

ADVANCES IN SUSTAINABLE MARINE FUELS TECHNOLOGY

Introduction

There has been an increased level of environmental consciousness in recent years, resulting in global sustainment efforts across all energy sectors. In the marine sector, this is evident by new efforts and policies to reduce emissions. Today, the marine industry primarily uses fossil fuels, specifically bunker fuels which are some of the heaviest and most polluting. These fuels produce particulate matter (PM), Sulfur Oxides (SO_x), Nitrogen Oxides (NO_x), ozone-depleting substances (ODS), and volatile organic compounds (VOCs) [1].

At the current growth rates, greenhouse gas emissions (GHG) from ships are set to increase by 250% by the year 2050 [2]. Indeed, shipping emissions are currently 2.8% of the total emissions and are expected to increase to 17% by 2050 [2]. For this reason, the International Maritime Organization (IMO) has adopted the International Convention for the Prevention of Pollution from Ships (MARPOL) [3]. The most recent annex of the convention, Annex VI, sets limits on SO_x emissions, NO_x emissions, ODS, and particulate matter. It also sets more stringent measures on specified control areas including the North American coasts, the Baltic Sea, and the English Channel. A target has been set for 2050, aiming to reduce GHG emissions by at least 50% and to achieve carbon neutrality by 2100. This can be accomplished by switching to alternative and sustainable marine fuels in addition to technological improvements. However, the Det Norske Veritas (DNV) - a company that performs risk and safety tests in the maritime industry [4] - projects that technical measures can only reduce air pollution at a maximum of 20%. As such, alternative fuels and energy sources are necessary to further reduce the GHG emissions [5].

Some of the more popular alternative fuel options being researched are ammonia, methanol, hydrogen, liquefied natural gas (LNG), biofuels, and dimethyl ether. LNG is the most researched sustainable fuel, commercially used in ships today, but concerns over methane leakage has led to research into alternative sources [6]. When researching different fuels for ships, a holistic approach must be considered including production, in addition to its combustion in engines. Additionally, feedstock choice, fuel production, and engine technologies must all be considered when evaluating emission levels, environmental impact, and safety. For advances in sustainable marine fuels, all these variables must be reviewed. A bibliometric review was conducted by Ampah et al. [7] that reviewed the research changes of alternative marine fuels from the past 2 decades. Recent trends have shown that researchers are becoming increasingly focused on three fuels: Hydrogen, ammonia, and methanol. For this reason, this paper will summarize the advances of these select three fuels as well as the technologies associated with them.

Hydrogen

Hydrogen as a marine fuel alternative has gained a lot of attention these past few years due to several promising characteristics - the most promising being that hydrogen produces zero carbon emissions while under combustion. Additionally, hydrogen has a very high gravimetric density at 120 MJ/kg [8], meaning it has a high amount of energy stored. It also has various renewable production methods and can be utilized with some existing technologies. Compatibility with existing technologies is also an important criterion for the short term since existing ships are subject to regulations regarding emission reduction and efficiency improvements [5].

However, the overall environmental attractiveness of hydrogen is also dependent on its production route. Over 95% of hydrogen produced today is considered to be "grey" hydrogen, meaning that it is produced from fossil fuels. This has contributed to approximately 830 million tons of carbon

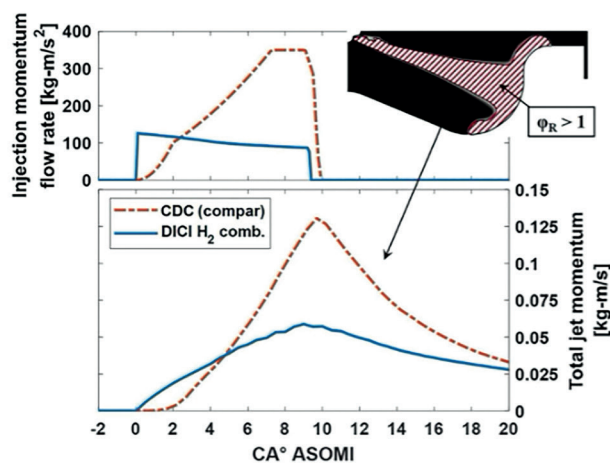


Figure 1 (left): Nozzle exit momentum flow rate (top) and jet momentum (bottom) for the CDC and DICI H₂ combustion cases [13].

such as wind or solar. Electrolyzers are a clean way of obtaining hydrogen without producing harmful emissions. They operate by applying an electric current so that the negatively charged hydroxide ions get attracted by the anode and the positively charged hydrogen ions get attracted by the cathode [10].

