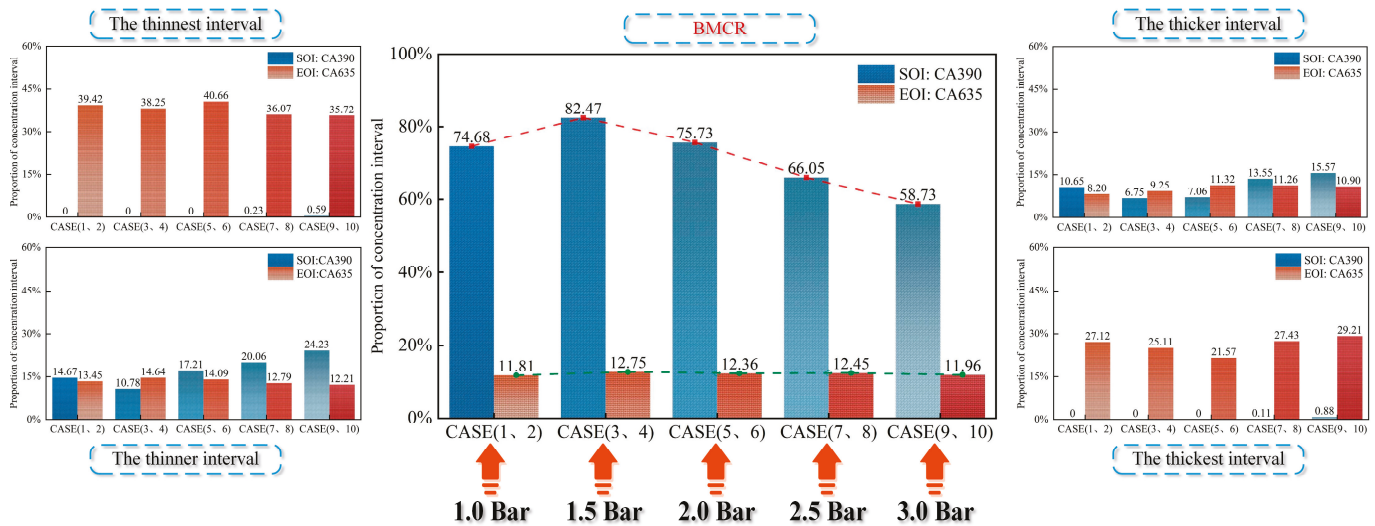


Figure 4. Percentage of each gas concentration interval at the moment of ignition.

3.1. Gas Jet Development Stage

The “gas jet development stage” means the gas injection stage. In this stage, the kinetic energy of the airflow within the cylinder is significantly lower than that of the gas jet. Thus, this phase is predominantly dominated by the inertial development of the gas jet, with relatively limited mixing between the gas and air [25]. Taking CASES 1, 3, 5, 7, and 9 as examples, the state of the gas jet was scrutinized with the injection device valves in the fully open position. The gas jet in CASE 1 was observed to continue its upward development after impacting the piston top, as illustrated in Figure 5. As the inlet pressure increased, the penetration distance of the upward-developing gas became increasingly shorter, which indicated that the adequacy of the gas jet development was becoming worse. A further

explanation of this conclusion can be gleaned from Figure 5. By observing the numerical variation in the back pressure in the upper-left corner of the contour, it was found that with the increase in intake pressure, the back pressure within the cylinder progressively ascended. Consequently, the hindering effect (from back pressure within the cylinder) on the development of gas jets in CASES 1, 3, 5, 7, and 9 was increasing, which was the principal cause for the gradual decline in the adequacy of gas jet development.

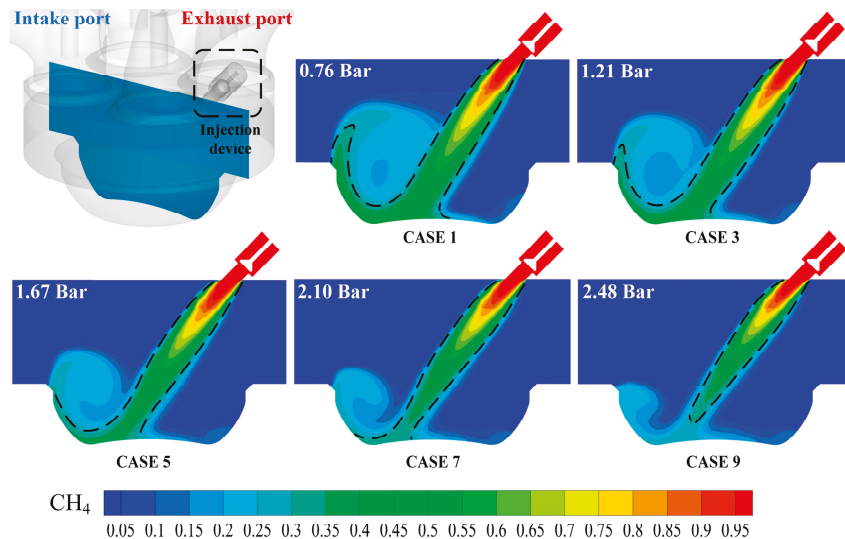


Figure 5. Gas jet at the moment of CA 420.

Additionally, the volume distribution of TKE exceeding $500 \text{ (m}^2/\text{s}^2)/\text{kg}$ for CASES 1, 3, 5, 7, and 9 is showcased in Figure 6. It could be plainly seen that the portion with relatively high TKE in the cylinder was primarily generated by the gas jet, as the volumetric shape of TKE in Figure 6 basically coincided with the development morphology of the gas jet depicted in Figure 5. Thus, the volumetric shape variations of TKE portrayed in Figure 6 also substantiated that the adequacy of gas jet development progressively diminished with increasing intake pressure. Combining the above analyses of TKE volume distribution and gas jet contours, it was determined that during the stage of gas jet development, the adequacy of gas jet development obeyed the sequence CASE 1 > CASE 3 > CASE 5 > CASE 7 > CASE 9.

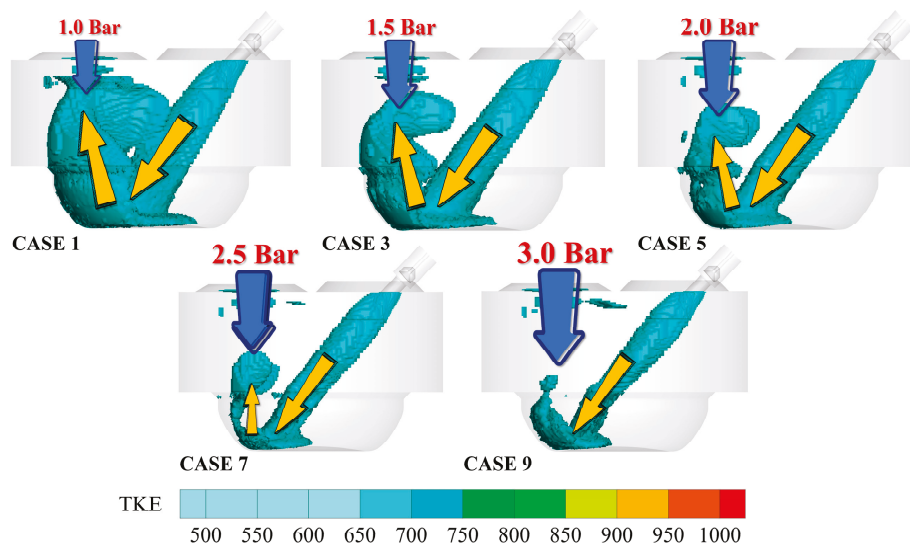


Figure 6. TKE above $500 \text{ (m}^2/\text{s}^2)/\text{kg}$ in the cylinder at the moment of CA 420.

3.2. Gas Core Mixing Stage

After having gone through the stage of gas jet development, the overall TKE and velocity of the gas jet in CASES 1, 3, 5, 7, and 9 began to decrease significantly. Subsequently, the analytical process transitioned into the major stage that determined the gas-mixing homogeneity at the ignition moment. The stage was hereby designated as the “gas core mixing stage”, with its corresponding process commencing from the EOI and terminating at the ignition moment. In this process, the high concentration of gas was extensively mixed with the air, thereby diluting to a more uniform range of gas concentrations. Therefore, it was more comprehensive to analyze the impact of TKE on gas mixing uniformity based on the core mixing stage. Simultaneously, considering the differing pulse width of gas injection among these five schemes, the numerical relationship between the MTKE (during the core mixing stage) and the BMCR proportion (at the ignition) was additionally dissected in this study. The specific formulas for the corresponding TKE and MTKE are given in (1) and (2).

$$\text{TKE} = \frac{\sum_i^N k_i \rho_i V_i}{\sum_i^N \rho_i V_i} \quad (1)$$

$$\text{MTKE} = \frac{\int_{\text{EOI}}^{700} \text{TKE} dt}{\Delta t} \quad (2)$$

where TKE is the unit mass turbulence kinetic energy; MTKE is the unit mass mean turbulence kinetic energy; k_i is the turbulence kinetic energy of the i th grid cell; ρ_i is the density of the i th grid cell; V_i is the volume of the i th grid cell; EOI is the ending time of injection; and Δt is the time interval between the EOI and the ignition timing.

The core mixing stages of CASES 1, 3, 5, 7, and 9 are labeled in Figure 7, where the area of the shaded portion represents the total turbulent kinetic energy (TTKE) of the core mixing stage, and the corresponding values (and the MTKE of this process) are detailed in Table 3. Upon meticulously examining the numerical variations in the table, it became clear that the TTKE in the core mixing stage of these five schemes was sequentially decreasing. Consequently, the gas mixing velocity in the core mixing stage of CASES 1, 3, 5, 7, and 9 was progressively declining. Under the influence of this mixing velocity, the phenomenon (analyzed in Section 3.1) of the stepwise reduced adequacy in the development of gas jet for CASES 1, 3, 5, 7, and 9 would lead to a consistent decrease in the BMCR percentage at the moment of ignition. However, the facts were slightly different, as the characteristic inflection point in the BMCR percentage occurred under the intake pressure of 1.5 bar, as illustrated in Figure 8. CASE 1 had a significantly lower percentage of BMCR at the ignition than CASE 3, which went against the overall decreasing trend of TTKE in the core mixing stage. Only when the intake pressure had exceeded 1.5 bar did the BMCR percentage at ignition time follow the declining trend of TTKE.

To elucidate the numerical relations between the MTKE (during the core mixing stage) and the BMCR proportion (at the ignition), the two groups of data enumerated in Table 3 were contrasted, as portrayed in Figure 8. It was apparent that when the intake pressure surpassed 1.5 bar, the decline trends of both BMCR proportion and MTKE were remarkably similar. This particular phenomenon indicated that under certain conditions, utilizing either a set of data from BMCR proportion or MTKE could approximately predict the changing trend of the other set.

Table 3. TTKE and MTKE of the core mixing process in CASES 1, 3, 5, 7, and 9.

	CASE 1	CASE 3	CASE 5	CASE 7	CASE 9
TTKE	31,544.20	28,361.69	25,467.12	23,014.58	21,423.63
ATKE	115.55	106.78	98.71	91.95	88.16

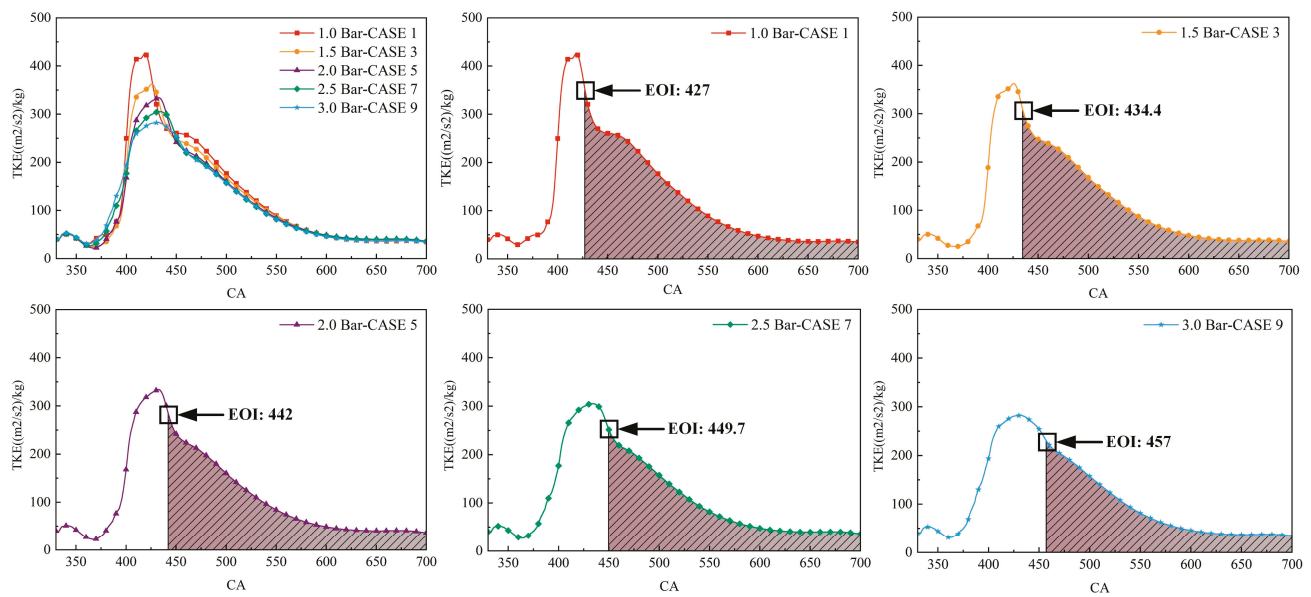


Figure 7. Core mixing stage of CASES 1, 3, 5, 7, and 9.

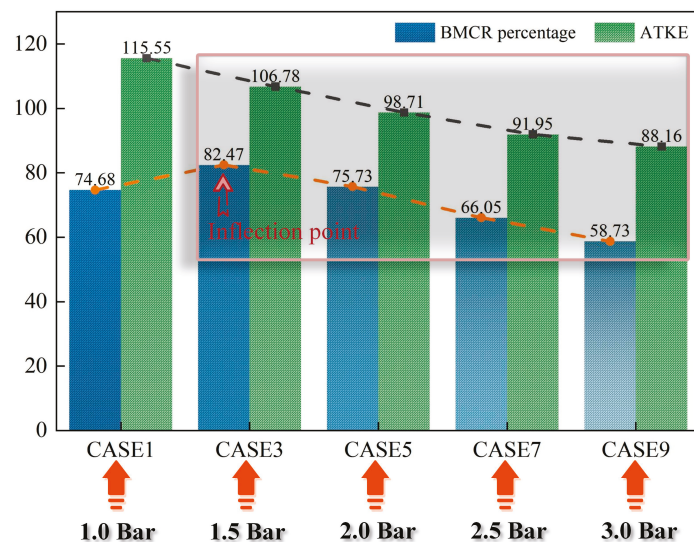


Figure 8. Comparison of numerical variation between BMCR percentage and ATKE in CASES 1, 3, 5, 7, and 9.

3.3. Differential Analysis of BMCR Proportions

Here, the reasons for the characteristic inflection point in the BMCR percentage under 1.5 bar intake pressure were analyzed. A comparison of gas volume distribution of CASE 1 and CASE 3 after EOI (CA 440) was performed, as shown in Figure 9. In comparison to CASE 3, CASE 1 exhibited a significantly higher concentration of gas beneath the intake valve, attributed to the longer penetration distance of the upward-developing gas in CASE 1 (analyzed in Section 3.1). Given the relatively weaker airflow movement beneath the conical valve (intake valve) employed in this study compared to other spaces within the cylinder, the gas located closer to the bottom of this valve performed inferior mixing performance with air. This disparity in airflow movement explained why the TTKE was higher in CASE 1 while the BMCR percentage at the ignition was lower relative to CASE 3. (The aforementioned analysis did not need to address the issue of insufficient comparison of high-concentration gas due to the inconsistent amount of air in the cylinder at the moment of CA 440, since the high-concentration gas was generally not fully mixed by the air for a short period of time after the EOI.)

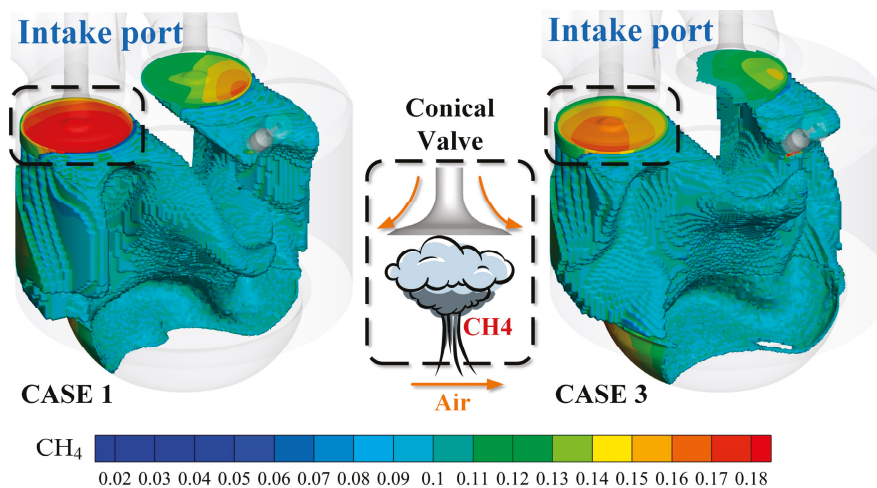


Figure 9. Gas volume distribution of CASES 1 and 3 at the moment of CA 440.

At this juncture, the predominant reason for the first increase and then decrease in the BMCR proportion of CASES 1, 3, 5, 7, and 9 was elucidated. To further visualize the disparity in gas mixing uniformity at ignition among these five schemes, the gas below a 2.5% concentration was hidden in Figure 10. The observations indicated that CASE 3 achieved the highest level of gas mixing uniformity, with a small percentage of low-concentration gas. In contrast, CASE 5 had a significantly worse spatial distribution of gas than CASE 3, even though it also had a relatively high percentage of BMCR.

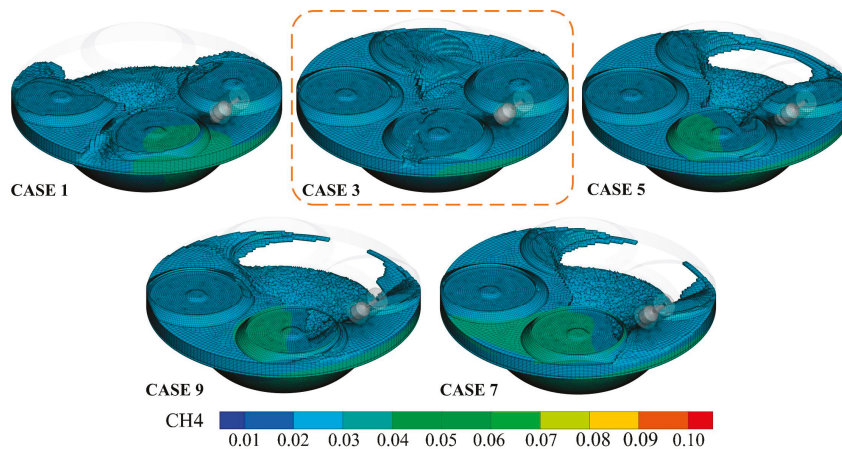


Figure 10. Gas distribution above 2.5% concentration in CASES 1, 3, 5, 7, and 9 at the ignition.

Finally, the causes behind the overall low and convergent BMCR percentage of CASES 2, 4, 6, 8, and 10 were conducted from two perspectives. Firstly, given that the EOI for these five scenarios was CA 635, the gas mixing time was notably shortened compared to CASES 1, 3, 5, 7, and 9. This directly led to their BMCR proportions dropping to around 12% at ignition. Secondly, it was observed from Figure 11 that the TTKE (during the core mixing stage) of CASES 2, 4, 6, 8, and 10 did not differ much. Consequently, fluctuations in the BMCR proportion due to differences in TTKE (during the core mixing stage) could be very subtle when the BMCR percentage values were already low.

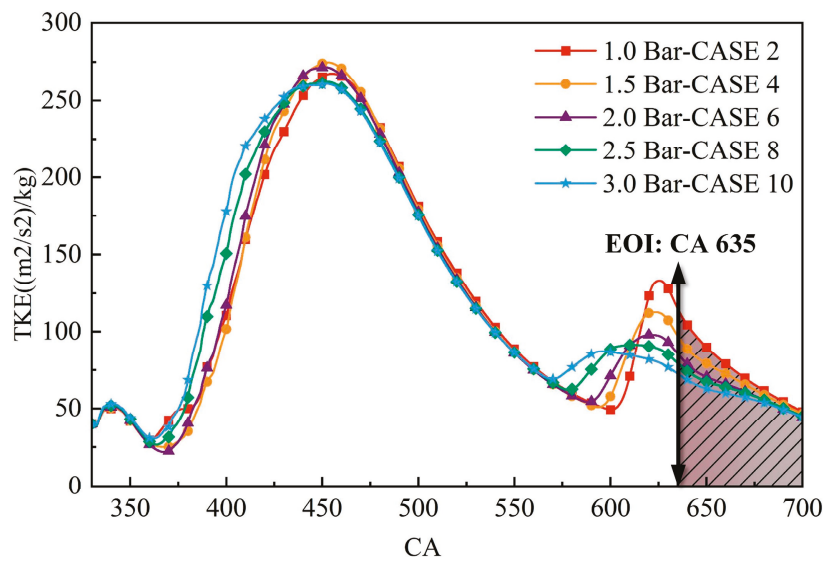


Figure 11. TKE variations in the cylinder of CASES 2, 4, 6, 8, and 10.

In addition, the gas distribution of CASES 2, 4, 6, 8, and 10 at the ignition was demonstrated, as shown in Figure 12. The gas mixing uniformity of these five schemes was relatively low, and the gas with a concentration of 2.5% or more was predominantly clustered around the periphery of the combustion chamber. When the spark plug was positioned at the center of the combustion chamber, all five schemes presented the disadvantage of uneven flame propagation at the moment of ignition.

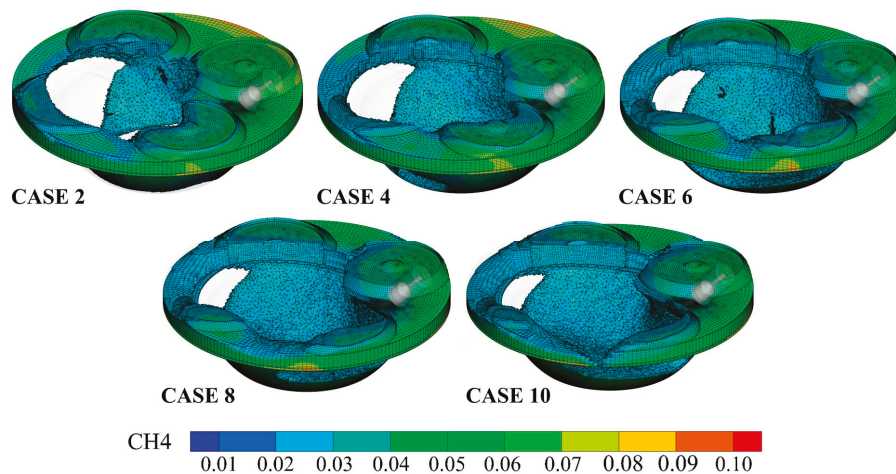


Figure 12. Gas distribution above 2.5% concentration in CASES 2, 4, 6, 8, and 10 at the ignition.

4. Conclusions

In this paper, the influence of TKE on gas mixing uniformity under various inlet pressures was investigated by establishing a CFD model of direct injection and mixing processes for natural gas engines. Concurrently, based on the proposed theoretical concept of core mixing stages, an analysis was conducted on the numerical relationship between the MTKE and the BMCR proportions. The primary research findings are outlined as follows:

- (1) Under identical intake pressure conditions, the earlier the gas injection timing, the greater the TTKE in the core mixing stage. Typically, a higher value of the latter facilitates improved gas mixing uniformity.
- (2) With 30° ATDC (CA 390) as the SOI, an elevation in intake pressure induces a corresponding increase in in-cylinder back pressure, which reduces the adequacy of gas jet development.

- (3) Given a particular injection timing situation, when the inlet pressure surpasses 1.5 bar, the diminishing tendency of the MTKE in the core mixing process exhibits a close similarity to that of the BMCR proportion. The changes in the uniformity of gas mixing at the ignition moment can be predicted by analyzing the numerical variations in the MTKE.
- (4) In the naturally aspirated state of the engine, the earlier injected gas jet will develop in large quantities towards the underside of the intake valves after impacting the piston crown. However, constrained by the intake valve structure and the airflow movement, high-concentration gas is usually retained below the intake valves, resulting in a decline in gas mixing uniformity.
- (5) In the future, the numerical correlation between the MTKE and BMCR proportions across diverse engine conditions will be thoroughly investigated.

Author Contributions: Methodology and software, Y.W. and T.W.; verification, W.G. and L.Z.; resources, Y.Z. and C.W.; writing original draft preparation, Y.W., T.W. and R.L. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Natural Science Foundation of China [Grant No. 52105260]; the Qinglan Engineering Project of Jiangsu Universities; Changzhou Sci & Tech Program [Grant No. CE20225049]; the Natural Science Research Project of Higher Education Institutions in Jiangsu Province [Grant No. 21KJB460008, 22KJA580002]; and the Jiangsu Province Postgraduate Practice and Innovation Project [Grant No. XSJCX23_13, SJCX-1632, and SJCX-1622]. The APC was funded by the National Natural Science Foundation of China; the Qinglan Engineering Project of Jiangsu Universities; the Changzhou Sci & Tech Program; and the Natural Science Research Project of Higher Education Institutions in Jiangsu Province [Grant No. 21KJB460008].

Data Availability Statement: The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding author.

Conflicts of Interest: The authors declare no conflicts of interest.

Nomenclature

NG	natural gas
CNG	compressed natural gas
TKE	turbulent kinetic energy
CFD	computational fluid dynamics
BMCR	best mixture concentration region
MTKE	mean turbulent kinetic energy
TTKE	total turbulent kinetic energy
IVO	intake valve opening time
IVC	intake valve closing time
EVO	exhaust valve opening time
EVC	exhaust valve closing time
DSP	digital signal processor
CA	crank angle
SOI	start of injection
EOI	end of injection

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Article

Decarbonization in Shipping—The Hopes and Doubts on the Way to Hydrogen Use

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Abstract: This article presents the initial processes of changing ship fuels aimed at reducing emissions of carbon dioxide and other greenhouse gases. A significant reduction in GHG emissions is only possible by using carbon-free fuels. The process of reducing CO₂ emissions was forced by legal regulations introduced in recent years by the International Maritime Organization and the Parliament of the European Union. The year 2050 was set as the target year for achieving the intended goals, but intermediate goals should be achieved already in 2030 and 2040. This article attempts to analyze the ongoing changes in the fuel market in maritime transport on the way to achieving the threshold of climate neutrality with this form of transport. A number of hopes related to this were indicated but also so were obstacles that may slow down this process. In 2023, there was an increased interest among shipowners in adapting ship engines to burn more ecological ship fuels. However, it is far from our expectations. Meeting the gradually increasing emission limits through imposed regulations was possible in the years 2020–2023 by using dual-fuel engines in which gaseous fuels, mainly LNG and LPG, were used for long periods of operation. The next step is the use of biofuels or synthetic fuels, which, however, will not meet the requirements after 2030. Interest is moving towards the use of ammonia and, ultimately, after 2040, hydrogen. The aim of this article is to analyze the ongoing processes and assess the directions of changes that justify the sense of the actions taken.

Keywords: decarbonization process; marine fuels; transient fuels; biofuels; ammonia; hydrogen

1. Introduction

The increase in Earth's temperature threatens the development of civilization. Human activity has contributed to the increase in the concentration of greenhouse gases in the Earth's atmosphere over the last two hundred years, which is especially visible in the 21st century. Despite the Earth Summit in Kyoto in 1997 and the signing of the protocol, greenhouse gas emissions, especially carbon dioxide, are increasing year by year. The actions taken are insufficient, and the temperature increase threshold of 1.5 °C compared to 1990 may be exceeded. Analyzing the share of maritime transport in global carbon dioxide emissions into the atmosphere over the last 20 years, it ranged from 2.5 to 3.3%, depending on the growth rate of cargo by sea. It is the cheapest form of transport, consuming the least amount of energy in terms of transport effect. In international shipping, the International Maritime Organization and, in shipping within the European Union, the Parliament of the European Union have taken actions aimed at reducing GHG emissions from fossil fuels, mainly fuels derived from crude oil processing, in favor of biofuels or synthetic fuels, and as a result, achieving the intended ecological effects [1–4].

The transition to alternative fuels was accelerated in 2020 when the International Maritime Organization (IMO) reduced the fuel sulfur limit in international shipping from 3.5% (m/m) to 0.5% (m/m).

The last step was taken in July 2023, when the IMO presented a revised greenhouse gas emission reduction strategy with numerical targets [2,3]. The 2050 goals have milestones in

2030 and 2040. The life cycle of greenhouse gases emitted into the atmosphere associated with ship fuels is taken into account to achieve the following targets:

- To achieve net-zero GHG emissions by or around 2050;
- As a minimum 5% to 10% uptake of zero GHG emission fuels, etc., by 2030;
- At a checkpoint of 40% reduction in CO₂ emissions (per transport work) by 2030 (compared to 2008) and the indicative checkpoints: 20% to 30% reduction in GHG emissions by 2030 (compared to 2008) and 70% to 80% reduction in GHG emissions by 2040 (compared to 2008).

The main goal is to achieve climate neutrality from international shipping by or around 2050.

The new rules entered into force on 5 June 2023 in the EU ports. Since 1 January 2024, the EU's Emissions Trading System has been extended to cover CO₂ emissions from all large ships (of 5000 gross tonnage and above) entering EU ports, regardless of the flag they fly (Figure 1).

EU ETS Extension to Maritime Transport						
Introduction Timeline						
	2023	2024	2025	2026	2027	2028+
Ship sizes and types		MRV review		ETS review		
Cargo/passenger ships* (5000+ GT)			First surrendering year on 2024 emissions			
Offshore ships (5000+ GT)	---	---				First surrendering year on 2027 emissions
Offshore and general cargo ships (400–5000 GT)	---	---			Inclusion on the EU ETS to be considered as part of the ETS review	
Greenhouse Gases						
Carbon dioxide (CO ₂)						
Methane (CH ₄) and Nitrous Oxide (N ₂ O)	---					
Phase in						
% of emissions to be surrendered as per EU ETS Directive	---	40%	70%	100%	100%	100%

*Ships already covered by the EU MRV regulation Under MRV scope Under MRV and EU ETS scope

Figure 1. European Union's Emissions Trading System extension to maritime transport (on base [5]).

When ships sail between European Union ports or at berth in port under the jurisdiction of an EU Member State, CO₂ emissions are counted as 100%, while if only one of the ports (exit or entry to a port) is located within the European Union, the emissions are counted at 50%.

An entity must buy or receive allowances to cover future emissions. The current price for a CO₂ certificate is approximately EUR 70 per ton of CO₂ emissions. If the fuel index for heavy fuel is 3.122, this means an additional cost of approximately EUR 220 per ton of fuel used.

The price of marine fuel is around USD 450–600 per metric ton. Purchasing carbon dioxide emission allowances will increase the cost of fuel by approximately 50%. DNV's Director of Environment for Maritime Eirik Nyhus also has a similar opinion. The EU ETS will lead to additional costs for the industry of roughly up to EUR 10 billion a year once fully implemented in 2026, due to the need to acquire carbon credits corresponding to GHG emissions. This will effectively increase fuel-related costs by about 50% [6].

Greenhouse gas emission limits (mainly carbon dioxide) in maritime transport were set by the IMO in 2015–2020, with specific limits at transitional stages, but generally, by the end of 2022, there have been minor changes in the use of new, more ecological marine fuels. An estimated 99.5% of the fuels used came from crude oil processing, with only 0.51% coming from other fuels such as LNG, LPG, ammonia, and hydrogen [4,7].

Important changes began to occur in 2023, when interest in bio-methanol, ammonia, and synthetic liquefied natural gas increased significantly.

Meeting the requirements imposed by the IMO will be necessary by 2050. To achieve this goal, intermediate steps must be completed in earlier years. Table 1 shows the schedule to achieve the indicative checkpoints. The year 2008 is the base year for the set target of reducing equivalent carbon dioxide emissions from maritime transport. Due to the fact that reducing emissions of other harmful substances into the atmosphere (nitrogen oxides, particulate matter, black carbon, and hydrocarbon slips) is more difficult to achieve, carbon dioxide emissions must be reduced to a greater extent. In 2040, the level of carbon dioxide equivalent emissions is to reach a minimum of -70% , which means that only carbon dioxide emissions must be reduced by approximately 90%.

Table 1. Annual greenhouse gas emissions from maritime transport in 2008 and 2021 and maximum emissions levels that will allow international shipping to reach the checkpoints [8] [unit: million tons CO_{2eq}].

GHG Emissions	2008 (Base Year)	2021 (Latest)	2030 (20% Reduction from 2008)	2040 (70% Reduction from 2008)
Life cycle GHG emissions (WtW)	731	798	585	219
GHG emissions (WtT)	110	122	88	33
GHG emissions (TtW)	621	676	497	186

Table 1 shows annual greenhouse gas emissions from maritime transport in 2008 and 2021 and maximum emissions levels that will allow international shipping to reach the checkpoints, taking into account two components well-to-tank (WtT) and tank-to-wake (TtW) and their sum well-to-wake (WtW).

2. Equivalent Energy for Different Marine Fuels

The world's annual demand for petroleum-based marine fuels is 300–330 million tons. As the weight of cargo by sea increases by approximately 3%, the demand for energy contained in the fuel also increases by 3% [4,9].

Assuming that the engine efficiency does not depend on the type of fuel burned, but only on the amount of energy generated in the combustion process, it is possible to estimate the quantitative demand for potential ship fuels with different calorific values. Other potential marine fuels have different lower calorific values. Assuming the same amount of thermal energy in the combustion process, the demand for these fuels will vary. The higher the calorific value, the lower the demand, and vice versa (Table 2).

Table 2. Amount of marine fuel in energy and volume equivalent [own elaboration].

Type of Marine Fuel	Equivalent Energy ¹ [million ton]	Equivalent Volume [million m ³]	Energetic Volume Density [MJ/m ³]	Global Production (Data from 2021 to 2023) [million ton]
Petroleum-based marine fuels	330	370	38.6	>330
Methanol	696.5	879.4	15.76	111
Ammonia	737	1080	12.82	150 ²
Methyl ester	370	425.3	32.6	74.8
S-LNG/bio-methane/LNG trade	285	433.8	31.9	no data/ 30/401.5
Liquefied hydrogen	115.5	1635	8.5	94

¹ taking the following into account: petroleum marine fuels 42 MJ/kg; bio-methanol 19.9 MJ/kg; ammonia 18.8 MJ/kg; methyl ester (biodiesel) 37.5 MJ/kg; S-LNG 48.6 MJ/kg; hydrogen 120 MJ/kg [4,10]. ² global production of renewable ammonia was zero in 2022.

When burning marine fuels from crude oil processing in 2022, carbon dioxide emissions would amount to approximately 1.03 Tg (1.03 billion tons). Due to the associated emissions of other greenhouse gases such as soot, nitrogen oxides, and sulfur from marine diesel engines, CO₂ equivalent emissions (CO_{2eq}) are sometimes used. The difference between CO₂ and CO_{2eq} is rather small, about 7–9% larger for CO_{2eq}, and is quite stable. This means that CO_{2eq} emissions amounted to 1.09 Tg.

Uniquely, fossil LNG offers significant GHG emissions reductions when used as a marine fuel compared with VLSFO—up to 23% on a full life cycle (well-to-wake) basis (without taking into account slip). By contrast, the use of fossil methanol (14% more), ammonia (47% more), and (liquid) hydrogen (64% more) produces emissions much higher than those associated with VLSFO due to the large amounts of electricity (largely derived from the combustion of fossil fuels) needed for their production (e.g., hydrolysis) and long-term storage [11].

The lower calorific value and lower density of alternative fuel require a much larger volume of fuel tanks. In the case of liquefied fuels (NH₃, LNG, and H₂), thermal insulation of the tanks is required, which additionally increases the required space for reserve fuel. The necessary increase in the required volume of fuel reserve tanks compared to currently traditional marine fossil fuels is up to approximately 2 to 7, respectively. For ships intended to transport cargo, this represents a significant reduction in available cargo space at the expense of increased space for fuel reserve tanks.

3. Expected Effects of Decarbonization of Marine Fuels

In March 2023, the European Parliament and the Council of Europe reached an agreement on the use of cleaner fuels, calling for a reduction in ship emissions by 2% by 2025 and 80% by 2050. The European Commission has introduced FuelEU regulations, effective starting from 1st January 2025, which assume a reduction in CO₂ equivalent emissions from shipping every 5 years, to the level of 18.23 g CO_{2eq}/MJ in 2050 (80% less compared to 2020) counting total well-to-wake emissions.

Under the initial agreement, container ships and passenger ships (using the most quantity of fuel and, at the same time, emitting the most GHGs into the atmosphere) starting from 2030 will be obliged to use a land-based power source to meet all energy needs when mooring at the quays of main EU ports (there are such intentions, as long as there are such possibilities in the port, because the demand for electricity reaches 2–5 MW per ship). Starting from 2035, it will also apply to other EU ports if these ports have shore power. Certain exceptions will apply, such as stays in a port of less than two hours, use of own zero-emission technology, or port calls due to unforeseen circumstances or emergencies [4].

The primary effect of reducing CO₂ emissions will depend on the amount of biodiesel and bio-methanol used. The transition to renewable fuels is necessary in the transitional process of the decarbonization of shipping [12]. This process will be supported by increasing the consumption of liquefied ammonia. It is possible to increase ammonia production by 20–30% per year. However, it should be noted that in 2022, ammonia production from renewable sources was close to zero. Storing liquefied ammonia in its production processes and using excess electricity (which cannot be used directly) from renewable sources can contribute to the stated goal of decarbonizing shipping [13,14].

Achieving the decarbonization goal by 2050, i.e., switching to a significant share of hydrogen as a primary energy source in shipping, will depend on the method of hydrogen production (its color), i.e., whether energy from “dirty” sources was not used in the process of its production.

Table 3 shows the possible decrease in CO₂ emissions from different marine fuels.

The technology of fuel production is important, especially the carbon footprint left in this process. If the primary source is fossil fuels, even if they are processed, they will be transitional fuels. In the case of the production of synthetic fuels or biofuels, recognizing

them as more or less ecological fuels depends on the amount of electricity used, and especially from what primary energy sources it was produced [4].

Table 3. Possible decrease in CO₂ emissions using different marine fuels [own elaboration].

Type of Marine Fuel	Fuel Factor [kg CO ₂ /kg of Fuel]	Decrease in CO ₂ Emissions ¹ [%]
Petroleum-based marine fuels	3.12–3.23	0
Methanol	2.9	10
Renewable bio-methanol	0	100
Ammonia with 15% MDO	0.46	85
Methyl ester/B100	3/0	5/100
Biodiesel/FAME/HVO/SVO	0–2	40–100
Fossil LNG/methane	2.75	23
Renewable bio-methane	0	100
S-LNG	0–5	–55–100
Renewable hydrogen	0	100

¹ HFO-MDO CO₂ emission = 100%.

Achieving the target of reducing greenhouse gas emissions from maritime transport will be possible if emission reductions are properly distributed according to the capacity and type of ship. For example, container ships with large carrying capacity, equipped with main engines with the highest power of 50–80 MW, must reduce emissions to a greater extent than the presented total target, because for small-capacity ships (a capacity below 400), fishing vessels, and specialized vessels, it will be difficult to achieve proportional indicators or it will be outside of the regulations. For example, the most carbon-polluting cargo shippers in 2022 were the following: MSC—10.5 million t CO₂, CMA CGM—5.4 million t CO₂, and Maersk—5.3 million t CO₂. Whereas the most polluting cruise companies in 2022 were the following: Carnival—2.5 million CO₂ t, MSC Cruises—1.4 million CO₂ t, and Royal Caribbean International—0.8 million t CO₂ [15].

Levels of ambition directing the 2023 IMO GHG Strategy are as follows [3]:

- Carbon intensity of the ship to decline through further improvement of the energy efficiency for new ships (these methods have been used for 50 years and their possibilities have essentially been exhausted);
- Carbon intensity for international shipping to decline (by using fuels considered more ecological, e.g., biofuels);
- Other targets to be achieved by 2050 were given earlier.

A significant barrier to the transition to alternative and renewable fuels is the distribution system and availability of the bunker network, or essentially its scarcity [13,14]. As a result, depending on the availability of fuel, ships may be bunkered locally in port shipping, coastal shipping, or within the ship's autonomy radius and the port (harbor roadstead)—the bunkering site. The first important step towards the decarbonization of shipping was the decision of shipowners of large container ships to switch to dual-fuel engines, with the option of long-term operation on liquefied natural gas (LNG). Currently, it is a fuel of fossil origin, but with limited gas leaks, CO₂ emissions are reduced by up to 23%. Technologies for producing synthetic LNG are energy-intensive and, as a result, do not still solve the problem of renewable energy. Actions have been taken to power engines with bio-methanol. This is a much better solution, allowing us to meet the requirements related to emission limits and, at the same time, being future-proof, enabling ships to be operated for many years until 2050. A similar effect can be achieved by switching to fueling the engines with ammonia. However, there remains the problem of the technology for obtaining ammonia, the production of which should use electricity generated from renewable sources [14]. One of the seriously considered proposals is the construction of ammonia storage facilities, produced at a time when there is a problem of surpluses in electricity production. Another considered option is the construction of hydrogen storage facilities near large wind or photovoltaic farms. An important problem is to obtain a high

energy recovery coefficient as the ratio of the energy obtained in end devices to the amount of primary energy used in the production of a given storage medium. In this way, it will be possible to enter the era of renewable fuels, including hydrogen.

Due to the dominant share of fuel costs in ship operation, the shipowner's decisions regarding adapting the ship's power plant to burn a different type of fuel must be balanced, and the assessment of the financial consequences will be a decisive factor when analyzing the selection of the optimal type of fuel.

4. Possible Additional Financial Costs and Environmental Losses

IMO regulations on international shipping regarding carbon dioxide emission limits from maritime transport impose an obligation on shipowners to meet them in order to continue operating their ships (there is a risk of their ships being scrapped). A direct reduction in GHG emissions by reducing fuel consumption as a result of increasing the overall efficiency of engines and optimizing the selection of the number of operating engines and their loads does not allow for meeting these requirements. Opportunities to increase overall propulsion efficiency have already been exploited. The subsequent improvement may be very small, perhaps a few percent. Reducing hull resistance can have a similar effect. Optimizing the cruise route means savings of 1–3%. It is no longer possible to achieve a reduction in fuel consumption by another 10–30% this way. The only option is to change the type of fuel burned to one currently considered more ecological (biofuels), especially those without carbon in the molecule (ammonia and hydrogen) [16,17]. Changing the type of marine fuel requires adapting the fuel system and engine. The use of fuel with similar density and calorific value and similar combustion process parameters requires slight changes in the fuel system (e.g., for synthetic hydrocarbon fuels). Unfortunately, the trace production of synthetic fuels, considered ecological, creates a significant barrier due to lack of availability and high prices. Bio-methanol may be a transition fuel until around 2040. The role of green ammonia will significantly increase if investments in ammonia synthesis are completed, increasing its production by 2030 at least tenfold, while reducing the price several times. Moreover, it is estimated that the technological processes of producing these fuels generate a significant carbon trace. Despite fluctuations in the price of marine fossil fuels (Figure 2), they remain competitive with the alternative fuels considered. Even after the introduction of emission fees in European Union ports (EU ETS), which will increase fuel costs by approximately 50%, this situation will not change significantly.

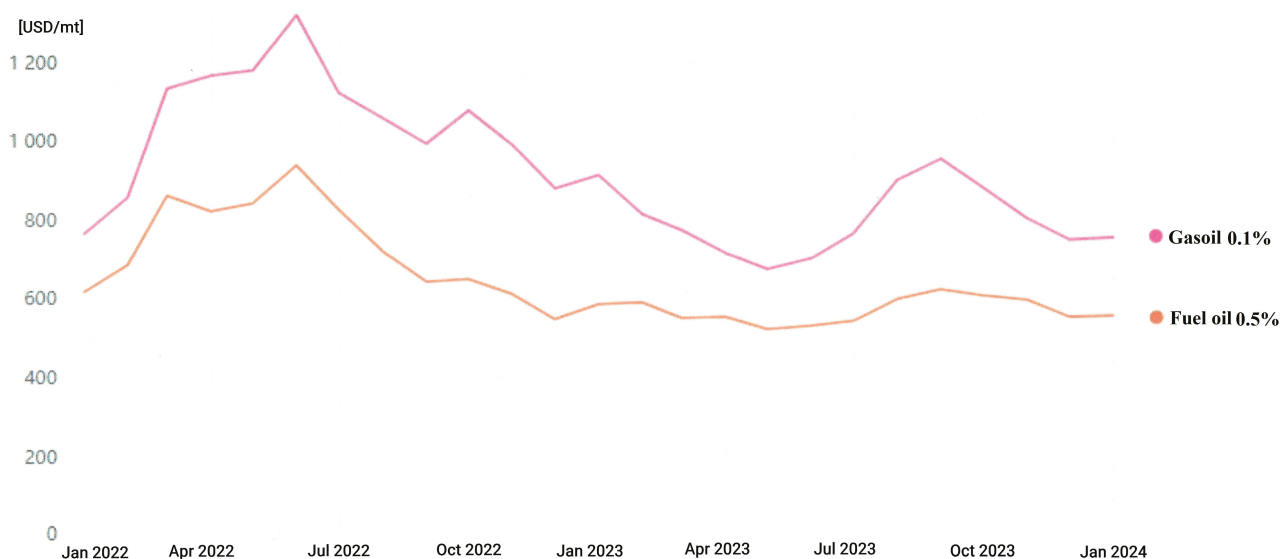


Figure 2. The price of marine fossil fuels in 2022–2024 [on base DNV Argus].

