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Ammonia and Hydrogen as Carbon-Free Fuels for Internal Combustion Engines: A Comprehensive Review on Combustion, Emissions, and Performance

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Abstract

The transition to carbon-free energy sources is critical for combating climate change. This review explores the potential of hydrogen (H_2) and ammonia (NH_3) as promising zero-carbon fuels for internal combustion engines (ICEs). It examines their production methods, highlighting the shift from carbon-intensive "grey" processes to renewable-based "green" production. The study contrasts the fundamental properties of H_2 and NH_3: hydrogen offers high reactivity and wide flammability but poses storage challenges, while ammonia features higher energy density and easier handling but suffers from low flame speed and high ignition resistance. The core analysis focuses on combustion characteristics, engine performance, and emissions. Hydrogen enables efficient lean-burn combustion in spark-ignition engines but risks NOx emissions and abnormal combustion. Its use in compression-ignition engines requires dual-fuel operation. For ammonia, strategies like hydrogen enrichment, dual-fuel operation, and advanced injection are essential to enhance combustion efficiency and stability. Although both fuels eliminate CO_2 emissions, controlling nitrogen oxides (NOx) and nitrous oxide (N_2O) remains a challenge. The review concludes that hydrogen and ammonia represent viable pathways for decarbonizing ICEs, with their synergistic use—using ammonia as a hydrogen carrier and enriching it with hydrogen—offering a particularly promising solution for a sustainable future.

Keywords

Carbon-free fuels, Hydrogen, Ammonia, Emissions, Performance, Dual-fuel combustion.

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1. Introduction

Fossil fuels have extensive drawbacks, together with their confined availability and deliver safety worries stemming from their excessive demand. Additional factors driving the push to move away from fossil fuels include the impact of climate change, which has caused a rise in global temperatures and various related environmental consequences. The primary provider is greenhouse gases (GHGs), which create an insulating layer in the atmosphere that traps heat, thus raising global temperatures. This issue is critical because the growing concentration of GHGs threatens the capability of future generations to maintain the quality of life we currently enjoy. The primary greenhouse gas released in large quantities is carbon dioxide, predominantly from burning fossil fuels. Transitioning to renewable and alternative fuels will significantly reduce carbon emissions and contribute to a sustainable future.

Today, an alternative fuel must be technically feasible and economically viable to produce and, above all, must reduce environmentally harmful emissions, including CO_2, to the greatest possible extent. Current alternative fuels such as ethanol, methanol, biodiesel, propane, ammonia, natural gas, and hydrogen can reduce engine emissions to varying degrees compared to emissions caused by conventional liquid hydrocarbon fuels. In this way, substitute carbon-free fuels, like hydrogen and ammonia, present promising avenues for replacing fossil fuels and curbing carbon dioxide emissions.

Hydrogen, as an energy carrier, is the only fuel that is potentially free of hydrocarbon, carbon monoxide, and carbon dioxide emissions. The physical and chemical properties of hydrogen differ significantly from those of conventional fossil fuels [1]; [2]. Hydrogen is a clean and renewable energy source, which has the advantages of a large diffusion coefficient, low ignition energy, high laminar flame speed, high adiabatic flame temperature, and small quenching distance. Furthermore, the combustion product of hydrogen is only water [3]. However, a major challenge with hydrogen is that it’s extremely low gas density makes high-pressure storage of the gas unaffordable [4]. Therefore, using hydrogen as the supplementary fuel on traditional gasoline and diesel engines can optimize the in-cylinder combustion of the gasoline mixture and reduce the harmful engine-out emissions [3]; [4[; [5]; [6]. In general, hydrogen, as a sustainable fuel of the future, will reduce global dependence on fossil fuel resources and the level of exhaust emitted from motor vehicles [7]; [1]. However, the quantities of emissions are highly influenced by the method of hydrogen production [8].