Hydrogen is particularly attractive for marine applications since ports have direct access to water to use as the feedstock for electrolysis. With the right infrastructure upgrades, it also has access to off-shore wind plants and tidal power, which can produce the renewable energy necessary for sustainable electrolysis. The largest electrolyzer project for obtaining green hydrogen is the Kuqa facility, located in Xinjiang, China, which was set to have a capacity of 650 ton/day of hydrogen production [9]. However, the output has been limited to only producing a third of the promised capacity. This impediment is due to safety concerns in response to an issue regarding the membrane of the electrolyzer which has been causing gas mixing of hydrogen and oxygen on the anode side. This mixing can pose an explosion risk if the concentration of the hydrogen gets too high [11], highlighting the need for major improvements to the membrane if the plant is to be successful. Nonetheless, the size of the Kuqa plant is expected to be surpassed by a new green hydrogen plant, the Ordos plant, by the same developers. It is not yet known when the plant will begin operation, nor has there been insight into any improvements to the electrolysis technology [12].

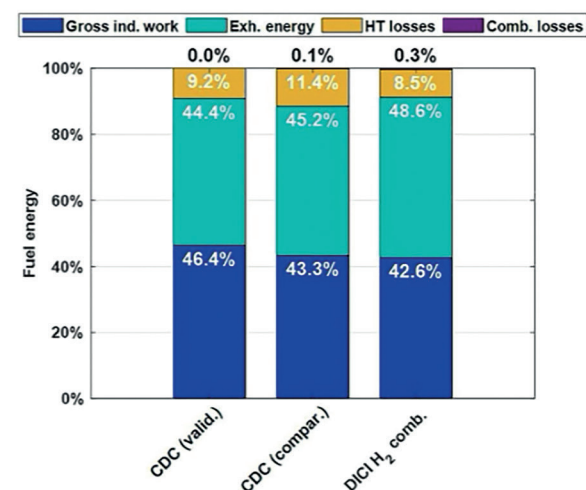


Figure 2 (right): Fuel energy distribution between gross indicated piston work (GIW), exhaust enthalpy, heat transfer (HT) losses, and incomplete combustion losses for different combustion cycles [13].

engines are limited by hydrogen's high ignition temperature, which would lead to higher NO_x emissions.

Babayev et al. further investigated the operation of a pure hydrogen CI engine concept that uses non-premixed hydrogen, meaning the hydrogen and air are not mixed prior to entering the combustion chamber. The researchers chose this approach since premixed engines typically have a lower efficiency and are more prone to safety issues. This engine utilized hydrogen pilot injections, smaller initial injections of hydrogen followed by the main injection. The results were compared to the results of the same engine using diesel fuel. Results indicated that the brake thermal efficiency of the hydrogen-fueled engine was higher than that of the diesel. However, the hydrogen jet momentum, which involves the speed the fuel sprayed into the chamber, was four times lower than the diesel jet momentum. This leads to ineffective global mixing in the combustion chamber, nonhomogeneous air-fuel mixing, and heat transfer loss. The pilot injection location at the TDC contributed to 5-10% of the total useful work, an indication of how useful it was to the engine's overall efficiency.

Figure 1 and 2 summarize these findings. Figure 1 depicts the injection momentum of the diesel in comparison to the hydrogen showing that the jet momentum of the conventional diesel combustion (CDC) was higher than hydrogen for most crank angle degrees (CA) after start of main injection (ASOMI). Figure 2 shows the fuel energy as well as the heat transfer

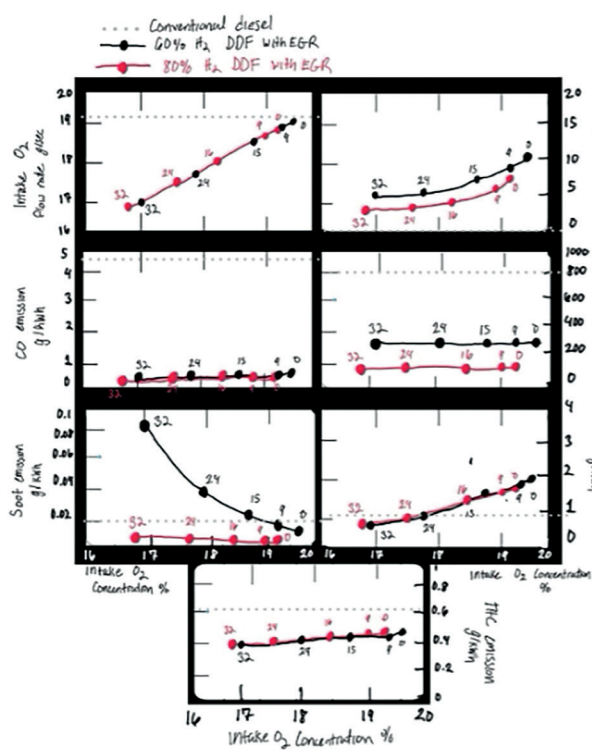


Figure 3 (left): Engine-out emissions for different H₂ energy share ratios, 20 kW [14].