Figure 3 shows the costs of generating 1 kWh of electricity in SOFC fuel cells for various types of fuel [18]. The list does not include the costs of fuel storage. For liquefied

hydrogen, these costs are significant, approximately 15–100 times higher than for other fuels, and at the same time, they generate higher costs (20–50 times higher) than subsequent energy conversion [18]. Similar costs will occur using modern marine diesel engines.

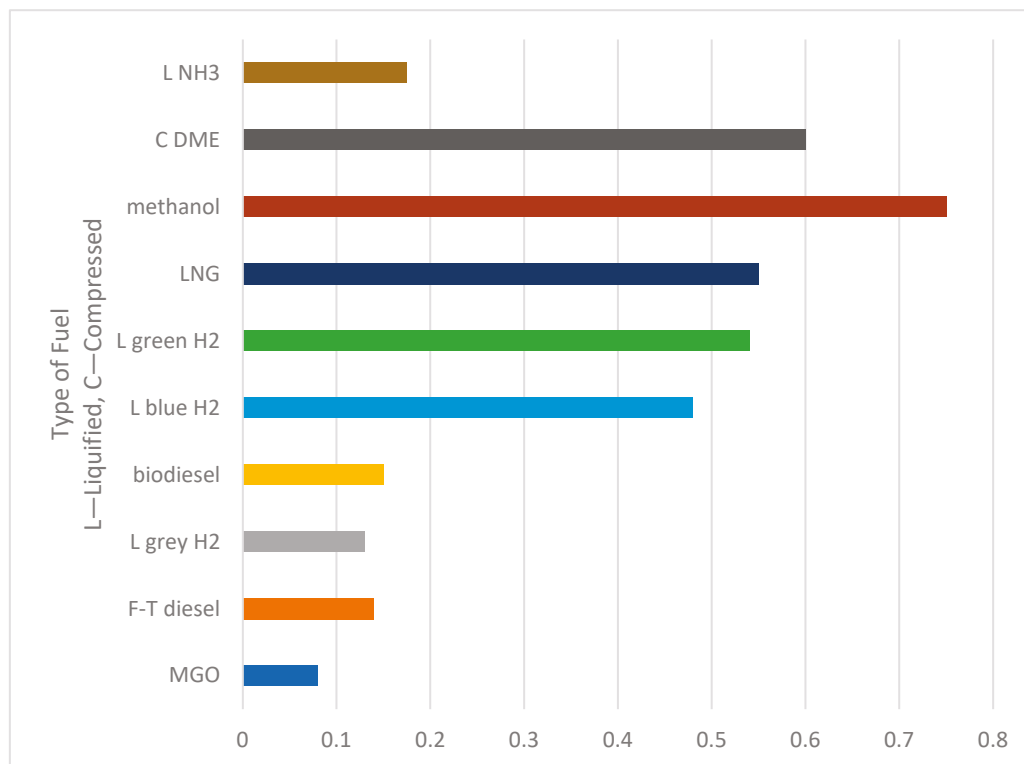


Figure 3. The cost in EUR per kWh produced energy in SOFC depending on the type of fuel at 55% efficiency (on base [18]).

For comparison, Table 4 shows the direct costs of generating 1 MWh of energy from marine diesel engines powered by various fuels.

Table 4. Direct cost in USD of MWh output from marine diesel engines powered by various fuels at prices from 2022 to 2023 (on-board system CAPEX not included) [own elaboration].

Type of Marine Fuel	Cost of 1 MWh in USD
Marine diesel oil (MDO)	80–100
Fossil liquefied natural gas (LNG)	60–150
Used cooking oil methyl ester (UCOME)	120–215
Bio-methanol	160–320
Bio-LNG (from biomass)	170–275
Bio-LNG (price forecast in 2035)	130–220
Liquid hydrogen (L-H2)	285–375
E-ammonia *	220–325
E-methanol *	240–320
E-LNG *	270–360

* electro-fuels.

Fossil fuels are by far the cheapest source of energy in maritime transport. Comparable costs of obtaining energy may only apply to fossil liquefied natural gas. This is related to the energy policy of many countries, which want to keep the prices of crude oil and fuels obtained from it low. This allows us to reduce the production costs of, among others, consumer goods, increasing demand and boosting the state's economy. The introduction of emission fees (essentially the purchase of greenhouse gas emission permits) in maritime

transport equalizes the costs of obtaining energy and favors the energy transformation. The introduction of Carbon Intensity Indicator (CII) requirements [19–23], due to the annual requirement to report CO₂ emission levels, will accelerate this process because shipowners will face a dilemma: make the necessary adaptations of the fuel system and engines themselves to ecological fuels or replace the ship with a new generation [19].

The characteristics of emissions of harmful substances into the atmosphere from the combustion of various ship fuels are presented in Table 5.

Table 5. Air pollutants and GHGs from marine fuel combustion [own elaboration].

Pollutant/Marine Fuel	HFO, MDO, MGO	LNG, Methane	Ammonia	Hydrogen
CO ₂ ¹	large quantities	large quantities 25% less	without a trace	without a trace
C _m H _n /VOC	trace amounts	trace amounts/slip	without a trace	without a trace
CO	trace amounts	trace amounts	without a trace	without a trace
NO _x	trace/needs SCR on EC area	Otto engines meet EC area without SCR	present/needs SCR on EC area	trace/probably needs SCR on EC area
SO _x	trace amounts	without a trace	without a trace	without a trace
PM	trace amounts	trace amounts	trace amounts	without a trace
Ammonia (catalyst)	low	without a trace	unknown	unknown
CH ₄ slip	not present	trace amounts	without a trace	without a trace
PAHs	trace amounts	trace amounts	without a trace	without a trace

¹ Fuel coefficients are presented in Table 3.

Taking into account the impact of fuel combustion products on the natural environment is important for assessing their suitability as marine fuels [24–26]. Efforts are being made to estimate product life cycle costs (LCCs) for marine fuels. An example of the actions taken is presented in Table 6.

Table 6. Life cycle equivalent (WtW) carbon dioxide (CO_{2EQ}) emissions and SO_x, NO_x, and PM emissions in kg per kWh using different alternative marine fuels (on base [27]).

Type of Marine Fuel	Pollutant			
	CO _{2EQ}	SO _x	NO _x	PM
MDO, SCR, 2-stroke	0.664	0.247×10^{-3}	1.24×10^{-3}	0.330×10^{-3}
MDO, SCR, 4-stroke	0.808	0.301×10^{-3}	1.51×10^{-3}	0.402×10^{-3}
Green NH ₃ , 5%MDO, SCR, 2-stroke	0.114	12.3×10^{-6}	1.02×10^{-3}	32.2×10^{-6}
Blue NH ₃ , 5%MDO, SCR, 2-stroke	0.418	12.3×10^{-6}	1.45×10^{-3}	37.1×10^{-6}
Green H ₂ , 1.5%MDO, 4-stroke	0.0503	4.67×10^{-6}	2.11×10^{-3}	14.7×10^{-6}
Blue H ₂ , 1.5%MDO, 4-stroke	0.397	4.67×10^{-6}	2.60×10^{-3}	20.2×10^{-6}

Switching to fuels such as ammonia and hydrogen brings a number of additional costs, but at the same time, a number of benefits compared to marine diesel oil, which are presented in [22]. The estimated environmental impacts associated with fuel switching in the WtW process are greater when using ammonia or hydrogen compared to MDO (by approximately 50%). Only for blue hydrogen during combustion in four-stroke engines is the estimated environmental impact factor (WtW) lower by about 30% [27].

So far, the assessment has been carried out by analyzing the environmental effects from the moment the fuel is in the ship's tank until the moment of gas emissions into the atmosphere after the combustion process (tank-to-wake—TtW). Currently, environmental impacts are analyzed from the point of extraction, processing, or production of fuel to the point at which the fuel reaches the ship's fuel tank (well-to-tank—WtT). The results of an environmental impact analysis that are the sum of both processes are considered to be more valuable (well-to-wake—WtW). In this case, alternative fuels, especially black hydrogen,

achieve much higher indicators, which is contrary to the assessment of their environmental friendliness. On the other hand, the “well-to-wake” (WtW) parameter of methanol is close to MDO, which means that bio-methanol will be preferred as a transition fuel [4].

5. The Influence of Ship Type and Size on the Choice of Transition Fuel or Hydrogen

The lack of suggestions and recommendations as to what type of marine fuel will be preferred in the coming years meant that shipowners did not decide to switch to low-emission fuels in 2023. The number and type of ships dominating a given shipowner’s fleet had the greatest impact on decisions regarding the fuel used on a ship, followed by its deadweight capacity, type of cargo transported, shipping line, etc. One of the options that has been under consideration for over 20 years is natural gas. For example, Table 7 shows the number of ships in operation and on order, powered by liquefied natural gas.

Table 7. Number of LNG-powered ships by type in operation or on order [4,25].

Type of Vessel	Number of Vessels in Operation	Number of Vessels on Order
Car/passenger vessels	43	7
Container ships	43	181
Crude oil tanker	49	40
Offshore supply vessels	36	1
Oil/chemical tankers	44	44
Tugs	22	16
Other	124	213
Total	361	502

For about 40 years, methane evaporating from the cargo space (boil-off gas, BOG) has been used as a fuel because the energy costs for re-liquefying it are too high. In the 1990s, BOG was burned in boilers, producing steam to power steam turbines. After dual-fuel engines entered the shipping market (after 2010), due to their greater overall efficiency, they dominated the LNG transport market. Currently, ship engines are being built mainly adapted to burn LNG, not only for LNG carriers, but during engine start-up, stoppage, and in emergency situations, typical liquid ship fuels are switched to. Only about 50 gas carriers carrying LPG as cargo use the LPG combustion option in dual-fuel engines. In the case of LNG carriers, whose fleet is much larger, this solution is used on 361 ships. The use of methane evaporation from the cargo space (BOG) requires moving the gas outside the tank and its further processing, e.g., use as fuel in the ship’s energetic systems (the simplest solution is combustion in steam boilers). Currently, due to the amount of BOG, dual-fuel engines are used, and the excess amount of gas not used as fuel is condensed again, even though it is uneconomical, but these are environmental protection requirements (methane must not be released into the atmosphere under normal ship operating conditions).

Due to the large share of container ships in the total GHG emissions from maritime transport, there has been interest in the use of dual-fuel ship engines that can burn natural gas for long periods of operation. Despite many benefits for the natural environment, the problem of the source of this gas remains. There should be a shift from the use of brown natural gas to synthetic gas, whose carbon trace in new technologies can be smaller and smaller using electricity from renewable sources.

Interest in methanol as a marine fuel, especially bio-methanol, has increased significantly, especially among container shipowners. The fleet of ships using methanol in 2022 was 25 ships, of which methanol was used on 22 chemical tankers, 1 ro-pax ship, and 1 tug. Of the 59 ships ordered, 47 are container ships, 4 offshore ships, 2 bulk carriers, and 1 cruise ship [25]. The ongoing changes would most affect ships that consume the largest amounts of fuel, hence the search for alternative fuels (bio-methanol will be recognized as an ecological fuel, thanks to which emission requirements will be met) [4].

However, there is a bottleneck related to the volume of current methanol production. The demand for methanol is not very high because it is produced approximately 75 million tons per year. For maritime transport, using it as a marine fuel, world production would have to increase more than 10 times. Natural gas is mainly used as a raw material for the production of methanol [9,28]. In 2023, only about 220,000 tons of bio-methanol were produced. The equivalent amount of energy, with marine fuel consumed in the amount of approximately 300 million tons, will be 630 million tons of methanol. In order to switch to methanol as a marine fuel, its production would have to be increased, which requires many investments in this field, but on the other hand, it would be possible within 10–20 years. If the fleet of ships using methanol as a fuel increases, its scarcity (unavailability) may constitute a significant barrier to its popularization. Moreover, the “well-to-wake” (WtW) parameter of methanol is similar to that of diesel fuel (MDO), which means that mainly bio-methanol should be used.

Successful tests of ammonia-fueled marine engines were carried out in 2020–2022. With the current design of the engine combustion chamber (too low compression ratio), it is required to use 5–15% of the pilot dose of diesel oil (MDO) to initiate and accelerate the combustion process. This gives hope for significant changes in the use of ecological fuel in maritime transport. The combustion of ammonia makes it possible to meet carbon dioxide emission limits by 2050, despite the additional combustion of light fuel. If a decision is made to switch to ammonia as a new marine fuel, many additional problems remain to be solved (storage, distribution network, and bunkering procedures), although this has been possible in the port of Singapore since 2023. However, the main problem will remain the most ecologically possible production of ammonia at reasonable production costs [28,29]. A good sign is the investments made in Australia and Southeast Asia in the production of green ammonia (from electricity from renewable sources) and blue ammonia production (USA and Canada), with some announcing intentions to provide ammonia as an energy source for the maritime sector. Renewable ammonia production is expected to reach 20 million tons in 2030 and as much as 540–1140 million tons in 2050 [30]. The demand for ammonia only in maritime transport, taking into account the equivalent amount of energy, in 2023 would be approximately 600–700 million tons.

Ammonia production will compete with hydrogen production as an energy storage source from renewable sources. The low volumetric energy density of hydrogen is a particularly significant disadvantage when used as a marine fuel. Due to the need to store large amounts of fuel (ship autonomy), this reduces the cargo space on these ships. The volumetric energy density of hydrogen is low and amounts to 5.14 GJ/m³ when stored in a compressed state at a pressure of 80 MPa (in order to equal the energy density of diesel oil, it should be compressed to a pressure of approximately 420 MPa) and slightly higher at 8.55 GJ/m³ when stored in a liquid state in cryogenic conditions at −253 °C. Moreover, hydrogen mixed with air creates a very wide flammability (and explosive) range, i.e., 4.1–75% (compared to 5–15% for methane), and its greenhouse effect potential (GWP) within 100 years is estimated at 11. The basic technology for obtaining hydrogen seems to be water electrolysis. Due to the high energy expenditure associated with compressing hydrogen or its condensation in order to increase its volumetric calorific value and the large losses associated with its storage, an alternative may be the processing of hydrogen into ammonia, the cost of which is several times lower in storage. In 2022, the number of ships powered by hydrogen as a fuel was six ships, i.e., three ro-paxes, one tug, one ro-ro, and one cruise ship. For comparison, the number of ships in international shipping exceeds 100,000. An increase in the fleet of ships whose main source of energy is hydrogen-powered fuel cells is expected [25]. This development will currently concern relatively small vessels sailing over short distances. It is estimated that, by 2030, the number of ships that use hydrogen as marine fuel will be well below 100, and their share in tonnage will be small (less than 0.1%) [4,25].

6. Problems to Overcome (Doubts) on the Way to the Hydrogen Era

There are many obstacles to the popularization of hydrogen as a primary energy source, including marine fuel. Due to its high chemical reactivity, hydrogen on Earth occurs primarily in chemical compounds. The most popular is water. It is essentially non-existent in gaseous form in the atmosphere. However, it may accompany deposits of certain raw materials. For example, in France, large deposits of white hydrogen associated with water have been discovered in the Massif Central. Hydrogen can be produced for industrial purposes using various technologies [31,32]. Depending on the production technology, hydrogen colors are distinguished:

- Black or brown—using black coal or lignite in the hydrogen-making process;
- White—is naturally occurring (in underground deposits);
- Yellow—is made through electrolysis using solar power;
- Pink—is generated through electrolysis powered by nuclear energy;
- Green—is made by using clean electricity from surplus renewable energy sources;
- Blue—is produced mainly from natural gas (steam reforming process);
- Turquoise—is made using a process called methane pyrolysis;
- Gray—is created from natural gas (without the use of carbon capture and storage).

In the process of black, brown, gray, and blue hydrogen production, in addition to consuming energy in the technological process, greenhouse gases (carbon dioxide, carbon monoxide, and black carbon) are also produced, which means that these technologies are not neutral to the natural environment. Currently, hydrogen is produced in over 90% by these methods. Other technologies are more environmentally friendly provided that electricity from renewable sources is used, especially excess energy that cannot be used on an ongoing basis.

6.1. Physical Properties of Selected Potential Marine Fuels

The physical properties of a substance are the basis for analyzing the possibility of its production, storage, and use. Table 8 shows selected physical parameters for three potential marine fuels. Fundamental differences occurring in the boiling point (especially when there are differences in these temperatures in relation to the ambient temperature, e.g., 15°C) and density are taken into account. This is important for the required thermal insulation, in order to reduce the amount of heat entering the liquid and, as a result, the amount of liquid converted into gas and the increase in pressure in the tank. Long-term storage of substances with a low boiling point requires large financial outlays on the construction of a thermal barrier and a system for removing gas outside the tank, re-liquefying it, or directly using it. The best situation is when the daily fuel demand equals or exceeds the daily rate of evaporation of the liquid in the tank.

Table 8. Comparison of physical parameters of selected potential marine fuels [own elaboration].

Parameter/Type of Fuel	Ammonia	Methane	Hydrogen
Molecular mass [kg/kmol]	17.031	16.043	2.016
Boiling point [°C; K] at 1 atm; T_{boiling}	−33.34; 239.81	−161.5; 111.6	−252.8; 20.27
T_{melting} Melting point [°C; K]	−77.7; 195.45	−182.5; 90.7	−259.2; 13.99
Critical temperature [°C; K]	132.4; 405.5	−82.59; 190.56	−243.8; 32.9
Medium specific heat [kJ/kgK] liquid, c_p	4.45	35.8	14.29
Density at boiling point [kg/m ³] liquid; gas	681.9; 0.86	422.8; 0.717	71; 0.09
R Heat of vaporization [kJ/kg]	1371.2	510	446.4
$\Delta T = T_{\text{amb}} - T_{\text{boiling}}$ [°C; K]	48.34	176.55	267.8
$\Delta T = T_{\text{boiling}} - T_{\text{melting}}$ [°C; K]	44.36	21	6.4
$Q = R + c_p \times \Delta T$ [kJ/kg]	1586.3	6830.49	4273.26
Physical state at a pressure of 1MPa and a temperature of +15 °C; 288.15 K T_{amb}	liquid	gas	gas

The amount of heat flux entering a tank with a liquid at a lower temperature than the surroundings depends on the following:

$$Q = k \times S \times \Delta T \quad [\text{kW}] \quad (1)$$

$$\frac{Q}{V} = k \times \left(\frac{S}{V} \right) \times \Delta T \quad \left[\frac{\text{kW}}{\text{m}^3} \right], \quad (2)$$

where

Q —the amount of heat flux entering a tank [kW];

k —heat transfer coefficient $\left[\frac{\text{kW}}{\text{K m}^2} \right]$;

S —the external surface of the tank $[\text{m}^2]$;

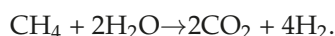
V —tank capacity (amount of liquid in the tank) $[\text{m}^3]$;

ΔT —temperature difference (ambient and liquid in the tank) [K].

Equation (2) shows that the daily relative evaporation rate can be reduced by building a tank with a larger volume, with the same heat transfer coefficient and temperature difference. By increasing the volume of the tank, its volume increases faster than the external surface. The greater the temperature difference, the greater the heat flow penetrating the tank. For liquefied hydrogen, this value is approximately six times higher than for ammonia.

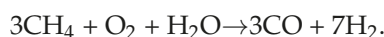
6.2. Methods of Hydrogen Production

Hydrogen can be produced in many chemical and electrochemical processes [33, 34]. Industrial-scale production requires technologies that are simple methods that use the least amount of energy possible. The steam reforming of natural gas is the most universal method. After removing contaminants from natural gas, it is exposed to steam at a temperature of 900 °C in the presence of a nickel-based catalyst (the method is known as Steam Methane Reformation—SMR). The overall reaction of the process is



The main disadvantage of this process is the emission of approximately 9 kg $\text{CO}_{2\text{eq}}$ per kg H_2 . If a carbon capture system (CCS) with an efficiency of 80–90% is additionally used, carbon dioxide emissions drop to approximately 1 kg CO_2 .

Partial oxidation and autothermal reforming (ATR) are other routes to produce hydrogen. This is a more efficient and compact reformer. Carbon monoxide and dioxide (after oxidation) generated in the production process must be captured by CCS and stored in a geological repository. The overall reaction of the process is



The production of greener hydrogen requires much higher investment costs than technologies based on its production from methane or by the gasification process of hard coal or lignite [33]. The share of green hydrogen in global production is approximately 4%. The basic technology for obtaining greener hydrogen is water electrolysis. It is necessary to develop and search for new zero-emission technologies.

6.3. Comparison of Storage Parameters for Ammonia, Methane, and Hydrogen

Hydrogen production and its current consumption at the point of production are very rare. As a result, there is a need to store hydrogen and transport it to its destination. This requires the construction of appropriate tanks for its storage and tank cars for transport or a network of pipelines for transmission. Due to the unfavorable physical parameters of hydrogen, it can be stored in two variants: liquefied or compressed. Table 9 compares the storage parameters of hydrogen, ammonia, and methane.

Table 9. Comparison of energy parameters of selected potential marine fuels [own elaboration].

Type of Fuel/Energy Parameter	Lower Calorific Value [MJ/kg]	Volumetric Energy Density [GJ/m ³]	Tank Volume Increase Factor for an Equivalent Amount of Energy ¹ (for MGO $\epsilon = 1$)	Daily Evaporation [%]
Marine gas oil (MGO)	42.7	36.6	1	0
Liquid ammonia	18.6	12.7	3	0–0.1
Liquid methane	50	23.4	1.6	0.1–1
Liquid hydrogen	120	8.5	12	1–3
Compressed hydrogen (70 MPa)	120	7.5	14	0

¹ without taking into account the increase in volume due to thermal insulation.

Fluid storage is possible in gaseous or liquid form. Due to significant differences (evaporation ratio for ammonia is 900, for methane 660, and for hydrogen 848) between the density of liquid and gas under normal conditions, the liquid state is preferred. This requires keeping the storage temperature below the critical temperature, and preferably at the boiling point. Due to the difficulties and costs of storing liquefied and compressed hydrogen, it can be processed into ammonia, the long-term storage of which is not a significant problem and does not cause high costs. This possibility should be considered, especially when marine engines adapted to burn ammonia are already available, and in some ports, it is possible to bunker it [27]. Ammonia may be a transition fuel until new competitive zero-emission hydrogen technologies are developed.

7. Analysis of the Ongoing Transformation Processes to Ecological Marine Fuels—Discussion

Including additional maritime transport charges (taxes) in the EU ETS may significantly increase costs. In 2022, the price of CO₂ emissions ranged from EUR 70 to 100 EUR/ton. With emissions of 3.12 tons of CO₂ per ton of HFO, this will increase the cost of fuel by approximately EUR 230–300. The cost of emissions will be an increase in fuel costs in ship operation by 30–50%, taking into account indirect costs which will be approximately 50%.

This is a proposal from the European Commission. The deadline for the implementation of the EU ETS depends on the results of negotiations between the Commission, the European Parliament, and the Council. It was planned to start billing in 2024, and these regulations will probably come into force starting from 2025 and may apply to large ships, over 5000 GT. Firstly, the amounts of fuel used in EU waters should be reported, and previously purchased CO₂ emission permits should be canceled. The obligation to pay emission fees applies to ships calling at EU ports. This may make maritime transport in EU ports less attractive (for economic reasons) and may increase the attractiveness of calling at ports outside the EU, with goods then delivered by land to EU countries. The introduction of additional fees is a big challenge for shipowners who will try to mitigate the effects of this process [4].

The aim of the introduced regulations is to reduce GHG emissions in EU maritime areas. The introduced fees will result in accelerated changes towards zero-emission fuels or fuels considered ecological, thanks to which CO₂ emissions from these biofuels will not be subject to fees. There are still too many unknowns at the moment. Shipowners are waiting for the final decisions of the EU administration. There is a risk that this may be a unilateral EU decision, without taking into account the opinions of shipowners, the International Maritime Organization, etc.

As of 2022, the number of ships in operation and ordered that do not use fossil fuels as marine fuel is presented in Table 10.

Table 10. Number of ships in operation and on order using non-fossil fuels ¹ [4,25].

Number of Vessels	Hydrogen	Methanol	LPG	LNG
In operation	6	25	51	361
Ordered ships by 2026	19	59	78	502
Total	25	84	129	863

¹ Biofuels are FAME, HVO, SVO, DME, F-T diesel, liquefied biogas (LBG), upgraded pyrolysis oil, and more.

Competition in the shipping market meant that large players in this market (owners of container ships, tankers, and car carriers) had to be the first to decide to switch to alternative fuels. This resulted in the adaptation of engines to burn LNG (dual-fuel diesel engine, DFD), even though it basically comes from natural gas deposits. Table 11 shows the number of ships in operation and on order, which use LNG as the basic fuel. There is a significant increase in orders for these types of ships. Further developmental trends depend on the recognition by the IMO and the EU Parliament of the color assigned to LNG due to its source, origin, and production technology.

Table 11. Number of vessels in service and on order using LNG as basic fuel [11].

Type of Vessel	Number of Vessels in Operation	Number of Vessels on Order
Cruisers	13	26
Ro-ro and ro-pax	32	16
Tanker	100	92
Container vessels	43	175
Car carriers	10	119
Bulk	18	50

Marine fuels considered as transient are produced mainly using electricity, and their production will have a significant share of fossil fuels as a primary energy source. There is a need for far-reaching changes in production processes, especially the storage of excess electricity on land and at sea so that the production of new-generation marine fuels can be emission-free. Another significant problem in the transition to green (or temporarily to blue) fuels is their availability for the shipping market. Attention should be paid to the development and acceleration of processes taking place in the energy sector on land. The changes taking place on land will force the acceleration of processes taking place in maritime transport and vice versa; what is happening with sea transport has a strong connection with what is happening onshore. It should be expected that the processes of changing primary energy sources in the production of electricity and new-generation fuels will occur faster at sea than onshore.

The ongoing changes in the choice of marine fuels and forecasts for the future can be tracked in many studies and scientific publications [7]. The possibilities of using fuel cells, despite significant progress, are currently insufficient in terms of power for propulsion and the demand for electricity [35]. On the other hand, technologies for capturing carbon dioxide from exhaust gases from ship engines make it possible to temporarily meet the emission reduction requirements (Carbon Intensity Indicator—CII) [19,36], but ultimately, these actions are insufficient. With this method, it is impossible to meet the “Fit for 55” requirements.

8. Conclusions

Already after the first fuel crisis in 1973–1974, the share of fuel costs in ship operations became significant. This was one of the main reasons for moving away from turbo-steam propulsion in ships to diesel engines. To this day, the main barrier to the development of maritime transport is fuel costs. The actions taken are always aimed at minimizing the ship’s operating costs, especially fuel.

The requirements to reduce GHG emissions from maritime transport force the shift to transitional fuels and, ultimately, to zero-emission fuels. The current price of production, storage, transport, and distribution of biofuels, transition fuels, ammonia, and hydrogen is much higher than fossil fuels. A system of emission fees (EU ETS) (a form of tax) has been introduced in EU countries to accelerate the transformation of marine fuels, which generates additional costs when using fossil fuels.

A ban on subsidies (public money) for maritime transport by countries will slow down the processes of change. The flag state of the ship makes independent decisions

on many matters that have not been determined by international regulations. One such situation is the recognition of a new type of fuel as ecological. At the same time, there may be pressure from the European Commission and the International Maritime Organization. Their assessment of the changes taking place may force a change in the decision of the flag state.

This article attempts to analyze the ongoing changes in the fuel market in maritime transport on the way to achieving the threshold of climate neutrality with this form of transport. A number of hopes related to this were indicated, but also so were obstacles that may slow down this process.

In 2024, interest in bio-methanol has increased significantly. The actions taken to increase its production may reach the threshold of approximately 30–60 million tons for maritime transport purposes in 2030. This is approximately 5–10% of the energy demand in this transport. Significant changes may concern the use of ammonia, especially in the green version. Investments made in Australia and Southeast Asia may achieve a production capacity of 60–100 million tons, which may constitute 10–15% of energy demand in maritime transport. This represents a significant breakthrough, but not yet a green revolution. A significant increase in the share of hydrogen as a marine fuel is unlikely to occur before 2040. As a result, the green revolution in maritime transport will be extended in time.

The process of transformation of marine fuels, still hardly noticeable in 2022, accelerated in 2023. Investments in the construction of low-emission fuel production infrastructure will result in a significant increase in the production of green hydrogen and, above all, green ammonia, a decrease in their prices, and an increase in interest in their use. Significant development is expected in the coming years, which will result in an increase in the share of renewable fuels in the marine fuel market. There is a need to provide practical solutions to remain competitive and compliant, and reduce risk in a rapidly changing world.

Author Contributions: Conceptualization, J.H. and A.L.; methodology, J.H.; validation, J.H., investigation, J.H. and A.L.; resources, J.H., data curation, J.H.; writing—original draft preparation, J.H.; writing—review and editing, J.H.; visualization, J.H. and A.L.; supervision, J.H.; funding acquisition, J.H. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding author.

Acknowledgments: The authors want to express sincere thanks to all the authors of the references.

Conflicts of Interest: The authors declare no conflicts of interest.

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Article

Dielectric Constant Predictions for Jet-Range Hydrocarbons: Evaluating the Clausius–Mossotti Relation and Correcting for Molecular Dipole Moments

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Abstract: The dielectric constant of aviation turbine fuel is leveraged by aircraft fuel quantity indicator systems (FQISs) using the Clausius–Mossotti relation, which assumes no significant dipole moments. For fossil-derived jet fuel containing relatively consistent fractions of polar aromatic molecules, this is appropriate. However, the interest in sustainable aviation fuels (SAFs) to reduce the carbon intensity of commercial aviation has brought attention to the uncertainty of the FQISs’ compatibility for low- or zero-aromatic fuels exhibiting dielectric constant values outside of the conventional Jet-A range. A dielectric constant model accounting for the varying dipole moments of both aromatic and non-aromatic jet-range hydrocarbons improves the community’s understanding of fuel composition on FQISs’ operability and provides a tool suitable for fuel performance property optimizations while maintaining compatibility with current aircraft systems. Here, the Clausius–Mossotti relation is first evaluated against a training dataset of 240 dielectric constant and density measurements (48 neat hydrocarbons each measured at five temperatures). Then, the dipole moment is calculated for each species of interest using open-source computational chemistry software, and a second-degree binomial regression is performed over the training data to correct for the error in the Clausius–Mossotti relation. The Clausius–Mossotti relation exhibited an R^2 value of 0.54, which increased to 0.92 when terms for the dipole correction were added to the model. The improved accuracy from this model establishes a computationally inexpensive framework for modeling theoretical fuel compositions that demonstrate improved performance characteristics (sooting propensity, thermal management, aircraft efficiency, etc.) while remaining within key limiting property constraints, such as the dielectric constant.

Keywords: sustainable aviation fuel (SAF); dielectric constant; property predictions; Clausius–Mossotti; computational chemistry; fuel-composition modeling

1. Introduction

Sustainable aviation fuel (SAF) has been identified as a leading prospect for meeting the decarbonization goals of commercial aviation [1]. To advance this technology, a joint effort by the United States’ Department of Energy, Department of Agriculture, Department of Transportation, and Federal Aviation Administration has put forth a number of domestic SAF production targets, including 3 billion gallons of SAF by 2030 and 35 billion by 2050 (10% and 100% of the United States’ projected fuel demand, respectively) [2]. Standing in the way of these goals are a number of obstacles, not the least of which is the compatibility of the current operational aircraft fleet with novel SAFs. Currently, in-flight fuel safety and performance characteristics are maintained by a maximum 50%v blending limit for SAF in

conventional petroleum-based fuels [3]. Ensuring full fleet compatibility past this limit is a critical step towards meeting the stated industry targets.

Many SAF compositions significantly vary from those of conventional petroleum jet fuel (Jet-A), and ongoing regulatory efforts are in place to ensure safe operation for aircraft utilizing SAFs. Due to the high cost of developing novel fuels, the community benefits from reliable predictive methods for fuel properties critical to engine and fuel system function. One of these properties, the dielectric constant, is central to an empirical version of the Clausius–Mossotti relation (C-M) with density used in capacitance-based fuel quantity indicator systems (FQISs) [4]. If this relationship for a prospective SAF is far outside of the expected fuel values used by the system, then a significant error in density can occur as a result, potentially leading to an incorrect indicated fuel mass on board the aircraft [5,6]. All of the currently approved (up to 50%v) low-aromatic SAFs would fall into this category if they were to be allowed up to 100%v [7,8].

The conventional fuel dielectric constant is highly dependent upon aromatic content. Existing SAF technologies that contain little-to-no aromatics, such as synthetic paraffinic kerosene (SPK) or cycloparaffinic kerosene (CPK), do not match the conventional fuel experience range for density as a function of the dielectric constant [9]. Both density and the relationship between density and the dielectric constant restrict, to varying degrees, the blend fraction of low-aromatic synthetic fuels, which are otherwise viewed favorably in terms of LHV, sooting propensity, and thermal stability [10].

An O-ring seal swell is an additional fuel property of concern to engine and aircraft manufacturers that is driven largely by aromatics in conventional fuels [11]. The inclusion of cycloalkanes at larger fractions is currently seen as a low-sooting alternative to induce adequate seal swell and density [12,13], but cannot be used to improve fuel gauging relative to the Jet-A range [7]. Understanding how to improve the viability of low- or zero-aromatic SAFs in the entirety of current aircraft systems requires accurate prediction methods for the properties of aromatic species and potential substitutes, namely certain cycloalkanes.

Here, the dielectric constant is predicted using a two-part model. First, QSPR polarizability predictions from Wang et al. [14] and density measurements are applied to the theoretical version of the Clausius–Mossotti relation, which assumes no permanent molecular dipole moments [15,16], to demonstrate its efficacy in jet fuel applications. Second, the permanent dipole moments of 240 molecules are calculated from first principles and are used as an independent variable in a second-degree binomial regression to predict the difference between the empirical dielectric constant data of Yang et al. [7] and the Clausius–Mossotti dielectric calculation. Adding the terms of this regression to the theoretical Clausius–Mossotti relation results in a new, computationally inexpensive dielectric constant prediction method that, when used in tandem with the blending rules verified by Yang et al. [7], can be easily implemented into fuel-composition optimizations to effectively forecast fuels that will maintain compatibility with current aircraft fuel systems, including FQISs, while exhibiting advantageous performance properties [10,17,18].

2. Materials and Methods

The 230 dielectric constant and density measurements (46 molecules at 10, 15, 20, 25, and 30 °C) found in Yang et al. [7] are utilized here along with 10 additional data points, 1,3,5-trimethylcyclohexane (TCI America, Portland, OR, USA, Purity >98.0%) and *cis*-1,3-dimethylcyclohexane (TCI America, Portland, OR, USA, Purity >99.0%), each at the same 5 temperatures as the previous study, for model development. The 10 added measurements can be found in Tables S1 and S2 of the Supplementary Information (SI). The temperatures considered here cover a moderate fraction of the expected range for an in-service jet fuel. However, historical jet fuel dielectric constant data [19,20] indicate a linear relationship on the Clausius–Mossotti plot for each fuel over a more comprehensive temperature range, −35 to 70 °C. Although currently unavailable, single-species dielectric constant data over a wider temperature range, which will improve modeling efforts, will be a focus of future experimental work. To provide further context towards the dipole

moments of jet-range hydrocarbons (C7 to C18), the permanent dipoles of 1827 molecules found in the NIST Web Thermo Tables Version 2-2012 [21] are computed and discussed.

Polarizability is a relatively easily predicted property, and multiple QSPR/QSAR models exist for this purpose [14,22]. Here, polarizability is predicted using Wang et al.'s Model 2E [14]. This is a simple QSPR model built with 420 experimental polarizability data points and has a coefficient of determination (R^2) equal to 0.9978. While the present study employs quantum mechanical calculations for the dipole moment, this empirical model was favored for predicting polarizability values. In addition to added simplicity, this choice is based on Wang et al.'s [14] comparison of Model 2E to quantum mechanical molecular polarizabilities, which showed superior performance of Model 2E relative to the experimental values.

The dipole moment represents the solution to the dipole operator with respect to the electronic wave function of the molecule at its ground electronic energy state [23]. These two steps, optimizing a molecule's atomic coordinates to its ground state and evaluating the wave function, are somewhat computationally expensive even for hydrocarbons. Additionally, molecules often have multiple electronic energy local minima, representing different electronic states for the same molecule. Accounting for all of these conformations requires additional iterations of an already time-consuming calculation.

Fortunately, easily accessible computational quantum chemistry software packages [24,25] exist for running calculations for the molecular dipole moment. With the species' isomeric SMILES string [26] and a random number generator 'seed' as inputs, RDKit Version 2023.09.05 [27] was used for obtaining initial atomic coordinates. Then, the Psi4 software package Version 1.9.1 [24] was employed to handle the quantum mechanical calculations using the Hartree–Fock method [23] and 6-31G** basis set [28,29]. To account for the presence of multiple local electronic energy minima, this computation was repeated with 100 different atomic coordinate seeds for each species in the database. The average of the 100 dipole moment calculations for each molecule was then stored for use in property predictions. Additionally, it is important to note that the basis set and level of theory used here are simplistic and computationally inexpensive relative to what can be found in work dedicated to determining optimal dipole calculation methods [23,30,31]. Improved dipole calculations would, in all likelihood, lead to improved dielectric predictions, at the cost of computational time not afforded to the work shown here.

As mentioned, the prediction method for the dielectric constant described here consists of two parts. The first part stems from the Clausius–Mossotti relation (Equation (1)) for the dielectric constant (ϵ_{CM}) with Avogadro's number (N_a), molar volume (V_m), and molecular polarizability (α) [15].

$$\frac{\epsilon_{CM}-1}{\epsilon_{CM}+2} = \frac{4\pi}{3} N_a \alpha V_m \quad (1)$$

Solving Equation (1) for the dielectric constant results in Equation (2).

$$\epsilon_{CM} = \frac{\frac{8\pi N_a \alpha}{3V_m} + 1}{1 - \frac{4\pi N_a \alpha}{3V_m}} \quad (2)$$

The original development of the Clausius–Mossotti relation was for applications to substances without a significant permanent dipole moment, such as noble gases or simple aliphatic hydrocarbons [15,16]. Hydrocarbons are generally considered non-polar due to the similar electronegativities of hydrogen and carbon (2.1 and 2.5, respectively). However, the hydrogen/carbon (H/C) ratio and structural differences between hydrocarbon classes (n-/iso-alkanes, cycloalkanes, aromatics, etc.) does introduce a small and varied dipole moment. This implies that Equation (2) may underrepresent the impact of dipole moments on the dielectric constant, or that, in other words, some hydrocarbons can have non-negligible permanent dipole moments. A more comprehensive overview of the Clausius–Mossotti relation in aviation applications can be found in the works of Yang et al. [7] and Kosir et al. [9].

Part two of the model presented here aims to address the potential impacts of the dipole moments of molecules. Using data for 48 neat molecules, the difference between the measured dielectric constant and the result of Equation (2) was calculated. A second-degree binomial regression was performed on this dataset with the dipole moment acting as the independent variable. Multiple forms of regression, with and without forcing the y-intercept term to zero, were considered. Ultimately, the second-degree binomial form with an intercept equal to zero was chosen for its high accuracy compared to the other forms considered and its semblance to the theoretical applications of dipole moments in dielectric constant calculations [32]. The results of the regression, including 5 k-fold cross-validation scores indicating no overfitting, can be found in Figure S1 and Table S3 of the SI. The dielectric constant prediction for a given species (ϵ) was computed according to Equation (3) as the sum of the Equation (2) result (ϵ_{CM}) and the output of this regression with the dipole moment (μ) as calculated by the method described above.

$$\epsilon_{CM,\mu} = \epsilon_{CM} + 0.9263\mu^2 + 0.2655\mu \quad (3)$$

3. Results and Discussion

3.1. Dipole Moment Calculation

Figure 1 shows the results of the dipole moment calculations for the NIST database of 1827 jet-range hydrocarbons. While confirmation of these values remains difficult due to the lack of available dipole moment data in the archival literature, this self-consistent dataset is convenient for understanding molecular dipole moments relative to hydrocarbon class and carbon number, as well as the variance of dipoles within these descriptors. It is suitable for relating Equation (2) model error to the calculated dipole moment; however, the coefficients of the regression are specific to the dipole calculation method presented in this article.

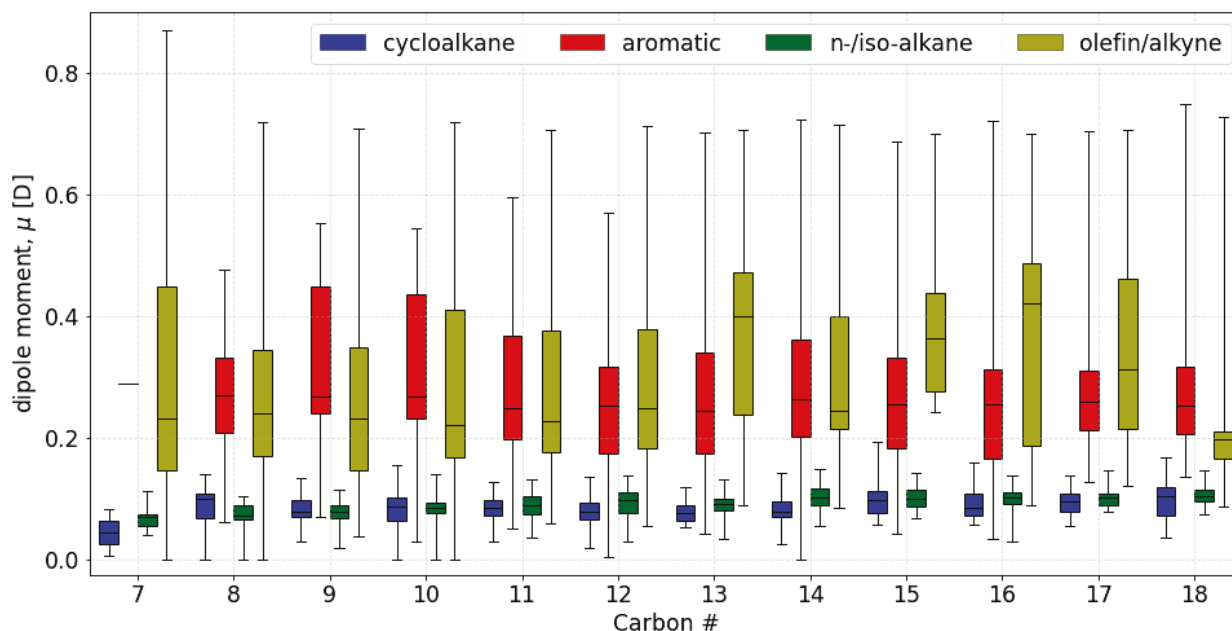


Figure 1. Calculated dipole moments sorted by carbon number and general hydrocarbon class. Cycloalkanes include mono, di, and tricycloalkanes. Aromatics include alkylbenzenes, di-aromatics, and cyclo-aromatics. Olefins include linear and branched alkenes, alkynes, and dienes.

The most polar hydrocarbons common to aviation turbine fuels, di-aromatics, have dipole moments well below 1 Debye (D), which is often considered non-polar within the context of heteroatom-containing hydrocarbons, as well as most inorganic compounds. For clarity, dipole moments are discussed here in terms that are relative to the ranges shown

in Figure 1. For example, a high dipole moment for a constituent fuel molecule would be 0.6 D.

As expected, *n*-, iso-, and cyclic alkanes all have a much lower mean dipole moment across all carbon numbers compared to unsaturates (aromatics, olefins, and alkynes). Unsaturated compounds also show a much higher variance within carbon number groups, with some species exhibiting lower dipole moments than many alkanes. This makes the identification of carbon-number trends among unsaturated compounds difficult. Alkanes show a slight increase in the dipole moment with higher carbon number, likely due to an increased opportunity for branching.

3.2. Model Performance

The dielectric constant measurements of 48 neat molecules at five temperatures were compared with values predicted from the Clausius–Mossotti relation (Equation (2)) using the measured density and QSPR-calculated polarizability [14] as inputs. As shown in Figure 2 and Table 1, the majority of *n*-, iso-, and cycloalkanes in the dataset show good agreement with this equation due to the relatively low dipole moments of most aliphatic hydrocarbons. However, the two additional cycloalkanes measured for this study, 1,3,5-trimethylcyclohexane and *cis*-1,3-dimethylcyclohexane, show a MARE nearly five times higher than the rest of the alkanes in the dataset and have the two largest dipole moments within the alkanes in the dataset. Since these molecules appear much nearer to the conventional fuel range compared to other alkanes, it is important to ensure that the dielectric constant can be correctly predicted for similar molecules. This is discussed further in Section 3.3. Additionally, for unsaturated molecules exhibiting higher dipole moments, Equation (2) consistently underestimated the dielectric constant leading to a poor overall R^2 of 0.54 for the Clausius–Mossotti relation. Given the importance of aromatics for meeting the conventional jet fuel range for the dielectric constant, and the potential impact of certain cycloalkanes as higher-performing substitutes for aromatics in synthetic fuels, Equation (2) alone is not sufficient for accurate predictions.

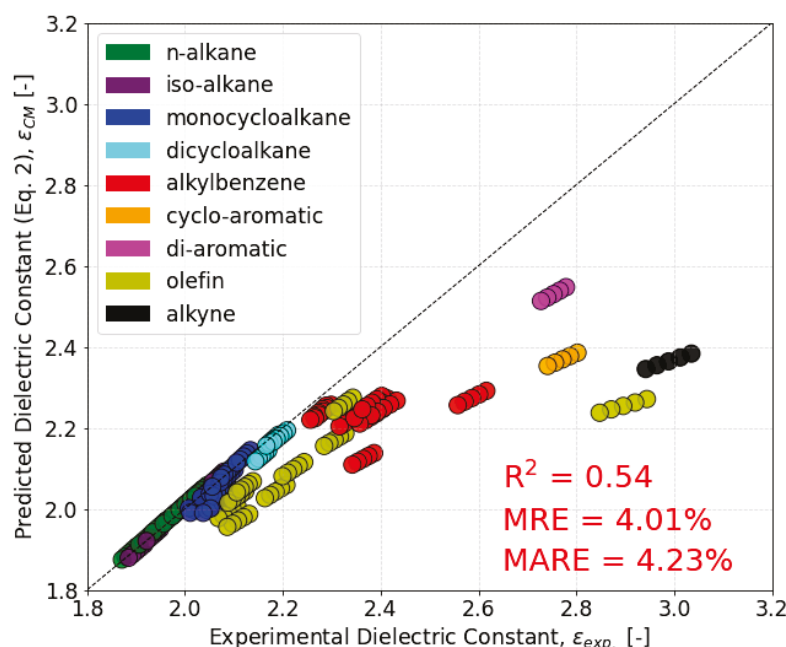
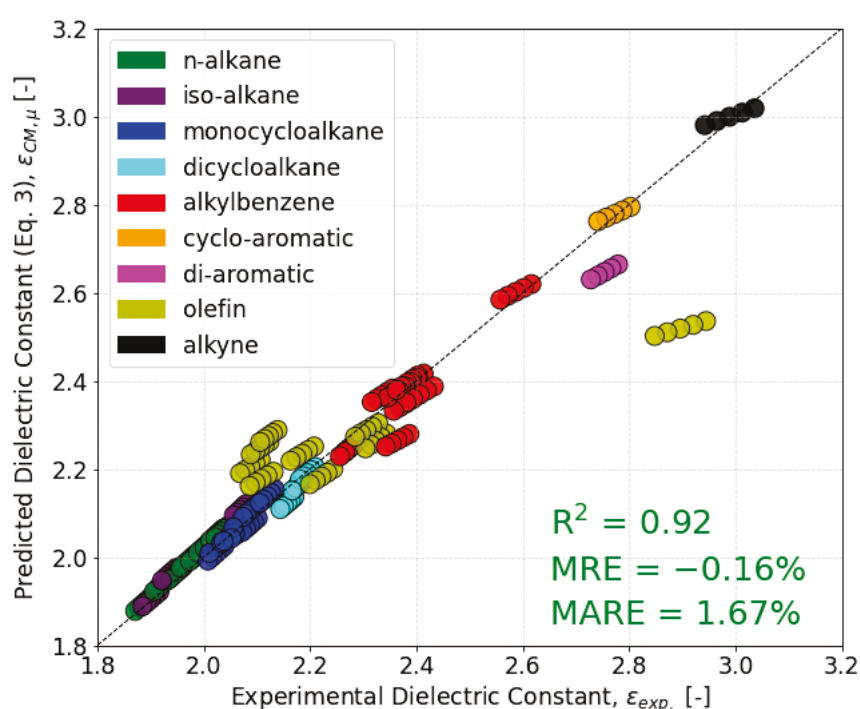


Figure 2. Unity plot for dielectric predictions via the Clausius–Mossotti relation (Equation (2)) with accuracy metrics for the entire dataset. R^2 = coefficient of determination, MRE = mean relative error, MARE = mean absolute relative error.

Table 1. Error metrics for the two dielectric constant models presented here.

HC Class	Clausius–Mossotti (Figure 2)		Dipole-Corrected Model (Figure 3)	
	MRE [%]	MARE [%]	MRE [%]	MARE [%]
N-alkane	−0.45	0.45	−0.97	0.98
Iso-alkane	−0.08	0.27	−1.16	1.16
Monocycloalkane	0.73	0.85	−0.02	0.43
Dicyclocycloalkane	0.78	0.78	0.82	0.82
Alkene	6.76	6.76	−0.77	4.80
Cyclo-aromatic	14.53	14.53	−0.24	0.35
Alkyne	20.89	20.89	−0.36	0.63
Di-aromatic	8.11	8.11	3.86	3.86
Alkylbenzene	5.98	5.98	0.61	1.27

**Figure 3.** Unity plot for dielectric predictions via the dipole-corrected Clausius–Mossotti model (Equation (3)) with accuracy metrics for the entire dataset.

The results for the dipole-corrected C-M model described by Equation (3) are shown in Figure 3 below. The Equation (3) predictions for alkanes remain mostly consistent with those from the standalone C-M relation, while the predictions for aromatics and olefins are most affected by the inclusion of a weighted dipole moment term. This is supported by Table 1, where the accuracy increases significantly for alkylbenzenes, cyclo-aromatics, and di-aromatics. The correction of these groups is the main contributor to the much-improved R^2 of 0.92 for the overall model.

Olefins did not show an obvious improvement with the dipole correction compared to the other hydrocarbon classes. While the MARE for these molecules slightly improved from 6.76% to 4.80% with the dipole moment correction, over half of the molecules see an overcorrection in the dielectric constant from the additional model term. This indicates that partial saturates, whether cyclic or linear, may have electronic or magnetic [9] properties that are beyond what is described by a singular dipole moment term. While this represents one limitation of the current work, it is of relatively low concern because jet fuel typically contains less than 2.5%v of olefins measured by ASTM D1319 [19,33].

Another impact of the dipole moment correction is the slight decrease in accuracy for n-alkanes, iso-alkanes, and dicycloalkanes. The change in accuracy between the two models

in Table 1 correlates with the dipole moment calculations found in Figure 1. Specifically, these molecules all have small, but nonzero, dipole moments. When applied to Equation (3), this confounds what is otherwise a highly accurate prediction from the C-M relation (Equation (2)) where no dipole moments are assumed. The error for these molecules in the dipole-corrected model still appears reasonably close to the unity line, although its impact on the relationship with density is more pronounced and will be discussed in Section 3.3.

Most of the monocycloalkanes behave similarly with regard to the dipole correction; however, the group at large sees a slight improvement in accuracy due to the much-improved predictions for 1,3,5-trimethylcyclohexane and *cis*-1,3-dimethylcyclohexane. These molecules exhibit higher polarity than the rest of the cycloalkanes, and thus are not well characterized by the Clausius–Mossotti model alone (Equation (2)). Because cycloalkanes are seen as desirable for improving the density and seal swell characteristics of SPK SAFs, which are almost entirely composed of *n*- and iso-alkanes, it is important to accurately capture the dielectric behavior of the entire spectrum of cycloalkanes. Additionally, the disproportionate influence of aromatic molecules on fuels meeting the Jet-A experience range for the dielectric constant implies that cycloalkanes exhibiting higher dipole moments could actually contribute positively towards SAFs meeting this property constraint.

3.3. Impacts on Model Application

This work provides a method for predicting the dielectric constant of aviation turbine fuel. However, as mentioned before, aircraft FQISs function under the assumption that the onboard fuel resembles the conventional fuel range on the Clausius–Mossotti plot. Using historical dielectric constant data for 172 fuels at 10°, 15°, 20°, 25°, and 30 °C from ARINC 611-1 and CRC 647 [19,20], the Jet-A experience range is shown in Figures 4 and 5 as a reference point to evaluate how the models presented here (Equations (2) and (3)) performed for each hydrocarbon class in a fuel-gauging application. The impact of hydrocarbon class in relation to the Clausius–Mossotti Jet-A range is discussed at length in previous work [7], so it will not be repeated. However, an important detail to point out in these plots is the close proximity in Figures 4b and 5b of the two additional cycloalkane molecules measured, 1,3,5-trimethylcyclohexane (thin diamonds) and *cis*-1,3-dimethylcyclohexane (stars), to the conventional fuel range.

Given the results shown in Figure 2, the results shown in Figure 4 are largely unsurprising. The placements of more polar hydrocarbons, aromatics (Figure 4c) and olefins (Figure 4d), are poorly predicted by the theoretical Clausius–Mossotti relation (Equation (2)). Barring the two additional cycloalkanes measured for this study, the cycloalkanes predictions from Equation (2) are found well below the Jet-A range, in general alignment with the experimental values. Figure 4a, on the other hand, demonstrates a consistent overprediction of the *n*-/iso-alkanes on the Clausius–Mossotti plot despite displaying low errors for Equation (2) predictions in Figure 1 and Table 1. Because these molecules have much lower density than the other hydrocarbon classes, errors in the dielectric constant are exacerbated on the Clausius–Mossotti plot. The small increase in dielectric error for *n*-/iso-alkanes in the dipole-corrected (Equation (3)) model further demonstrates this effect on the Clausius–Mossotti plot in Figure 5a. However, because these molecules display relatively little variance across species for FQIS implications (or O-ring seal swell, for that matter), they can be adequately represented in fuel-composition optimizations with the properties of a commercially available SPK or iso-paraffinic solvent.

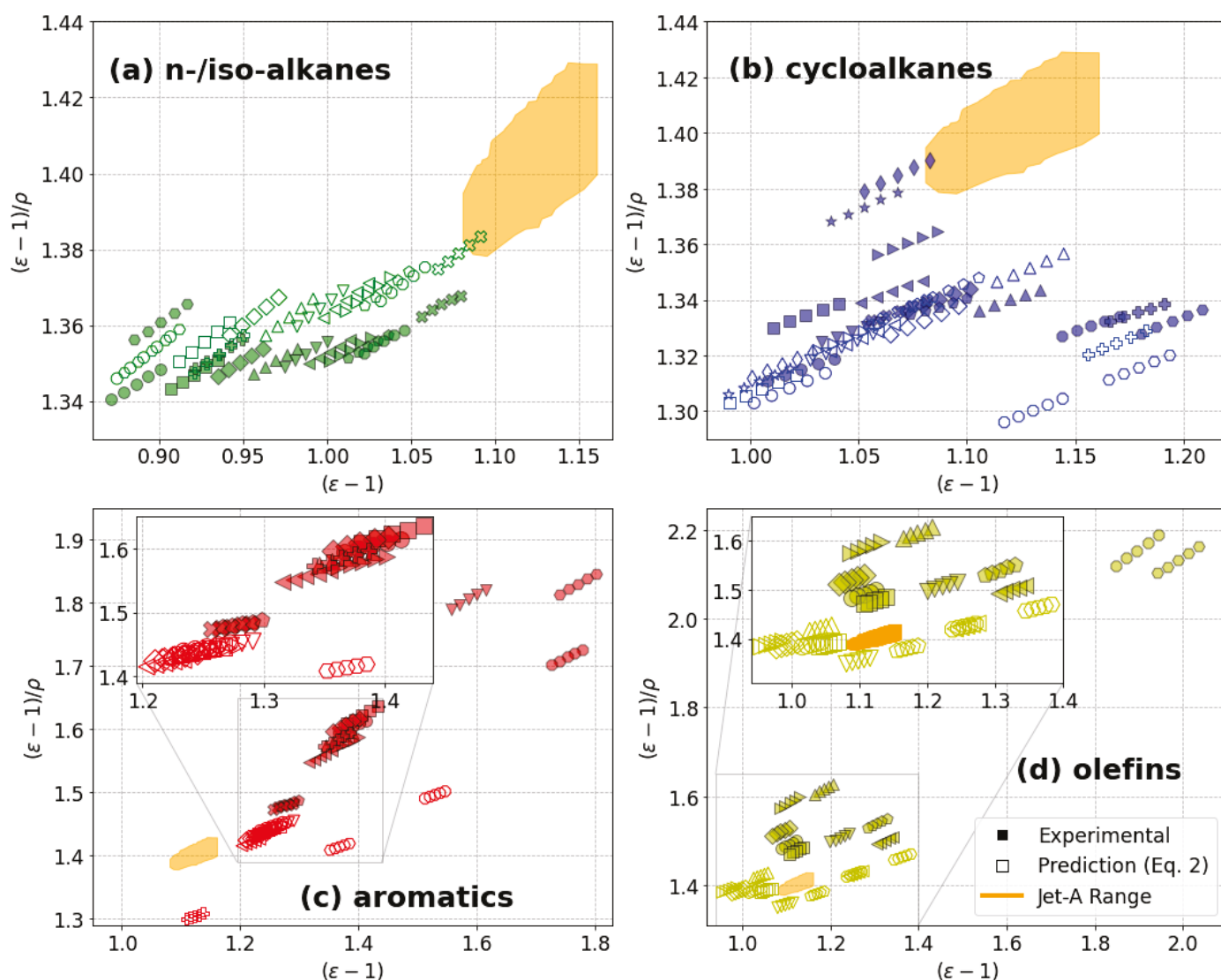


Figure 4. Clausius–Mossotti plots containing experimental results (closed symbols) and predictions from the Clausius–Mossotti relation shown in Equation (2) (open symbols). Each subplot (and color) focuses on one general hydrocarbon class: n-/iso-alkanes (a), cycloalkanes (b), aromatics (c), olefins, and alkynes (d). Each molecule is identified by a unique shape. The Jet-A experience range, based on ARINC and CRC historical data, is shown in orange.

Figure 5b–d show predictions more consistent with the experimental values for cycloalkanes and aromatics. The improved prediction capabilities for aromatics offer the opportunity for identifying the most desirable species for improving FQISs' compatibility while taking the sooting impacts of the molecule into consideration. Additionally, the improvement in accuracy for 1,3,5-trimethylcyclohexane (thin diamonds) and *cis*-1,3-dimethylcyclohexane (stars) indicate this method's potential to forecast the dielectric constant values for more polar cycloalkane species that may offer some benefit in reducing the need for aromatics in aviation fuel. The improvement in prediction accuracy for molecules near the Jet-A range comes at the cost of some cycloalkanes showing overpredictions on the y -axis of the Clausius–Mossotti plot. This underlines that there are other electromagnetic properties impacting the dielectric constant that are uncharacterized by this model. However, the range of species near the Jet-A range on the Clausius–Mossotti plot is fairly narrow, making experimental validation of these molecules for model applications much simpler than evaluating the entirety of jet-range hydrocarbons.

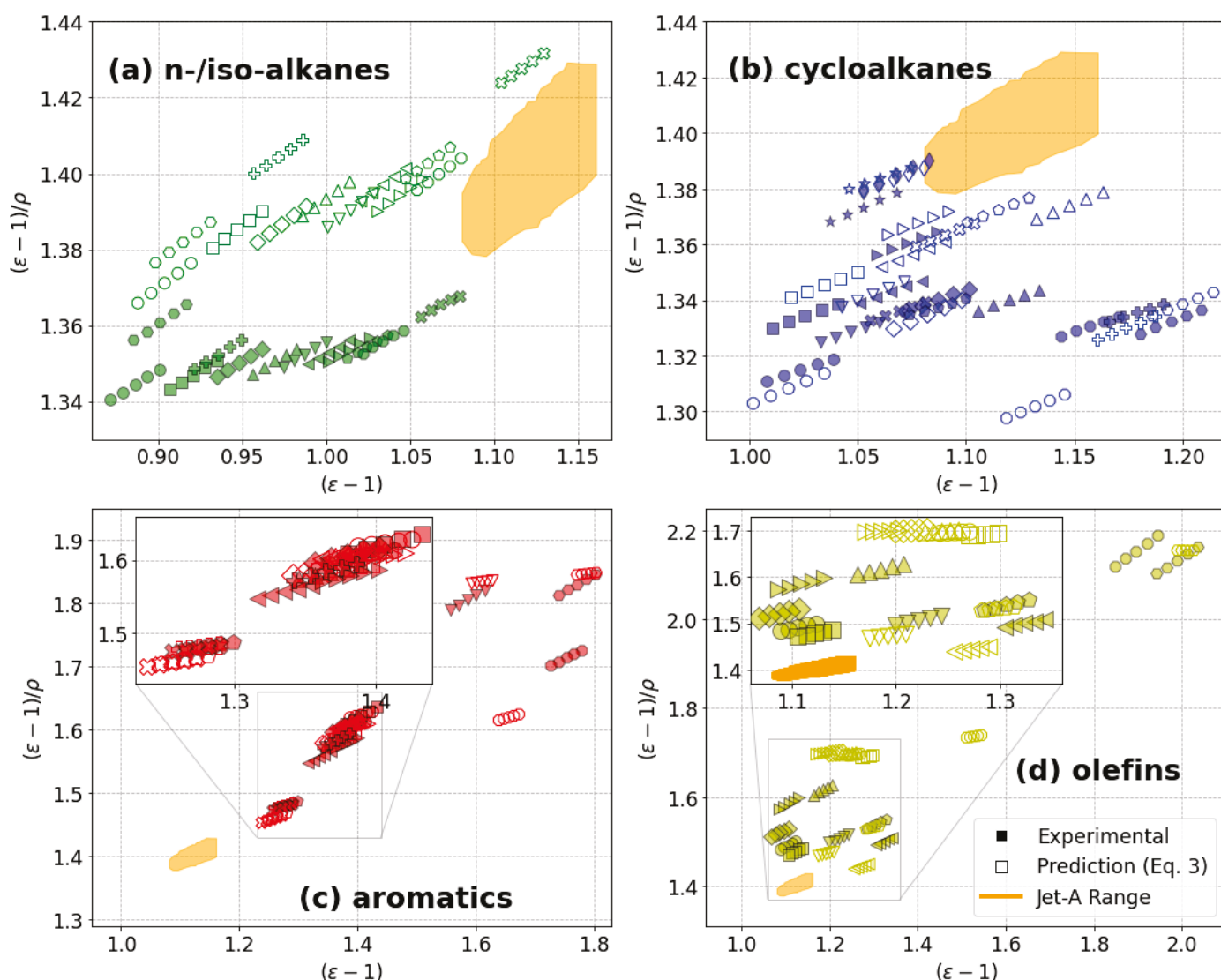


Figure 5. Clausius–Mossotti plots containing experimental results (closed symbols) and predictions from the dipole-corrected Clausius–Mossotti relation shown in Equation (3) (open symbols). Each subplot (and color) focuses on one general hydrocarbon class: n- and iso-alkanes (a), cycloalkanes (b), aromatics (c), olefins, and alkynes (d). Each molecule is identified by a unique shape. The Jet-A experience range, based on ARINC and CRC historical data, is shown in orange.

With this in mind, Figure 6b illustrates that certain cycloalkanes from the NIST database may positively contribute towards fulfilling the constraints of the Clausius–Mossotti Jet-A range when using the dipole-corrected model (Equation (3)) for dielectric constant prediction. Alternatively, Figure 6a shows that predictions made on the same database using only the Clausius–Mossotti relation (Equation (2)) significantly impact the solution space for modeling FQIS-compatible fuel compositions from this database.

While not insignificant, the applications of the dipole-corrected model presented here are limited to research or production efforts at low fuel readiness levels [34] seeking to evaluate fuel compositions in relation to the Jet-A range on the Clausius–Mossotti plot. This model does not sufficiently capture the temperature dependence of the dielectric constant, which is leveraged in aircraft FQISs in the form of the gauging slope and intercept [9]. A closer look at Figure 3 shows that the slope of the temperature series for many molecules is not consistent with the unity line. This is likely the result of some temperature dependency that has not been assessed for some of the model inputs, namely polarizability and the dipole moment. Although some work has been performed to show

the impact of temperature on the electronic properties of molecules [35,36], accurately calculating this dependency is beyond the scope of this work.

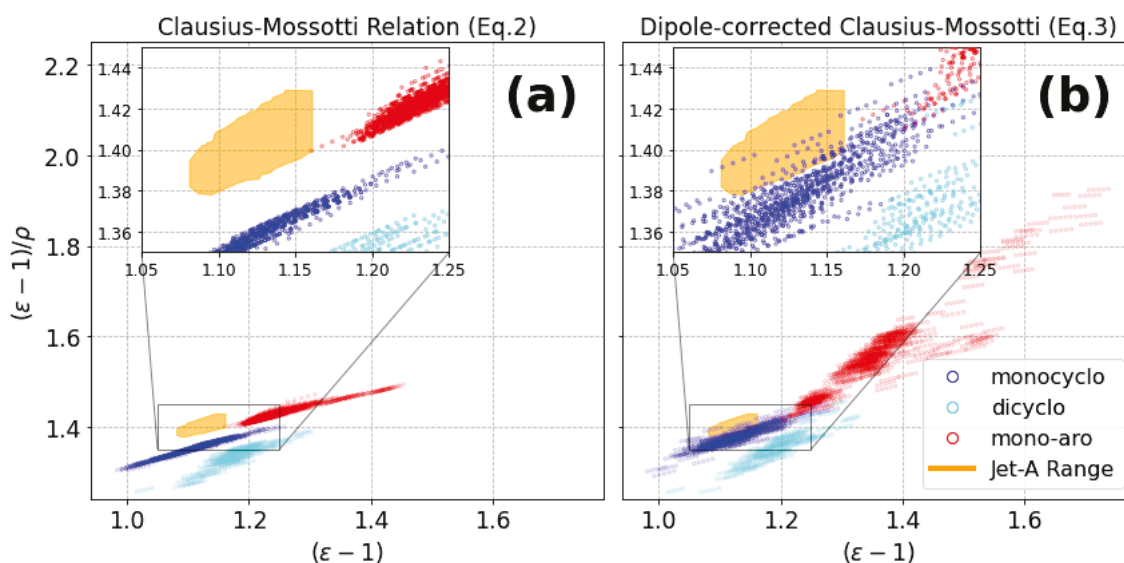


Figure 6. Clausius–Mossotti plot displaying predictions from (a) the Clausius–Mossotti relation (Equation (2)) and (b) the dipole-corrected model (Equation (3)) for the NIST database molecules of interest for blending with current SPK products (monocycloalkanes, dicycloalkanes, and monoaromatics). The Jet-A range is shown in orange as a reference point.

4. Conclusions

This work evaluated the Clausius–Mossotti relation (Equation (2)), which assumes negligible molecular dipole moments, for predicting the dielectric constant of aviation jet-range hydrocarbons and proposes Equation (3) as a more accurate prediction method using a simple correction for dipole moments calculated using open-source computational chemistry software. Both models (Equations (2) and (3)) were evaluated over a training dataset of density and dielectric constant measurements for 48 neat molecules at five temperatures each. The relatively high dipole moments of aromatic molecules led to poor prediction accuracy over the entirety of the dataset ($R^2 = 0.54$, $MRE = 4.01\%$, $MARE = 4.23\%$) when Equation (2) was used. With the addition of model terms accounting for the dipole moment, Equation (3) showed significantly improved error metrics ($R^2 = 0.92$, $MRE = -0.16\%$, $MARE = 1.67\%$) by more accurately capturing the behavior of aromatics and polar cycloalkane species. Both models showed low accuracy for olefins, which is of little concern due to their relatively low concentration in jet fuels. Predictions from both models had small error metrics for the dielectric constant values of n-/iso-alkanes, but presented exacerbated inaccuracies on the Clausius–Mossotti plot used in fuel-gauging applications, due to the low density of these molecules. More computationally intensive dipole moment calculations would likely improve these predictions and may be the subject of future work. Despite this, the authors suggest the current dipole-corrected model (Equation (3)) as appropriate for use in exploratory fuel-composition optimizations where the n-/iso-alkane fraction of the solutions can be represented with existing SPK products to highlight the influence of aromatics and cycloalkanes on fuel performance and operability properties, e.g., sooting propensity, energy density, volumetric density, elastomer O-ring seal swell, and dielectric constant-based FQISs, that are currently of high interest to the community.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/en17184700/s1>, Tables of dielectric constant and density measurements added to the dataset of Yang et al. [7] for use in model development (Tables S1 and S2).

Plot of regression performed to generate the dipole-correction term in Equation (3) (Figure S1). Cross-validation R^2 scores for dipole moment regression (Table S3).

Author Contributions: C.F.: conceptualization, formal analysis, investigation, methodology, validation, visualization, writing (original draft), and writing (review and editing). D.C.B.: data curation, software, and writing (review and editing). R.B.: formal analysis, supervision, and writing (review and editing). J.H.: conceptualization, resources, funding acquisition, and project administration. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the United States Federal Aviation Administration (FAA) Office of Environment and Energy through ASCENT, the FAA Center of Excellence for Alternative Jet Fuels and the Environment, Project 65 through FAA Awards Number 13-C-AJFE-WASU-035 (PI: Joshua Heyne) under the supervision of Ana Gabrielan, and Project 66 through FAA Award Number 13-C-AJFE-WASU-036 under the supervision of Bahman Habibzadeh, Ana Gabrielan, and Prem Lobo. Any opinions, findings, conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the FAA.

Data Availability Statement: Dielectric constant and density measurements for the two additional molecules measured for this study, 1,3,5-trimethylcyclohexane and cis-1,3-dimethylcyclohexane, can be found in the supporting material for this article. Readers are directed towards the work of Yang et al. [7] for the remaining 46 molecules used here. Molecular dipole moment data can be made available upon request.

Acknowledgments: The authors would also like to thank Harrison Yang of Washington State University for his assistance in collection of dielectric constant data and insights about the results.

Conflicts of Interest: The authors declare no conflicts of interest.

Nomenclature

α	Molecular polarizability.
ASTM	ASTM International.
C-M (or CM)	Clausius–Mossotti relation.
CPK	Cycloparaffinic kerosene.
D	Debye.
ϵ	Dielectric constant.
FQIS	Fuel quantity indicator system.
μ	Permanent dipole moment.
N_a	Avogadro’s number.
NIST	National Institute of Standards and Technology.
QSPR/QSAR	Quantitative structure property/activity relationship.
R^2	Coefficient of determination.
SAF	Sustainable aviation fuel.
SPK	Synthetic paraffinic kerosene
V_m	Molar volume.

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Article

Research and Analysis of Explosion-Proof Diesel Engine Performance Based on Different Exhaust Gas Cooling Systems

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Abstract: As stringent emission regulations and safety standards for explosion-proof diesel engines become more critical, the demand for efficient exhaust cooling systems has increased. Traditional cooling systems, typically relying on cooling and purification water tanks, have limitations in terms of safety, performance, and emissions control. To address these challenges, a novel dry exhaust gas cooling system was developed, incorporating a heat exchanger and exhaust dilution cooling device, replacing the conventional water-based cooling systems. This study explores the performance of the dry exhaust gas cooling system through a series of experiments including explosion-proof testing of the exhaust system, whole machine explosion-proof testing, exhaust temperature measurements, surface temperature evaluations, and exhaust gas composition analysis. The system's performance was compared to both wet and combined dry + wet exhaust gas cooling systems. Results showed that the dry exhaust cooling system maintained its explosion-proof integrity during all tests, with the highest exhaust temperature at 68.5 °C and a surface temperature of 130.8 °C—both of which comply with safety standards. Notably, the dry exhaust system also demonstrated improved power output and reduced fuel consumption by over 4% compared to the other systems. Furthermore, it significantly lowered harmful exhaust emissions, reducing CO, HC, NOX, and CO₂ levels by 55%, 71%, 68%, and 82%, respectively, when compared to the wet exhaust cooling system. In comparison to the dry + wet system, these reductions were even more pronounced—63%, 75%, 66%, and 94%, respectively. The findings suggest that the dry exhaust gas cooling system offers a safer, more efficient, and environmentally friendly alternative to conventional exhaust cooling systems in explosion-proof diesel engines.

Keywords: explosion-proof diesel engine; dry exhaust cooling system; explosion-proof design; exhaust emissions

1. Introduction

With the continuous development of the Chinese economy, modern mechanized mining in coal mines has been dramatically improved, and auxiliary transportation equipment in coal mines has become a vital component of the underground transportation system, undertaking tasks such as transporting personnel, materials, and equipment [1–3]. In China, explosion-proof diesel engines are generally designed and modified based on the

original engine's intake, exhaust, and cooling systems, making them flexible, safe, and cost-effective for later maintenance. They have become the coal mines' main power source for auxiliary transportation equipment [4].

Currently, the cooling systems of explosion-proof diesel engines used in China are all wet, while the explosion-proof diesel cooling systems used abroad are divided into dry and wet types. The wet exhaust cooling system design has been widely used, and researchers at home and overseas have also achieved many results. Fan Jiangpeng designed an exhaust purification technology scheme which can reduce the emission of exhaust pollutants while meeting the requirements of flame suppression and cooling during the experimental process [5]; Cai Yueyun and Li Kaixuan both conducted a comprehensive analysis and design of the explosion-proof diesel engine exhaust water tank [6,7], Li Baolin et al. conducted research and analysis on the explosion-proof diesel engine exhaust cooling and purification box, and modified it. Through experiments, it was shown that the improved water tank significantly reduced the smoke emissions [8]. Zhang Lei et al. designed a new type of four-element combined exhaust gas post-treatment system to address the severe exhaust pollution of explosion-proof diesel engines. The optimization parameters of key components and exhaust purification performance were studied through simulation and experimental research. The results showed that based on meeting the non-road national emission requirements, there was no significant impact on power and the economy [9]. Ferdinando designed a diesel engine exhaust purification control strategy based on a neural network prediction model to improve the exhaust purification efficiency of explosion-proof diesel engines. By predicting the particle size of diesel engine exhaust in real-time, the urea injection situation of SCR was adjusted to ensure the exhaust purification efficiency [10]. An SCR thermal management control strategy for transient cycle conditions was designed to improve the efficiency of SCR reduction reactions. It increases the exhaust gas temperature by controlling the amount of diesel exhaust treatment fluid, thereby improving the efficiency of the SCR reduction reaction [11]. Liu Xin et al. studied the absorption efficiency of exhaust particulate matter in explosion-proof diesel engine exhaust gas treatment water tanks under different water levels and operating conditions using laser example timers. They proposed suggestions through simulation experiments [12]. Zhang Siwan et al. used CFD simulation software to study the effects of smoke barriers, gas inlet velocity, initial liquid level height, and other factors on the performance of exhaust gas treatment tanks. They designed the optimal design and obtained results through experimental platforms. While meeting explosion-proof requirements, they significantly improved engine efficiency [13].

Although wet cooling systems with water tanks are widely used in explosion-proof diesel engines in China, according to the standard MT990-2006 "General Technical Conditions for Mining Explosion-proof Diesel Engines" for explosion-proof diesel engines, Article 4.10.1 stipulates that "before the exhaust gas of explosion-proof diesel engines is discharged, it should be cooled and purified by a water tank". In contrast, Article 4.6 of GB20800.3-2008 "General Rules for Explosion proof Technology of Reciprocating Internal Combustion Engines for Explosive Environments Part 3: Class I Internal Combustion Engines for Underground Mining Area Tunnels with Methane and/or Combustible Dust", which is equivalent to EN1834.2-2000 (EU Explosion-proof Diesel Engine Standard), stipulates that explosion-proof diesel engines can use exhaust flame arresters and spark arresters as two explosion-proof methods, and does not require the use of a cooled and purified water tank. Article 4.9 also specifies the technical requirements for dry and water-based spark arresters. The difference between domestic and international standards related to explosion-proof diesel engines has led to the requirement for imported explosion-proof diesel engines that have obtained the EU explosion-proof diesel engine certificate to be

equipped with a cooling and purification water tank when applying for use in China, resulting in functional redundancy and waste. At the same time, due to the large volume of the cooling and purification water tank and the need to equip it with a corresponding water replenishment tank, it is not conducive to the layout of emission after-treatment devices, making it an obstacle to the emission upgrade of explosion-proof diesel engines and increasing the burden and maintenance costs on workers.

Moreover, due to the fact that the wet cooling system has exhaust gas passing through a water washing tank, the exhaust resistance is increased, and the power performance of the diesel engine is reduced. Compared with the wet cooling system, using a dry exhaust gas cooling system to replace the cooling and purification water tank has become a direction for developing explosion-proof diesel engines in China. Compared to others, The research on dry cooling systems for explosion-proof diesel engines in China is very slow, and the research results include: Matsumoto Researchers have studied a dry exhaust after-treatment system consisting of a catalytic converter (DOC), a particulate filter (DPF), and a flame arrester [14]. Tian Wei et al. conducted data simulation of the jet dry exhaust pipe process of explosion-proof diesel engines using CFD simulation software and studied the influence of critical structural parameters on its performance, providing a basis for the structural improvement and optimization of jet dry exhaust pipes [15]. Wang Yuan proposed methods to improve the emissions of exhaust pollutants from explosion-proof diesel engines, including dry cooling, fuel injection electronic control system, EGR, and exhaust post-treatment [16]. Cavan M installed DPF+SCR on small non-road diesel engines, significantly controlling the emissions of significant pollutants PM and NOX from non-road diesel engines [17]; JOENSOO et al. developed a urea injection control strategy for SCR components in standard rail direct injection diesel engines, which improved the reduction rate of NOX [18]; FERDINANDO et al. developed a diesel engine exhaust purification control strategy based on a neural network prediction model, which adjusts the urea injection of SCR by predicting the particle size of diesel engine exhaust in real-time, thereby ensuring exhaust purification efficiency [10]; TAE et al. designed an SCR thermal management control strategy for transient cycle conditions, which increases the exhaust gas temperature by controlling the amount of diesel exhaust treatment fluid, ensuring the efficiency of SCR reduction reaction [11]. At present, mainstream research institutions and manufacturers at home and abroad mainly use engine purification technologies such as electronic fuel injection systems, boost intercoolers, and exhaust gas recirculation (EGR), as well as the three-way catalytic exhaust aftertreatment technology of “oxidation catalyst+particulate filter (DPF)+selective catalytic reduction (SCR)” to treat diesel engine exhaust pollutants [19,20]. The integration of explosion-proof engines in monorail cranes, essential for coal mine safety, benefits from advancements in speed control systems like MPC and fuzzy adaptive PID controllers (Hai Jiang et al., 2023) [21], while innovative piston designs and fuel injection strategies for ultra-low emissions could further enhance safety and performance in line with future emission regulations (Gabriele Di Blasio et al., 2023) [22].

This article analyzes and compares the explosion-proof performance, surface temperature, exhaust temperature, power, torque, fuel consumption rate, exhaust back pressure, and concentrations of CO, HC, NOX, and CO₂ in exhaust gases of explosion-proof diesel engines equipped with dry (dry exhaust gas cooling system), wet (cooling purification water tank), and dry + wet exhaust gas cooling systems based on current relevant standards. The performance and emission performance of explosion-proof diesel engines with different exhaust cooling systems are compared to determine whether they meet the standard requirements.

2. Model Selection of Explosion-Proof Diesel Engines with Different Exhaust Cooling Systems

2.1. Selection of Experimental Prototype

The explosion-proof diesel engine selected for this experiment is a 74.5 kW diesel engine produced by a particular company. The main technical parameters of the explosion-proof modified engine are shown in Table 1.

Table 1. Basic parameters of explosion-proof diesel engine.

Project	Parameter
Type	Straight, 4-cylinder, 4-stroke, water-cooled, turbocharged intake
Air intake method	Turbo
Number of cylinders $\times$ bore $\times$ stroke	$4 \times 105 \times 127$
Total piston displacement (L)	4.4
Compression ratio	18.2
Rated speed (r/min)	2200
Rated power (kW)	62
prototype	1104D-E44Tmodel
Electronic fuel injection	KXJ24BOSCH

Explosion-proof diesel engines of around 60 kW are widely used in coal mine auxiliary transportation systems for products such as 5-ton and below material transport vehicles, personnel transport vehicles, and small monorail cranes. They have a large loading capacity and are representative of explosion-proof diesel engines.

2.2. Explosion-Proof Design of Fuel Injection System

The source engine used in this experiment is equipped with the electronic high-pressure standard rail fuel injection system produced by BOSCH company. Compared with other fuel injection systems, it has the advantages of good fuel economy, good emission indicators, reliable electronic control work, fault diagnosis function, and fast response speed. After the explosion-proof diesel engine is upgraded to the non-road National III emission stage, it has become the primary type of fuel injection system for explosion-proof diesel engines. The explosion-proof transformation of the fuel injection system can be divided into aspects such as explosion-proof isolation of the electronic control ECU, intrinsic safety connection of sensors, explosion-proof transformation of the fuel injection solenoid valve and other actuators, mainly including the electronic control box, throttle actuator, fuel injection solenoid valve, rail pressure sensor, etc., as shown in Figure 1:

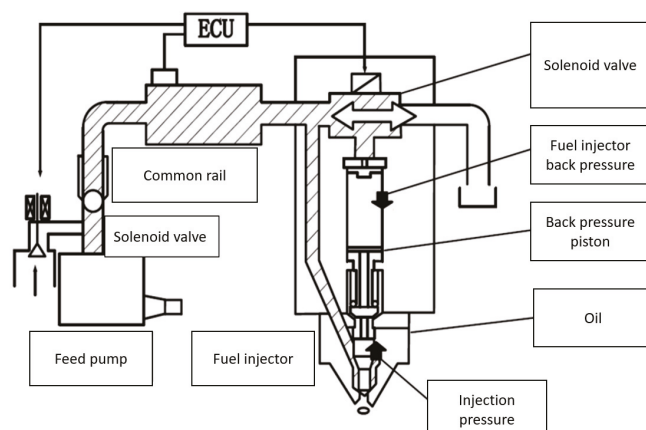


Figure 1. Schematic diagram of explosion-proof diesel engine fuel injection.

2.3. Explosion-Proof Design of Intake System

The main content of the explosion-proof modification of the diesel engine intake system selected for this experiment is to add an intake flame arrester and an air shut-off valve, which are used to prevent the flame generated by internal combustion of the explosion-proof diesel engine from spreading to the outside and to block the intake of the explosion-proof diesel engine during emergency shutdown. As shown in Figure 2:

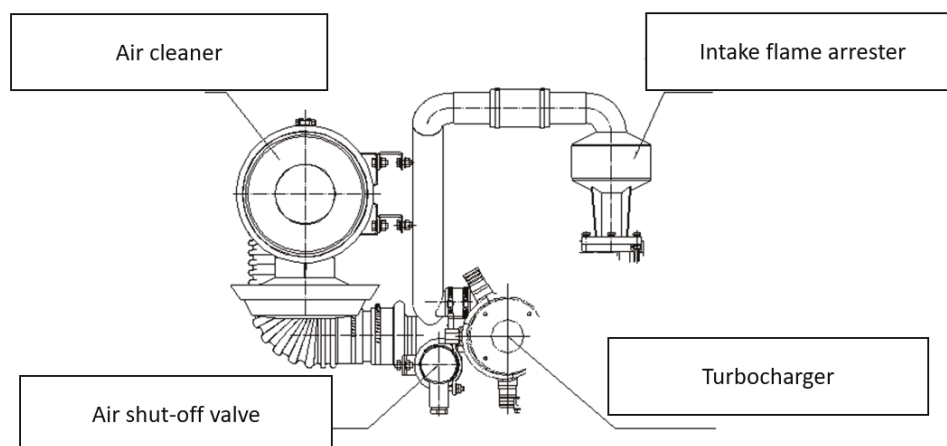


Figure 2. Explosion-proof diesel engine intake system diagram.

2.4. Explosion-Proof Design of Exhaust System

The initial exhaust temperature of a diesel engine is generally above 500 °C, and the temperature of the exhaust manifold and exhaust pipe is also above 200 °C, which may ignite the accumulated coal dust and cause safety accidents. Therefore, Article 378 of the Coal Mine Safety Regulations stipulates that the exhaust temperature at the exhaust port of an explosion-proof diesel engine shall not exceed 77 °C, and its surface temperature shall not exceed 150 °C. Therefore, it is necessary to perform cooling treatment on the exhaust system of diesel engines. The main method is to add cooling water jackets in the exhaust pipes and turbocharger where the exhaust passes through, and circulating water is used to bring heat to the radiator to dissipate it. Additionally, an exhaust cooling device is added at the end of the exhaust to ensure that the exhaust temperature does not exceed the standard. The structural type is the main research content of this experiment.

2.4.1. Explosion-Proof Design of Wet Exhaust Gas Turbine System

The most widely used exhaust system for explosion-proof diesel engines in the domestic market is the wet exhaust system, as shown in Figure 3. In addition to using exhaust pipes with water jackets and turbochargers, the main characteristic of wet exhaust systems is using cooling and purification water tanks to reduce exhaust temperature. Its advantages are mature technology and simple structure. The main disadvantages are reflected in its large volume and the inconvenient layout of the supporting water tank. During use, a large amount of water is consumed, and it is necessary to add water regularly, resulting in the wastage of water resources. Particles in high-temperature exhaust come into contact with water, cool and condense, and adhere to the exhaust flame arrester, causing significant exhaust back pressure and affecting power and emission performance.

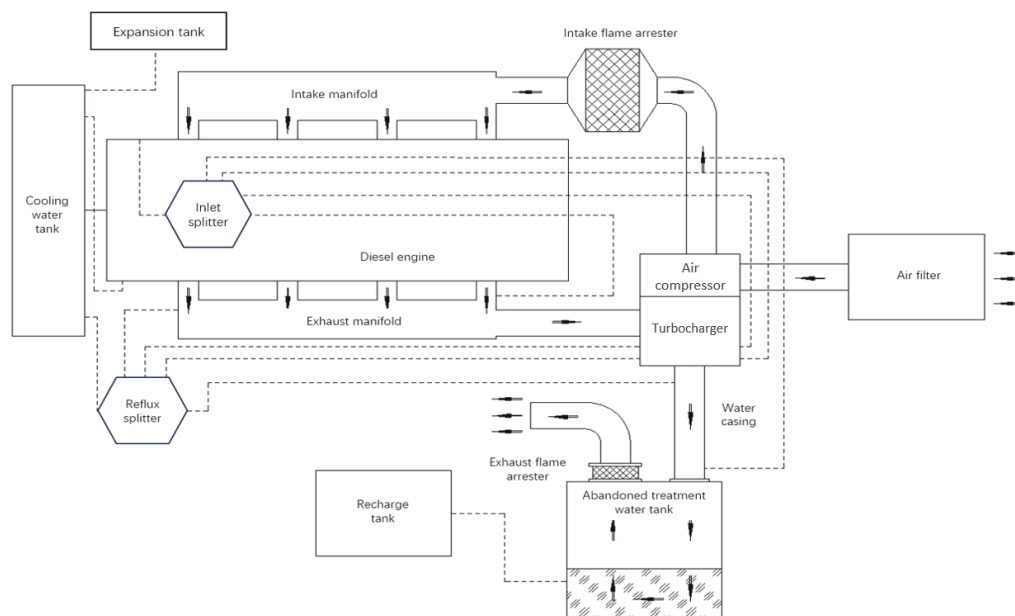


Figure 3. Design diagram of wet exhaust cooling system for explosion-proof diesel engine.

2.4.2. Explosion-Proof Design of Dry Exhaust Gas Cooling System

Compared to wet exhaust systems, dry exhaust systems have a lighter and simpler structure, save space, significantly reduce vehicle weight, and do not have the resistance effect of exhaust flame arresters, resulting in better power and emission performance. The main renovation content is to design a two-stage condenser structure and heat exchange component scale based on the exhaust volume and initial exhaust temperature, as well as the dilution amount and size of the exhaust dilution device, to ensure that the exhaust temperature meets regulatory requirements; Design the layout of two-stage condensers and exhaust flame arresters based on exhaust back pressure, real-time power, and emission data to minimize power loss caused by explosion-proof renovations. The dry exhaust system in this experiment mainly consists of a first-stage condenser, a second-stage condenser, exhaust bellows, an exhaust dilution device, and an exhaust flame arrester. As shown in Figure 4.

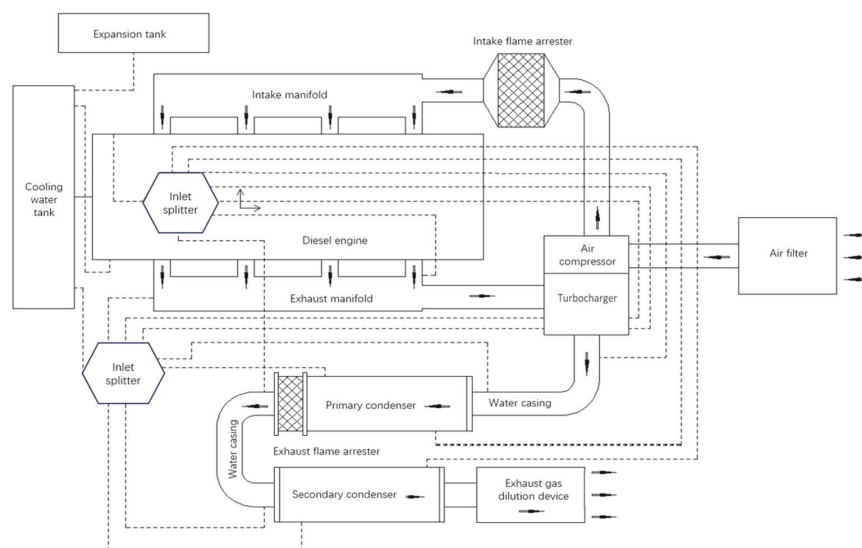


Figure 4. Design diagram of explosion-proof diesel engine dry exhaust cooling system.

2.4.3. Explosion-Proof Design of Dry and Wet Exhaust Gas Cooling System

The dry and wet exhaust gas cooling system mainly consists of a dry exhaust gas cooling system added to a cooling purification water tank, as shown in Figure 5. This structure is commonly used in imported diesel engines that meet the EU explosion-proof diesel engine standards. After entering the domestic market, a cooling and purification water tank was added to the original structure to meet the domestic explosion-proof requirements, making its overall structure large and complex.

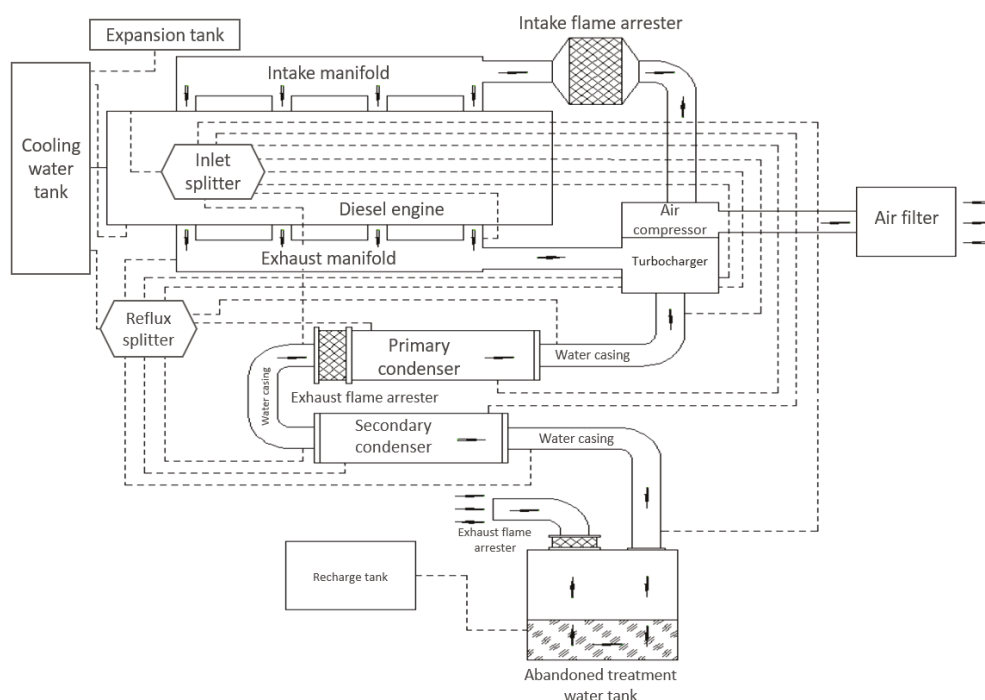


Figure 5. Design diagram of explosion-proof diesel engine dry exhaust cooling system.