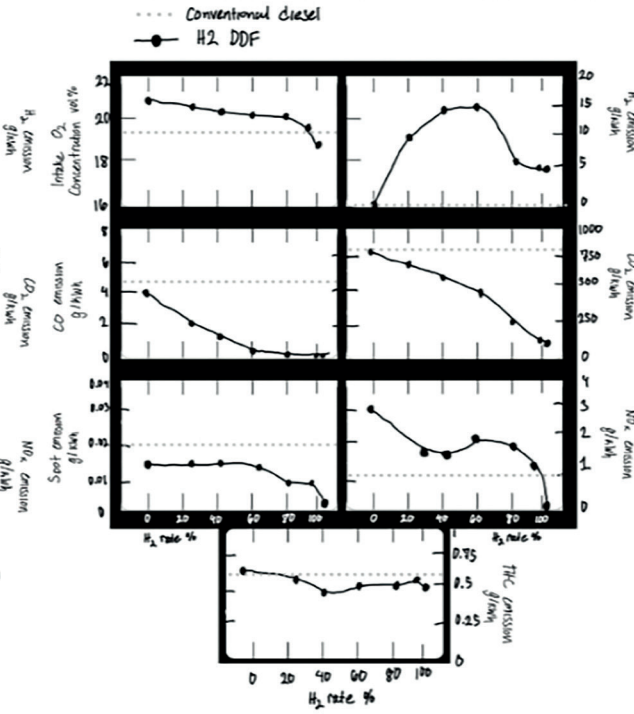


Figure 4 (right): Engine-out emissions for different EGR rates (%), H₂ share ratio of 60% and 80% at 20 kW [14].

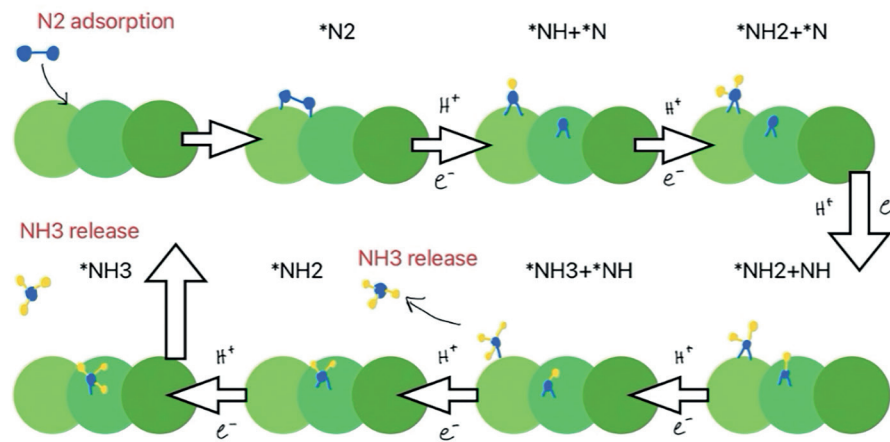


Figure 5: NRR adsorption of N₂ on a catalyst to produce ammonia [17].

losses, exhaust energy, and gross indicated work. Hydrogen as a fuel in non-premixed CI engines has several benefits over diesel, but still requires more research and innovation before being technologically ready to use in ships.

In another study on dual-fuel engines using hydrogen, Dimitriou et al. [14] analyzed a similar engine that used hydrogen and diesel. Although the study focuses on the prospects of hydrogen fuel for the automotive industry, the results can benefit research regarding the marine fuel industry as well. The research group assessed different combustion strategies such as exit gas recirculation (EGR), as well as various diesel injection pressures and patterns that are known to affect exhaust emissions. EGR is a technique used in conventional automotive engines to reduce NO_x emissions. This method works by recirculating some of the exhaust gases back into the combustion chamber with fuel and air. Based on the results, the researchers found that factors such as an increased pre-injection rate, as well as a long dwell angle, have a positive effect on combustion efficiency. Also, the inclusion of EGR reduced NO_x emissions by up to 75% but also resulted in higher soot emissions. This means that with the EGR, reduction of both types of emissions could not be achieved.