3. Preparation for the Experiment

3.1. Explosion-Proof Test

3.1.1. Test Equipment

The explosion-proof testing equipment adopts an explosion-proof testing platform built according to the MT990-2006 “General Technical Conditions for Mining Explosion-proof Diesel Engines” standard. This platform can verify the explosion-proof performance of the intake and exhaust systems and the entire machine of the explosion-proof engine. It is divided into an intake and exhaust system explosion-proof test platform (Figure 6A) and a complete machine explosion-proof test platform (Figure 6B). The main technical parameters of the testing equipment are shown in Table 2.

Table 2. Capability Table of Main Experimental Equipment for Explosion Proof Test.

Serial Number	Equipment Name	Main Parameter
1	Hydraulic dynamometer	0~4000 rpm, Used for loading explosion-proof diesel engines
2	High and low-concentration methane sensor	Measurement range: 0~10%, Measure methane concentration
3	Oxygen sensor	Measurement range: 0~25%, Measure oxygen concentration
4	Water ring vacuum pump	Power: 7.5 kW; Gas volume 3.6 m ³ /min, Extract mixed gas



(A) Electric dynamometer



(B) Particle weighing device



(C) Gas content analysis device

Figure 6. Non-road country III emission standard detection system.

3.1.2. Test Conditions and Working Conditions

Place the three fully assembled explosion-proof exhaust gas cooling systems (without water in the cooling purification box) in a sealed test space. Inject explosive gas containing methane into the interior and ensure that the concentration inside and outside the intake system chamber is uniform, igniting the combustible gas inside the chamber. The methane concentration should be controlled between 7% and 9%, and the oxygen concentration should be controlled between 18% and 21%. The ignition source should be arranged at different positions, such as near the flame arrester, the branch pipe, and the middle of the system. Single or multiple ignition points can be set up depending on the volume and structure. The experiment shall be conducted at least ten times.

The performance testing of the explosion-proof diesel engines with three different exhaust cooling systems began with the installation of the engines on the test bench. Once in place, the engines underwent a preheating phase to ensure they were ready for testing. During this period, the cooling water temperature was carefully monitored, and once it reached 70 °C, the engines were considered sufficiently warmed up to proceed to the next phase.

After the preheating, the engines were operated with no load at a speed of 50% to 60% of their calibrated rated speed. This allowed the engines to stabilize under a low-load condition before moving to more demanding test scenarios. The test area was then sealed off, and a mixture of methane, oxygen, and air was introduced into the enclosed space to simulate the required explosion-proof conditions. The methane concentration was maintained between 7% and 9%, while the oxygen concentration was carefully controlled to remain between 18% and 21%. These conditions were maintained for a 10-min period to ensure the engines operated under the specific environmental parameters.

Once the engines had run for 10 min under these controlled conditions, the throttle and dynamometer were adjusted to increase the engine speed to between 60% and 90% of the rated speed, and the power was set to operate at 50% to 80% of the rated power. The engine was then run at these adjusted parameters for 3 min, simulating typical operational conditions. Following this, the engines were gradually unloaded, and the speed was decreased. The throttle was slowly closed, and the engine was decelerated until it was completely shut down. If needed, the air shutoff valve was also closed to ensure the engine ceased operation fully. The entire testing procedure lasted for a total of 15 min, ensuring that all performance aspects of the explosion-proof diesel engines were thoroughly examined under these controlled and simulated conditions.

3.1.3. Test Equipment

The testing equipment used in this experiment is a non-road national III emission standard detection system based on explosion-proof diesel engines used in coal mines, as shown in Figure 6. The testing system mainly includes an electric dynamometer, torque sensor, throttle controller, data acquisition system, intake air conditioning, fuel consumption meter, particulate matter sampling device, particulate matter weighing bin, explosion-proof test bin, gas analyzer, CVS full flow sampling system and operation console. It can detect the concentrations of NOX, CO, HC and CO₂ particulate matter in the exhaust pollutants of mining explosion-proof diesel engines. The main technical parameters of the testing equipment are shown in Table 3.

Table 3. Capacity Table of Main Experimental Equipment for Exhaust Emissions.

Serial Number	Equipment Name	Main Parameter
1	Siemens electronic dynamometer	400 kW, used for loading mining diesel engines
2	HBM torque sensor	5000 N. m, $\pm 0.5\%$ FS, for torque and speed measurement
3	AVL fuel consumption meter	$\pm 0.15\%$ FS for fuel consumption measurement

Table 3. Cont.

Serial Number	Equipment Name	Main Parameter
4	Intake flow meter	$\pm 1\%$ FS for measuring intake flow rate
5	AVL gas analyzer	$\pm 0.3\%$ FS, testing for concentrations of CO, NOX, HC, etc.
6	Particulate matter sampling device	Pre-sampling temperature $\leq 52\text{ }^{\circ}\text{C}$, filter paper 47 mm, for particulate matter entering
7	Microgram balance	Row Sampling
8	Explosion-proof test chamber	$\pm 2\text{ }\mu\text{g}$, measure the mass of particulate matter
9	High-flow automatic gas distribution	$4\text{ m} \times 8\text{ m} \times 2\text{ m}$, providing a sealed environment for explosion-proof testing

3.1.4. Test Conditions and Working Conditions

After completing the design of different cooling systems for explosion-proof diesel engines, prototype bench tests were conducted to investigate the impact of varying cooling system designs on the power and economy of explosion-proof diesel engines. To ensure the accuracy of experimental data, the experimental platform conditions are as follows:

The diesel used in the explosion-proof diesel engine experiment is No. 0 diesel, and the engine oil used is 15 W-40 diesel engine oil provided by the source engine manufacturer.

During the experiment, the laboratory intake system adjusted the intake condition of the explosion-proof diesel engine, stabilizing the intake temperature at $(25 \pm 3)\text{ }^{\circ}\text{C}$ and the intake humidity at $(50 \pm 5)\%$.

The laboratory air conditioning system adjusted the environmental conditions of the explosion-proof diesel engine during the experiment, maintaining the ambient temperature at $(25 \pm 5)\text{ }^{\circ}\text{C}$.

The test conditions are mainly based on GB 20891-2014, “Limits and Measurement Methods for Exhaust Pollutants from Diesel Engines for Non-Road Mobile Machinery (China’s Third and Fourth Stages),” and the specific test parameters are shown in Table 4.

Table 4. Performance Experiment Working Condition Parameters Table.

Serial Number	Diesel Engine Speed	Load Percentage
1	Rated speed	100
2	Rated speed	75
3	Rated speed	50
4	Rated speed	10
5	Intermediate speed	100
6	Intermediate speed	75
7	Intermediate speed	50
8	Idling	0

4. Experimental Data Analysis

4.1. Explosion-Proof Test

The explosion-proof diesel engine equipped with three different exhaust cooling systems did not experience any explosion during the exhaust system explosion-proof test and the overall explosion-proof test, meeting the standard requirements.

4.2. Performance Test

4.2.1. Exhaust Temperature

Based on the explosion-proof diesel engine’s basic parameters, adjust the engine to operate under different working conditions. After the return water temperature is balanced, measure the exhaust temperature of the explosion-proof diesel engine equipped

with three different exhaust cooling systems under different working conditions, as shown in Figure 7.

The dry exhaust gas cooling system maintains a higher exhaust temperature at all operating points compared to the other two cooling systems because the exhaust gas does not directly contact water. At the maximum torque point, which corresponds to the fifth operating point, the air-fuel ratio is at its lowest, as shown in Figure 8. This leads to higher combustion chamber temperatures, resulting in an increase in the initial exhaust temperature. As a result, this operating point has the highest exhaust temperature. The exhaust temperature of the dry cooling system, optimized for exhaust temperature, can reach up to 68.5 °C, which is about 4 °C higher than the wet cooling system, but still below the 70 °C threshold, thus meeting the standard requirements.

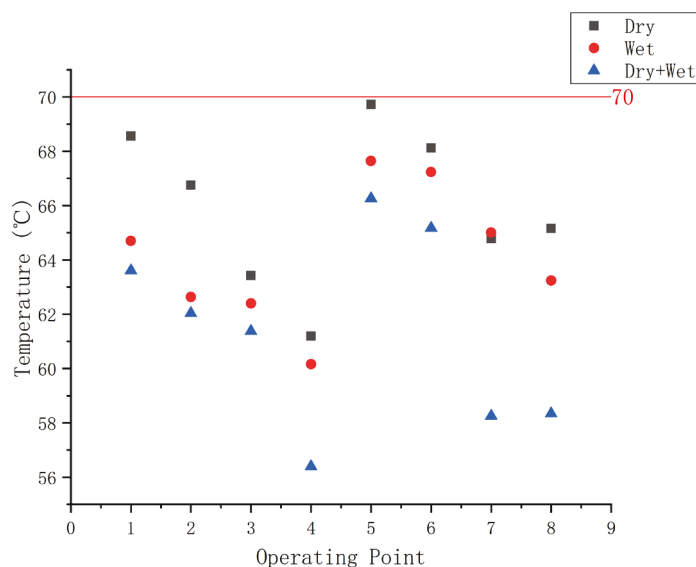


Figure 7. Exhaust temperature comparison.

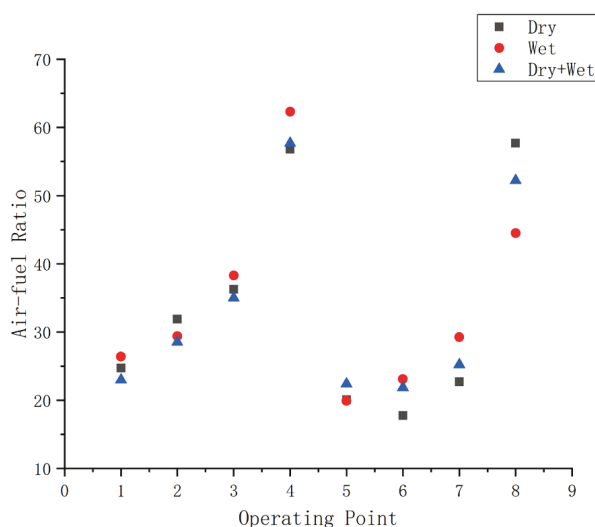


Figure 8. Air fuel ratio comparison.

4.2.2. Surface Temperature

When the cooling water temperature reaches 70 °C, adjust the explosion-proof diesel engine to the rated speed and rated power and run it stably for 1 h. The highest surface temperature of the explosion-proof diesel engine based on three cooling systems is shown in Figure 9:



(a) Wet emission system



(b) Dry emission system



(c) Dry and wet emission system

Figure 9. Maximum surface temperature map of explosion-proof diesel engines with different exhaust cooling systems.

As shown in the figure above, the dry exhaust cooling system differs from the wet and dry + wet cooling systems because it cannot be cooled by water channels, due to the absence of a cooling purification water tank. Its highest surface temperature occurs at the connection flange of the exhaust dilution device, as shown in Figure 9b, reaching 130.8 °C. In comparison, the wet exhaust cooling system, shown in Figure 9a, has a maximum exhaust temperature about 40 °C higher, but still below 150 °C, which meets the standard requirements. For the dry + wet cooling system in Figure 9c, its highest surface temperature is lower than that of Figure 9a, but higher than that of Figure 9b, due to the presence of water channels. Overall, the highest surface temperature in Figure 9c lies between those in Figure 9a,b, and all three cooling systems comply with the standard requirements.

4.2.3. Power, Torque Performance, and Fuel Consumption

According to the power, torque, fuel consumption, and exhaust back pressure measured under different operating conditions, the three cooling system diesel engine data are shown in Figure 10.

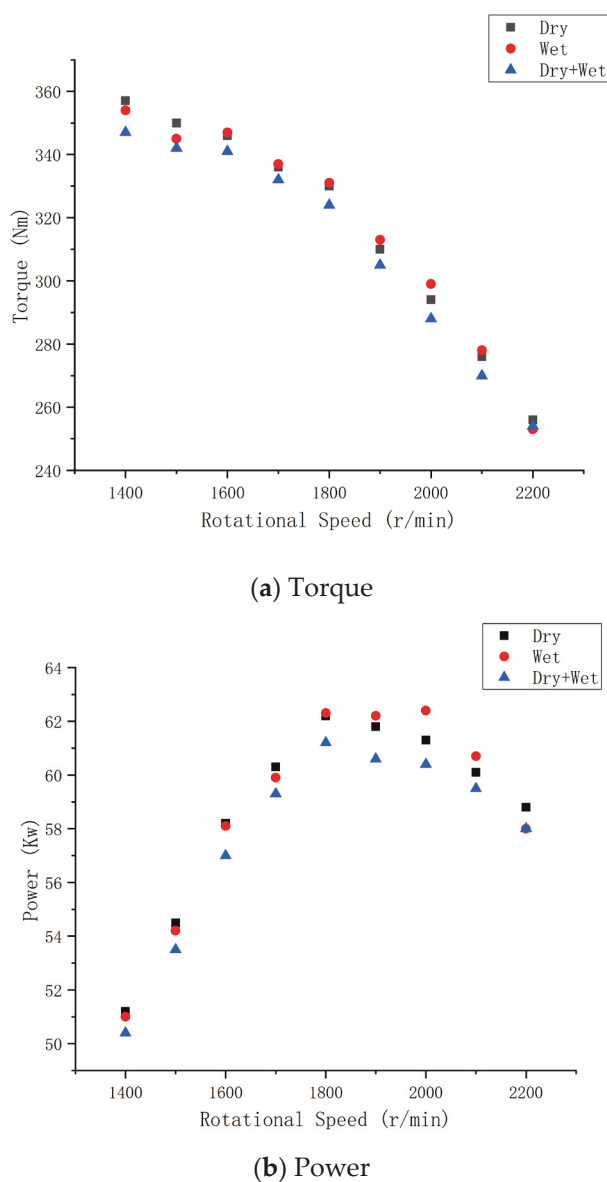
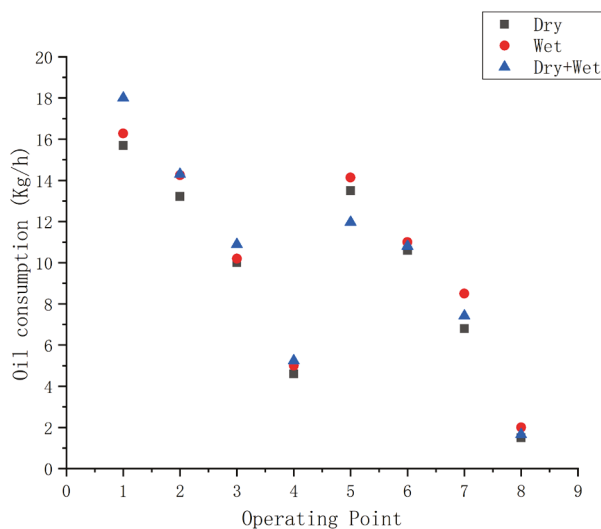
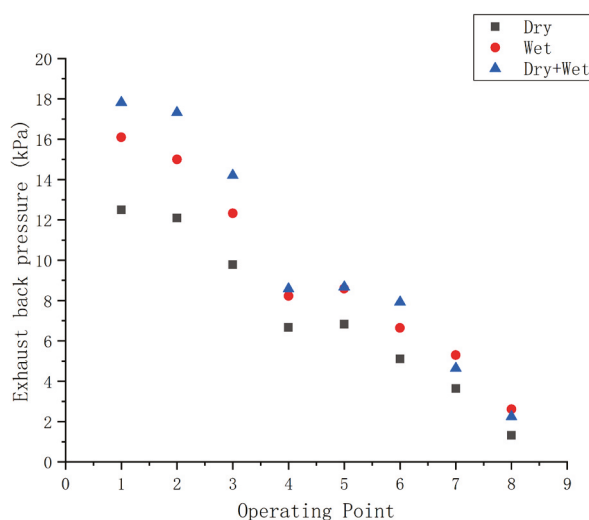


Figure 10. Cont.



(c) Fuel consumption



(d) Exhaust back pressure

Figure 10. Comparison of power and economic performance between different exhaust cooling systems.

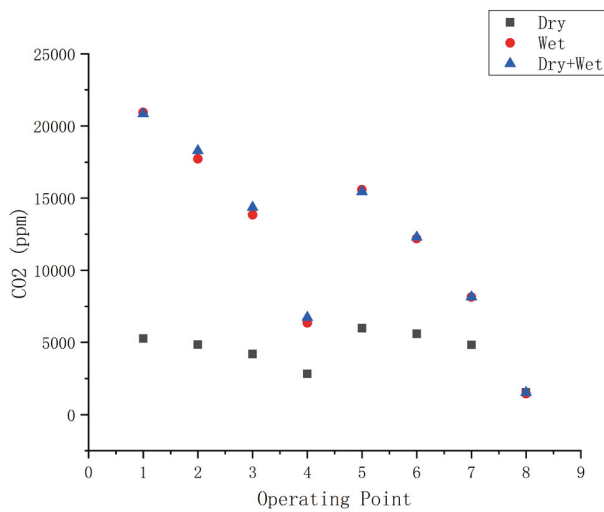
Because the exhaust gas in the dry exhaust cooling system does not pass through a water tank, it avoids direct contact with water. This prevents particles in the exhaust gas from mixing with water and solidifying on the surface of the exhaust flame arrester after cooling. As a result, the dry exhaust cooling system achieves the best exhaust back pressure performance (see Figure 10d), which is 22% lower than that of the wet exhaust cooling system. The exhaust flow is smoother, leading to a 1% increase in the rated power and a 2% increase in the maximum torque compared to the wet exhaust cooling system (see Figure 10a). Fuel consumption is also reduced by 4% (see Figure 10c).

In comparison to the dry + wet exhaust cooling system (see Figure 10b), the dry exhaust cooling system also shows a 1% increase in rated power, a 2% increase in maximum torque (see Figure 10a), and a 13% reduction in fuel consumption (see Figure 10c).

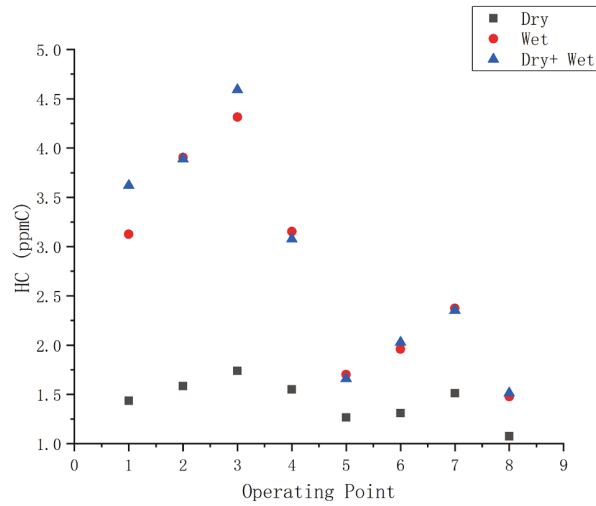
4.2.4. Emission Concentrations

While keeping other structures unchanged, adjust explosion-proof diesel engines equipped with different exhaust cooling systems to achieve the operating parameters shown in Table 4. According to the sampling method specified in GB 20891-2014, "Emission Limits and Mea-

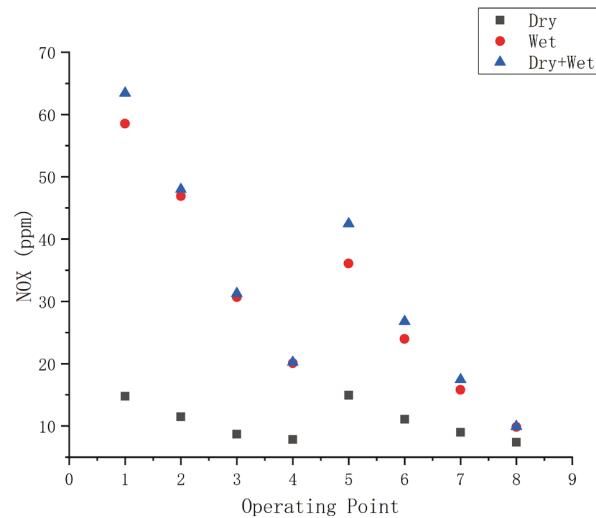
surement Methods for Exhaust Pollutants of Diesel Engines for Non-Road Mobile Machinery (China’s Third and Fourth Stages)”, the emission results shown in Figure 11 are weighted.



(a) CO₂

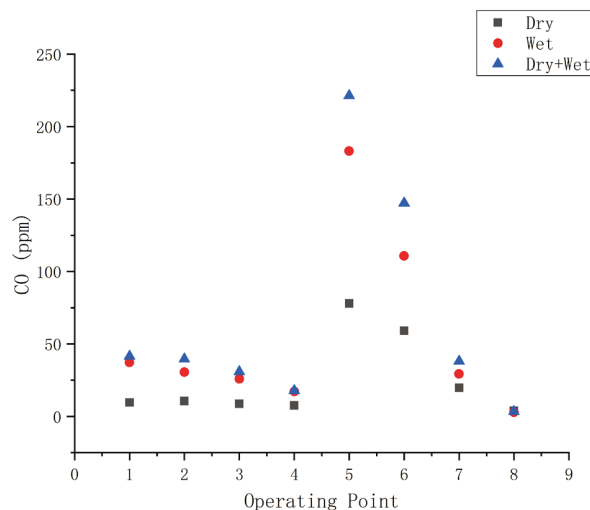


(b) HC



(c) NO_x

Figure 11. Cont.



(d) CO

Figure 11. Exhaust emission diagrams of explosion-proof diesel engines with different exhaust cooling systems.

As shown in Figure 11a–d, the dry exhaust cooling system significantly outperforms both the wet and dry + wet systems in terms of exhaust emissions. Unlike the wet and dry + wet systems, the dry exhaust cooling system does not require a water tank, preventing exhaust particles from mixing with water and solidifying on the surface of the exhaust flame arrester after cooling. This results in the best exhaust back pressure performance. With lower exhaust back pressure, the system reduces exhaust resistance and improves turbocharger efficiency.

Additionally, the dry exhaust cooling system incorporates an exhaust dilution device that uses exhaust power to generate negative pressure for better dilution. As a result, its emission performance is significantly lower than that of the wet exhaust cooling system: 55% lower in CO, 71% lower in HC, 68% lower in NO_x, and 82% lower in CO₂. Compared to the dry + wet exhaust cooling system, the dry system shows reductions of 63% in CO, 75% in HC, 66% in NO_x, and 94% in CO₂.

5. Conclusions

The study demonstrates that the dry exhaust gas cooling system meets the required explosion-proof performance standards while offering several operational advantages over the wet exhaust system.

Explosion-proof Performance: The dry exhaust gas cooling system passed both the exhaust system explosion-proof test and the whole machine explosion-proof test. Although the exhaust and surface temperatures were slightly higher than with the wet system (about 4 °C and 40 °C respectively), it still meets the necessary safety standards.

Fuel Efficiency and Power Performance: The dry exhaust cooling system reduces exhaust back pressure by 22% compared to the wet system, resulting in a 1% increase in rated power and a 2% increase in maximum torque. Additionally, fuel consumption is reduced by 4% compared to the wet system and 13% compared to the combined dry + wet system.

Emissions Reduction: The dry exhaust cooling system significantly reduces emissions, with CO, HC, NO_x, and CO₂ levels 55%, 71%, 68%, and 82% lower than the wet exhaust system, respectively. Compared to the dry + wet system, the reductions are 63%, 75%, 66%, and 94%, respectively.

6. Future Perspectives

Future improvements could focus on further enhancing the thermal efficiency and emissions reduction of the dry exhaust cooling system, potentially integrating advanced filtration and catalytic technologies. Additionally, optimizing system design for varying operational conditions in coal mines could enhance both performance and safety, meeting stricter environmental regulations in the coming years.

Author Contributions: Conceptualization, Z.S., G.L., C.C., C.M. and M.K.B.; Data curation, H.W., Q.L. and X.Z.; Formal analysis, Y.W.; Investigation, Y.W., Q.L. and C.M.; Methodology, Z.S., H.W., G.L., K.S., C.C. and S.A.M.; Resources, K.S.; Software, C.M.; Supervision, Z.S. and C.M.; Validation, C.M.; Visualization, X.Z. and C.C.; Writing—original draft, G.L. and Q.L.; Writing—review & editing, S.A.M. and M.K.B. All authors have read and agreed to the published version of the manuscript.

Funding: The author(s) disclosed receipt of the following financial support for the research, authorship, and/or publication of this article: This research is supported by National Natural Science Foundation of China (Grant number: 52274155).

Data Availability Statement: Data are contained within the article.

Conflicts of Interest: Authors Z.S. and C.C. were employed by the company National Mining Product Safety Mark Center Co., Ltd., authors H.W., G.L., Y.W., Q.L., X.Z. and K.S. were employed by the companies Hebei Coal Science Research Institute Co., Ltd. and Hebei Maian Testing Service Co., Ltd. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Article

Improvement Efficiency and Emission Reduction in Used Cars for Developing Regions Using Gasoline–Bioethanol Blends

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Abstract: Energy demand is continuously increasing owing to rapid technological developments and population growth. Additionally, it has been shown that the consumption of fossil fuels contributes to the emission of gases that increase the greenhouse effect. An alternative for addressing the problems of greenhouse gas emissions and dependence on oil is to replace fossil fuels with biofuels. This article presents the combustion gas emissions and performance assessment of a used car using gasoline–bioethanol blends at concentrations free of mechanical risk to contribute information for energy transition. The tests were carried out using the mixtures E0, E5, and E10 at speeds of 1500, 2500, and 4500 rpm for the evaluation of emissions. Meanwhile, for the performance assessment, the speed was varied from 2500 rpm to 8000 rpm. The vehicle was analyzed under functional operating conditions, and no mechanical modifications were made to the alcohol mixtures. Testing was performed using a gas analyzer with non-dispersive infrared (NDIR) electroluminescence and electrochemical cells to measure the emissions, and a computerized chassis dynamometer was used to measure the torque and speed. From the results shown here, it can be concluded that the use of bioethanol at low concentrations in the range without mechanical risk, such as E0, E5, and E10, can be utilized in used cars and in functional operating conditions, improving the thermal efficiency of the engine by 2% and 1.2% with the E5 and E10 mixtures. The specific consumption increased up to 3% with the E10 mixture owing to the lower energy capacity of the mixture. Meanwhile, HC polluting emissions decreased by up to 8.44%, 20%, and 100 at speeds of 1500 rpm, 2500 rpm, and 4500 rpm, respectively. The nitrogen oxide emissions decreased by up to 5% for mixtures E5 and E10. The results presented in this article may be useful for decision making in the use of biofuels in automobiles used in the energy transition. In addition, our study can be taken as a reference for studies on cars that are more than 20 years old.

Keywords: air/fuel ratio; gas emissions; gasoline–bioethanol blends; performance assessment; used car; greenhouse effect; human health

1. Introduction

Energy demand is continuously increasing owing to rapid technological developments and population growth. It is estimated that approximately 35% of energy demand is covered by petroleum fuels [1]. Furthermore, in the last decade, the transportation sector has accounted for approximately 19% of global oil consumption and is responsible for 20–23% of CO₂ emissions related to the consumption of fossil fuels [2,3]. Not forgetting that the quality of crude oil affects gas emissions in used cars, its extraction becomes relevant, making it possible to consider more efficient technologies [4,5]. Likewise, it has been shown on several occasions that the consumption of these fuels contributes to the emission of gases that increase the greenhouse effect [6–8].

One of the problems with the use of fossil fuels is that they are not a renewable resource, and it is estimated that oil reserves are reduced between 2% and 5% each year, considering the proven crude reserves of which there is certainty currently [9]. An alternative to addressing the problems of greenhouse gas emissions and dependence on oil is to replace fossil fuels with biofuels [10–12].

At the end of the 20th century, biofuels, such as ethanol, methanol, and butanol, were proposed as alternatives to partially or totally replace gasoline [13]. Ethanol is one of the most used biofuels in the world, producing 95% from agricultural sources such as corn, sugarcane, barley, and agricultural waste, making it a sustainable biofuel [14–17]. Among the main benefits of using ethanol as a biofuel are its economic advantages. Ethanol is generally cheaper than gasoline; the estimated cost of producing a liter of bioethanol in Mexico ranges from USD 0.50 to 0.70, while a liter of regular gasoline is approximately USD 1.20. This price difference contributes to reducing the overall cost of gasoline–ethanol blends by an average of 5%. Additionally, there are significant environmental benefits, as ethanol helps reduce the emission of harmful gases [18,19]. In addition, it offers social benefits by generating jobs for fuel production in the agricultural sector. The use of this fuel is aligned with the concept of sustainability, which seeks to contribute to the economic, environmental, and social aspects, and ethanol-blended gasoline has been increasingly adopted worldwide as a strategy to address pressing concerns related to energy security and air pollution [20–22].

It has been found in internal combustion engines that gasoline–ethanol mixtures offer better performance results and a reduction in greenhouse gas emissions owing to their high antiknock degree [23–26]. This allows for its use with high-compression-ratio engines, which increases its thermal efficiency and allows for a better air/fuel ratio, as shown [7,27,28]. Also, there are works in which it is evident that for a gasoline–ethanol mixture, it is considered that the effect of adding ethanol to gasoline is to oxygenate the fuel. Similarly, the air/fuel ratio decreased considerably as the amount of ethanol in the mixture increased [29,30]. However, when gasoline–ethanol mixtures with large percentages of ethanol are used, it is necessary to make important modifications to the engine owing to the deterioration generated on some engine components [31]. For 20% ethanol mixtures, surface treatment or anodizing the surface of the carburetor is required in carburetor systems, while no modification is required for electronic injection systems [32]. However, several researchers have shown that gasoline–ethanol mixtures up to 15% can be used in new or modified vehicles without additional changes, apart from changing the fuel lines [31,33]. To use percentages equal to or less than 10% ethanol (E10) in automobiles, it is not necessary to make any modifications [7,34–37].

In 2012, the government of El Salvador [38], with the support of a company, developed tests on 4-, 12-, and 36-year-old cars without any modification for the use of E0, E5, E10, and E15 ethanol blends. The authors showed that the cars did not have damage to their components, that power improved in some cases, and that CO and HC emissions were

reduced. However, the production cost of biofuel that year was 110% higher than the international price. In the same sense, in Mexico, projects have been developed to include ethanol in gasoline in such a way as to reduce dependence on hydrocarbons. This has contributed to encouraging the production of biofuels in the country and to issuing an official agreement for the use of cleaner fuels [39–42]. Finally, studies such as [43–45] have given recommendations on how to convert a car to run ethanol in Spain, described which cars can run on ethanol in the US, and presented warnings about the risks of using ethanol in older cars in Bolivia. However, in most cases, the information is general, referring to high ethanol concentrations and/or cars prepared for ethanol blends from the factory.

As far as it has been possible to search the literature, there are no published works with detailed results of performance and emission parameters in the entire operating range of a used car without mechanical modifications using gasoline and ethanol blends at low concentrations. Therefore, in this work, the performance and emissions of an 18-year-old automobile are evaluated under functional operating conditions using gasoline–bioethanol mixtures at low concentrations: E0, E5, and E10. The objective is to demonstrate that vehicles up to 18 years old can use ethanol at low concentrations with gasoline, with lower polluting emissions and favorable results in terms of power, thermal efficiency, and specific fuel consumption during the energy transition period.

2. Materials and Methods

The materials and methods used to develop this project are presented in this section. A description of the test rig and the fuels used, as well as the experimental procedure for the evaluation of performance and emissions with gasoline–bioethanol blends, are presented below.

2.1. Test Rig

The evaluation of gasoline–bioethanol mixtures at low concentrations was carried out in a used car and using torque, speed, and emission meters. The description of each of the components used for the evaluation is presented in this section. A test rig layout is shown in Figure 1, where one can see the used car, gas analyzer, and chassis dynamometer. Each of these components is described as follows.

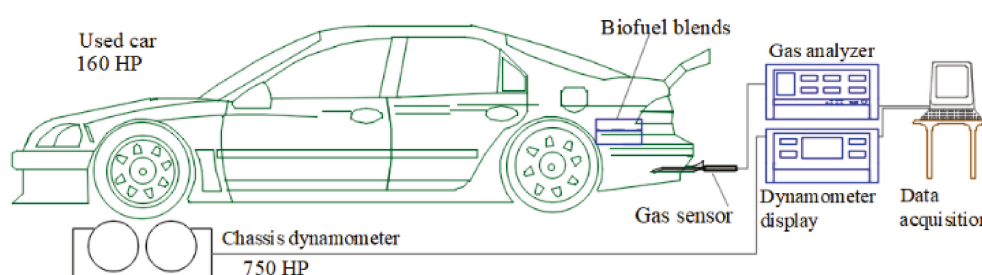


Figure 1. Test rig layout.

2.1.1. Tested Vehicle

The vehicle used in this project was a 6th generation Honda Civic 2000 model car with a B16A2-DOHC-VTEC engine. The history of this vehicle is as follows: between 2001 and 2010, a turbocharger was installed in the vehicle to increase its power. The exhaust system, injection system, suspension system, and programming of the engine control unit (ECU) of the car were modified. This set of modifications increased the overall power of the engine from 160 HP to approximately 200 HP. However, such modifications accelerate engine wear, causing perforations in the pistons and cylinder wear. Consequently, the vehicle was abandoned. Under these conditions, vehicles were acquired in 2017 for the development of this project. The vehicle traveled approximately 150,000 km. Once the mechanical history

of the vehicle and the actual conditions of the car at the time of acquisition were known, pertinent corrections and adjustments were made so that the vehicle was close to the original operating conditions. These corrections and adjustments included the repair of oil leaks, the replacement of the exhaust manifold, the installation of a custom stainless-steel catalyst, and engine adjustment by changing the rings, pistons, and liners. Once these adjustments were made, the vehicle was tuned by changing the oil, spark plugs, and air filters. The ECU was reprogrammed using the original manufacturer's parameters. All reconstruction activities were carried out by Mario René Grijalva Estrada due to the experience he has in this regard, along with the support of specialized technicians. The procedure followed for the rehabilitation of the vehicle and the tests carried out can be consulted in [46]. The characteristics of the engine used, both from the technical sheet and those from the current conditions, are listed in Table 1.

Table 1. Technical characteristics of the factory and current engine.

Parameter	Technical Sheet	Current
Engine identification	EK4vttecDochvTi	EK4vttecDochvTi
Engine type	L4 16 V	L4 16 V
Bore x stroke	86 mm × 77.4 mm	86 mm × 77.4 mm
Displacement	1595 cm ³	1595 cm ³
Compression ratio	10.2:1	10.2:1
Maximum power in Hp @ rpm	160 Hp @ 7600	79.7 Hp @ 7650 rpm
Maximum torque Nm @ rpm	150 Nm @ 7000 rpm	64.1 Nm @ 3950 rpm
Acceleration (0–100 km/h)	7.5 s	8.5 s
Maximum speed	195 Km/h	143 km/h
Combined consumption	7.5 Km/L	11 km/L

2.1.2. Gas Analyzer

The equipment used for the evaluation of combustion gas emissions was a 5-gas analyzer that uses the principle of non-dispersive infrared electroluminescence (NDIR) and electrochemical cells. The gas analyzer has a vacuum pump that sucks the exhaust gases through a probe to pass them into the analyzer, where the emission of infrared light is projected through the sample. An infrared receiver determines the amount of remaining light, thus obtaining the amount of each of the three gases that can be calculated using this method: carbon monoxide (CO), carbon dioxide (CO₂), and unburned hydrocarbons (HC). Oxygen levels were measured using an oxygen sensor. The amount of nitrogen oxide (NO_x) was measured using an electrochemical cell particle separator. The specifications of the gas analyzer are listed in Table 2.

Table 2. Specifications of the gas analyzer [47].

Parameter	Range	Precision
Hydrocarbons, HC (hexane), ppm	0–2000	1
Carbon monoxide, CO, %	0–15	0.01
Carbon dioxide, CO ₂ , %	0–20	0.1
Oxygen, O ₂ , %	0–25	0.01
Nitrogen oxide, NO _x , ppm	0–5000	1

2.1.3. Chassis Dynamometer

The equipment used for the performance evaluation is a 2WD 7500 chassis dynamometer, which allows for free rotation of the drive wheels. The device allows for the measurement of the torque, engine rotation speed, and travel speed (from 0 to 100 km/h). The dynamometer specifications are presented in Table 3.

Table 3. Chassis dynamometer specifications [48].

Parameter	Range	Precision
Mark	Dynocom	-
Model	2WD 7500 series	-
Timing accuracy	-	$\pm 0.1 \mu\text{s}$
Power, kW (Hp)	559.5 (750)	1%
Torque, kNm (lbf ft)	10.68 (7500)	1%
Engine speed, rpm	7500	$\pm 1/100\text{th rpm}$
Travel speed, km/h (mph)	362 (225)	$\pm 1/1000\text{th MPH}$

2.2. Used Fuels

The fuels used for the evaluated mixtures are described in this section. The gasoline used in this project is the so-called “magna gasoline” with 87 RON octane, 0.5% water content, (magna gasoline has 1.27% water content according to [49], while according to [50], it is 0.001% vol), marketed in Mexico by the Mexican company PEMEX. The bioethanol used in the mixture was produced from cane distillate, with 96% alcohol sold by Medric, in 20 L drums, with a maximum of 1% water content [7]. Table 4 lists the properties of the fuels used in this study.

Table 4. Gasoline and ethanol properties.

Parameter	E0	E100	References
Boiling temperature, (°C)	38.8	78.5	[7]
Flash point, (°C)	−40	13	[51,52]
Autoignition temperature, (°C)	250	363	[7]
Density at 20 °C, (g/cm ³)	760	790	[51,52]
Kinematic viscosity, 20 °C, (cSt)	0.704	1.5	[53,54]
Water content, %	0.5	1.0	[51,52]
Water solubility	insoluble	miscible	[7]
Vapor pressure, (mmHg, 20 °C)	48.7–58.6	43	[7]
Lower heating value, (kJ/kg)	44,000	26,810	[7]
Higher heating value, (kJ/kg)	47,300	29,670	[7]
Total acid number (mg/g KOH)	0.05	0.5	[51,52]
Distillation residue (vol %)	1	1.4	[52,55]
Distillation temperature for 10% recovery (°C)	70	78	[52,55]
Octane number, (RON/MON)	91/80	109/98	[7]
Stoichiometric ratio, A/F	14.7	9.0	[7]

The mixtures evaluated were E0, E5, and E10, with 0, 5, and 10% bioethanol in gasoline, respectively. These mixtures can be used without any modifications in most vehicles [37,56,57]. For the preparation of each mixture, the amount of ethanol and gasoline needed was measured according to the required concentration, x , calculated as follows:

$$x = \frac{V_E}{V_T} = \frac{V_E}{V_G + V_E}, \quad (1)$$

where V_E and V_G are the volumes of the bioethanol and gasoline, respectively. V_T is the total volume. To prepare the mixtures, a 1 L graduated container and 3 special gasoline containers with sight glass and a drain were used: two 20 L and one 10 L container. The preparation of the mixture was carried out as follows: (1) the amount of ethanol required for the desired mixture was introduced into the 10 L container; (2) the gasoline required for the desired mixture was introduced into a 20 L container; (3) the measured ethanol was placed in the second 20 L container, and then the measured gasoline was introduced; (4) once the two fuels were introduced, the solution was mixed for 20 min to ensure that the mixture was homogeneous. This alternative fuel was supplied to the vehicle tank.

2.3. Experimental Procedure

The experimental procedure followed for the evaluation of both the air/fuel ratio, performance parameters, and emissions is presented in this section. The used car under functional operating conditions, described in Section 2.1.1, was evaluated in two stages using the alternative fuel blends described in Section 2.2. The first stage was the measurement of the torque and speed using the chassis dynamometer described in Section 2.1.3. The second stage consisted of measuring the combustion gas emissions using the gas analyzer described in Section 2.1.2. The relative ratio of the E0 mixtures was also evaluated. The procedure followed for each stage is described in this section.

2.3.1. Relative Air/Fuel Ratio Tests

The gas analyzer provides the value of lambda, λ , which is determined from the Brettschneider equation, as shown in [58–60], which has the form:

$$\lambda = \frac{CO_2 + \frac{CO}{2} + O_2 + \frac{NO}{2} + \left(\frac{H_{CV}}{4} \times \frac{kp}{kp + \frac{CO}{CO_2}} - \frac{O_{CV}}{2} \right) \times (CO_2 + CO)}{\left(1 + \frac{H_{CV}}{4} - \frac{O_{CV}}{2} \right) \times (CO_2 + CO + C_f \times HC)}, \quad (2)$$

where H_{CV} is the atomic ratio of hydrogen to carbon in the fuel, O_{CV} is the atomic ratio of oxygen and carbon in the fuel, C_f is the number of carbon atoms in each HC measured molecule, and Kp is the assumed ratio of the CO_2 concentrations, CO , H_2O , and H_2 , determined from:

$$kp = \frac{CO \times H_2O}{CO_2 \times H_2} = 3.5, \quad (3)$$

The air/fuel ratio for the E0 mixture was determined using the lambda value measured at different engine speeds, as suggested in [61], by:

$$AF_{ac} = \lambda AF_{stq}, \quad (4)$$

where AF_{ac} is the actual air/fuel ratio, while AF_{stq} is the stoichiometric air/fuel ratio equal to 14.6 kg_a/kg_f, taken from the same source.

2.3.2. Torque and Speed Tests

Prior to the performance measurements and as suggested in the standard [62], as well as after verifying that the drive wheels, in this case, the front ones, were in good condition, the vehicle was preheated, keeping the engine at a speed rotation of 1500 rpm for 10 min. Measurements of the torque and engine rotation speed for the evaluation of automobile performance using alternative fuel mixtures were performed as described in this section. The car was mounted on the dynamometer with the front wheels on the roller and secured with adjustable tie rods. A fan was placed in front of the vehicle. The vehicle's ECU was linked to a chassis dynamometer computer. The engine rotation speed increased from 2500 rpm to 7500 rpm with the respective vehicle speed changes. The specific speed ranges in rpm were chosen as recommended in [63]. This procedure was followed for each alternative fuel mixture: E0, E5, and E10.

2.3.3. Combustion Gas Emission Tests

Flue gas measurements were performed as recommended in the standards [62,64]. As a preliminary stage, the vehicle was warmed for 20 min at an engine speed of 1000 rpm. Once the vehicle was preheated, the gas analyzer probe was placed in the exhaust pipe as close as possible to the exhaust manifold. From this moment, the engine was accelerated to 1500 rpm, and the vehicle was maintained at this rotation speed for 5 min to obtain the parameters in

a stable state. This procedure, of accelerating to a given speed and maintaining it for 5 min for steady state, was repeated at 2500 rpm and 4500 rpm for each alternative fuel mixture, E0, E5, and E10. The steady state of carbon dioxide, with the data saved every 30 s for 5 min, is presented in Figure 2, where it can be seen that the maximum standard deviation of the data was 0.135% for the E5 mixture at 1500 rpm. All emission gases evaluated here were analyzed in a steady state, and the standard deviation was lower than that of CO₂. Emissions were evaluated in this speed range because it is the range in which a used vehicle operates under functional operating conditions.

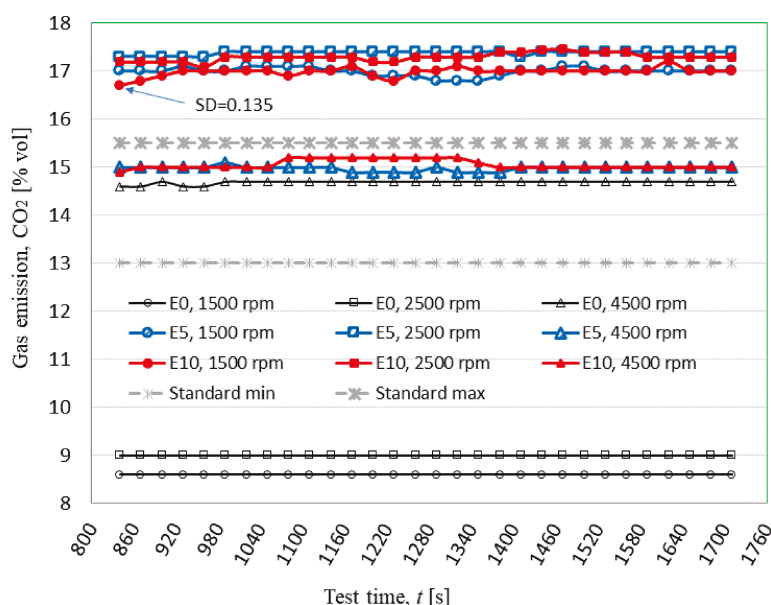


Figure 2. Emissions of carbon dioxide in a steady state. Minimum and maximum standard [65].

2.4. Data Reduction for Performance Assessment

For the evaluation of the performance parameters, the measured torque and speed data in rpm were analyzed for an Otto cycle, such as the one shown in Figure 3, and according to [61]. From the figure, it can be noted that the gasoline–bioethanol mixture, through combustion with air, is fed as heat supplied to the cycle, Q_{in} . The combustion of the fuel mixture produces the work, W , of the engine. The energy that is not used for the production of work is expelled as combustion gases through the exhaust heat, Q_o . Data reduction is described below.

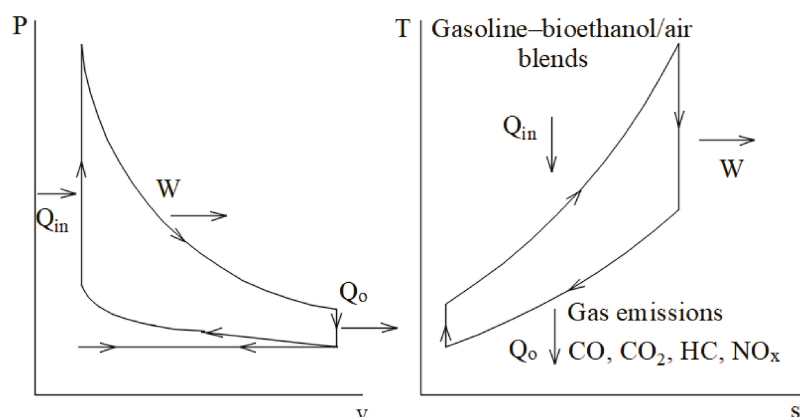


Figure 3. Diagram of the Otto cycle, which the evaluated car follows.

With the torque and speed data measured as described in Section 2.3.2, the thermal efficiency and specific fuel consumption, as well as their behaviors under different operating

conditions, were obtained as described in this section, according to what is suggested in [61]. With the torque (τ) and engine speed (N), the data measured as described here, the engine power, $\dot{W}$, was computed.

$$\dot{W} = 2\pi N\tau, \quad (5)$$

The thermal efficiency and specific fuel consumption, as well as their behaviors under different operating conditions, were obtained, as described in this section. The work of one cycle is calculated as follows:

$$W = \frac{\dot{W}n}{N} = Q_{in} - Q_o, \quad (6)$$

where N is the engine speed in rpm, τ is the torque measured in Nm, and n is the number of revolutions per cycle. The air mass, m_a , was determined under the atmospheric conditions of Mexico City ($T_1 = 25^\circ\text{C}$ and $P_1 = 77.38\text{ kPa}$) at the inlet of the cylinder as:

$$m_a = \frac{P_1 V_1}{RT_1}, \quad (7)$$

where the total volume, V_1 , is determined from:

$$V_1 = r_c V_c, \quad (8)$$

In this equation, the compression ratio r_c is obtained from the engine specifications. The volume of the combustion chamber, V_c , was calculated as:

$$V_c = V_d / (r_c - 1), \quad (9)$$

where the displaced volume, V_d , is determined from:

$$V_d = N_c \frac{\pi}{4} B^2 S, \quad (10)$$

Here, N_c is the number of cylinders in the engine, and B and S are the diameter and stroke of the piston, respectively. On the other hand, the heat supplied to a cycle is determined as:

$$Q_{in} = m_f Q_{HV} \eta_c, \quad (11)$$

where η_c is the combustion efficiency equal to 98%, as considered in [34], and Q_{HV} is the heating value of the mixture taken from [24,57], which is 42,604 kJ/kg, 40,578 kJ/kg, and 39,820 kJ/kg for E0, E5, and E10, respectively. The quantity of fuel, m_f , is determined by:

$$AF_{ac} = \frac{m_a}{m_f}, \quad (12)$$

where the air fuel ratio, AF_{act} , for each of the mixtures was taken from [66], in which, for each mixture, it was 14.6 kga/kgf, 14.1 kga/kgf, and 13.5 kga/kgf for E0, E5, and E10, respectively. According to [61], the thermal efficiency (η_t) and specific fuel consumption (SFC) are determined as:

$$\eta_t = \frac{W}{Q_{in}}, \quad (13)$$

$$SFC = \frac{\dot{m}_f}{\dot{W}}, \quad (14)$$

where the fuel flow, $\dot{m}_f$, is determined from:

$$\eta_t = \dot{W} / \dot{m}_f Q_{HV} \eta_c \quad (15)$$

3. Results

The results obtained from the evaluation of gasoline–bioethanol mixtures at low concentrations in used cars are presented in this section. The results are presented first, for the evaluation of the air/fuel ratio for the E0 mixture. Next, the performance and emission results in used cars under functional operating conditions, using E0, E5, and E10 mixtures, are presented.

3.1. Lambda and Air/Fuel Ratio

The lambda (λ) value was measured using an oxygen sensor and vehicle ECU. The data obtained for the E0 mixture at different engine speeds are shown in Figure 4a, where it can be seen that throughout the test period, lambda had values of 0.77 for the speeds 1500 rpm and 2500 rpm and 1.0 for 4500 rpm, respectively. The behavior of the lambda value in this engine during testing suggests that the engine control unit (ECU) adjusts the air/fuel mixture to maintain operational stability. At low and medium RPM, the engine exhibits a rich mixture ($\lambda = 0.7$) to ensure proper functioning, while at high RPM, a lambda value of 1 is achieved to optimize the performance. This phenomenon is particularly significant in the context of engine wear after more than 150,000 km, which can influence the combustion efficiency and mixture regulation. In all the cases, the lambda value was below 1.05, which is the value of the Mexican NOM-041 standard [65]. With these lambda values, the air/fuel ratio AF_{act} was calculated at different speeds measured for E0. The results are shown in Figure 4b, where rich mixtures at low speeds and nominal mixtures at 4500 rpm can be seen. From the Figure, it can be seen that at rotation speeds of 1500 rpm and 2500 rpm, the mixtures are rich or contain excess fuel.

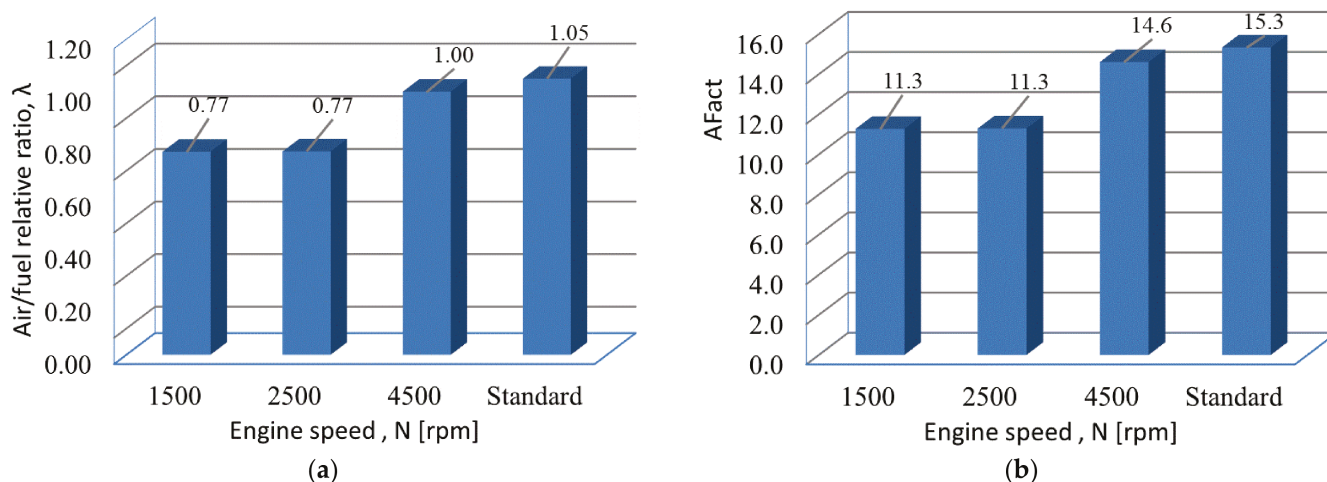


Figure 4. (a) Relative air/fuel ratio, λ . (b) Actual air/fuel ratio, AF_{act} .

3.2. Performance Assessment

Performance assessment parameters, such as the torque, power, thermal efficiency, and specific fuel consumption, are presented in this section. For the analysis, the torque and speed of the motor were measured using the roller dynamometer described in Section 2.1.3. On the one hand, the brake power was obtained using the dynamometer, while the thermal efficiency and specific fuel consumption were determined semiempirically, that is, using the measured data of the torque, τ ; engine speed, N; and using a mathematical model of the Otto cycle, developed as shown in [61].

3.2.1. Torque and Power Results

The torque and power results at speeds from 2500 rpm to 8500 rpm with each ethanol–gasoline blend are shown in Figure 5, where it can be seen that the maximum torque is reached at an engine speed of 3500 rpm. The maximum power was achieved at an engine speed of 7500 rpm. To evaluate the influence of the ethanol mixture on the performance, the analysis was performed in the range of 3000–4500 rpm. This is because it is the common operating range of a passenger car and the range evaluated by the SEMARNAT standard [65]. From the figure, it can be seen that at 4500 rpm, the torque increased by approximately 3%, while the power decreased by approximately 10%. This decrease in power is due to the lower calorific value of the mixture, as also stated in [55], where the authors evaluated the performance of a motorcycle using E30 mixtures.

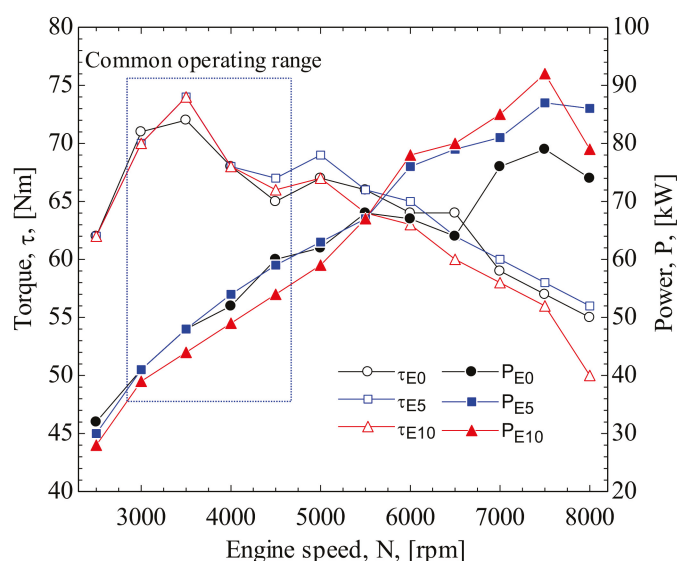


Figure 5. Power and torque at different rotation speeds for the three mixtures tested.

3.2.2. Thermal Efficiency Results

The behavior of the thermal efficiency of the engine for the three mixtures—E0, E5, and E10—at different engine speeds is presented in Figure 6. Like power, the analysis of thermal efficiency is carried out between the speeds of 3000 rpm and 4500 rpm due to the common operating range and the application of the above regulations for cars. From the figure, it can be seen that the thermal efficiency grows from 0.255 at 2500 rpm to 0.295 at 3500 rpm, which is the maximum thermal efficiency achieved for E0. From there, the thermal efficiency decreases to approximately 0.265 at 4500 rpm for the same mixture. An increase in efficiency until a maximum is reached is expected due to the maximum torque reached in this angular velocity range, where complete combustion and, therefore, efficient heat conversion are achieved [65]. The sharp decrease in efficiency from 3500 rpm to 4000 rpm is due to the decrease in torque. However, because the power is increasing, combustion can continue in optimal conditions. From the figure, when the engine reaches the maximum torque at 3500 rpm, the efficiency increases by 2% and 1.2% with the E5 and E10 mixtures, respectively. The increase in thermal efficiency with ethane mixtures is mainly due to the complete combustion of the fuel, facilitating the efficient conversion of heat, as also concluded in [55].

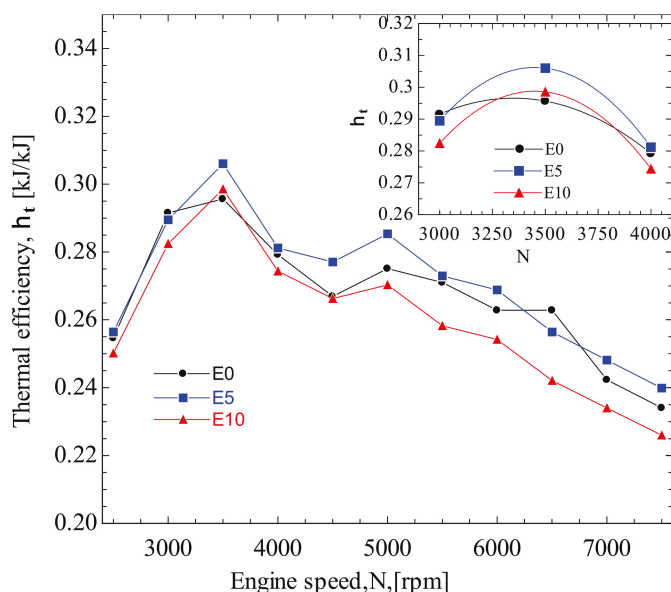


Figure 6. Influence of fuel concentration on thermal efficiency at different engine speeds.

3.2.3. Specific Fuel Consumption Results

The specific fuel consumption of the engine at different speeds and for the three mixtures—E0, E5, and E10—are presented in Figure 7. As in the cases of power and thermal efficiency, the analysis was carried out in the operating range of 3000 rpm to 4500 rpm for the standard and safe operating range, as stated. As shown in the figure, when the maximum torque is reached at 3500 rpm, the specific fuel consumption increases up to 1.4% and 5.6% for the E5 and E10 mixtures, respectively. The increase in specific fuel consumption is due to the low energy content of the mixture, as concluded in [55].

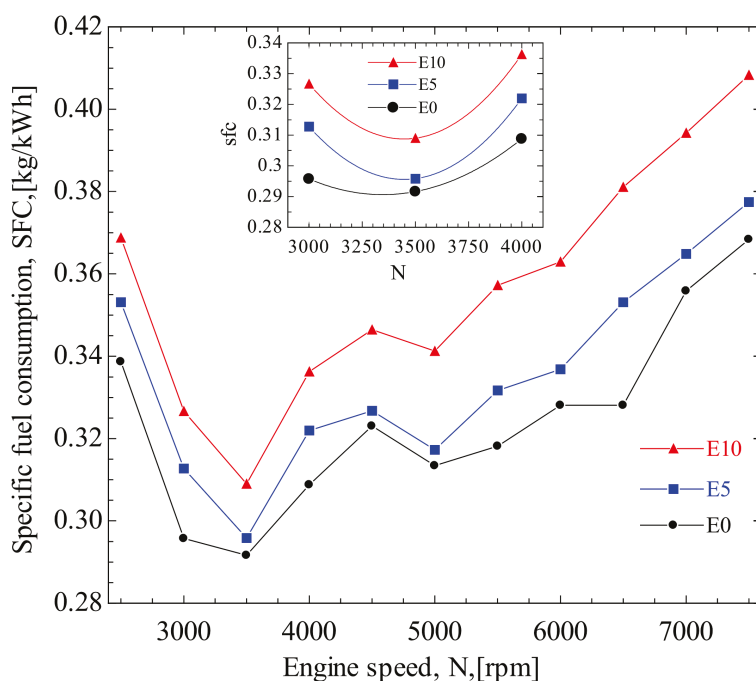


Figure 7. Influence of mixture concentration on specific fuel consumption at different engine speeds.

3.3. Combustion Gas Emission Assessment

The analysis of automobile combustion gas emissions using E0, E5, and E10 gasoline–ethanol mixtures is presented in this section for the five most representative combustion gases—carbon

monoxide, CO; carbon dioxide, CO₂; oxygen, O₂; unburned hydrocarbons, HC; and nitrogen oxides, Nox—with the aim of contributing information to the energy transition. The results were compared with the maximum values allowed by the standard [65] applied to cars with verification hologram 1 in the metropolitan area of the Valley of Mexico, which has approximately 22,000,000 inhabitants [67]. It is important to mention that the control of polluting emissions is necessary in cities that are densely populated with cars, such as Mexico City, with approximately 4288 cars/km², compared to cities less populated by cars, such as Paris, with 2215 cars/km², or Tlaxiaco, Oaxaca, Mexico, with 1495 cars/km². These numbers were obtained by combining the information found on the pages of such cities regarding the number of cars and the area of the district.

Figure 8 presents the emissions of carbon monoxide (CO), showing that if CO emissions are analyzed when the engine operates at a constant speed of 1500 rpm, the CO emissions decrease by up to approximately 39% when 10% ethanol is added to gasoline. A decrease of approximately 6% was observed when the engine was operated at 2500 rpm. When the engine operated at 4500 rpm and 5% and 10% ethanol was added to gasoline, the CO emissions remained almost constant at 0.1% and 0.2%, respectively. These values were within the limits allowed by the standard. This behavior of reducing CO emissions when ethanol is added to gasoline is similar to that shown in [55–57]. With the results of carbon monoxide reduction between speeds of 2500 and 4500 rpm, it can be expected that when driving in cities or highways at speeds greater than 2500 rpm, CO emissions will decrease.

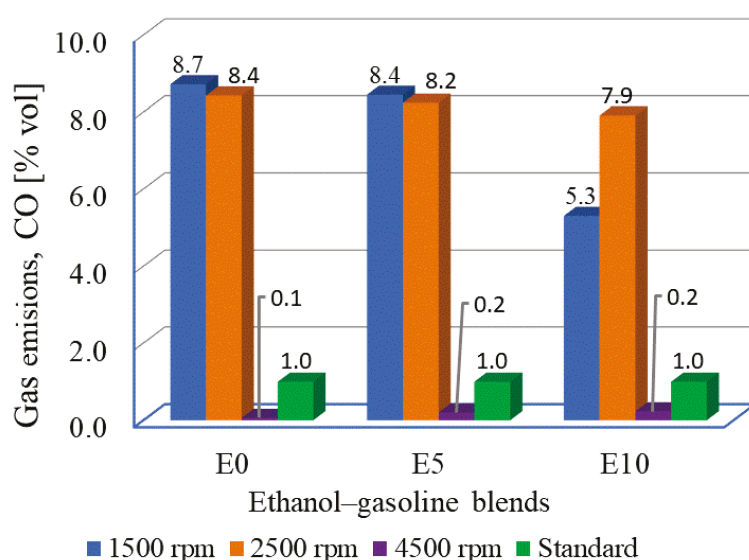


Figure 8. Influence of ethanol in gasoline on CO emissions.

The percentage of CO₂ emitted by the vehicle is presented in Figure 9, where it can be seen that if the car operates only with gasoline (E0), the CO₂ emissions increase by up to 41% when the speed increases from 1500 rpm to 4500 rpm. The engine behavior was improved by adding ethanol at a speed of 4500 rpm. The increase was 2.6% in the E10 mixture compared with that in the E0 mixture. At this speed, the values are below 15.5, as suggested by the standard. An increase in CO₂ emissions with the increase in ethanol in gasoline has also been reported in [55–57], where the authors concluded that it was due to the greater amount of oxygen in the fuel mixture.

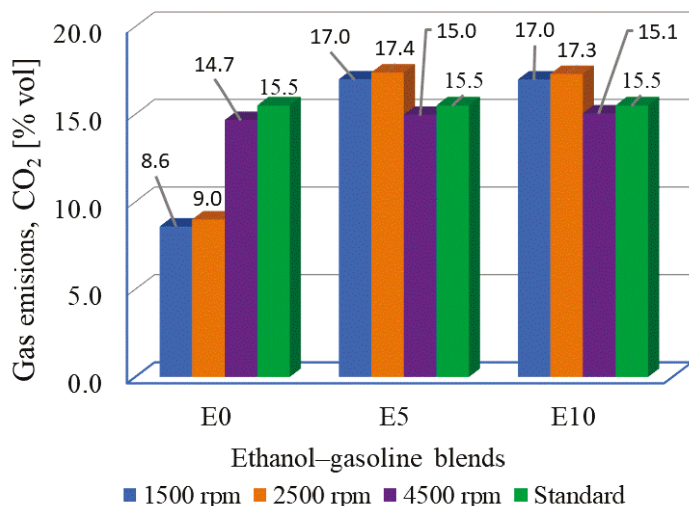


Figure 9. Influence of ethanol in gasoline on CO₂ emissions.

The amount of oxygen emitted from the gases indicates the oxygen left over from the air during the combustion process. The emission of this gas is shown in Figure 10, where it can be observed for E0 that excess oxygen decreases with speed. The same behavior was observed at 4500 rpm when ethanol was added to gasoline. The excess oxygen decreased to approximately 42% when 10% ethanol was added to gasoline. In all cases, the oxygen emission was below 2%, which is the maximum value allowed by the standard [65].

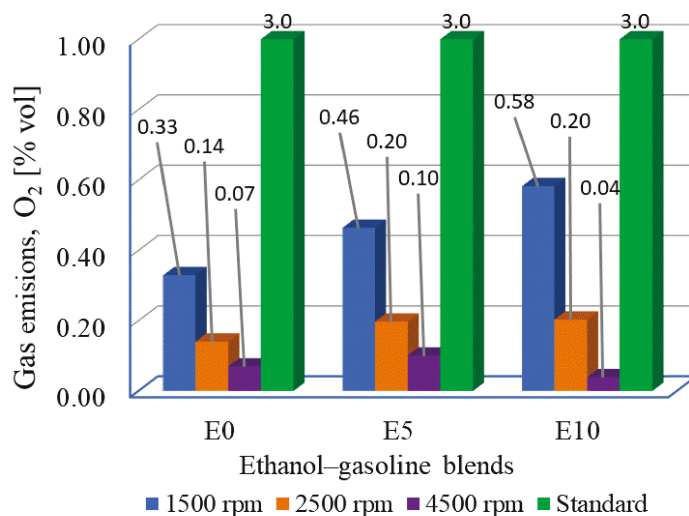


Figure 10. Influence of ethanol in gasoline on O₂ emissions.

The emission of hydrocarbons is presented in Figure 11, where it can be seen that with the addition of bioethanol, the HC emissions decreased by 8.44%, 20%, and 100% at speeds of 1500 rpm, 2500 rpm, and 4500 rpm, respectively. These results are expected mainly because of the oxygenation of the fuel due to the oxygen content of ethanol, which contributes to improved combustion. Similar results for the decrease in hydrocarbons were reported in [55–57].

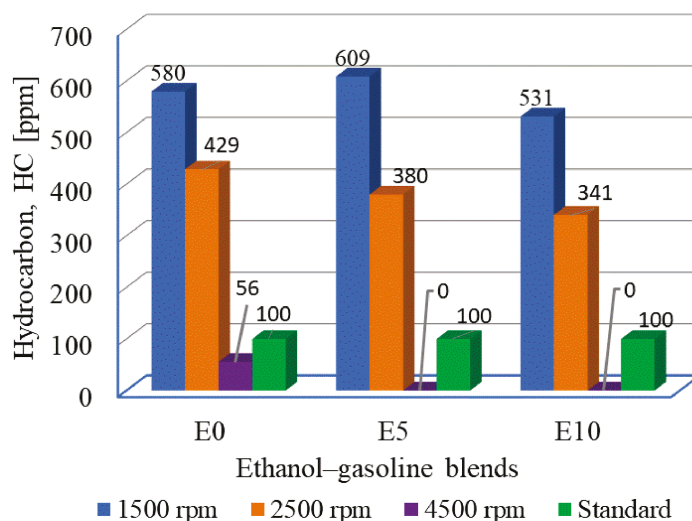


Figure 11. Influence of ethanol in gasoline on HC emissions.

Figure 12 shows the NO_x emissions with respect to the concentration of ethanol in gasoline at different speeds and compared with the maximum values allowed by the standard [65] for vehicles with hologram 1, as mentioned previously. However, when focusing only on the influence of the ethanol content in gasoline, it can be seen that when the engine operates at a low speed of 1500 rpm, the NO_x emissions decrease by 4% when 10% ethanol is added. Meanwhile, when the engine is operated at 2500 rpm and 4500 rpm, the emissions increase from 11 to 34 ppm and from 9 to 22 ppm, respectively. This may be due to the increase in oxygen in the fuel, which, when combined with nitrogen in the air, improves combustion, thereby increasing the combustion temperature and NO_x emissions. The same conclusion was reached regarding the increase in nitrogen oxides in motorcycles with 30% ethanol [55,57]. As can be seen in the figure, although the NO_x emissions increased when ethanol was added to gasoline, in all cases, the values achieved are not even equal to 2% of the value allowed by the standard for large cities.

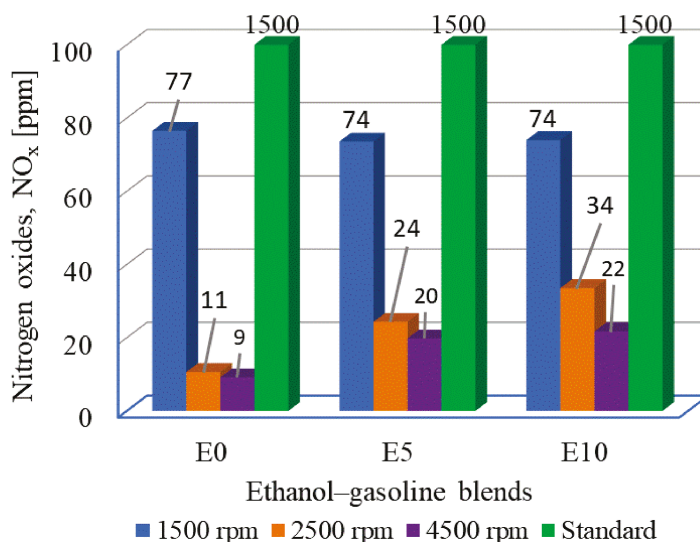


Figure 12. Influence of ethanol in gasoline on NO_x emissions.

Figure 13 shows the emission of combustion gases at 4500 rpm, which is within the functional or common operating range. From the figure, it can be seen that CO_2 emissions practically remain the same in the three mixtures. Oxygen decreases by approximately 40%, while unburned hydrocarbons are eliminated by 100% for the two bioethanol mix-

tures. From the results, it can be concluded that adding bioethanol to gasoline at low concentrations contributes to the reduction of pollutants from used cars.

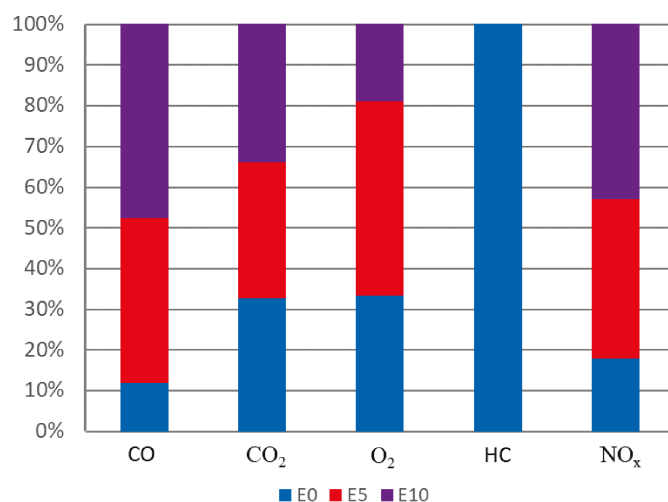


Figure 13. Emission of combustion gases in used car at 4500 rpm.

4. Conclusions

The following conclusions can be drawn from the results: The CO emissions remained almost constant with different gasoline–bioethanol mixtures. Meanwhile, the HC emissions decreased by approximately 50% with the E10 mixture. This improvement is mainly due to the oxygen content of the mixture, which improves combustion. On the other hand, although the CO₂ and NO_x emissions increased by approximately 2.6% and 10%, respectively, in both cases, the quantities emitted were always lower than the values allowed by the standard. Similarly, regarding the performance assessment, it can be observed that the power decreases by approximately 10% with the E10 mixture. The thermal efficiency and specific fuel consumption increased by 1.2% and 5.6%, respectively. The decrease in power and increase in fuel consumption were due to the lower energy content of the mixture. Meanwhile, the increase in thermal efficiency is due to the higher oxygen content of the fuel, which improves combustion. From the results shown here, it can be concluded that ethanol at low concentrations in the range without mechanical risk, such as E0, E5, and E10, can be used in used cars and in functional operating conditions, improving the thermal efficiency of the engine by 2% and 1.2% with the E5 and E10 mixtures. Meanwhile, HC polluting emissions decreased by up to 8.44%, 20%, and 100 at speeds of 1500 rpm, 2500 rpm, and 4500 rpm, respectively. On the other hand, future studies on ethanol mixtures at higher concentrations and in different types of used cars are suggested to generalize the results. The results found here could contribute to the modernization of older vehicles with ethanol-compatible systems. The above results can push us to take advantage, for example, of the fact that in Mexico, the production of biofuels has already been promoted, in addition to the fact that regulations for the use of cleaner fuels have just been published.

Author Contributions: Conceptualization, A.Z. and M.R.G.; methodology, A.Z., M.R.G. and R.H.; software, J.d.J.R., G.R. and B.A.R.; validation, M.R.G., J.d.J.R., A.F. and B.A.R.; formal analysis, A.Z., M.R.G., V.Y.M., R.H., I.C. and O.G.; investigation, A.Z., M.R.G., G.R., I.C. and O.G.; resources, A.Z., V.Y.M. and I.C.; data curation, J.d.J.R., G.R. and B.A.R.; writing—original draft preparation, A.Z.; writing—review and editing, A.Z., M.R.G. and B.A.R.; visualization, A.Z., J.d.J.R., I.C. and A.F.; supervision, J.d.J.R., R.H., I.C. and O.G.; project administration, A.Z.; funding acquisition, A.Z., J.d.J.R., V.Y.M. and R.H. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Instituto Politécnico Nacional, grant number SIP20240435.

Data Availability Statement: The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding author.

Acknowledgments: This study was financially supported by the Science Research Grant SIP20240435 from the Instituto Politécnico Nacional of Mexico. Grijalva acknowledges the financial support provided by the National Board of Science and Technology, CONAHCYT, of Mexico.

Conflicts of Interest: The authors declare that this study received funding from the National Board of Science and Technology, CONAHCYT. The funder was not involved in the study design, collection, analysis, interpretation of data, the writing of this article or the decision to submit it for publication. The authors declare no conflicts of interest.

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Article

Investigation of Water-in-Diesel Emulsion Behavior Formulated for Performance Conditions in a Single-Cylinder Diesel Engine

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Abstract: The search for alternative fuels is driven by increasing environmental and health concerns across the globe. Water-in-diesel emulsions (WiDEs) have been explored over the years as a potential fuel for diesel engines to mitigate emissions of greenhouse gases, especially nitrogen oxides and smoke. Researchers have been developing and testing different formulations of emulsified fuels with the common goal of stabilizing the mixture and minimizing pollutant emissions without significantly compromising engine performance. In this work, a novel approach is taken by developing a hydrophilic emulsion formulation optimized for engine operating temperatures, overcoming the storage-related stability issues that most studies focus on. Two different mixtures of WiDE were heated and supplied to a Hatz 1B40 single-cylinder diesel engine. The engine was coupled to an eddy current dynamometer to measure speed, torque, and power values. Emissions of carbon monoxide (CO), carbon dioxide (CO₂), hydrocarbons (HCs), nitric oxide (NO), and oxygen (O₂) were measured by an AVL DiGas 1000 exhaust gas analyzer. Smoke emissions were measured by an AVL DiSmoke 480. This study represents a contribution to the field of alternative fuels for diesel engines by providing experimental evidence that formulating WiDE for operating temperatures can be advantageous and significantly improve thermal efficiency and reduce emissions of NO and smoke at specific engine operating conditions, with a maximum reduction of 46.86% for NO emissions and a maximum reduction of 83.67% for smoke emissions obtained when compared to diesel.

Keywords: water-in-diesel emulsion; micro-explosion; hydrophilic emulsion formulation; Hatz engine; AVL analyzer; alternative fuel

1. Introduction

Motivated by an inspiring lecture and since its invention by Rudolf Diesel in 1897 [1], diesel engines have been used as one of the most efficient options in the realm of internal combustion engines [2–4]. The reduced values of specific fuel consumption are, however, opposed by pollutant emissions that directly impact the environment and our health, especially nitrogen oxides (NO_x), particulate matter, and smoke [5,6], mostly due to its heterogeneous combustion [7] leading to localized fuel-rich zones and higher temperatures [8]. Several emission reduction technologies have been implemented over the years [9]. Diesel particulate filters [10], selective catalytic reduction [11], diesel oxidation catalysts [12], and exhaust gas recirculation [13] are examples of some after-treatment systems significantly contributing to the reduction in pollutant emissions. However, not

only do these systems increase the total weight of the engine, but they also significantly increase its cost [14]. Water-in-diesel emulsion (WiDE) is an alternative fuel capable of adapting to the thermodynamic cycle of compression-ignition engines (CI), while reducing fuel consumption and emissions [15,16]. For this alternative fuel, small water droplets are dispersed in a continuous diesel medium [15,17]. Due to surface tension and other actuating forces, these two phases are unable to remain static, and even though short time stability may occur, stability for longer periods is not attainable [18]. To solve this issue, two pathways can be followed [19]: producing the emulsion instantaneously and rapidly feeding it to the engine fuel system [20–22], or adding emulsifiers and having it stabilized for a longer period [23–25]. Even though the first option would eliminate any storage issues [26], it is more complex to achieve and overall less explored. The second option is more common and has been widely adopted by different researchers [27]. It involves the addition of surfactants, which are emulsifying substances responsible for lowering the interfacial tension of the system [28], making it easier for water droplets to disperse in the fuel, forming micelles [29]. These surface-active agents are labeled as amphipathic molecules due to their dual nature of hydrophilic and lipophilic parts [30]. The lipophilic tail of a surfactant is usually composed of a hydrocarbon and therefore turns towards the oil phase [31]. The polar head (hydrophilic) defines the ionicity of the surfactant and turns towards the water [18]. Based on their charge, they are classified as anionic, cationic, zwitterionic, or non-ionic (neutral charge) [32]. Non-ionic surfactants are often adopted for WiDE fuels as their ability to not dissociate into ions prevents the worsening of exhaust emissions, making them relatively non-toxic when compared to the other types [33]. By stabilizing the mixture, they allow the emulsion to be safely supplied to the fuel lines without risking phase separation and possibly shutting down the engine [34]. Emulsions can be divided into macroemulsions, kinetically stable nanoemulsions, and thermodynamically stable microemulsions [35–37]. Nanoemulsions and microemulsions are preferred for fuel applications as they exhibit higher shelf life, lower viscosity, and lower energy required to emulsify [37]. Several benefits have been found from utilizing WiDE fuels when it comes to performance and pollutant emissions. When sprayed into a hot combustion chamber, the surfaces of the fuel droplets start heating. As the boiling point of water is lower than diesel, the dispersed water molecules reach their superheated stage first, evaporating and splitting the parent droplet in violent processes known as puffing and micro-explosion [38,39]. An initial larger droplet of fuel is split into smaller ones, increasing the surface area in contact with the surrounding air [40], leading to better air/fuel mixing in the engine cylinder. This secondary atomization [41] can potentially lower the emission of some pollutants after combustion.

Many researchers have investigated the effects of WiDEs on CI engines; however, achieving a strong correlation between the different parameters remains challenging. Experimental conditions, such as engine type, equipment used, applied load, fuel properties, water properties, surfactants used, ratio of the mixture, mixing method [42], and others, significantly vary between the different studies. More recently, Tamam et al. [43] tested an emulsifier-free WiDE with water percentages of 3, 6, 9, 15, and 20 by mass at 20, 40, 60, and 80% engine loads in a 5900 cc common rail turbocharged diesel electric generator and found that increasing water content resulted in a reduction in brake-specific fuel consumption (BSFC), an increase in brake thermal efficiency (BTE), and a reduction in NO_x emissions and smoke opacity. Okumuş, Kaya, and Kökkülünk [44] tested WiDEs with water percentages of 5, 10, and 15 by mass with a fixed surfactant ratio of 2% by mass of Tween 80 and Span 60 in a 510 cc single-cylinder diesel engine under full load conditions at engine speeds of 1500 and 2800 rpm and found a 5.22% and 5.46% respective power reduction with emulsified fuel usage, an increased BSFC of 7.42% and 8.96%, and

lower NO_x emissions, with a maximum reduction of 16.85% for the 10% water content emulsion, when compared to diesel. Woo and Lee [17] developed WiDEs composed of 10 and 20% water by mass and 2% surfactant content of polyglyceryl-4 oleate and tested them on a 2200 cc common rail diesel engine at brake mean effective pressures (BMEP) of 2, 4, 6, 8, and 10 bar at engine speeds of 1000, 1500, and 2000 rpm, adjusting injection timing to optimize pollutant emissions. They found increased exhaust gas temperatures with retarded injection timing and reduced NO_x emissions. These emissions decreased with the increase in water content. For the 20% water content WiDE, PM emissions were almost non-existent by retarding the injection timing according to the amount of NO_x emissions. They found that combustion duration is correlated with water content and not injection timing, decreasing the duration with the increase in water content. They also found that low-load conditions lead to ignition delay, requiring injection timing calibration to control the combustion process. Mondal and Mandal [25] prepared a WiDE with a 10% water and 2% surfactant ratio of Tween 80 and Span 80 by volume via ultrasonication and tested it in a 661 cc single-cylinder diesel engine at loads of 2, 4, 6, 8, 10, and 12 kg, injection pressures of 160, 190, 210, and 250 bar at a speed of 1500 rpm, and found reduced brake-specific energy consumption and a maximum BTE increase at 210 bar of 3.3% when compared to diesel. They found that NO_x and smoke emissions were lower than diesel, increasing and decreasing, respectively, with the increase in injection pressure. Maximum reductions were also found at 210 bar with values of 32.6% and 51.9%, respectively. Emissions of carbon monoxide (CO) were higher for the emulsified fuels at every load condition.

Most of these studies target the utilization of WiDE fuels that are stable at ambient temperatures, therefore optimizing the formulation for storage purposes [45]. This often leads to an unbalanced emulsion formulation when temperature and pressure naturally increase from the fuel tank to the fuel injectors, affecting its thermodynamic stability and producing unoptimized results. As prior studies generally focus on storage stability, the surfactants and mixing methods utilized are aimed at preventing phase separation between the oil, water, and surfactant at room temperature. The increased temperatures, pressures, and shear forces encountered in the fuel system easily destabilize conventional formulations, deteriorating combustion and increasing emissions.

This study addresses this crucial gap by suggesting a novel WiDE formulation explicitly designed for engine operating states, ensuring stability at this condition rather than ambient storage. This approach not only mitigates the risk of phase separation in the fuel in the fuel tank but also improves secondary atomization effects as water droplets remain uniformly dispersed until fuel injection occurs, improving combustion and reducing some exhaust emissions. By offering an opposing alternative to ambient-stable emulsions, this work advances the field of WiDE beyond its current limitations by developing an emulsion formulation that is scalable and adaptable to emerging fuels to be used in diesel engine architectures.

2. Materials and Methods

EN590 diesel fuel from Galp (Lisbon, Portugal), deionized water, a hydrophilic surfactant (Cocamide DEA) from FarmaQuímica Sur (Malaga, Spain), and a lipophilic co-surfactant (Span 80) from TCI (Tokyo, Japan) were acquired to perform the different tests. Two different emulsions were prepared in the laboratory by mechanical homogenization, a low-energy mixing method. The goal was to obtain stable emulsions with different percentages of water at the temperature of 40 °C, similar to the temperature of the fuel in the fuel tank of high-capacity diesel engines during operation conditions, mostly due to heat transfer from the fuel return lines. After several trial-and-error attempts, and based on Serôdio's work formulations [46], two different blends were obtained: an 8% WiDE and a 16% WiDE.

The first one is composed of 89% diesel fuel, 8% deionized water, and 3% of total surfactant concentration (91% Cocamide DEA and 9% Span 80). The second one is composed of 78% diesel fuel, 16% deionized water, and 6% total surfactant concentration (95% Cocamide DEA and 5% Span 80). All percentages are by mass. Commonly used surfactants may degrade or be less efficient at higher temperatures found during engine operation, leading to phase separation and worse secondary atomization. If they are ionic, they are toxic, and, by dissociating into ions, they worsen emissions. Our formulation of Cocamide DEA and Span 80 addresses these limitations as the surfactants have high thermal stability, are non-ionic and therefore non-toxic, derive from renewable sources, aligning with current sustainability targets, and, in addition, they support higher shear stresses often found during fuel injection at higher pressures. During laboratory tests, it was also discovered that an increase in water concentration needed to be followed by a corresponding increase in surfactant concentration. The same happened for the hydrophilic–lipophilic balance of the surfactant mixture. These combined allowed to obtain two stable emulsions at the temperature of 40 °C. This stability was verified by pointing a flashlight on one side of the flask and observing the light on the other side after passing through the emulsion medium. This is an indication that the water droplet size is low enough and that the emulsion formulation used for each case was ideal and optimized for the temperature of 40 °C. Figure 1 shows diesel fuel and both emulsions in their initial state, prior to exposure to the thermostatic bath. The equipment and material used during the tests are shown in Figure 2.

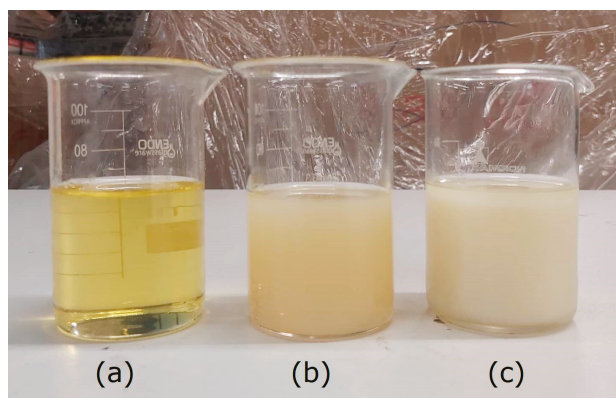


Figure 1. Diesel fuel (a), 8% WiDE (b), and 16% WiDE (c) at ambient temperature ($T = 15\text{ }^{\circ}\text{C}$).

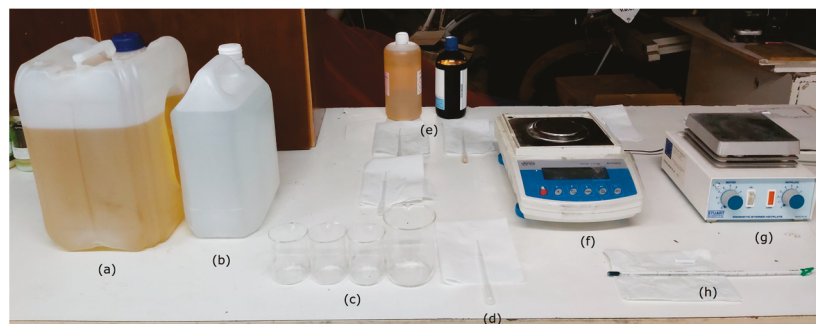


Figure 2. Laboratory equipment and material: diesel fuel (a), deionized water (b), beakers (c), pipette (d), surfactants (e), analytic balance (Radwag AS 310/C/2, Radwag, Macclesfield, UK) (f), magnetic stirrer (Stuart Scientific SM3, Salford Scientific, Salford, UK) (g), and thermometer (Enviro-Safe, SP Bel-Art, Wayne, NJ, USA) (h).

After obtaining the different fuels, properties such as density, viscosity, and heating value were measured using a hydrometer, an Oswald viscometer, and a bomb calorimeter, model 6050 from Parr. These measurements are shown in Figures 3 and 4, and Table 1.

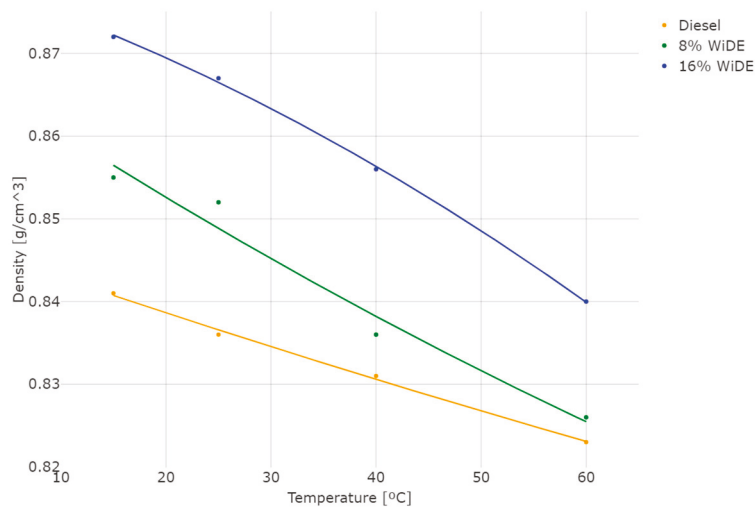


Figure 3. Density of the different fuels.

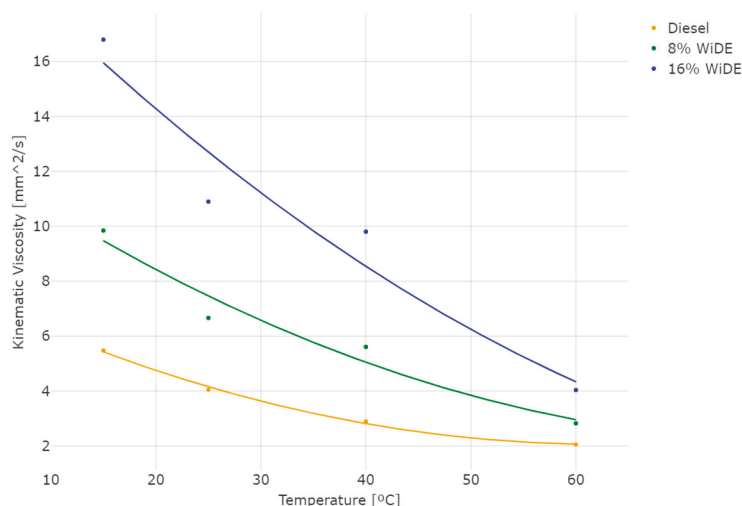


Figure 4. Kinematic viscosity of the different fuels.

Table 1. Heating value of the different fuels.