Figure 3 shows various graphs depicting different emission levels as hydrogen rate percentage increases at 20 kW operation. Soot, CO, CO₂, and total hydrocarbon (THC) emissions are decreased for any addition of hydrogen to the dual engine. The NO_x emissions are higher at many percentages due to the increase in temperature in the combustion chamber. Figure 3 quantifies the emissions at different EGR rates, showing that NO_x emissions were reduced up to 40% in the case of 80% EGR. Carbon and THC emission levels showed no significant difference with the EGR while a high EGR rate for the 60% H₂ case increased soot emissions.

Ammonia

Ammonia is another promising alternative formed from the reaction between nitrogen and hydrogen. Although ammonia

production uses hydrogen as a feedstock, there are several benefits to using ammonia fuel over hydrogen. For one, ammonia transport and storage is more established with existing infrastructure and methods for its handling. Furthermore, ammonia storage is easier than hydrogen because it exists as a liquid at temperatures below -33.6 °C. Storage at low temperatures of ammonia is almost sixteen times cheaper than hydrogen storage [15]. However, sustainability in an environmental context depends highly on the feedstock used and the emissions produced during

upstream production processes. Over 70% of ammonia production comes from natural gas steam reforming and most of the remainder is from coal gasification to obtain the hydrogen [16].

The ammonia production from natural gas or coal is part of a larger process called the Haber-Bosch Process which involves the combination of hydrogen and nitrogen obtained from air by a cryogenic process. Ammonia production from this process is responsible for about 1.4% of global CO₂ emissions, not including the CO₂ emissions from natural gas extraction [17], highlighting the importance of finding an alternative production method. Despite this drawback, the Haber-Bosch Process is responsible for most ammonia production, of which over 80% is used in agricultural fertilizers [18]. There is ongoing research to find methods to bypass the Haber-Bosch process and obtain the same amount of ammonia without needing a hydrogen source.

One method of bypassing is through the nitrogen electrochemical reduction reaction (NRR) which is carried out in an electrochemical cell. Nitrogen is fed to the cell where it reacts with protons and electrons to produce ammonia [19]. Since this method does not require a hydrogen source, it is potentially a greener alternative to the Haber-Bosch process. In addition, Nitrogen is naturally abundant, contributing further to the attractiveness of the NRR process for ammonia synthesis.

A drawback of this method is that the typical catalysts used in this reaction show low activity and are not very selective due to competing reactions [20]. Figure 5 below roughly shows the NRR method and how it produces ammonia.

A major limitation of using ammonia as a fuel is its poor performance in combustion engines due to its low flammability, high NO_x emissions, and low flame speed [21]. For this reason, solid oxide fuel cells (SOFCs) are becoming increasingly researched. In these devices, chemical energy is directly converted into electrical energy through electrochemical reactions. In addition, NO_x emissions are also produced at negligibly low levels [15] and SOFCs eliminate any pretreatment requirements of the ammonia [20]. Hendriksen et al. [22] conducted a study to confirm the feasibility of an ammonia-fed SOFC by comparing it to a nitrogen/hydrogen mixture-fed SOFC because conventional SOFCs are typically fed hydrogen fuels. Researchers found that above temperatures of 700°C, there is a negligible difference between the cell voltage measured in the H₂/N₂-fed SOFC and the ammonia-fed SOFC, as shown in Figure 6. However, below 675°C the cell voltage of the ammonia-fed SOFC was significantly lower. Long-term durability tests (after 1400 hours) also showed that the degradation rate was not significant between the two different feeds, shown in Figure 7. Overall, the researchers confirmed the feasibility of SOFCs with a direct ammonia feed at high temperatures (800-850°C).