Fuels	Lower Heating Value (MJ/Kg)	Lower Heating Value (MJ/L)
Diesel	42.53	35.77
8% WiDE	38.77	33.15
16% WiDE	35.42	30.89

A Hatz 1B40 single-cylinder from Hatz (Ruhstorf, Germany), naturally aspirated, direct-injection (DI) diesel engine was tested under different load conditions in an eddy current dynamometer. Its specifications are shown in Table 2. An AVL DiGas 1000 model 2301 exhaust gas analyzer and an AVL DiSmoke 480 opacimeter from AVL (Graz, Austria) were used to measure emissions of CO, carbon dioxide (CO₂), hydrocarbons (HCs), nitric oxide (NO), oxygen (O₂), and smoke. Table 3 summarizes its specifications.

Table 2. Hatz 1B-40 specifications.

Engine Specifications	Parameters Values
Operation cycle	4-stroke
Cylinders	1
Valves per cylinder	2
Bore [mm]	88
Stroke [mm]	76
Displacement [cm ³]	462
Injection system	DI
Injection pressure [bar]	200
Compression ratio	20.5:1
Cooling system	Air cooling
Rated torque [Nm]	23.4
Rater power [kW]	7.3

Table 3. AVL DiTest gas 1000 model 2301 and AVL DiSmoke 480 opacimeter specifications.

Measuring Ranges	Accuracy
CO: 0–15% vol.	±0.03% vol.
CO ₂ : 0–20% vol.	±0.5% vol.
HCs: 0–30,000 ppm vol.	±10 ppm vol.
O ₂ : 0–25% vol.	±5% of Maximum
NO: 0–5000 ppm vol.	±1% vol.
Opacity	±0.1%
Absorption: 0–99.99 m ^{−1}	±0.01 m ^{−1}

The tests were performed at 25, 50, 75, and 100% of the maximum considered engine load at four different engine speeds (1500, 2000, 2500, and 3000 rpm) for the different fuels. As this diesel engine is composed of a governor (a mechanical device responsible for controlling fuel injection based on speed and load conditions), different fuel viscosities lead to different injection delays. To mitigate this and provide a fairer comparison between the fuels without modifying injection timings, a thermostatic oil bath was added for heating the emulsions to attain more similar viscosities to diesel fuel in the fuel tank during engine operation. The selected temperatures were 45 °C for the 8% WiDE and 55 °C for the 16% WiDE. Ambient conditions were also monitored during tests with temperature varying from 15.9 to 16.1 °C, relative humidity from 67 to 73%, and pressure from 937 to 942 hPa. Figure 5 shows the experimental setup during fuel testing.

For each operating condition, a run-up period was applied to warm the engine to reach its operating temperature. Performance data were collected from sensors every 250 ms via the Arduino 1.8.16 software, using the LabVIEW 2019 19.0f2 software to synchronize both microcontrollers. Emission data were collected every 50 ms with AVL DSS 2.0 software. The mean value of the different measured parameters was calculated for each condition of the total forty-eight experiments. Data analysis of the different results was conducted under R 4.1.3 software.

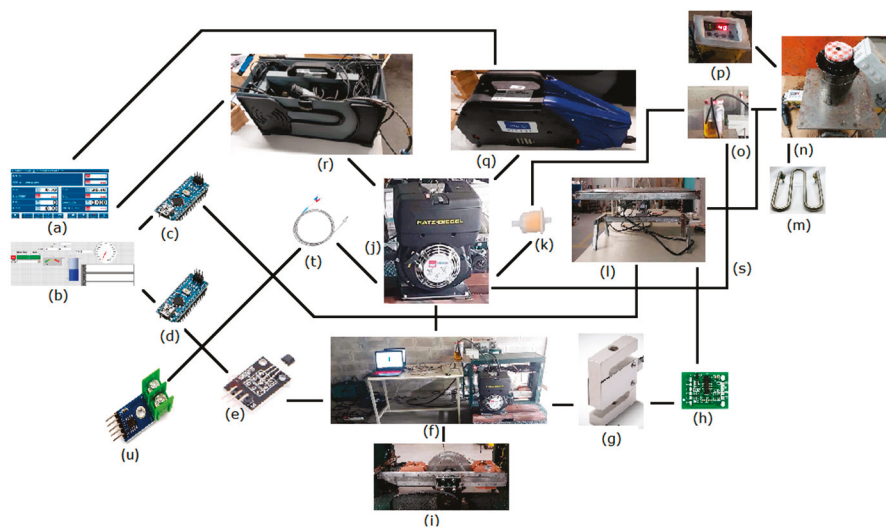


Figure 5. Test-bench layout: (a) emission data acquisition; (b) performance data acquisition; (c) Arduino 1; (d) Arduino 2; (e) Hall effect sensor (speed); (f) test-bench; (g) load cell for torque measurement; (h) HX711 load cell amplifier; (i) eddy current dynamometer; (j) diesel engine; (k) fuel filter; (l) load cell and fuel tank balance for fuel consumption measurement; (m) heating unit; (n) thermo-static oil bath for emulsion fuel tank; (o) diesel fuel tank; (p) fuel temperature sensor; (q) opacimeter; (r) gas analyzer; (s) fuel return; (t) type K thermocouple; and (u) MAX6675 thermocouple amplifier.

3. Results and Discussion

The following figures represent the corrected data gathered during the experiments for the different engine and emissions parameters. For each case, a two-dimensional plot is displayed. For each load condition, four different engine speeds were tested. After analyzing how the different parameters behaved for each engine speed, their values were averaged, obtaining a mean value for BMEP and a mean value for BSFC, BTE, CO, CO₂, HCs, NO, O₂, and smoke for each load condition. As BMEP is calculated from engine speed, the following plots represent BMEP on the x-axis and the different parameters on the y-axis.

3.1. Brake-Specific Fuel Consumption

As can be seen in Figure 6, the BSFC of the 16% WiDE is higher when compared to the 8% WiDE at every load condition. It is also higher than diesel fuel in every condition except at the maximum load condition, where it is lower. The BSFC of the 8% WiDE is lower than diesel fuel at the lowest and highest load conditions, and higher in the 1.698 and 2.492 bar load conditions. For the 16% WiDE, the BSFC decreases with an increase in engine load. For diesel fuel, the BSFC decreases between 0.789 and 2.492 bar and then increases until 3.585 bar. For the 8% WiDE, BSFC remains constant between 0.789 and 1.698 bar and then decreases until 3.585 bar. The occurrence of puffing and micro-explosions in emulsion droplets may be responsible for increasing the force acting on the piston during the expansion stroke [47], increasing the burning rate, and reducing the fuel flow needed to achieve a certain power, reducing BSFC in some cases. In contrast, the increased spray penetration and injection duration due to different fuel properties and the lower energy content of the fuel may increase this parameter [48].

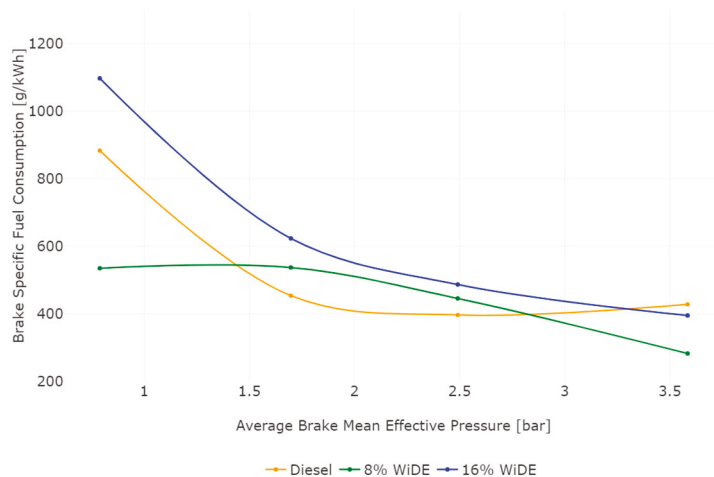


Figure 6. Average BMEP vs. BSFC.

3.2. Brake Thermal Efficiency

Regarding BTE, as seen in Figure 7, the 8% WiDE exhibits higher values compared to the 16% WiDE at every load condition. The BTE of diesel fuel is lower than in the 8% WiDE and similar to the 16% WiDE at 0.789 bar, higher than both emulsions at 1.698 bar, lower than both emulsions at 3.585 bar, and higher than the 16% WiDE but lower than the 8% WiDE at 2.492 bar. For the 16% WiDE, BTE increases with engine load. For diesel fuel, it increases with engine load until 2.492 bar and then decreases until 3.585 bar. For the 8% WiDE, it remains constant between 0.789 and 1.698 bar and then increases until 3.585 bar. As BTE is inversely proportional to BSFC, the curves are oppositely similar. Due to the reduced lower heating values of the emulsions (less diesel and therefore less energy content) [49], BTE can also improve, as the lower potential energy of the emulsified fuel molecules is better harvested for producing useful work, and less energy is lost in the form of heat.

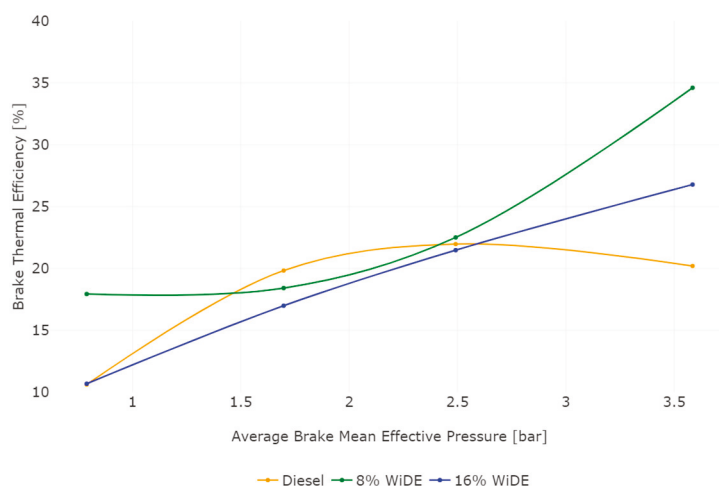


Figure 7. Average BMEP vs. BTE.

3.3. Carbon Monoxide Emissions

As shown in Figure 8, regarding CO emissions, they are always lower for diesel fuel compared to both emulsions. These results are in accordance with the most recent literature [50]. For the 8% WiDE, they are lower compared to the 16% WiDE at the minimum and maximum load conditions and higher at 1.698 and 2.492 bar. These emissions decrease for diesel fuel and the 16% WiDE with the increase in engine load and increase between 0.789 and 2.492 bar, followed by a decrease until 3.585 bar for the 8% WiDE. Higher CO

emissions for the emulsions can be a result of the incomplete combustion of some fuel molecules, possibly due to the excess carbon atoms present in the surfactants that were not fully combusted, lack of mixture uniformity, lower combustion chamber temperature, cylinder pressure, slow soot burning, and lower O_2 availability preventing CO from oxidizing to CO_2 , and different properties of the emulsified fuels leading to different spray characteristics after the injector [51]. On the other hand, a lower cetane number of diesel fuel due to its shorter ignition delay may reduce these emissions [52].

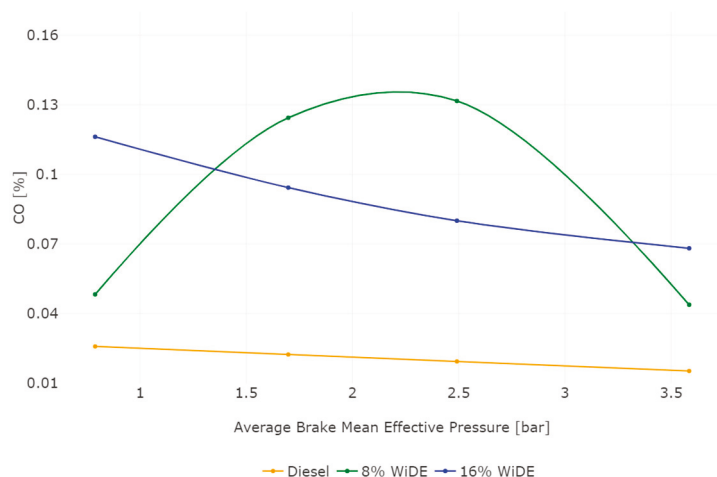


Figure 8. Average BMEP vs. CO.

3.4. Carbon Dioxide Emissions

As seen in Figure 9, CO_2 emissions, for every fuel tested, increase with increasing engine load. The CO_2 emissions of diesel are always lower than the emulsions at every load condition. Similar to CO emissions, CO_2 emissions for the 8% WiDE are lower than the 16% WiDE at the minimum and maximum load conditions and higher at both mid-load conditions. As a complete combustion of a hydrocarbon with O_2 would only produce CO_2 and water vapor, the higher CO_2 emissions of the emulsions can be due to better combustion properties and favorable conditions for CO oxidation into CO_2 [53]. Better burning characteristics can lead to a more complete combustion and therefore emit more CO_2 [54], increasing with engine load for all cases as more fuel is being burned per engine cycle.

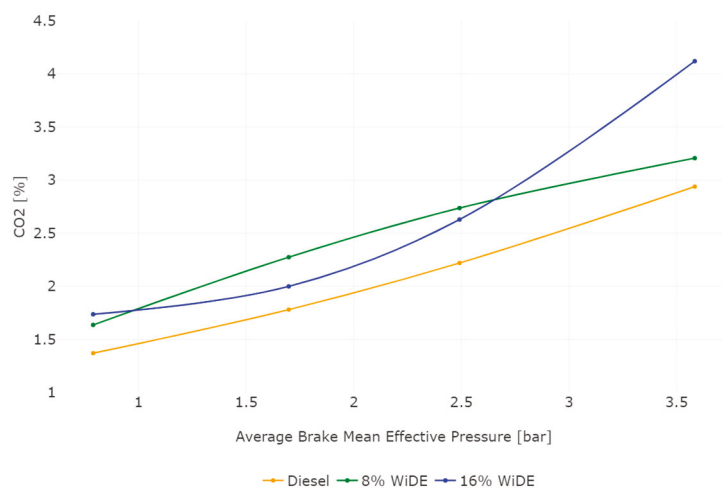


Figure 9. Average BMEP vs. CO_2 .

3.5. Hydrocarbon Emissions

As for HC emissions, as shown in Figure 10, they are lower for diesel at every load condition compared to the emulsions. These findings follow the most recent literature [55]. For diesel fuel, they remain overall constant throughout the different load conditions. For the 16% WiDE, they decrease between 0.789 and 2.492 bar and then increase until 3.585 bar. For the 8% WiDE, they decrease between 0.789 and 1.698 bar, remain similar between 1.698 and 2.492 bar, and then decrease until 3.585 bar. Similar to CO emissions, these emissions are also a result of the incomplete combustion of fuel molecules, strongly influenced by the air–fuel ratio, combustion temperature [56], and cylinder pressure [57]. The higher HC emissions for the emulsions may also be due to increased hydrogen and carbon atoms in the emulsifiers. Puffing and microexplosions may also increase the spray penetration length, leading to spray wall impingement and spray wall wetting [58]. The production or breakdown of HC compounds resulting in the formation of intermediate products can also explain this increase [59].

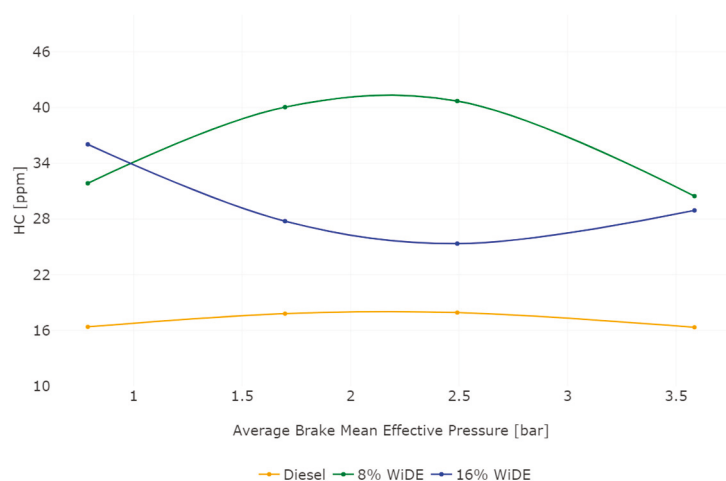


Figure 10. Average BMEP vs. HC.

3.6. Nitric Oxide Emissions

Regarding NO emissions, in Figure 11, for all fuels tested, they increase with increasing engine load. For diesel fuel, these emissions are always higher compared to the emulsions, except at 0.789 bar, where the NO emissions of the 8% WiDE are slightly higher, and 3.585 bar, where the NO emissions of the 16% WiDE are higher. The NO emissions of the 16% WiDE are lower than the 8% WiDE at 0.789 and 1.698 bar and higher at 2.492 and 3.585 bar. The reduction in NO emissions for WiDEs is in accordance with the most recent literature [60]. As the water molecules dispersed in the emulsified fuels need to absorb some of the heat produced during combustion to change their state from liquid to vapor, it was expected that the combustion temperature would drop as a consequence of this heat sink effect mechanism [61]. It was also expected that an increase in the water content of the emulsion would lead to a further reduction in the combustion temperature, which would prevent most of NO from being formed [62,63]. This only happened significantly for the 1.698 bar load condition, where NO emissions of diesel are higher, followed by the 8% WiDE, followed by the 16% WiDE. For the single case where NO emissions from diesel were significantly lower than the 16% WiDE, higher rates of premixed combustion and increased ignition delay may explain that occurrence [64]. An increased engine temperature, owing to different injection delays and ignition timings due to differences in fuel properties and the occurrence of intense micro-explosions in the combustion chamber, may also have contributed to increased burning rates and improved combustion, therefore increasing these emissions [65], as longer ignition delays lead to slower combustion and more time

available for NO formation in the combustion chamber [64]. This can be confirmed by Figure S1 in the Supplementary Material describing the outer engine block temperature over different engine speeds for the three different fuels, which are significantly higher for the 16% WiDE. Increased engine temperatures lead to higher NO emissions as the increased heat facilitates the dissociation of molecular nitrogen, which then reacts with oxygen from the air, therefore increasing these emissions. The unique case where NO emissions for the 8% WiDE were higher than diesel at the lowest load condition also corresponded to the trends observed in [66], where a 25% engine load was the only condition reporting higher emissions of NO for the emulsified fuels compared to diesel.

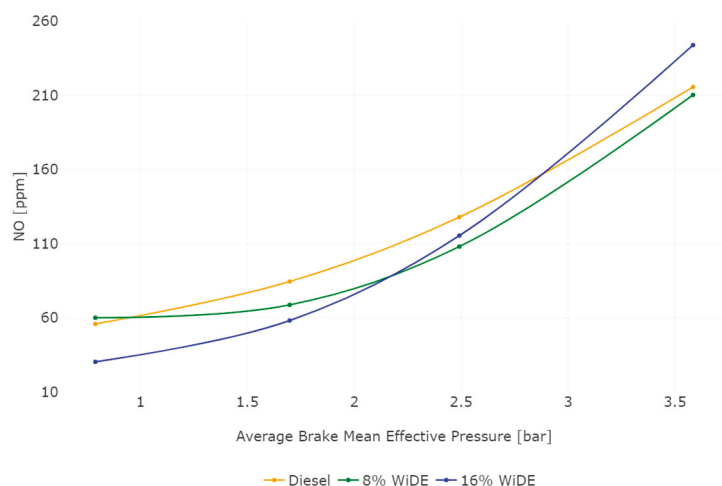


Figure 11. Average BMEP vs. NO.

3.7. Oxygen Emissions

As can be seen in Figure 12, regarding O_2 emissions, for all fuels, they decrease with increasing engine load. At every load condition, O_2 emissions for diesel are higher than the emulsions. For the 8% WiDE, these emissions are higher than the 16% WiDE at the minimum and maximum load conditions, similar at 2.492 bar, and lower at 1.698 bar. Lower values of O_2 content measured by the gas analyzer in the exhaust system may be an indication that the extra O_2 available in the emulsified fuels from the water molecules was used to react with fuel molecules and form other chemical compounds, assuring a more complete combustion [67]. If it was not used, it would be expected that O_2 emissions measured in the exhaust would be higher.

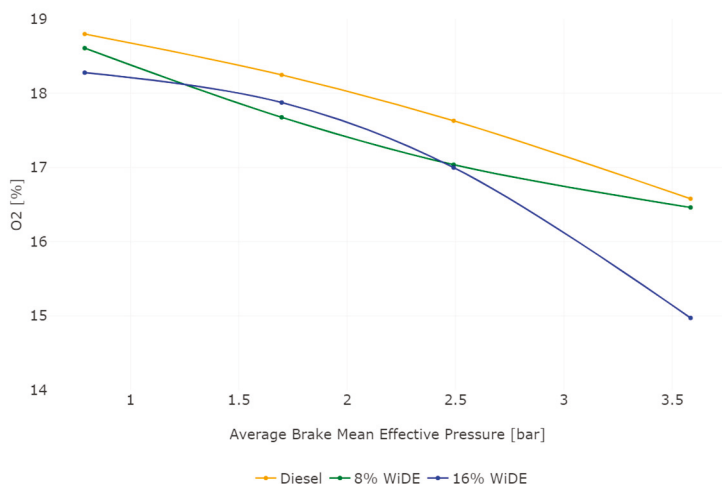


Figure 12. Average BMEP vs. O_2 .

3.8. Smoke Emissions

As for smoke emissions, shown in Figure 13, for the 8% WiDE, they increase with increasing engine load. For diesel, they increase between 0.789 and 2.492 bar and then decrease until 3.585 bar. For the 16% WiDE, these emissions increase between 0.789 and 1.696 bar and then decrease until 3.585 bar. The smoke emissions of diesel are always higher than the emulsions, similar to most recent studies [68]. These emissions are also always higher for the 16% WiDE compared to the 8% WiDE, except at the maximum load condition where these emissions are lower. As smoke is typically formed when the combustion is incomplete, producing soot, primarily composed of carbon particles, the reduction in fuel-rich zones, characteristic of diesel's heterogeneous combustion due to the oxygenated fuels [69], an improved mixing rate due to puffing and micro-explosions [70], and a longer ignition delay due to slightly different properties of the emulsified fuels increasing the time for the emulsion to vaporize, mix, and auto-ignite initiating the combustion process [71] may explain these lower emissions. In addition, the decomposition of some water vapor into hydroxyl, atomic oxygen, and hydrogen radicals at high temperatures can oxidize soot in fuel-rich zones, reducing smoke emissions and improving fuel efficiency [72]. It was also expected that an increase in water content would further reduce the smoke emissions; however, this only happened at the maximum load condition. At lower load conditions, the engine is operating under lower temperatures and pressures, making the conditions less suitable for the additional water present in the higher water content emulsion to fully vaporize and be more effective at further reducing smoke emissions. For these cases, the mixture composed of reduced water content was found to be more efficient and adaptable to these conditions, therefore resulting in decreased smoke emissions. This trend was also observed in [43], who reported an increase in smoke opacity by increasing water content from 8% to 16% under certain load conditions.

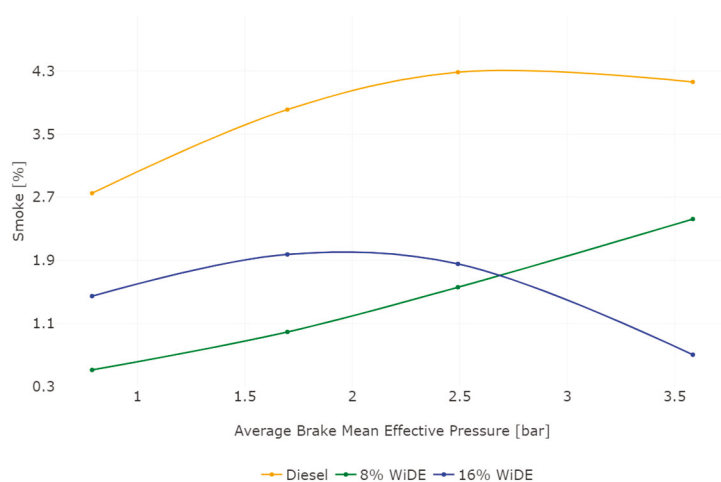


Figure 13. Average BMEP vs. smoke.

4. Conclusions

This research evaluates the viability of utilizing water-emulsified diesel fuels stabilized with non-ionic surfactants formulated for operating temperatures of CI engines under hydrophilic surfactant formulations. After analyzing the different results regarding various engine and emissions parameters, some conclusions can be drawn.

At every load condition, oxygen and smoke emissions are reduced for both emulsions. At every load condition, CO, CO₂, and HC emissions are increased for both emulsions. NO emissions are reduced for both emulsions at every load condition except during the minimum load for the 8% WiDE and the maximum load for the 16% WiDE. For the 8%

WiDE, TE is improved at every condition, except during a 50% load. For the 16% WiDE, TE is only improved during maximum load conditions.

In addition, it is also expected that sulfur oxide emissions would be lower for WiDEs as less diesel, and therefore less sulfur, is present in the fuel. Possible changes in injection timing when utilizing WiDEs may also reduce some of the pollutant emissions from incomplete combustion, especially CO and HC. This possibility should be explored in future works.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/en18030610/s1>.

Author Contributions: Conceptualization, P.O., F.B., R.S. and J.S.; methodology, P.O., F.B., R.S. and J.S.; software, P.O.; validation, P.O., F.B. and R.S.; formal analysis, P.O.; investigation, P.O., F.B. and J.S.; resources, P.O. and F.B.; data curation, P.O. and R.S.; writing—original draft preparation, P.O.; writing—review and editing, P.O., F.B., R.S. and J.S.; visualization, P.O., F.B., R.S. and J.S.; supervision, F.B.; project administration, F.B.; funding acquisition, P.O. and F.B. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by FCT through an individual PhD Grant 2021.07535.BD and C-MAST through projects UIDB/00151/2020 (<https://doi.org/10.54499/UIDB/00151/2020>) and UIDP/00151/2020 (<https://doi.org/10.54499/UIDP/00151/2020>).

Data Availability Statement: The original contributions presented in this study are included in the article/Supplementary Material. Further inquiries can be directed to the corresponding author.

Acknowledgments: The authors would like to thank the University of Beira Interior, Center for Mechanical and Aerospace Science and Technologies and the University of Castilla—La Mancha, Department of Fuels and Engines for the space, equipment, and materials provided during the development of this work.

Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

BMEP	brake mean effective pressure
BSFC	brake-specific fuel consumption
BTE	brake thermal efficiency
CI	compression-ignition
CO	carbon monoxide
CO ₂	carbon dioxide
DI	direct injection
HC	hydrocarbons
LHV	lower heating value
NO	nitric oxide
NO _x	nitrogen oxides
PM	particulate matter
O ₂	oxygen
WiDE	water-in-diesel emulsion

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Article

Evaluation of Rheological and Lubrication Properties of Selected Alcohol Fuels

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Abstract: This article presents the results of a study on the rheological and lubricating properties of selected alcohol fuels. Methanol, ethanol, and 2-propanol are investigated, for which density, kinematic, and dynamic viscosity are determined at selected temperatures in the range of 15–60 °C. In addition, the water content of the studied fuels is determined. Based on the measurements, the coefficient of temperature change for density and the relative percentage decrease in kinematic viscosity with increasing temperature are calculated. Subsequently, regression models are built to describe the value of density and viscosity of the tested liquid alcohol fuels as a function of temperature. Next, the fuels under study are subjected to the evaluation of antiwear properties using a high-frequency reciprocating rig (HFRR). For each fuel, the corrected wear scar size $WS_{1.4}$, which is a measure of lubricity, the average coefficient of friction, and the relative percentage decrease in oil *FILM* thickness during the conduct of the HFRR test under standardized conditions, are determined. The measurements are carried out at a standardized temperature of 25 °C in accordance with standardized methods for a time equal to 75 min. Due to the low lubricity of the tested fuels, additional tests are performed at a reduced time equal to 30 min. In this case, all fuels show a similar $WS_{1.4}$ value, which ranges from 384 μm for methanol through 422 μm for 2-propanol to 426 μm for ethanol. The wear marks on the samples after the execution of the test are used to draw additional qualitative conclusions about the lubricating properties of the tested alcohols. The results obtained are summarized, and possibilities for their use in further research are provided.

Keywords: alcohol fuel; methanol; ethanol; 2-propanol; lubricity; viscosity; density; HFRR test; high-frequency reciprocating rig; tribological wear

1. Introduction

In recent years, growing interest has arisen in using alcohol fuels to power internal combustion engines as an alternative to fossil fuels. The use of alcohol as fuel in engines has been known for more than a century [1,2]. Today, due to the implementation of climate agreements, including “Fit for 55”, the use of alcohols as gasoline admixtures [3] and stand-alone fuels [4] is growing. This is especially true for low-carbon fuels and the use of bio-based fuels such as biomass or biofuels [5].

Due to the phase-out of lead in all grades of gasoline and the adverse health and environmental impacts of tert-butyl methyl ether (MTBE), the synthesis of higher alcohols,

particularly ethanol, from syngas has attracted considerable interest. Low molecular weight alcohols such as ethanol have replaced other admixtures as octane enhancers in automotive fuels. Adding alcohols to petroleum products allows the fuel to burn more completely in the presence of oxygen, which increases combustion efficiency and reduces air pollution. To best utilize alcohols as alternative fuels, the engine or vehicle can be redesigned, or one or more admixtures can be added to ethanol or methanol to improve its properties [6]. Alternative fuels such as alcohols are widely used as admixtures in CI engines. Alcohols have economic advantages in diesel engines compared to conventional diesel fuel and can be used as an additive in compression ignition engines without any engine modifications [7]. Methanol fuel (CH_3OH) is considered one of the optimal fuels for internal combustion engines [8,9]. In addition, ethanol ($\text{C}_2\text{H}_5\text{OH}$) is considered as one of the most important components of biodiesel fuel and a promising alternative fuel in combustion engines [10–13]. On the other hand, the use of the studied alcohols as promising stand-alone fuels for industrial and marine internal combustion engines is driven by their low cetane number and high octane number, making them excellent fuels for spark-ignition engines. At the same time, these fuels exhibit low autoignition propensity, which significantly limits their application in compression-ignition engines.

A potential solution to these challenges is the use of dual-fuel engines powered by alcohol, where the ignition of the alcohol-air mixture is initiated by the autoignition of a pilot dose of diesel-type fuel. These solutions are currently being intensively developed by leading global manufacturers of large and high-power internal combustion engines, including MAN, Wärtsilä, and WinGD. The technological advancements pursued by these manufacturers mainly focus on methanol, as it is the low-carbon fuel with the fewest carbon atoms per molecule. Such engines are already commercially available and essentially represent the only alternative to low-carbon fuels such as LNG/CNG, LPG, or ethylene.

All the fuels mentioned in the previous sentence can be considered transitional fuels; however, the market will ultimately shift its focus toward carbon-free and low-carbon fuels. Carbon-free fuels such as hydrogen and ammonia still pose significant challenges related to proper storage, corrosive effects, and low volumetric energy density. Among low-carbon fuels, methanol appears to be the most promising option, and it is analyzed in our publication alongside two other low-carbon fuels. All the fuels examined in this article present significant challenges concerning their impact on engine component wear. They were selected and studied within this context. Currently, ethanol and methanol attract attention mainly due to their presence in the market and their potential to improve safety and reduce the negative impact of climate change. Methanol and ethanol are considered as promising oxygen admixtures in reducing CO and NO_x emissions [14,15]. In addition, many esters processed from methanol and ethanol have been used as admixtures blended with diesel fuel in diesel engines [16–20]. Methanol and ethanol are among the most promising alternative sources in terms of low emissions and low costs to replace conventional fuels. They are produced mainly from renewable sources, which makes them more valuable and makes it easier to meet demand in the event of overconsumption.

Aliphatic alcohols with the shortest hydrocarbon chains with one hydroxyl group are methanol, ethanol, and propanol. Propanol exists in the form of two isomers: 1- and 2-propanol. The basic characteristics of methanol, ethanol, and 2-propanol (isopropanol, propan-2-ol), i.e., alcohols used as the fuel in this study, are summarized based on various sources in Table 1.

Table 1. Physicochemical properties of the analyzed alcohol fuels [3,21–23].

Parameter	Fuel		
	Methanol	Ethanol	2-Propanol
Density at 20 °C (g/cm ³)	0.791–0.792	0.805–0.812	0.784–0.787
Kinematic viscosity at 20 °C (mm ² /s)	0.757	1.333	2.826
Dynamic viscosity at 20 °C (mPa·s)	0.599	1.078	2.220
Molar mass (g/mol)	32.040	46.068	60.110
Calorific value at 15.5 °C (MJ/kg)	19.90	26.80	31.00
Lower explosive limit in air at atmospheric pressure (% vol.)	5.5	3.3	2.0
Upper explosive limit in air at atmospheric pressure (% vol.)	50	19	13
Excess air factor (-)	6.40	9.00	~10.33
Boiling point at atmospheric pressure (°C)	64–65	78–79	81–83
Flash point (in a closed crucible) (°C)	11–12.0	12–18.3	11.7–15
Autoignition temperature (°C)	455–470	373–425	350–425
Octane number (research) RON (-)	108.7	107.4	112.5
Cetane number CN (-)	5	5–15	~12

Alcohols have a low cetane number (low self-ignition tendency), so they are unsuitable as a stand-alone fuel for compression-ignition engines [24]. However, they are used together with pilot liquid hydrocarbon fuel in dual-fuel compression-ignition engines [25], and due to their high octane number, they can be used in spark-ignition engines [26]. Recently, methanol has attained the most popularity as a carbon fuel containing only one carbon atom [27].

One significant challenge of using alcohols as fuel is their lubricity and corrosive effects [28,29], which can result in accelerated wear and damage to machinery powered by such fuel [30]. This also applies to other alcohols used as a stand-alone fuel [31]. In the case of internal combustion engines, the use of alcohol fuels, among others, is considered in the context of their components in blends with diesel oils [32], blends with gasoline [33], or the use of these fuels alone after appropriate treatment with admixtures that improve lubricity [34,35].

Despite a very rich literature describing studies of blending fuels of different types and various aspects of the use of alcohol fuels, the authors did not find any cross-discipline articles that compile the basic rheological and tribological properties of the simplest aliphatic alcohols, which is the motivation for conducting the experiment, that are summarized in this article.

Further research will focus on improving the lubrication properties and reducing corrosion caused by alcohol fuels, which will allow their wider use in combustion engines, and on optimizing fuel mixtures to increase combustion efficiency and reduce harmful emissions.

2. Materials and Methods

The employed experiment used certified alcohol fuels: methanol p.a. 99.85% (PTH CHEMLAND Zbigniew Bartczak, Stargard, Poland), ethanol p.a. 96.00% (Honeywell Specialty Chemicals Seelze GmbH, Seelze, Germany), and 2-propanol p.a. 99.80% (PTH CHEMLAND Zbigniew Bartczak, Stargard, Poland).

In order to holistically assess the effect of the tested fuels on the wear of engine components (i.e., precision injector pairs, fuel pumps, and valves) that can seize, selected rheological and tribological parameters were measured. The procedure adopted in the

experiment is shown in Figure 1. A summary of the measurement data is provided in Appendix A.

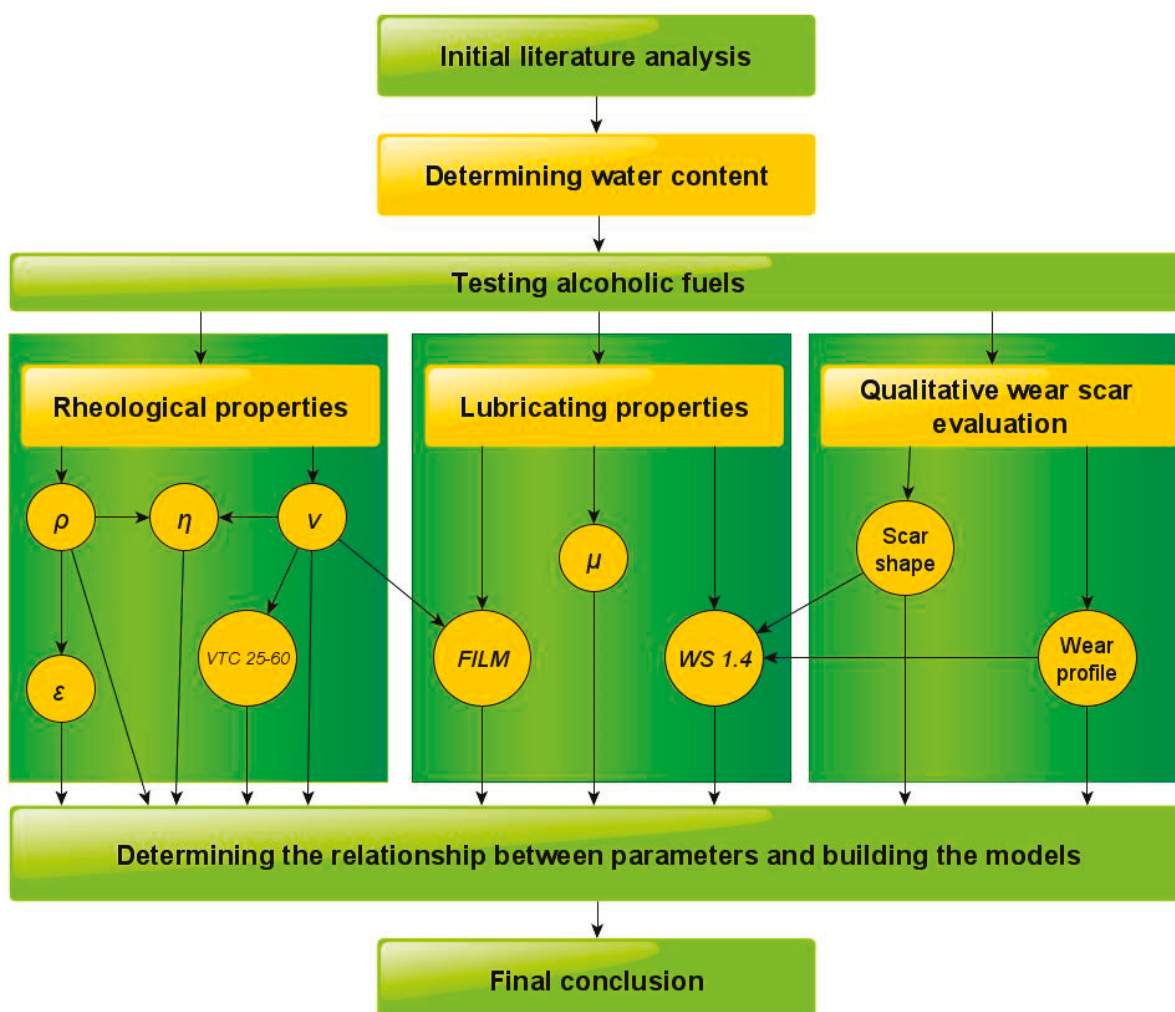


Figure 1. Scheme adopted for the experiment.

Considering the hygroscopic nature of alcohols, the water content was measured for each fuel to best describe the material used in the experiment. This water content testing was determined using the Karl–Fischer method with an 831 KF Coulometer (Metrohm, Herisau, Switzerland). The measured water content in the tested fuels is presented in Table 2.

Table 2. Measured water content of the tested fuels.

Parameter	Fuel		
	Methanol	Ethanol	2-Propanol
Water content (% m/m)	0.02	5.50	0.13

The rheological properties of alcohols were described using viscosity. Based on the measured values of kinematic viscosity and density, the dynamic viscosity was calculated. The reference density measurement of the petroleum products is usually taken at 15 °C [36]. The viscosity of petroleum-based fuels and lubricating oils is usually determined at 40 °C and 100 °C [37].

In the present experiment, the density of each fuel was determined at 15 °C, 25 °C, 40 °C, and 60 °C, while the kinematic and dynamic viscosities were determined at 25 °C, 40 °C, and 60 °C. The lower value is limited by the capabilities of the measuring apparatus, while the upper value relates to the proximity to the boiling point for one of the fuels tested, i.e., methanol, which is 64–65 °C. Each measurement of the density and kinematic viscosity was made twice, and the value that is recorded is the average of the two measurements. Dynamic viscosity was calculated based on the measured density and kinematic viscosity. Information about the instruments used and the standards according to which the measurements were made, as well as the accuracy of the measurements, is summarized in Table 3.

Table 3. Information on the apparatus and methods used to determine the rheological parameters of the alcohol fuels under study.

Parameter	Apparatus Used	Standard of Measurement Implementation	Accuracy of Measurement	Accuracy of the Temperature Setting
Density	DMA 4500 density analyzer with an oscillating U-tube (Anton Paar GmbH, Graz, Austria)	ISO 12185: 2024 [36]	$5 \times 10^{-5} \text{ g/cm}^3$	0.02 °C
Kinematic viscosity	Cannon-Fenske Opaque glass capillary viscometer (Paradise Scientific Company Ltd., Dhaka, Bangladesh) and a TV 2000 viscometric bath (Labovisco bv, Zoetermeer, The Netherlands)	ISO 3104:2023 [37]	0.1%	0.01 °C

In the next step, the variation of density and kinematic viscosity as a function of temperature was evaluated. For this purpose, the coefficient of temperature change in density and the relative percentage decrease in kinematic viscosity with increasing temperature were found. Regression models were also built to describe the variation of density, kinematic viscosity, and dynamic viscosity as a function of temperature. For each model, the quality of the model fit to the experimental data was evaluated using the coefficient of determination. A summary of the developed models is provided in Appendix B.

The tribological properties of the tested fuels were determined using the high-frequency reciprocating rig (HFRR) from which the corrected wear scar $WS_{1.4}$ (lubricity [38]) was found, as well as the average coefficient of friction and the relative percentage decrease in oil *FILM* thickness during the execution of the HFRR test. Considering the high wear intensity of the samples separated by a layer of test fuels, the measurements were performed at a test execution temperature of 25 °C in accordance with ISO 12156:2023 [39], ASTM D6079-22 [40]. The ASTM D6079 standard is essentially identical in content to the other two standards, CEC F-06-96 [41] and ISO 12156:2023. The difference concerns the testing of low-lubricity fuels, where only the ASTM D6079 standard allows for lubricity testing at temperatures lower than 60 °C. Moreover, CEC F-06-96 is now obsolete [42]. It should be noted that the HFRR apparatus used meets the measurement requirements in accordance with both ASTM D6079 and ISO 12156:2023 standards. The lubricity tests were carried out at a standard time τ of 75 min and a shortened test execution time τ of 30 min. In addition to the quantitative evaluation of lubricity and auxiliary indicators, a qualitative assessment was made on the wear scar produced during each HFRR test. Information

on the apparatuses used, and the standards according to which the measurements of tribological parameters were carried out are summarized in Table 4.

Table 4. Information about the apparatuses and methods used to determine the tribological parameters of the alcohol fuels under study.

Parameter	Apparatus Used	Standard of Measurement Implementation	Accuracy of Measurement	Accuracy of the Temperature Setting
Lubricity	HFRR V1.0.3 tribometer [43] and HFRR microscope [44] (PCS Instruments, London, UK)	ASTM D6079-22 [40]	50 μm	80 μm
Average coefficient of friction	Cannon-Fenske Opaque glass capillary viscometer (Paradise Scientific Company Ltd., Dhaka, Bangladesh) and a TV 2000 viscometric bath (Labovisco bv, Zoetermeer, The Netherlands)	HFRR V.1.0.3 procedure [43]	Auxiliary parameter Not applicable	Auxiliary parameter Not applicable
Percentage decrease in oil <i>FILM</i> thickness		HFRR V.1.0.3 procedure [43]	Auxiliary parameter Not applicable	Auxiliary parameter Not applicable

In view of the fact that lubricity is not a fundamental physical quantity, its measurement accuracy is not specified. Instead, the standards include information on the repeatability and reproducibility of the measurements, which are determined based on statistical analyses of results obtained in different laboratories for a given set of samples.

3. Results and Discussion

3.1. Rheological Indices

The density of the alcohol fuels tested as a function of their temperature is shown in Figure 2. The dotted lines show the curves approximating each set of measurements. Ethanol has the highest density, and 2-propanol has the lowest.

The density ρ_t (kg/m^3) of each of the studied alcohols, likewise for fossil fuels, decreases approximately linearly with increasing temperature and can be determined at a given temperature t ($^{\circ}\text{C}$) relative to the reference density ρ_{15} (kg/m^3) of a given liquid at 15°C according to a relationship commonly used in engineering applications, which is described by the following formula [45]:

$$\rho_t = \rho_{15} - \varepsilon(t - 15), \quad (1)$$

where ε ($\text{kg}/(\text{m}^3 \cdot ^{\circ}\text{C})$) is the coefficient of temperature change for liquid density.