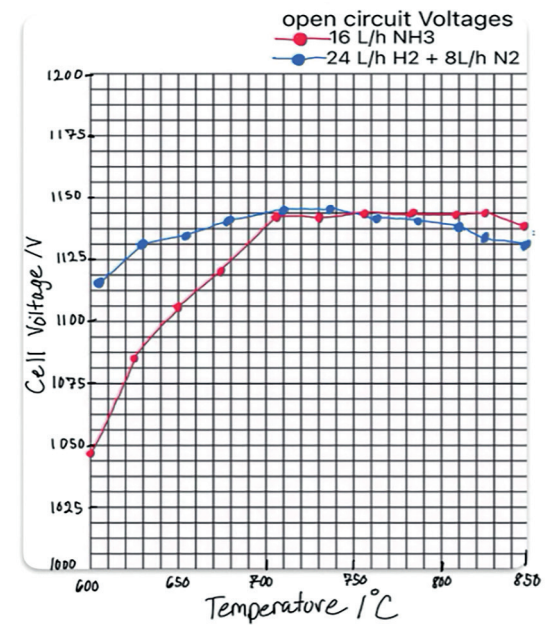


Figure 6: Open circuit voltage (OCV) measured in a flow of ammonia or an equivalent flow of N₂/H₂ [22].

Although ammonia-fed SOFCs are feasible Hendriksen et al. [22] stated the ammonia-fed SOFC was only similar to the H₂/N₂ SOFC at high temperatures, including above 800°C. For this reason, one of the major routes for scientists aiming to improve SOFC technology is to reduce its operating temperatures, specifically to below 600°C [23]. In investigating SOFC operating temperatures, Wang et al. [24] claim that the conventional anode in ammonia-fed SOFCs, Ni/yttria-stabilized zirconia (Ni/YSZ) is an efficient catalyst but tends to suffer from rapid deactivation at lower temperatures. They investigated the effect of including barium in the catalyst, forming a Ba-Ni/YSZ, by comparing its activity to the conventional anode. Barium was chosen to modify the catalyst because prior research had shown that this element was more active in promoting ammonia decomposition with Ni-based catalysts than without it. Results demonstrated a 100% ammonia conversion at 600°C with Ba-Ni/YSZ, while Ni/YSZ was only at 45% as shown in Figure 8. This shows that the investigated catalyst could be a potential alternative to the standard anode since it is able to accomplish complete conversion at lower temperatures.

	Degradation Rate (mV/kh)		
	Current density (A/cm ²)	<1000h	>1000h
750 °C, NH3	0.70	40-80	20-40
750 °C, H2 + N2	0.70	20-50	20
700 °C, NH3	0.42	50-150	20-50
650 °C, NH3	0.20	40-70	15-40

Figure 7: Voltage degradation rates for long-term tests with ammonia gas feed to a 5 by 5 square centimeter cell [22].

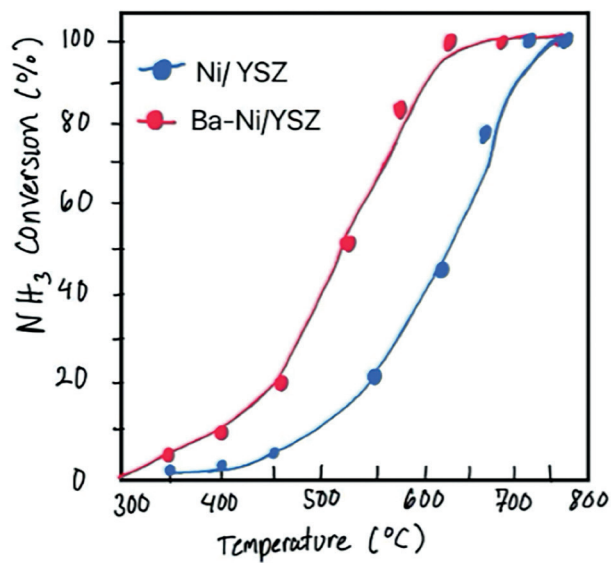


Figure 8: NH₃ conversion of Ba-Ni/YSZ and Ni/YSZ catalysts at 300 °C–750 °C [24].

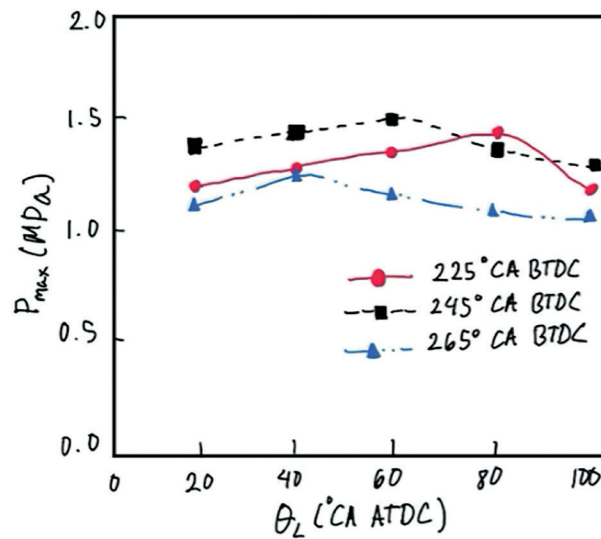


Figure 9 (left): Effect of LPG injection timing (θ_L) on maximum cylinder pressure (P_{max}) [27].

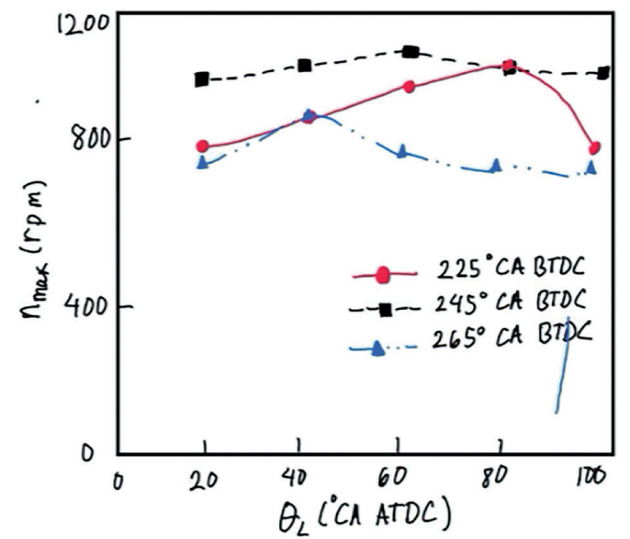


Figure 10 (right): Effect of LPG injection timing (θ_L) on maximum transient engine speed (n_{max}) [27].

Methanol

Methanol is another potential marine fuel alternative that has the advantage of being liquid at standard temperature and pressure. This allows for easier storage and transportation over gas fuels such as ammonia and hydrogen. In addition, methanol can burn very cleanly and can have a sustainable production method depending on the feedstock [25]. However, about 98 million tons are produced each year, with nearly all of it being from fossil fuels. The life-cycle CO₂ emissions from methanol production account for 10% of the total chemical sector emissions [26]. Despite methanol being very clean-burning and having the potential to reach current and future maritime pollution regulations, upstream methanol production processes must also be considered to evaluate the fuel's environmental impact properly. Methanol obtained from biomass sources such as sewage, wood residue, agricultural waste, and landfill waste has the potential to allow lower overall emissions.

A major obstacle in methanol-powered engines researchers are trying to overcome is its cold start difficulty in spark ignition engines. Methanol's low vapor pressure in combination with a high latent heat of vaporization causes this difficulty in lower temperatures [27]. As a result, engine performance decreases and certain emissions such as formaldehyde may increase [28]. To combat this issue, Gong et al. [27] tested the effect of an injection strategy on cold start firing by adding liquified petroleum gas (LPG) to the SI engine. A single-cycle fuel injection strategy was used, meaning the fuel is injected only once per compression cycle. A dual-fuel port injection for the two fuels was also used. Different fuel injection parameters were altered and investigated such as methanol and LPG injection timing, and the amounts of each fuel injected.

It was found that one of the most important factors in reliable firing during cold starts is the minimum amount of LPG injected. Other results were also obtained such as optimal LPG injection timing represented as crank angle degrees (°CA) past the at-top dead center (ATDC) location which are depicted in Figures 9 and 10. Maximum cylinder pressure and maximum transient engine speed were plotted against different injection timings and an optimal LPG injection timing of 57°CA ATDC was observed.

Although this research shows that LPG can be a reliable auxiliary fuel for methanol engines, the sustainability of the LPG fuel itself must also be considered. LPG fuel produces at least 95% less SO_x emissions and 20% less CO₂ emissions than conventional bunker fuel [29]. This is an improvement to current fuels, but it is important to note that in order to reach the IMO goal of zero carbon by the turn of the century, other auxiliary fuels may need to be considered for such a dual-fuel engine.

Conclusion

There have been many advances in sustainable marine fuels, including improvements in both the production processes of these fuels as well as the engines utilizing them. The three potential fuels this paper summarizes, hydrogen, ammonia, and methanol, are just a few of many that are currently being explored. These fuels have the potential to minimize GHG emissions considerably and may help reach future environmental goals when paired with new technologies. It is important to note, however, that although long-term goals include carbon-zero marine emissions and other stringent measures, short-term goals must reflect a transitional period where existing ships need prompt solutions to meet regulation. Other prospects include biofuels, nuclear power, LNG, ethanol, and dimethyl ether, all of which are being explored and investigated for both short-term and long-term use.

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