For the tested alcohols and the temperature difference between 15°C and 60°C , the coefficient ε can be calculated using the densities at the relevant temperatures, i.e., ρ_{15} (kg/m^3) and ρ_{60} (kg/m^3), according to the following relationship:

$$\varepsilon = \frac{|\rho_{60} - \rho_{15}|}{60 - 15} = \frac{|\rho_{60} - \rho_{15}|}{45} \quad (2)$$

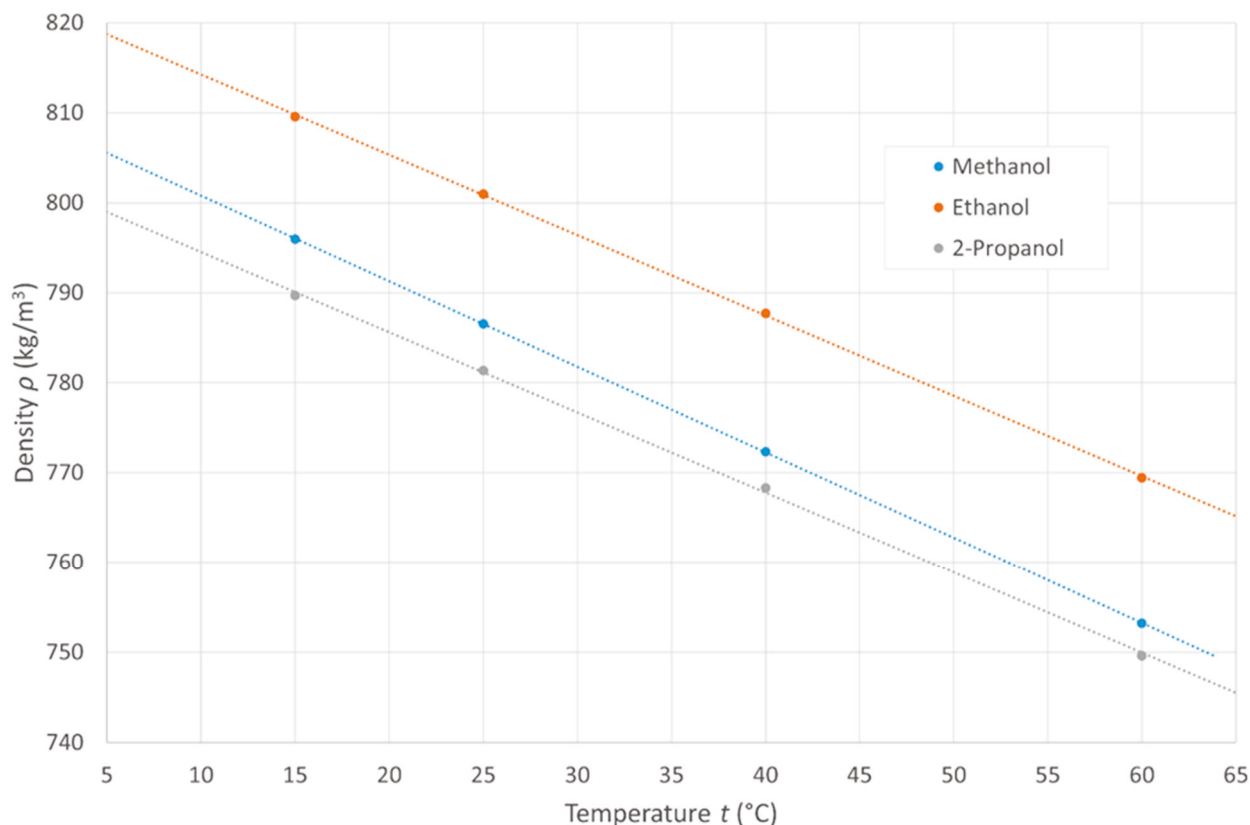


Figure 2. Measured densities of the alcohol fuels under study.

The values of the densities of the tested fuels at a reference temperature of 15 °C, the ϵ coefficient for the measured densities of the tested alcohols, and the R^2 coefficient of determination that describes the fit of the model (1) to the measured data are shown in Table 5. For all three tested alcohols, the coefficient of determination was $R^2 > 0.999$, so the model has a very good fit with the data.

Table 5. Indicators characterizing the model of temperature change for the density of alcohol fuels under study.

Alcohol	P15 (kg/m ³)	ϵ (kg/(m ³ ·°C))	R^2 (–)
Methanol	795.96	0.9507	0.9999
Ethanol	809.59	0.9820	0.9998
2-Propanol	789.71	0.8907	0.9994

The kinematic viscosities of the tested fuels are shown in Figure 3. The dotted lines indicate the curves approximating the change in kinematic viscosity as a function of temperature. The highest kinematic viscosity is 2-propanol, and the lowest is methanol. With increasing viscosity, the thickness of the oil film increases, which may translate into less wear for the contacting components separated by a layer of test fluid.

The kinematic viscosity γ_t (mm²/s) of a liquid is a function of dynamic density and density at a given temperature t (°C), as described by the relationship:

$$\gamma_t = 1000 \frac{\eta_t}{\rho_t}, \quad (3)$$

where η_t (mPa·s) is the dynamic density of the liquid, and 1000 is the conversion factor of the units of measurement.

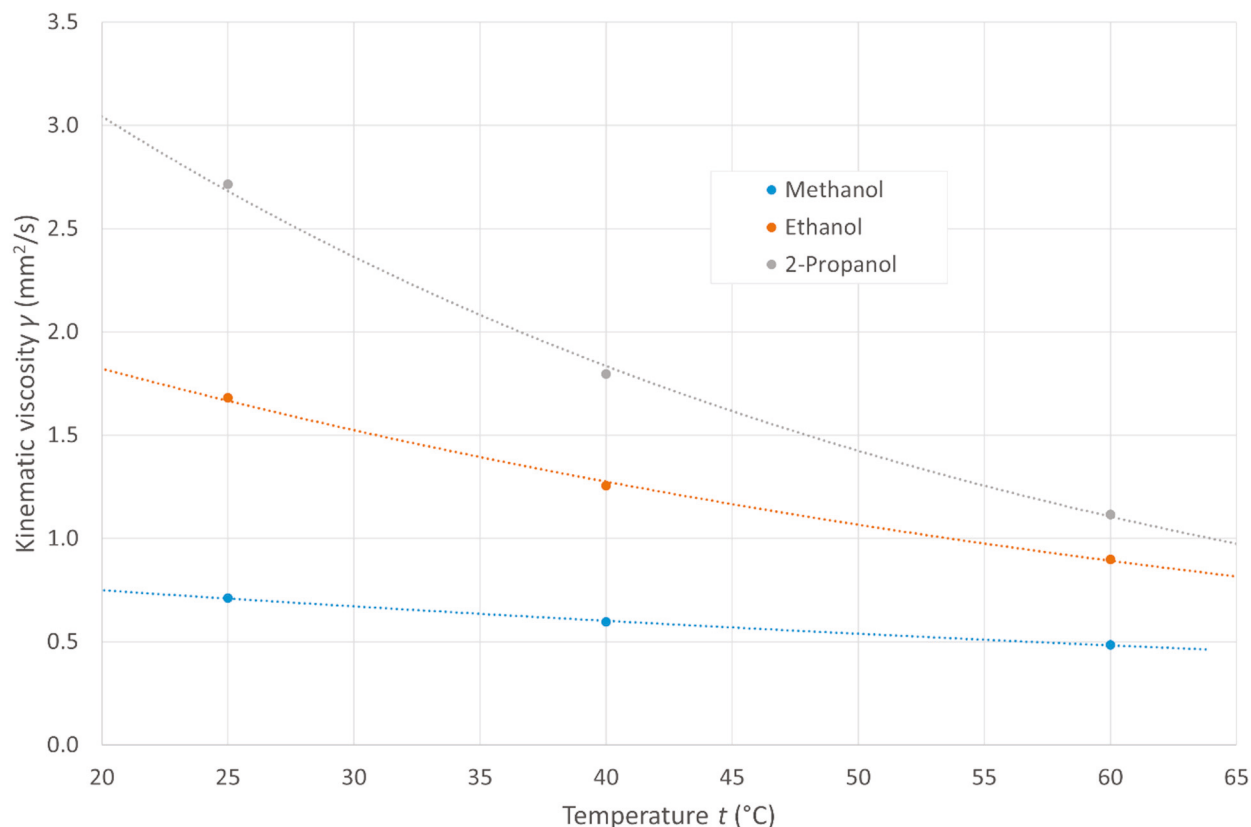


Figure 3. Measured kinematic viscosities of alcohol fuels under study.

The dynamic viscosity of a liquid decreases with increasing temperature according to the exponential Arrhenius–Guzman relationship, i.e.,

$$\eta_t = Ae^{-\frac{\Delta E}{R_C T}}, \quad (4)$$

where A is the mass- and molar-volume-dependent characteristic constant for a given liquid, ΔE is the activation energy of viscous flow, R_C involves Clapeyron’s gas constant (i.e., $8.31446261815324 \text{ J} \cdot \text{mol}^{-1} \text{ K}^{-1}$), and T (K) is the absolute temperature ($T = t + 273.15$).

Taking into account the almost linear dependence of the density of the tested fuels on temperature according to Equation (1), the relationship between kinematic viscosity and temperature, similar to the case of dynamic viscosity, can be approximated by the exponential relation (4) in the form of a function described by the following:

$$\gamma_t = a_1 e^{-a_2 t}, \quad (5)$$

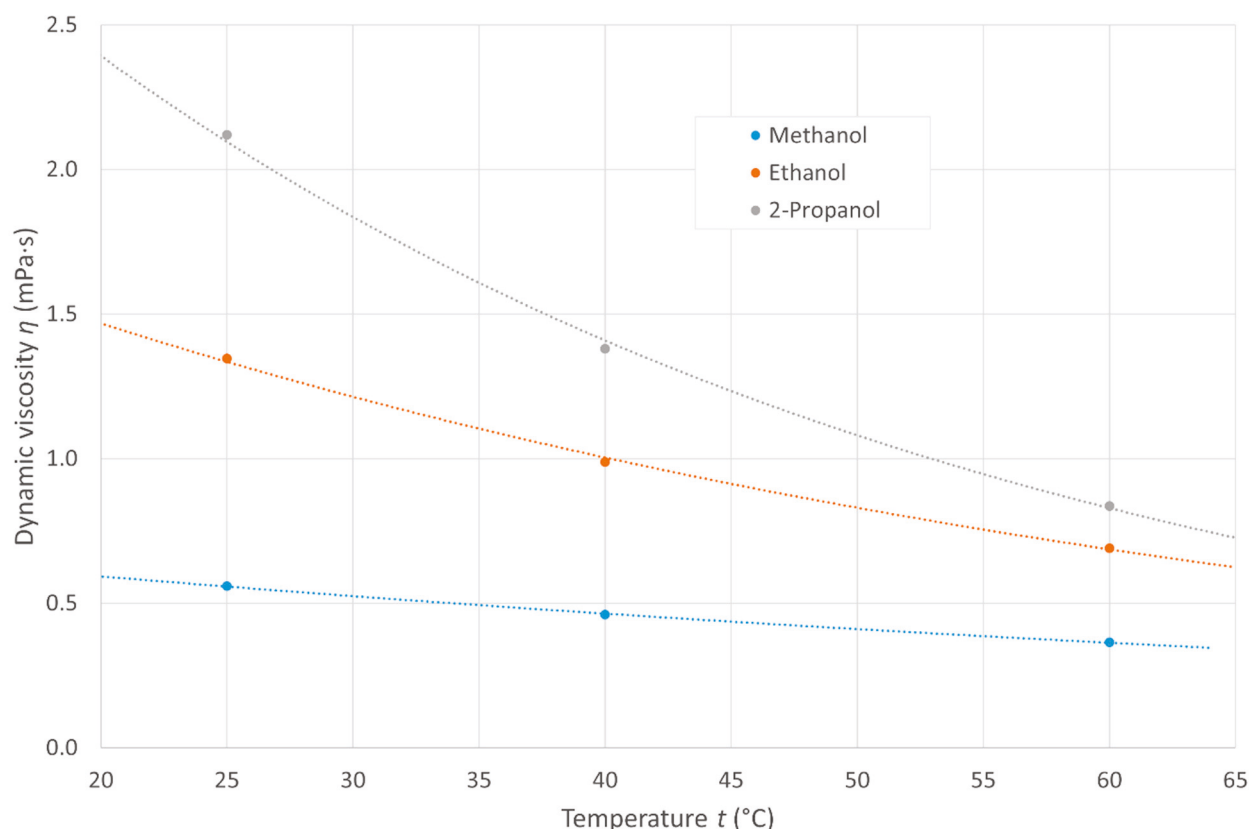
where a_1 (mm²/s) is the scale factor of the temperature model of kinematic viscosity and a_2 (1/°C) is the shape factor of the temperature model of kinematic viscosity.

The values of the coefficients a_1 and a_2 for the measured kinematic viscosities of the tested alcohols, as well as the coefficient of determination R^2 , which describes the fit of model (5) to the measured data, are shown in Table 6. For all three tested alcohols, the coefficient of determination was $R^2 > 0.998$, so the model is again a very good fit.

Dynamic viscosity was calculated using the transformed relation (3) for the tested fuels. The values of dynamic viscosity as a function of temperature are shown in Figure 4. The dotted lines indicate the curves approximating each set of measurements.

Table 6. Calculated coefficients of the exponential dependence of kinematic viscosity on the temperature of alcohol fuels under study.

Alcohol	a_1 (mm ² /s)	a_2 (1/°C)	R^2 (–)
Methanol	0.9336	0.011	0.9989
Ethanol	2.6041	0.018	0.9982
2-Propanol	5.0489	0.025	0.9983

**Figure 4.** Dynamic viscosities of the tested alcohol fuels calculated from measurements.

As an analog to relation (5), according to Equation (3), the dynamic viscosity as a function of temperature can be approximated by an exponential relationship in the form of a function described by the following:

$$\eta_t = b_1 e^{-b_2 t}, \quad (6)$$

where b_1 (mPa·s) is the scale factor of the temperature model of dynamic viscosity and b_2 (1/°C) is the shape factor of the temperature model of dynamic viscosity.

The values of the coefficients b_1 and b_2 for the calculated dynamic viscosities of the tested alcohols, as well as the coefficient of determination R^2 describing the fit of the model (6) to the measured data, are shown in Table 7. For all three tested alcohols, the coefficient of determination was $R^2 > 0.998$; again, the model is a very good fit.

A parameter commonly used to describe the variation of viscosity of petroleum products as a function of temperature is the viscosity index VI [46,47]. In the case of the fuels analyzed in the experiment, it is not possible to determine this parameter since it is necessary to know the viscosity of the product at 40 °C and 100 °C in order to determine VI ; unfortunately, all the tested alcohols have boiling points below 100 °C. To determine the temperature variation of viscosity, the modified viscosity-temperature coefficient (VTC), presented in the literature [48] and determined from previous studies [49], was used and

adapted for present purposes. In the present experiment, the modified coefficient was designated VTC_{25-60} (%) and defined as the relative percentage decrease in kinematic viscosity (mm^2/s) of the tested oil γ_{25} and γ_{60} determined at 25 °C and 60 °C, respectively, relating to the viscosity at 25 °C, as described by the relationship:

$$VTC_{25-60} = 100 \frac{\gamma_{25} - \gamma_{60}}{\gamma_{25}} \quad (7)$$

The largest decrease in viscosity with increasing temperature is shown by 2-propanol and the smallest by methanol. The values of VTC_{25-60} (%) of the tested alcohols are summarized in Table 8.

Table 7. Calculated coefficients of the exponential dependence of dynamic viscosity on the temperature of the alcohol fuels under study.

Alcohol	b_1 (mPa·s)	b_2 (1/°C)	R^2 (–)
Methanol	0.7575	0.012	0.9992
Ethanol	2.1469	0.019	0.9984
2-Propanol	4.0652	0.026	0.9985

Table 8. Temperature change in the kinematic viscosity of the fuels under study.

Parameter	Fuel		
	Methanol	Ethanol	2-Propanol
VTC_{25-60} (%)	32.02	46.58	58.88

The tested fuels show similar rheological properties and an analogous nature for the changes in individual parameters. Due to the highest viscosity and potentially thickest oil film, the best lubrication conditions will be provided by 2-propanol, followed by ethanol and, finally, methanol.

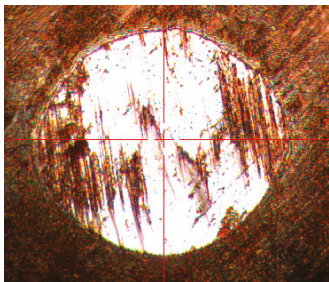
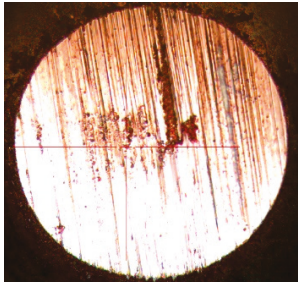
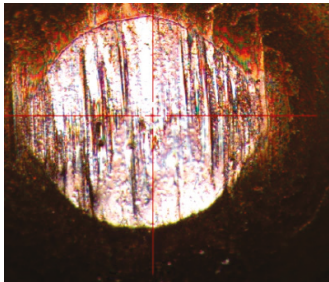
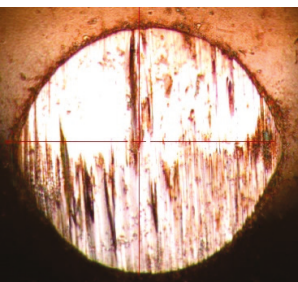
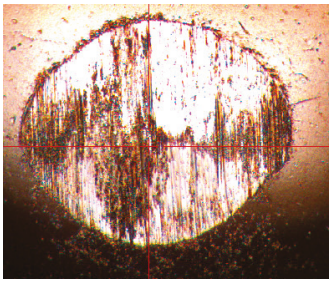
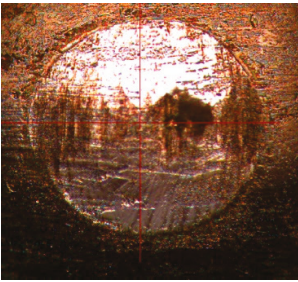
3.2. Lubricity and Auxiliary Indicators

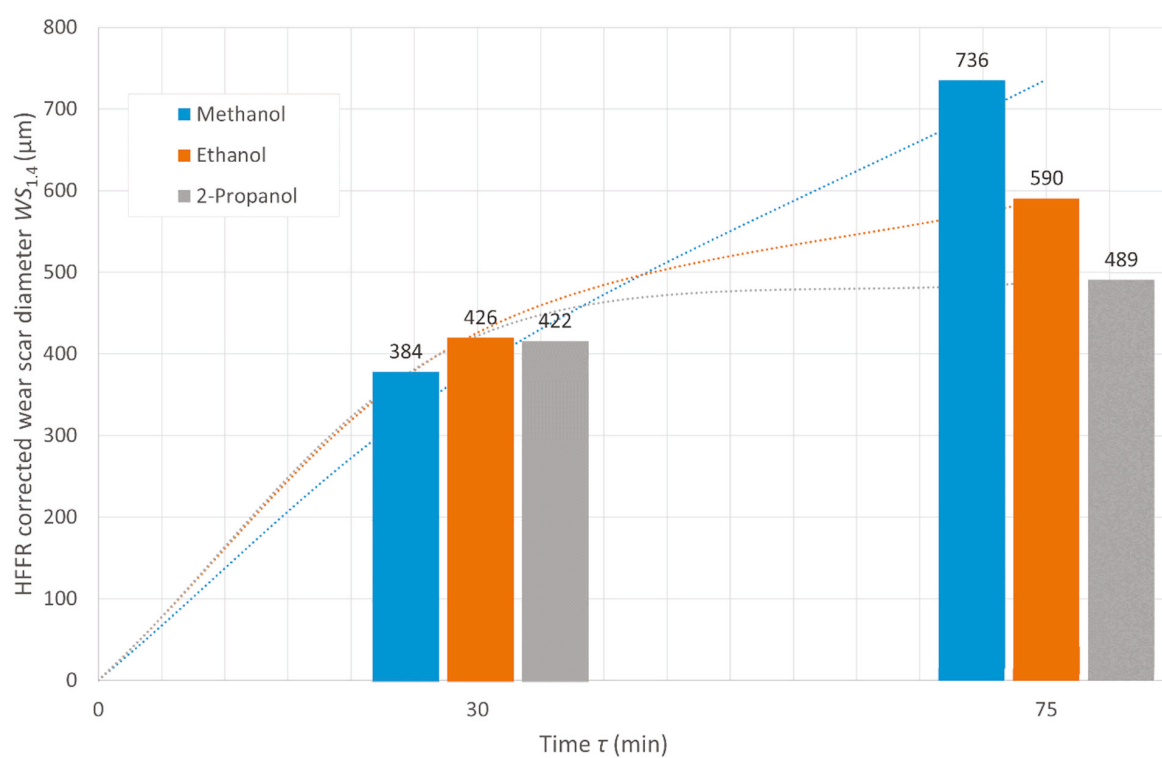
The recorded wear traces of the tested alcohol fuels obtained from HFRR tests at 25 °C for the adopted test execution times are shown in Table 9. All the obtained wear traces are similar in character. The shape of the wear trace is uniform in both directions of the measurement, making it similar to a circle.

The dominant type of wear takes the form of parallel grooves running the entire length of the scar, indicating the dominant influence of plastic deformation. For all tested samples, point-like wear is also evident, which is associated with local micro-cutting, plastic deformation, and scratching of the sample. Thus, for all the tested fuels, the occurrence of analogous phenomena in the wear zone can be assumed.

The corrected magnitude of the wear scar of the tested alcohols is shown in Figure 5. For the standard conditions of the test implementation, according to ASTM D6079-22 at 25 °C and 75 min, the largest wear scar (worst lubricity) was shown by methanol, where the $WS_{1.4}$ value was 736 μm , followed by ethanol with a $WS_{1.4}$ value of 590 μm , and the best lubricity is shown by 2-propanol with a $WS_{1.4}$ value of 489 μm . It should be noted that these values correspond to poor antiwear properties.

Table 9. Recorded wear scars of the sample during the HFRR test of the alcohols under study.

Fuel	Test Execution Time $\tau = 30$ min	Test Execution Time $\tau = 75$ min
Methanol		
Ethanol		
2-Propanol		

**Figure 5.** Measured values of the corrected average wear scar during the HFRR test of the alcohol fuels under study.

According to the Worldwide Fuel Charter 6th ed. [42] for diesel fuels, the maximum lubricity value of HFRR at 60 °C is 460 µm for fuels cat. 1, 2, and 3 and 400 µm for fuels cat. 4 and 5. According to the EN 590:2022 standard [50], the maximum lubricity value of HFRR at 60 °C is 460 µm. According to the standard for petroleum distillation marine fuels ISO 8217:2024 [51], where the maximum permissible value of $WS_{1.4}$ is 520 µm, which is supposed to ensure adequate durability of precision vapors in the fuel apparatus, only 2-propanol meets analogous requirements. In the case of methanol and ethanol, the value of the corrected wear scar exceeds the normative values, assuming that such values would be obtained at 60 °C. The measurements due to the high volatility of the fuels analyzed were made at the lower temperature of 25 °C, which is indicated in ASTM D6079-24 [40] for fuels of this type. A previous study for diesel fuels shows that the $WS_{1.4}$ values determined for tests at 25 °C are about twice as low as for measurements made at 60 °C [52].

However, the lubricity results obtained are better than the analogous ones obtained using the HFRR test for many additive-free gasoline fuels [53]. For example, European conventional gasoline has $WS_{1.4} = 799$ µm, CaRFG2 gasoline has $WS_{1.4} = 872$ µm, CEC RF-83-A-91 gasoline has $WS_{1.4} = 711$ µm, commercial UK gasoline has $WS_{1.4} = 792$ µm, and Finland City gasoline has $WS_{1.4} = 861$ µm [52].

Due to the low lubricity of the tested alcohols, additional measurements were made for the modified standard conditions, i.e., measurement at the standard temperature of 25 °C, but with a shortened measurement time τ of 30 min. In this case, all fuels show a similar $WS_{1.4}$ value, which ranges from 384 µm for methanol through 422 µm for 2-propanol to 426 µm for ethanol. Based on the presented results, it can be concluded that, after a certain measurement duration is exceeded, the wear increases due to a decrease in the amount of the test substance separating the contacting samples due to evaporation caused by friction heating of the samples.

The authors determined the measurement uncertainty values based on the calibration certificates of the measuring instruments used. A summary of the calculated measurement uncertainty values for the analyzed parameters is shown in Table 10. The assessment of measurement uncertainty for secondary and auxiliary quantities was not included in the mentioned table due to their specific nature. The indicated uncertainties refer to normative values.

Table 10. Summary of the uncertainties of the obtained measurement results for each parameter.

Parameter	Symbol	Unit	Methanol	Ethanol	2-Propanol
Density @ 15 °C	$U(\rho_{15})$	kg/m ³	0.3509	0.3509	0.3509
Kinematic viscosity @ 40 °C	$U(\nu_{40})$	mm ² /s	0.0148	0.0148	0.0148
Lubricity (HFRR wear scar diameter) @ 25 °C	$U(WS_{1.4})$	µm	37.3	37.3	37.3

The average coefficient of friction of the tested fuels during the execution of the test is shown in Figure 6. For a standard HFRR test time τ of 75 min, the highest coefficient of friction equal to 0.369 was obtained for methanol, followed by 0.361 for ethanol, and the lowest value of 0.290 was found for 2-propanol. With a shortened test time τ of 30 min, the highest coefficient of 0.411 was obtained for 2-propanol, next 0.377 for ethanol, and the lowest for methanol at 0.235.

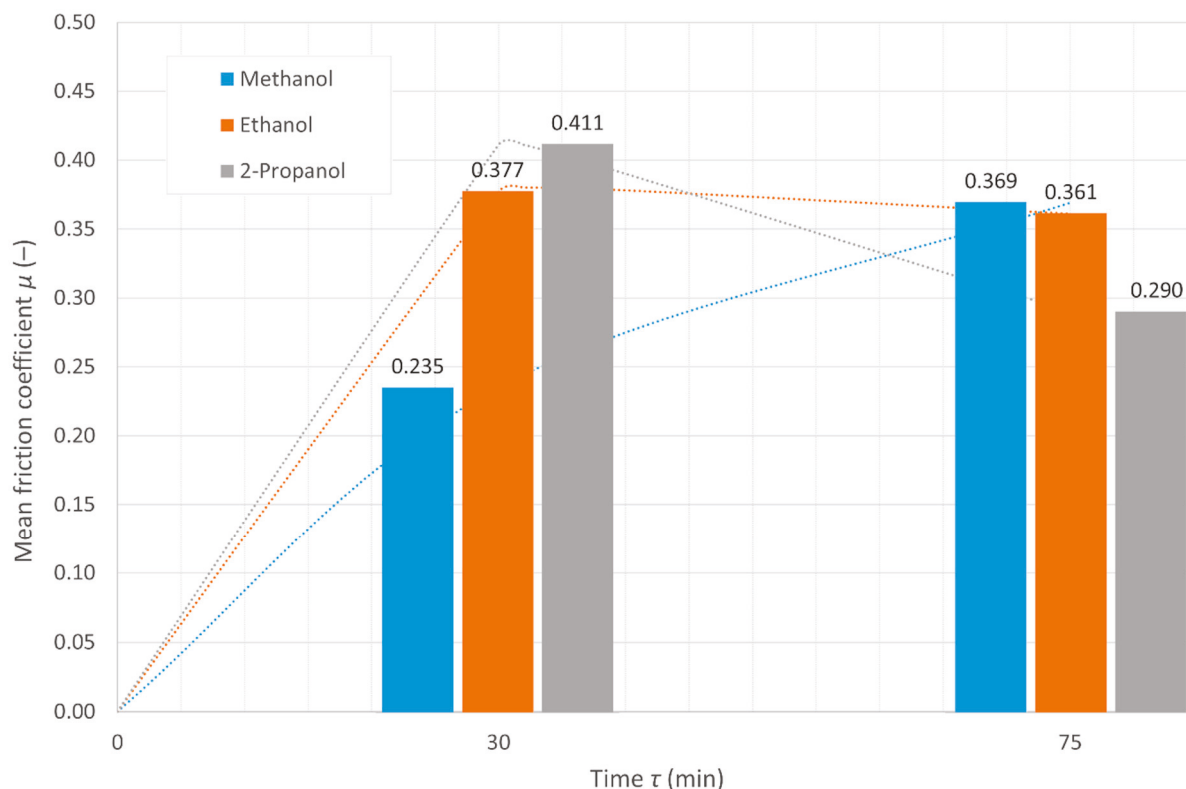


Figure 6. Measured values of the average coefficient of friction during the HFRR test of the alcohol fuels under study.

The average coefficient of friction for the tested alcohols and test execution times is in the range of 0.235–0.411. The values obtained are close to the values of the average coefficient of friction during the HFRR test of gasolines at 25 °C, where the example gasolines obtained a coefficient in the range of 0.320–0.530 [52]. The obtained values of the average coefficient of friction, on the other hand, are much higher than those obtained for diesel fuels, which, at a measurement temperature of 25 °C, are 0.125–0.149, for example, for the distillation fuels for diesel engines [52].

The value of the percentage decrease in oil film *FILM* thickness during the execution of the HFRR test is shown in Figure 7. For both the standard test execution time of 75 min and the test shortened to 30 min, the highest oil *FILM* thickness at the end of the test execution was obtained for methanol, then for 2-propanol, and the highest film thinning was obtained for ethanol. The very low *FILM* parameter values of 24% and 32% for methanol and $\leq 16\%$ for ethanol and 2-propanol indicate a significant reduction in lubricating *FILM* thickness and periodic metallic contact of the connected samples during the execution of the HFRR test.

The *FILM* parameter values do not correlate with the viscosity values obtained for individual fuels during previous tests, as shown in Figures 3 and 4, where a lower viscosity is often paired with lower *FILM* parameter values. Such a relationship occurs, for example, for fuel-diluted fresh lubricating oils [54] or fuel-diluted used lubricating oils [55].

In the present experiment for the tested fuels, the mentioned relationship between *FILM* thickness and substance viscosity was not observed, which is presumably due to the fact that the implementation of the HFRR test refers to the evaluation of the ability of individual fuels to form a boundary layer and the analysis of the boundary friction that takes place under these conditions. In contrast, viscosity has a direct effect on the separation of contacting components during the time when the lubricating substance is applied at the appropriate pressure, that is, during hydrostatic or hydrodynamic lubrication. Then, liquid

or mixed friction takes place. An additional factor affecting the obtained results is the low boiling point of the fuels under testing, which results in an accelerated depletion of the amount of the test substance relative to the petroleum-based fuels during the execution of the HFRR test.

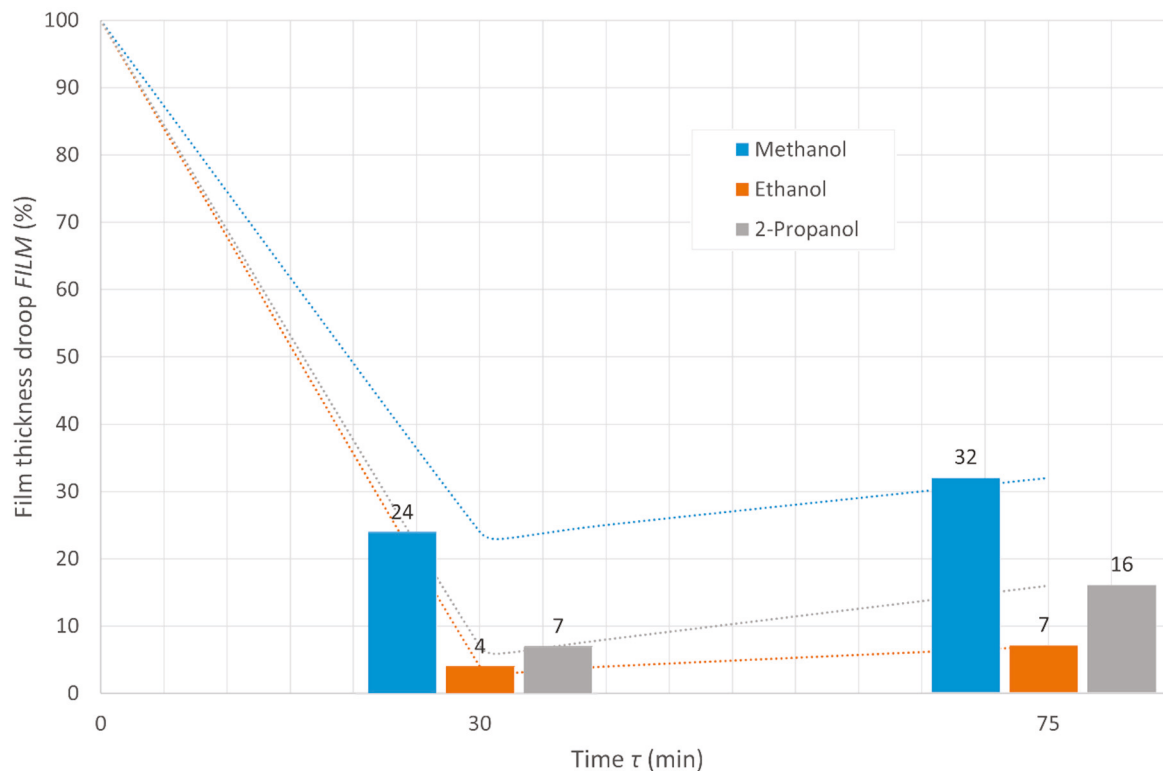


Figure 7. Measured values of thickness drop (resistance) of tested alcohol fuels acting as lubricants during the HFRR test.

4. Conclusions

This study confirmed the low lubricity of the fuels under investigation. Thus, their use in engines may require the use of mixtures of these fuels with hydrocarbons or the application of admixtures to improve the lubricity and, thus, reduce the wear intensity of the components of the tribological pairs lubricated with these fuels.

The lubricity of fuel, and consequently its impact on engine component wear, can be improved by lowering the fuel temperature in the fuel supply system and by using chemical additives that enhance fuel lubricity. Indirectly, the negative impact of fuel on the wear of combustion chamber components, such as cylinder liners, pistons, and piston rings, can be minimized by selecting a lubricating oil that is appropriately matched to the fuel. This approach is analogous to the practice used in industrial and marine engines powered by liquid hydrocarbon fuels with low sulfur content, such as very low sulfur fuels (VLSF) and ultra-low sulfur fuels (ULSF).

The obtained results relating to the rheological characteristics of the studied alcohols can be the basis for further analysis. This is especially true for the developed models of density, kinematic viscosity, and dynamic viscosity, which can be used in subsequent experiments since they provide a very good match between the calculation results and empirical data.

The experiment, as expected, showed that the antiwear properties of alcohols are low. The lubricity is much worse than that of diesel oils, while it is close to that of gasoline. This makes it necessary to use various admixtures to improve the lubricity of pure alcohol fuels and fuels that are mixtures of alcohols, alcohols and gasolines, and alcohols and diesel oils.

The obtained results can be used in further research aimed at optimizing the properties of fuels enriched with bioalcohols or alcohol-based fuels, which is becoming a much more important issue for road users who want to reduce their fossil fuel use. Moreover, the new generation of fuels, in addition to providing adequate ignition and caloric properties, must also exhibit appropriate characteristics to guarantee the reliability, durability, and operational safety of the internal combustion engines that these fuels will power.

Author Contributions: Author conceptualization, L.C., W.W. and M.S.; methodology, L.C., W.W. and M.S.; software, L.C. and M.S.; validation, L.C., W.W. and M.S.; formal analysis, L.C., W.W. and M.S.; investigation, L.C., W.W. and M.S.; resources, L.C., W.W. and M.S.; data curation, L.C. and W.W.; writing—original draft preparation, L.C., W.W. and M.S.; writing—review and editing, L.C., W.W. and M.S.; visualization, L.C., W.W. and M.S.; supervision, L.C.; project administration, L.C.; funding acquisition, L.C. All authors have read and agreed to the published version of the manuscript.

Funding: This research was partially funded by the Ministry of Science and Higher Education (MNiSW) of Poland, grant number 1/S/KSO/25.

Data Availability Statement: All data are available for this paper upon reasonable request.

Conflicts of Interest: The authors declare no conflicts of interest. The funders had no role in the design of the study, the collection, analysis, or interpretation of data, the writing of the manuscript, or the decision to publish the results.

Abbreviations

A	characteristic constant for a given liquid
a_1, a_2	coefficients of the equation approximating kinematic viscosity
ASTM	American Society for Testing and Materials
b_1, b_2	coefficients of the equation approximating dynamic viscosity
CN	cetane number
ΔE	activation energy of viscous flow
FILM	percentage decrease in film thickness of lubricant during the HFRR test
HFRR	high-frequency reciprocating rig
ISO	International Organization for Standardization
R_C	Clapeyron's gas constant
R^2	coefficient of determination
RON	research octane number
T	absolute temperature expressed in K
t	relative temperature expressed in °C
U	uncertainty
VI	viscosity index
VTC	viscosity-temperature coefficient
VTC_{25-60}	relative percentage decrease in kinematic viscosity with an increase in temperature
$WD_{1.4}$	normalized HFRR wear scar diameter
γ_t	kinematic viscosity at temperature t (°C)
ε	coefficient of temperature change for density
μ	friction coefficient
η_t	dynamic viscosity at temperature t (°C)
ρ	density
ρ_{15}	density at 15 °C
ρ_{60}	density at 60 °C
ρ_t	density at temperature t (°C)
τ	test execution time

Appendix A

Table A1. Measurement data.

Parameter	Temperature (°C)	Time (min)	Unit	Methanol	Ethanol	2-Propanol
Kinematic viscosity	25	N/A	mm ² /s	0.712	1.681	2.714
	40	N/A		0.597	1.256	1.797
	60	N/A		0.484	0.898	1.116
Density	15	N/A	kg/m ³	795.96	809.59	789.71
	25	N/A		786.56	800.96	781.36
	40	N/A		772.33	787.73	768.31
	60	N/A		753.18	769.45	749.63
Water content	N/A	N/A	(% m/m)	0.02	5.50	0.13
Lubricity	25	30	µm	384	426	422
	Coefficient of friction		N/A	0.235	0.377	0.411
	FILM parameter		%	24	4	7
	25	75	µm	736	590	489
	Coefficient of friction		N/A	0.369	0.361	0.290
	FILM parameter		%	32	7	16

Appendix B Empirical Models

Appendix B.1 Density $\rho_t(\text{kg/m}^3) = f[t (\text{°C})]$

Methanol: $\rho_t = 795.96 - 0.9507(t - 15)$

Ethanol: $\rho_t = 809.59 - 0.9820(t - 15)$

2-Propanol: $\rho_t = 789.71 - 0.8907(t - 15)$

Appendix B.2 Kinematic Viscosity $\gamma_t(\text{mm}^2/\text{s}) = f[t (\text{°C})]$

Methanol: $\gamma_t = 0.9336e^{-0.011 \cdot t}$

Ethanol: $\gamma_t = 2.6041e^{-0.018 \cdot t}$

2-Propanol: $\gamma_t = 5.0489e^{-0.025 \cdot t}$

Appendix B.3 Dynamic Viscosity $\eta_t(\text{mPa}\cdot\text{s}) = f[t (\text{°C})]$

Methanol: $\eta_t = 0.7575e^{-0.012 \cdot t}$

Ethanol: $\eta_t = 2.1469e^{-0.019 \cdot t}$

2-Propanol: $\eta_t = 4.0652e^{-0.026 \cdot t}$

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Article

Effects of Ethanol–Diesel Blends on Cylinder Pressure, Ignition Delay, and NO_x Emissions in a Diesel Engine

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Abstract: This study examined how adding ethanol to diesel fuel affects combustion characteristics, cylinder pressure and NO_x emissions in an AVL engine. The research focused on key engine parameters, including autoignition delay, in-cylinder pressure rise rates, the peaks of the mean in-cylinder temperature and NO_x emissions. Three fuel types were tested: pure diesel (DF) and blends with 10 and 20% ethanol by volume (DF10 and DF20). The results obtained indicate that increasing the ethanol content in diesel fuel significantly affects the combustion process of the fuel mixture, particularly in its early stage, reducing the benefits of the pilot fuel injection. Moreover, it was observed that the combustion of the DF20 mixture leads to a substantially higher pressure increase in the cylinder, exceeding the values recorded for pure diesel fuel by approximately 25%. Furthermore, the study revealed that ethanol addition increases the peaks of the mean in-cylinder temperature, with a recorded difference of up to 60 °C between pure diesel fuel and DF20. Since NO_x formation is highly temperature-dependent, this temperature rise is likely to result in higher NO_x concentration. Additionally, a slight effect of ethanol on increasing the ignition delay angle was observed. This remained minor, and did not exceed approximately 1 CA. These findings highlight the complex relationship between ethanol content in diesel fuel, combustion dynamics, and emissions. They emphasize the need for optimizing the injection process for ethanol–diesel blends to balance the benefits of ethanol addition with potential challenges related to combustion efficiency, engine load and NO_x concentration.

Keywords: diesel; combustion; ethanol

1. Introduction

The blending of ethanol with diesel fuel, known also as e-diesel or oxygenated diesel, has gained significant attention due to its potential to improve combustion characteristics and reduce emissions in diesel engines [1]. The first studies, conducted in the 1980s with ethanol and diesel blends, did not show technical obstacles for the exploitation of such fuel, which was an important step toward green energy after the global fuel crises in the 1970s triggered awareness among many countries of the availability of oil [2]. The well-recognized advantages of ethanol's addition to diesel, as a renewable and oxygenated fuel, include enhanced combustion efficiency and reduced harmful pollutants [3–5]. While different

techniques have been adopted for the use of ethanol in diesel engines, like dual injection, alcohol fumigation and alcohol–diesel emulsification, blending is usually preferred instead of the others as it allows for the prevention of phase separation and modification of the engine system [6]. Ethanol combines many different properties, such as higher oxygen content, lower viscosity, higher latent heat of evaporation, etc., resulting in a positive effect on engine performance and emissions. While lower viscosity results in better atomization than a higher latent heat evaporation increase in the volume efficiency, higher oxygen content reduces HC and CO emissions. At the same time, blending ethanol and diesel fuel faces problems such as poor miscibility and instability of phase separation depending on ambient temperature [7]. Ethanol solubility with water is based on the fact that the hydroxyl group found in ethanol and connected to its saturated carbon atom enables it to bond with hydrogen [8]. Besides that, alcohols generally have a lower derived cetane number (DCN) than diesel fuel, in such a way that contributes to an increase in the ignition delay, resulting in a more intense pre-mixed combustion phase and greater noise due to the associated in-cylinder pressure peaks [9,10]. However, due to the difference in ethanol, their chemical properties compared to diesel, especially higher oxygen content, improvement in the engine performance, combustion dynamics and emissions, should be observed [11,12].

Research typically involves a single-cylinder or multi-cylinder diesel engine equipped with sensors to measure cylinder pressure, temperature and emissions. Various blend ratios (e.g., E10, E20, E30) are tested to evaluate their impact on engine performance and emissions. Analyzing the accuracy of the engine in-cylinder pressure measurements necessitates a unique approach, as no reference instruments or calibration standards exist for the complete measurement system. Skrzek et al. [13] performed in-cylinder pressure measurements in a single-cylinder experimental internal combustion engine to propose an estimation method for that kind of measurement and to assess its repeatability. In order to solve the issue of repeatability, they proposed two methods: in the first, the in-cylinder pressure was recorded in the successive cycles immediately after the end of ignition, and in the second, the engine was cranked by a starter. The investigation of cylinder pressure changes in diesel engines fueled with diesel and its blends with ethanol is crucial for understanding combustion characteristics, performance and emissions. Diesel engines are widely used for their efficiency and durability, but concerns about fossil fuel depletion and environmental pollution have led to the exploration of alternative fuels, such as ethanol blends [14].

In a study by Smith et al. [15], the performance effects of ethanol were investigated, specifically focusing on the impact of ethanol–diesel blends on engine performance. They found that low-level ethanol blends (up to 10%) improved combustion efficiency and reduced emissions without significantly affecting engine power output. Similarly, Chen et al. [16] conducted engine testing with ethanol–diesel blends and observed improvements in thermal efficiency and combustion stability, particularly at higher ethanol concentrations. However, they noted a slight decrease in peak torque with increasing ethanol content.

The effects of diesel-ethanol blends on ignition characteristics have been studied by other researchers [17–19]. Recent studies by Li et al. [20] investigated the influence of ethanol–diesel blends on ignition properties. Their findings indicated that ethanol addition decreased ignition delay times, promoting more rapid and consistent combustion initiation compared to conventional diesel fuel. The presence of ethanol in the blend enhances ignition characteristics, leading to more rapid and stable combustion. Xu et al. [21] employed computational simulations and experimental validations to assess the impact of ethanol–diesel blends on combustion efficiency. Their results suggested increased combustion efficiency with ethanol blending, attributed to enhanced fuel atomization and more complete combustion in the frame of improved combustion kinetics [22].

Research conducted by Zhang et al. [23,24] explored the combustion stability of ethanol–diesel blends across varying blend ratios. The results suggested that higher ethanol concentrations enhanced combustion stability and reduced combustion duration, attributed to ethanol's higher octane rating and improved air–fuel mixing. Similarly, Zhao et al. [25] analyzed the heat release characteristics of ethanol–diesel blends to assess their combustion behavior. Their investigations revealed alterations in heat release profiles with ethanol blending, resulting in smoother combustion with moderated peak pressure and temperature gradients.

The atomization characteristics of diesel–ethanol blends, such as spray tip penetration, play an important role in engine performance and emission characteristics [26]. The study by Jimenez et al. [27] examined the effects of ethanol blending on fuel properties such as viscosity, density and cetane number. They found that ethanol–diesel blends exhibited altered fuel properties, which influenced combustion characteristics and engine performance. Han et al. [28] investigated the impact of ethanol–diesel blends on fuel atomization and spray characteristics. Their results indicated changes in spray morphology and droplet size distribution, affecting fuel–air mixing and combustion efficiency. Studies by Wang et al. [29,30] utilized advanced imaging techniques to analyze flame propagation characteristics in diesel engines fueled with ethanol–diesel blends. Their research highlighted enhanced flame stability and faster combustion propagation, attributed to ethanol's higher laminar flame speed and improved air–fuel mixing.

Shi et al. [31,32] investigated the impact of ethanol–diesel blends on combustion characteristics and emissions in diesel engines. The researchers conducted experimental tests using various ethanol–diesel blends and examined parameters such as combustion efficiency, ignition delay and emissions of CO, HC and PM. Results indicated that ethanol–diesel blends improved combustion efficiency and reduced emissions of CO and HC, while PM emissions showed a slight decrease, highlighting the potential of ethanol blends in enhancing diesel engine performance and emissions characteristics. Liu et al. [33,34] investigated the correlation between combustion characteristics of ethanol–diesel blends and emissions reduction. Their study revealed a direct relationship between improved combustion efficiency and reduced emissions of particulate matter, nitrogen oxides, and unburned hydrocarbons. Zhou et al. [35] conducted experiments on exhaust emissions from diesel engines fueled with ethanol–diesel blends and reported lower levels of nitrogen oxides (NO_x) emissions due to reduced peak combustion temperatures and altered combustion characteristics.

Cylinder pressure is a critical parameter in evaluating engine performance [36–38]. Studies [39,40] show that blending ethanol with diesel generally results in lower peak cylinder pressures due to ethanol's lower cetane number, which delays combustion initiation. The heat release rate in diesel engines is influenced by the fuel blend. Ethanol blends often show a higher rate of heat release in the premixed combustion phase due to ethanol's higher volatility and oxygen content, which enhance the mixing and combustion process [41,42]. Garg [43], through meticulous analysis of the combustion data, did not observe significant changes in the engine in-cylinder pressure and the start of injection using ethanol–diesel blends at full load condition, while he observed a reduction in peak firing pressure by up to 6%, and retarding of the start of injection and combustion achieved by 2 deg crank angle at part load operation.

In conclusion, ethanol–diesel blends exhibit promising potential for enhancing combustion characteristics in diesel engines, including improved ignition properties, combustion stability and reduced emissions. However, further research is warranted to optimize blend compositions, address compatibility issues and assess long-term engine performance and durability under real-world conditions [44].

To deepen the understanding of the effect of ethanol blends on the combustion process in an experimental diesel engine, various diesel–ethanol blends were tested using the following techniques:

- Analysis of engine indicator diagrams, enabling a comprehensive evaluation of the fuel combustion process.
- Comparative analysis of profiles of the fuel injector control signal.

2. Materials and Methods

During the investigation, the laboratory apparatus shown in Figures 1 and 2 was used to carry out the planned experiment. A key component of the applied research setup was the 5402 series diesel research engine manufactured by AVL. This state-of-the-art device was designed specifically for advanced scientific investigations in the automotive industry. It should be noted that the tested engine operated without a diesel particulate filter (DPF), a feature that typically affects exhaust gas composition and engine performance characteristics.

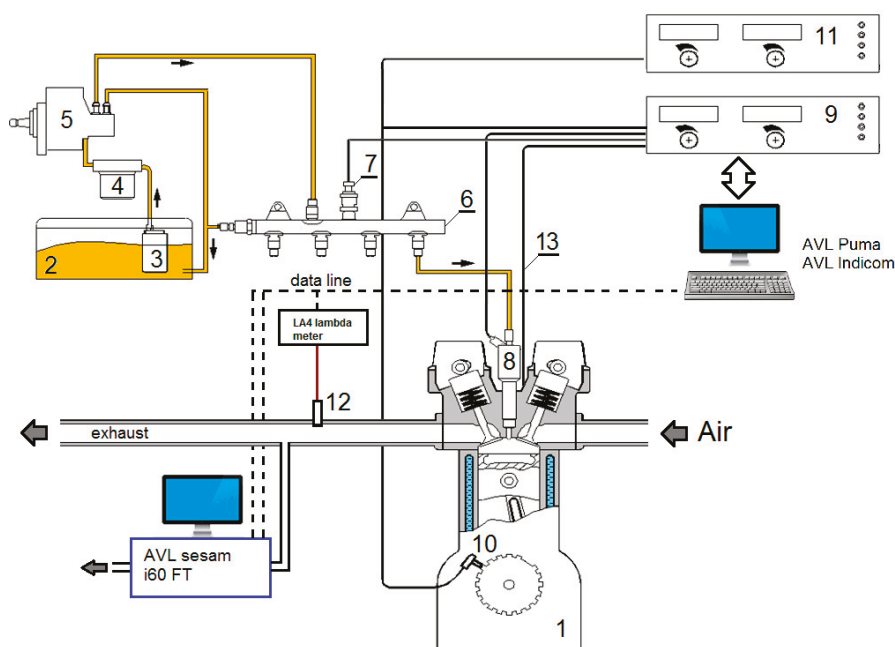


Figure 1. The schematic diagram of the research setup equipped with the AVL 5402 engine: 1—tested engine, 2—fuel tank, 3—fuel pump, 4—fuel filter, 5—high-pressure fuel pump, 6—fuel rail, 7—fuel pressure sensor, 8—fuel injector, 9—signals amplifier, 10—crankshaft angle sensor, 11—crankshaft angle encoder, 12—oxygen sensor, 13—in-cylinder pressure signal wire.

To simplify the research process, both the turbocharging system and the exhaust gas recirculation (EGR) system were deactivated. This decision was made to minimize the complexity of the research setup, enabling a more controlled and precise evaluation of the engine's basic performance parameters without interference from ancillary systems. Such an approach enhances result reproducibility and allows for a better understanding of the fundamental working processes occurring in the tested engine.

The research stand was meticulously designed and built by AVL Co., located in Graz, Austria, a leader in research and development technologies for the automotive sector. It was specifically commissioned for use at the Casimir Pulaski University of Radom (URad.). The collaboration with AVL Co. underscores the commitment to leveraging cutting-edge tools and expertise to achieve high-quality research results.



Figure 2. Actual view of the research setup equipped with the AVL engine.

The AVL 5402 series research engine is a renowned unit specifically crafted for rigorous scientific experimentation. Featuring a cylinder outfitted with 4 valves and a direct fuel injection system engineered by BOSCH Co., the engine's key specifications are delineated in Table 1.

Table 1. Selected data of the AVL 5402 engine.

Parameter	Value
Engine capacity, cm ³	511
Cylinder number	1
Injection timing	ECU controlled
Top power without supercharging	6 kW
Compression ratio	17.5
Fuel injection max. pressure	180 MPa
Crankshaft speed at idle run	750
Fuel injection system	Common Rail

As previously indicated, the engine subjected to examination in this research employs a CR injection system, meticulously regulated by a programmable engine control unit (ECU). The injection timing parameters used in this study remained constant for all tested fuels at a specific measurement point. In particular, the requisite experimental procedures were systematically replicated under constant engine operating conditions. Specifically, these conditions were characterized by discrete torque values: 5, 10, 15, 20 and 25 Nm, corresponding to engine speeds of 1200, 1700 and 2200 rpm. Thus, a total of 15 distinct engine operational states were delineated, wherein alterations in pressure within the combustion chamber were recorded for 100 consecutive cycles, specifically for the tested fuel. At each such measurement point, a fuel injection was split into 2 doses, i.e., pilot and main dose. An example of the course of changes in the signal controlling the opening of the fuel injector, changes in cylinder pressure and a graphical interpretation of the fuel auto-ignition delay angle is shown in Figure 3.

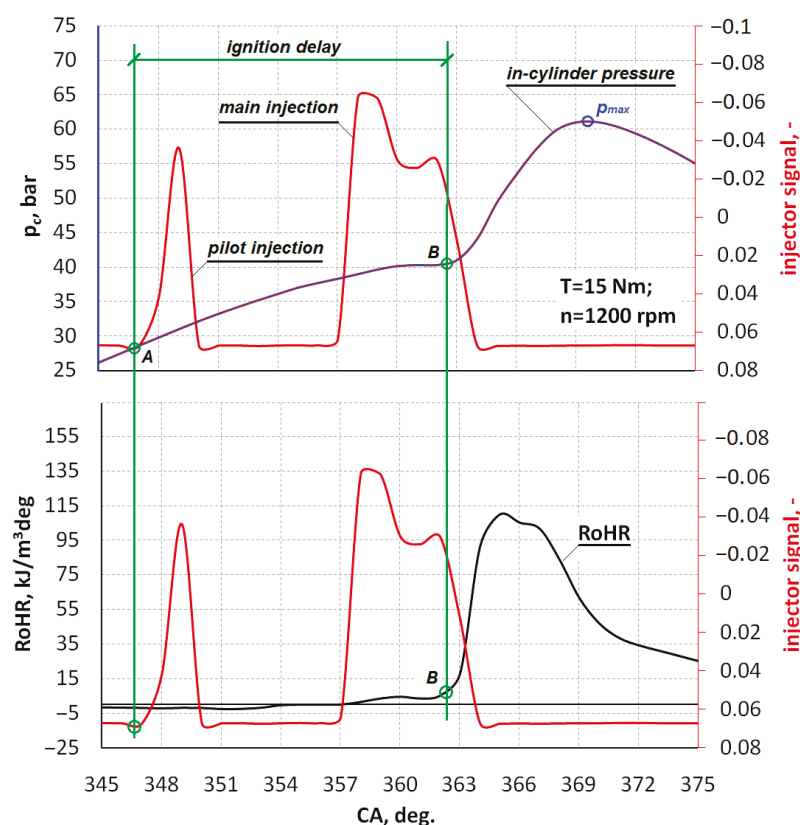


Figure 3. Graphical interpretation of determining the fuel auto-ignition delay angle and the corresponding the rate of heat release (RoHR).

According to Figure 3, the auto-ignition delay (ID) was defined as the crank angle interval between the start of pilot fuel injection and the onset of fuel combustion. The ignition point was identified based on the in-cylinder pressure trace and the corresponding rate of heat release (RoHR) profile. To accurately determine the ID, a characteristic point B on the RoHR curve was identified, indicating a rapid increase in heat release, which signifies the start of the combustion process. In this example, the injection of the pilot fuel dose began at point A, i.e., 12.5 degrees before TDC (top dead center = 360 CA deg.), and the start of combustion occurred at point B, i.e., 2.5 degrees after TDC. In this case, the auto-ignition delay angle was 15 degrees. The maximum in-cylinder pressure value (p_{max}) is also indicated in Figure 3. The variation in this parameter was assessed in this study too.

In the case of a diesel engine, an important operational parameter is the rate of pressure rise $dp/d\alpha$ (bar/CA) in the combustion chamber. An excessively high value of this parameter is unfavorable as it can lead to overloading of components in the crank–piston system. The rate of pressure rise in the cylinder is distinguished by its average and maximum values. In this article, the maximum value of the pressure rise in the cylinder was determined due to the rapidly occurring fuel combustion process.

As mentioned, the analysis of the combustion process was conducted using the AVL research engine, employing blends of ethanol (ET) and diesel fuel (DF). In this case, the results obtained for diesel fuel served as a reference point for evaluating the impact of ethanol addition to this fuel. The experiment involved the use of diesel fuel that meets the requirements of the European standard EN 590 for the summer season. This fuel served as a reference point for engine studies conducted with blends of the specified DF and ET with a purity of 99.9%. The research involved blends of DF containing 10% and 20% ET (by volume), labeled DF10 and DF20, respectively. The selected physicochemical parameters of the tested fuels are presented in Table 2.

Table 2. Selected physicochemical properties of tested fuels.

Parameter	Reference	ET	DF	DF10	DF20
Density @ 15 °C, g/cm ³	[45]	0.788	0.833	0.828	0.824
Viscosity @ 40 °C, mm ² /s	[46]	1.11	3.45	3.21	2.97
LHV, MJ/kg	[47]	28.4	43.9	42.3	40.7
Surface tension, mN/m	[48]	22.3	32.1	31.3	29.9
CN	[49]	-	51	-	-
Lubricity *, µm	[50]	1057	370	-	-
DCN **, -	[51]	8	-	-	-
FP, °C	[52]	12	60	26	24
CFPP, °C	[53]	<−50	0.0	-	-
Latent heat of vaporization, kJ/kg	-	846	250	309	368
Stoichiometric air/fuel ratio, kg/kg	-	9.0	14.7	13.9	13.4

* taken from ref. [54]. ** taken from refs. [55,56].

Table 2 presents the selected physicochemical properties of the tested fuels: ET, DF and DF10 and DF20 blends. The addition of ET to DF affects several properties of the resulting fuel, which are critical to the combustion process in the engine. The reduction in density and viscosity of the blends with increasing ethanol content may enhance fuel atomization but simultaneously decrease the stability of the fuel film on the cylinder walls. The lower heating value (LHV) of the blends indicates a reduced amount of energy available during combustion, which could lead to a decrease in engine energy efficiency. On the other hand, the higher latent heat of vaporization of ethanol, which increases with its proportion in the blend, significantly lowers the cylinder temperature during fuel evaporation. This may prolong ignition delay and alter the characteristics of the initial combustion phase. The lower surface tension of the blends promotes better fuel atomization, but may also influence the mixture formation process within the cylinder. It is noteworthy that ET has a very low derived cetane number (DCN = 8), which reduces the self-ignition capability of the blend compared to DF (CN = 51), potentially necessitating modifications in injection and ignition strategies to optimize engine performance. The low lubricity of ET compared to DF may lead to the increased wear of fuel system components, particularly at higher ethanol concentrations in the fuel. Taken together, these properties underscore the need for precise adjustments to engine operating parameters, such as injection pressure, ignition timing, and heat management strategies, to balance the benefits of using ethanol with the potential technical and operational limitations.

The evaluation of the combustion process of the tested fuel was performed based on the registered pressure changes in the cylinder. For this purpose, the sensor GU22C made by AVL was used. Necessary measurements were taken every 1 degree of crankshaft angle (CA). For each measurement point, 100 consecutive engine cycles were recorded for further analysis. More details of the measurement test stand are widely explained in ref [13].

In this study, the concentration of nitrogen oxides (NO_x) in the exhaust gases was measured using the AVL i60 FT infrared spectrometer. This advanced exhaust gas analysis device enables precise determination of the concentrations of individual nitrogen oxides (such as NO and NO₂), as well as the total NO_x content. The analysis of NO_x emissions was supported by the assessment of temperature changes in the cylinder, which were calculated in the AVL system using the equation of the state of the gas and the measured air flow into the engine.

The test bench used in the study enabled the measurement of λ values using a Bosch LSU 4.2 wideband oxygen sensor integrated with the LA4 lambda meter made by ETAS GmbH.

3. Results

Figure 4 shows pressure variation traces recorded in the cylinder of the AVL engine fueled with the investigated fuels (DF, DF10, and DF20), along with the corresponding rate of heat release (ROHR) curves. These in-cylinder pressure traces were recorded for the engine operating with torque of 5, 10, 15, 20 and 25 Nm at crankshaft speeds of 1200, 1700 and 2200 rpm.

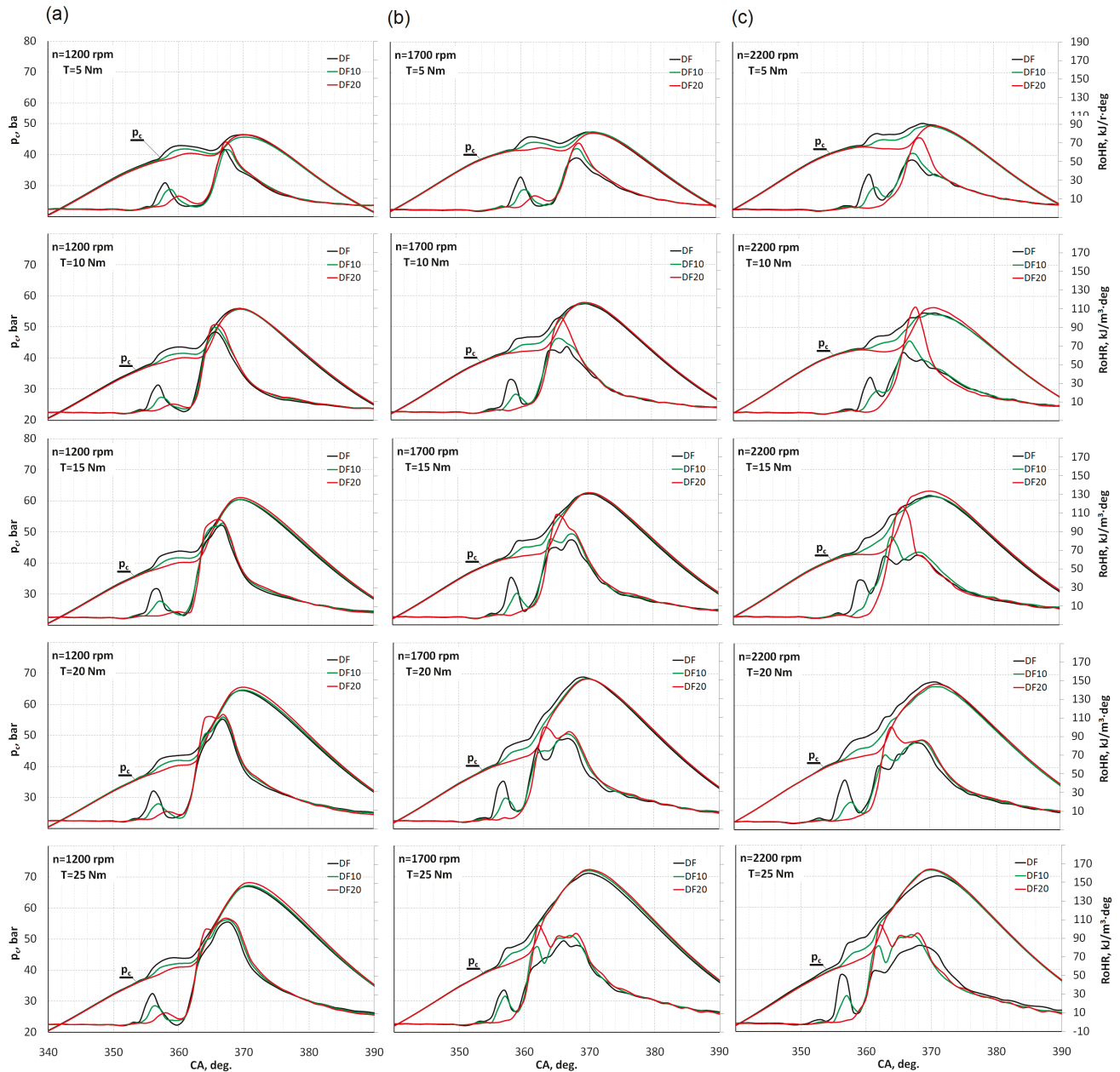


Figure 4. Recorded in-cylinder pressure (p_c) and corresponding rate of heat release (RoHR) curves for the AVL research engine operating at: (a) 1200, (b) 1700 and (c) 2200 rpm.

Based on the assessment of Figure 4, several key conclusions can be formulated. It can be confirmed that an increase in the load on the tested engine was accompanied by an adequate increase in cylinder pressure. No significant differences in the maximum pressure value were observed depending on the type of fuel tested. However, it should be pointed out that fuel containing more ethanol resulted in a smaller pressure rise immediately after injecting the pilot dose into the combustion chamber. Additionally, the influence of increas-

ing ethanol concentration in the blend with diesel fuel on the advance of the combustion angle and the corresponding higher pressure rise rate in the combustion chamber after the injection of the main fuel dose can be observed. These general relationships will be the subject of further analysis in this work. The key parameter in evaluating the combustion process in a diesel engine is the angle of ignition delay. For the purposes of this study, the definition of this parameter has been adopted in accordance with the previously presented Figure 3. As mentioned, the fuel injection parameters were constant at a specific measurement point for all fuels tested. In this way, the influence of these fuels on the auto-ignition delay angle was assessed. For this purpose, the waveforms were used, an example of which is shown in Figure 5.

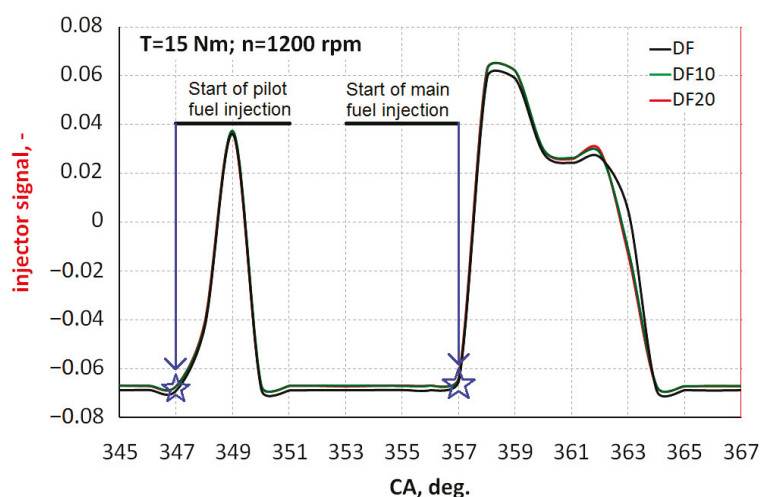


Figure 5. Example waveforms of the injector signal recorded for the AVL engine operated with 15 Nm at 1200 rpm.

Figure 5 shows the profiles of the fuel injector control signal in the AVL engine fueled with the tested fuels. The indicated figure confirms that the injection parameters for the tested fuels were the same. For example, in an engine operating with a torque of 15 Nm at 1200 rpm, the pilot injection began 13 degrees before TDC (360 degrees CA), while the main injection started 3 degrees before TDC. Figure 5 clearly shows that with constant injection parameters, only the change in ethanol content in diesel fuel has an effect on the changes in pressure in the combustion chamber. Specifically, it can be observed that with the increase in ethanol content in diesel fuel, there is a smaller increase in pressure in the combustion chamber after the injection of the pilot dose, which is visible in the previously shown Figure 4. This could be justified by the influence of the higher latent heat of vaporization of ethanol added to diesel fuel. In such a case, the increased heat of vaporization of the pilot fuel dose containing ethanol restricts the temperature and pressure rise during the initial phase of the combustion process, which, in turn, may contribute to prolonging the ignition delay period. Consequently, the combustion process in its main phase, i.e., after the injection of the main fuel dose, occurs with greater intensity. This could be due to a greater accumulation of fuel in the engine cylinder, which ignites abruptly throughout its volume, resulting in correspondingly larger pressure increases in the combustion process. This is confirmed in Figure 6, which illustrates the impact of the tested fuels on the maximum pressure rise rate $(dp/d\alpha)_{\max}$ during their combustion in the AVL engine. A value of this parameter that is too high is unfavorable, as it indicates an excessive noise and load on the crank–piston system. A $(dp/d\alpha)_{\max}$ value of 8–10 bar/°CA is considered a critical threshold, based on the authors' experience and further supported by findings reported in the literature, e.g., in ref. [57]. Above this value, the engine begins to operate with

a characteristic knocking sound, which is undesirable and may lead to engine damage. In the case of the examined engine, it was found that this load is the smallest for diesel fuel combustion. However, the increasing addition of ethanol to diesel fuel results in correspondingly larger pressure increases in the combustion chamber, which is not always favorable. The largest pressure increases in the cylinder of the examined engine occurred in the case of burning the DF20 mixture. They were even about 25% higher compared to the combustion of pure diesel fuel (DF).

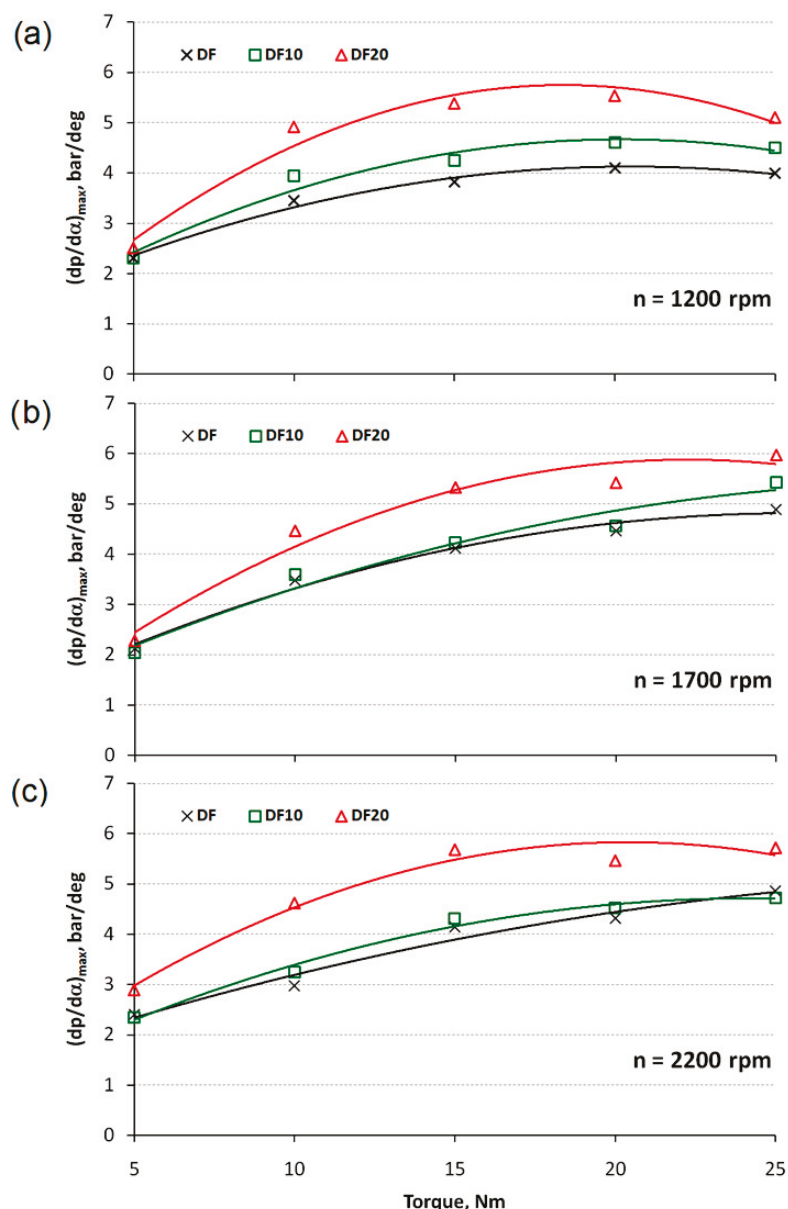


Figure 6. Curves of the pressure rise rate $(dp/d\alpha)_{max}$ obtained for the AVL research engine at: (a) 1200, (b) 1700 and (c) 2200 rpm.

The results suggest that the combustion of the DF20 mixture results in an adequately higher pressure increase in the cylinder, exceeding those observed in the combustion of pure diesel fuel (DF) by approximately 25%. It is essential to note that these pressure increases are not always advantageous, as they may lead to a temporary overload of the crank–piston system. Nevertheless, it was observed that the type of fuel tested did not significantly impact the maximum pressure values recorded in the examined engine. The

differences in the maximum pressure values in the cylinder of the examined engine, as seen in Figure 7, do not exceed 4%.

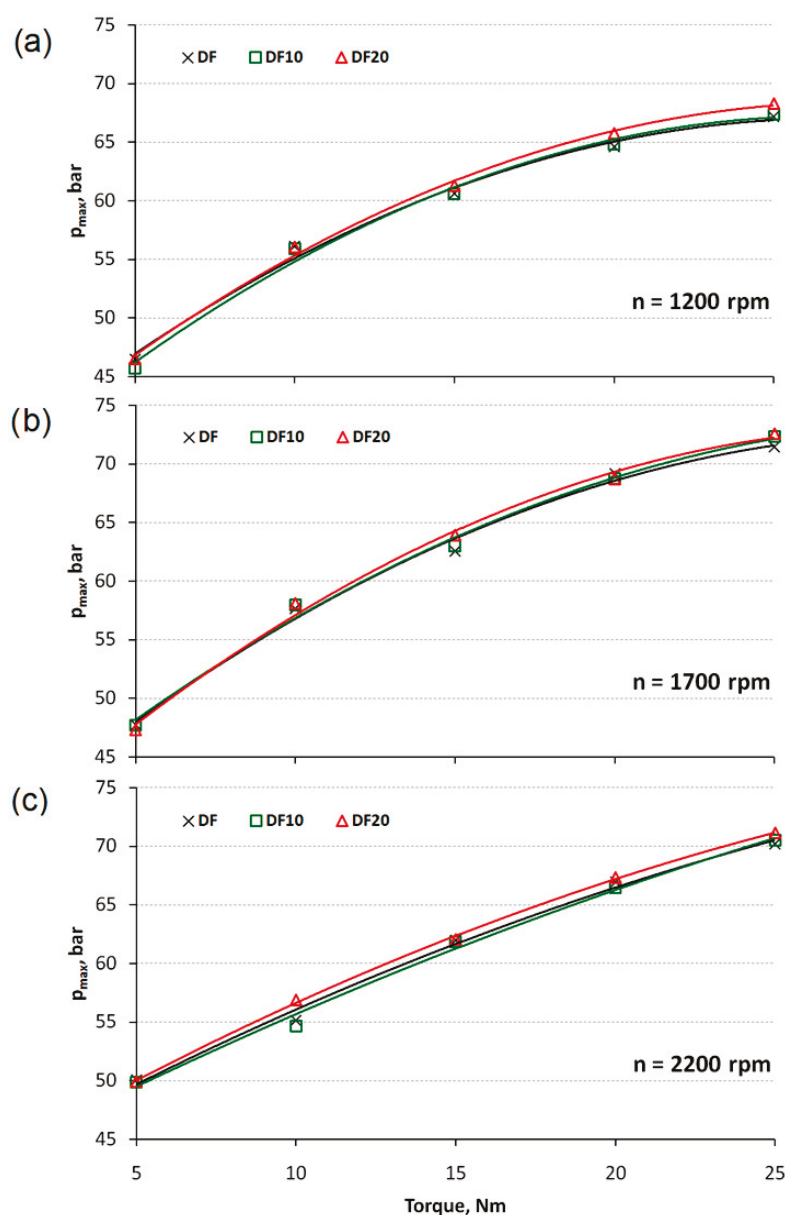


Figure 7. The influence of the tested fuels on the maximum pressure in the AVL engine cylinder recorded at: (a) 1200, (b) 1700 and (c) 2200 rpm.

Taking into account the registered parameters of the engine work, the AVL Concerto v.4.4. software was utilized to determine the peaks of the mean in-cylinder temperature values during the combustion process of the tested fuels, as the increase in temperature is correlated with NO_x concentrations. For this reason, Figures 8 and 9 present curves illustrating the effect of ethanol addition to diesel fuel on the variation not only in the peak mean in-cylinder temperature, but also in the resulting NO_x concentrations. Based on the assessment of this figure, it can be unequivocally stated that the increasing addition of ethanol to diesel fuel increases the peaks of the mean in-cylinder temperature of the examined engine. The maximum difference in this temperature value was 60 °C. In this case, lower temperatures were obtained for the combustion process of diesel fuel, while correspondingly higher temperatures were observed for the DF20 mixture.

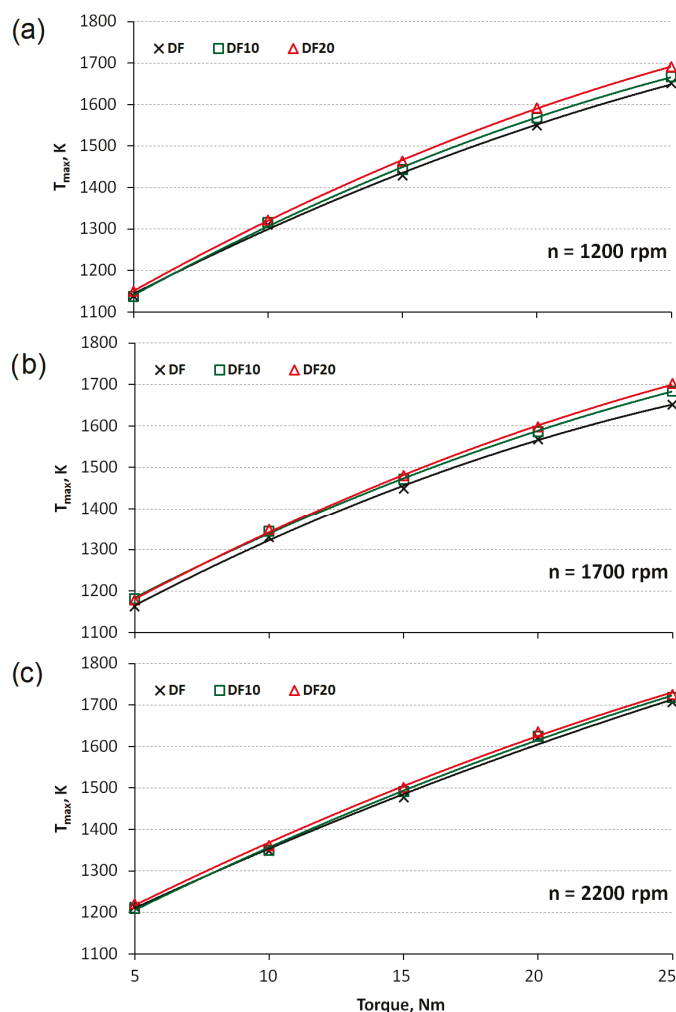


Figure 8. Variations in the peaks of the mean in-cylinder temperature obtained from the AVL engine at (a) 1200, (b) 1700, and (c) 2200 rpm.

The increase in the peaks of the mean in-cylinder temperature observed for DF20 can be attributed not only to the physical properties of ethanol, such as its higher oxygen content, but also to the altered chemical kinetics of the combustion process. Ethanol promotes leaner combustion and may lead to faster reaction rates in certain phases of the combustion cycle, contributing to increased heat release and higher peak temperatures. Studies on these dependencies are not widespread. However, in the work [58] regarding the combustion of ethanol-biodiesel mixtures, it was observed that ethanol accelerates reactions in the early stages of combustion, which can lead to higher peak temperatures, but generally decreases the overall combustion rate in the later stages, especially in the context of the ethanol-biodiesel/n-heptane mixture.

Recent studies have highlighted the importance of chemical kinetics in understanding combustion phenomena in diesel-ethanol blends, particularly in Premixed Charge Compression Ignition (PCCI) engines. A detailed simulation-based analysis by [59] demonstrates that the auto-ignition timing and combustion characteristics of ethanol–diesel mixtures are strongly influenced by the premixed ratio and the homogeneity of the in-cylinder charge. The use of a detailed kinetic reaction mechanism in that work allowed for the prediction of ignition delay, pressure rise, and heat release behavior for various ethanol volume fractions, including 20%. These findings confirm that even moderate ethanol additions substantially affect the combustion process, and that such effects can be interpreted and anticipated through chemical kinetic modeling.

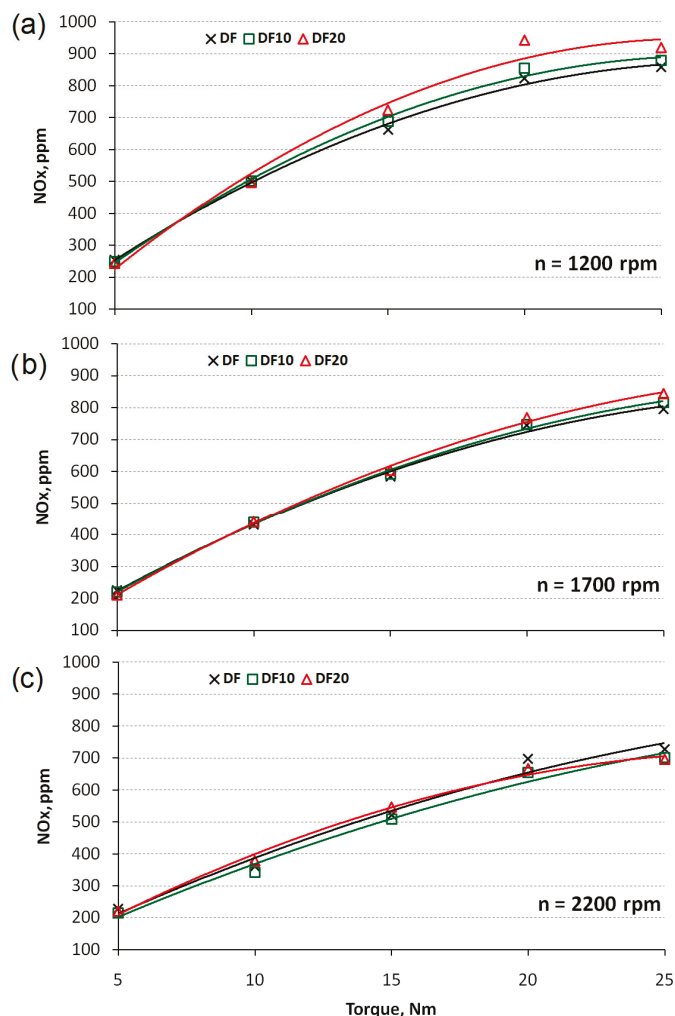


Figure 9. Variations in NO_x emissions obtained from the AVL engine at (a) 1200, (b) 1700, and (c) 2200 rpm.

The observed increase in the peaks of the mean in-cylinder temperature with the addition of ET to DF, as demonstrated by the DF20 mixture, is likely to lead to adequately higher concentrations of nitrogen oxides (NO_x). This is because NO_x formation is highly temperature-dependent, with higher combustion temperatures promoting more intense thermal NO_x generation through the Zeldovich mechanism. Consequently, the increased cylinder temperatures associated with the DF20 mixture can contribute to elevated NO_x concentrations compared to pure diesel fuel combustion.

For all engine operating conditions with the tested fuels, the lambda values were determined, as the quality of the air–fuel mixture, i.e., its enrichment or lean-burn, has a significant impact on the NO_x formation process. In the case of diesel fuel, the range of obtained lambda values was from 1.32 to 3.61, depending on the engine load and the speed of the crankshaft. For the DF10 fuel, lambda values ranged from 1.35 to 3.66, and for DF20, from 1.37 to 3.70. An increase in lambda values indicates a leaner fuel mixture, which, according to current knowledge, favors a higher NO_x emission, as confirmed in this study. However, it should be noted that the higher lambda values observed for the DF10 and DF20 fuels are partly due to the lower calorific value of ethanol, requiring a higher fuel flow to maintain the same engine load, which results in a greater air–fuel ratio and an apparent increase in lambda. Despite this, the mixtures with ethanol remain leaner, contributing to the observed trend of higher NO_x emissions.

However, it should be noted that some studies available in the literature [60] have shown that the addition of ethanol to diesel fuel may lead to a reduction in NO_x emissions—an effect that was not confirmed in the present study. These discrepancies may result from significant differences in the combustion systems and engine operating parameters used, which further complicates the formulation of generalized conclusions regarding the influence of ethanol on nitrogen oxide emissions.

This study also determined the effect of ethanol concentration in the tested diesel fuel on the change in fuel ignition delay (ID). The obtained results are presented in Figure 10. When evaluating the results presented in this figure, a significant impact of increasing engine load on the decreasing ignition delay of the tested fuels can be observed. This is a well-known phenomenon resulting from the influence of higher combustion chamber temperature on the shortening of the physical preparation period of the fuel for autoignition.

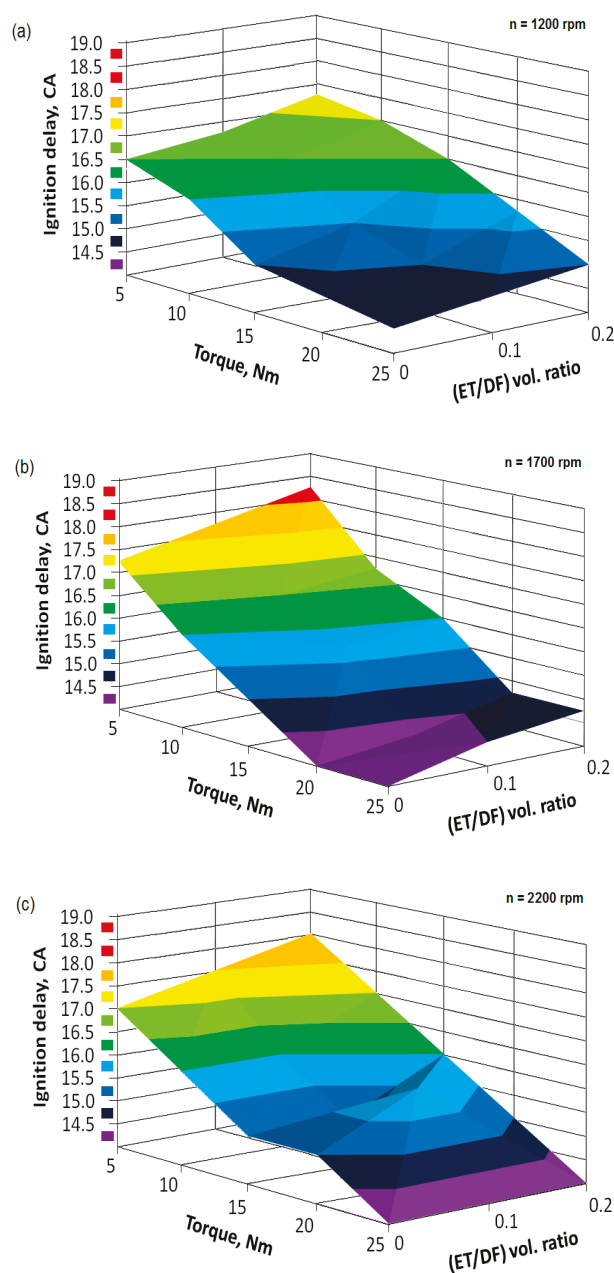


Figure 10. Variations in ignition delay in the AVL engine powered by the tested fuels at: (a) 1200, (b) 1700 and (c) 2200 rpm.

The ignition delay (ID) was measured with an accuracy of 1 °CA and then the values were converted to time units (milliseconds), taking into account the engine crankshaft speed. The obtained results are presented in Table 3. When evaluating the results presented in this table, a significant impact of increasing engine load on the decreasing ignition delay of the tested fuels can be observed. This is a well-known phenomenon resulting from the influence of higher combustion chamber temperature on the shortening of the physical preparation period of the fuel for autoignition.

Table 3. Ignition delay expressed in milliseconds for diesel fuels containing 0, 10 and 20% ethanol by vol. at different engine speeds and loads.

Fuel	rpm	5 Nm	10 Nm	15 Nm	20 Nm	25 Nm
DF	1200	2.22	1.94	1.94	1.81	1.81
DF10	1200	2.22	1.94	1.94	1.81	1.81
DF20	1200	2.22	2.08	2.08	1.94	1.81
DF	1700	2.29	1.81	1.81	1.67	1.81
DF10	1700	2.29	1.81	1.94	1.67	1.81
DF20	1700	2.29	1.81	1.94	1.67	1.67
DF	2200	2.08	2.01	1.94	1.67	1.81
DF10	2200	2.08	2.01	1.81	1.81	1.81
DF20	2200	2.08	1.94	1.81	1.81	1.81

The analysis of the results showed in Table 3 confirms that for DF10 fuel, the ignition delay values were practically identical to those of pure diesel fuel, regardless of engine speed and load level. This suggests that ethanol at this concentration does not significantly affect the ignition process under the tested conditions.

For the fuel with 20% ethanol addition (DF20), a slight tendency toward increased ignition delay was observed, particularly at lower load levels (5–15 Nm) and lower engine speed (1200 rpm). In these cases, ID values were approximately 0.14 ms higher than those for DF, corresponding to a difference of 1 degree of crankshaft rotation. Since the ID was determined based on crank angle measurements with a resolution of 1°, the observed differences fall within the inherent measurement uncertainty.

Therefore, it must be emphasized that the detected changes in ID, although numerically present, are minor and potentially within the margin of error associated with the applied method. A resolution of 1 CA corresponds to approximately 0.14 ms at 1200 rpm, 0.088 ms at 1700 rpm and 0.076 ms at 2200 rpm. As a result, slight variations in ID may not necessarily reflect actual combustion phenomena, but rather the limitations of the measurement resolution.

Based on these considerations, it can be concluded that the influence of ethanol addition on ignition delay under the tested conditions becomes discernible only at a higher ethanol content (20%), and even then, only within a narrow range of engine operating conditions. However, due to the resolution limits of the measurement method, these differences should be interpreted with caution.

Future research should focus on several key areas, including kinetic analysis of the combustion process, which would provide a deeper understanding of the chemical and physical mechanisms involved in engines using ethanol–diesel blends. Such analysis could further help explain the influence of various parameters, such as ignition delay and peak cylinder temperature, on combustion efficiency and the resulting exhaust emissions. Additionally, optimizing fuel injection strategies could improve efficiency and reduce emissions. Studies on the effect of these blends on engine durability could also provide valuable insights into their long-term operational reliability.

4. Conclusions

This study investigates the effect of ethanol addition to diesel fuel on combustion characteristics in an AVL engine. The focus was on engine parameters such as autoignition delay, in-cylinder pressure rise rates, and maximum cylinder pressure. The fuels tested were diesel-ethanol blends with 10 and 20% ethanol by volume (DF10 and DF20). The results demonstrated a significant impact of ethanol on the combustion process, particularly in the early stages. The higher latent heat of vaporization of ethanol reduced the benefits of pilot fuel injection by limiting the initial thermal preparation of the cylinder charge, affecting the combustion speed. The combustion of the DF20 mixture resulted in a 25% higher pressure rise in the cylinder compared to the pure diesel fuel (DF), although this pressure increase could lead to temporary overloading of the crank–piston system. Despite this, the type of fuel did not significantly impact the maximum pressure values in the engine. Temperature peaks during combustion, which are correlated with NO_x emissions, were also analyzed using AVL software. The results showed that increasing ethanol content led to a rise in these temperature peaks, with a maximum difference of 60 °C observed between DF20 and pure diesel. Higher cylinder temperatures are likely to increase NO_x concentrations due to the temperature dependence of NO_x formation. The study also confirmed that increasing engine load reduced ignition delay, a phenomenon caused by higher combustion chamber temperatures. Ethanol addition had a minor effect on ignition delay, increasing it by up to 1 CA. These findings highlight the complex relationship between ethanol content, combustion characteristics and engine performance, emphasizing the need for optimizing injection processes to balance combustion efficiency and NO_x emissions.

Author Contributions: Conceptualization, K.G. and R.S.; methodology, K.G. and D.T.; validation, R.L. and R.S.; data curation, D.T.; writing—original draft preparation, K.G.; writing—review and editing, R.L. and R.S.; visualization, D.T.; supervision, K.G. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding author.

Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

AFR	Air fuel ratio
ASTM	American Society for Testing and Materials
CA	Crank angle
CFPP	Cold filter plugging point
CI	Compression ignition
CN	Cetane number
CP	Cloud point
CO	Carbon monoxide
CO ₂	Carbon dioxide
COV _{MIP}	Coefficient of variation in mean indicated pressure
DCN	Derived cetane number
DF	Diesel fuel
DF10	10% ET by vol. in blend with 90% DF by vol.
DF20	20% E by vol. in blend with 80% DF by vol.
EN	European norm

FAME	Fatty acids methyl esters
FP	Flash point
HC	Hydrocarbon
IQT	Ignition quality tester
MIP	Mean indicated pressure
LHV	Lower heating value
NO _x	Nitrogen oxides
PP	Pour point
rpm	Revolutions per minute
RoHR	Rate of heat release
SD	Standard deviation
T	Torque
TDC	Top dead center
THC	Total hydrocarbons
λ	Excess air ratio (-)

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ISBN 978-3-7258-8442-1