Ammonia is one of the green fuels that is now receiving lots of curiosity as a possible substitute for fossil fuels, along with ethanol, methanol, and methyl ester [9]; [10]; [11]; [12]; [13]. It serves as an efficient carrier of hydrogen (17.8% by mass) in liquid form, can be easily stored under minimal pressure, and ranks among the most widely produced chemicals worldwide. Ammonia, in addition to being carbon-free, offers several advantageous features. This substance has a respectable energy density, can be conveniently stored in either liquid or gas form, and is among the most widely produced chemicals globally. Its infrastructure is robust, and it efficiently acts as a hydrogen transporter.

Ammonia provides safer transportation attributes in contrast to hydrogen. It is easily liquefiable for storing at moderate pressures (150 psi) at normal temperature, much like liquid propane, or at -33 degrees Celsius for storage at atmospheric pressure. With an octane number higher than 110, ammonia contains 17.8 percent hydrogen by weight, and compared to liquid hydrogen, it stores 30% more energy [14]. Due to its high flame speed and low ignition energy, hydrogen carries a significant risk of flashback. Additionally, hydrogen needs to be stored at high pressures at room temperature (from 2500 to 10000 psi) or as a liquid when cooled to -250 degrees Celsius [15]. These two storage methods incur higher costs compared to the tanks required for ammonia storage, due to the need for more robust construction or colder storage conditions. Moreover, for the final stage of hydrogen purification, ammonia doesn't need energy and can be easily separated with just 16% of the fuel's energy [16].

When it comes to handling, including storage and transportation, ammonia has a significant advantage over hydrogen, which needs an extra stage in its production. According to techno-economic research, using ammonia as an energy carrier by converting hydrogen into it makes sense [17]. This is because processing hydrogen requires more energy than producing and handling ammonia, both of which should be used as fuel.

This study explores fuel for engines by reviewing the process of ammonia and hydrogen production. It also describes the chemical and physical properties of ammonia and hydrogen fuel to identify their main advantages and disadvantages for use in internal combustion engines. Finally, this paper presents a comprehensive review of the results of using ammonia and hydrogen as a fuel in the internal combustion engines.

2. Production Methods

2.1. Production of Hydrogen

Hydrogen has become one of the most useful alternatives to fossil fuels today due to its properties such as great range of flammability, minor quenching distance, minimal ignition source energy, great diffusivity, and low density [18]. Since hydrogen is one of the many elements in the environment, it is easily available [19]. Hydrogen is not available in its pure form in nature (atmosphere). However, it can be produced from hydrogen-containing compounds such as fossil fuels, hydrogen sulfide, biomass, and water. To acquire hydrogen, it must first be separated from the other elements in the combination [18].

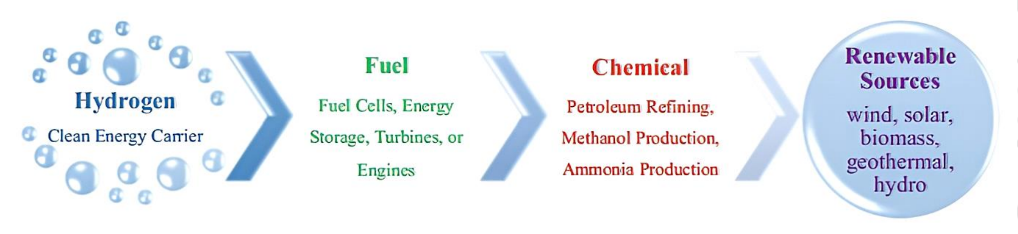

Fig1. hydrogen – a flexible, reliable, and environmentally friendly energy carrier in future energy networks [20]

Various methods are currently used to produce hydrogen [21]. Currently, the most widely used method to produce hydrogen is steam methane reforming. In this case, the efficiency of hydrogen production is very high (65–75%) and the costs are relatively low. However, in this case, hydrogen production results in high levels of CO_2 emission [22]. Another widely used method of hydrogen production is coal gasification. In this case, however, the efficiency of hydrogen production is low (45%) and CO_2 emissions are high. Electrolysis of water is another method of producing hydrogen, but it requires the use of large amounts of electricity and is therefore very expensive. In this case, the level of CO_2 emissions depends on the electricity source. Less common methods can also be used to produce hydrogen, such as biomass gasification, biomass-derived liquid reforming, or microbial biomass conversion [23]. However, only the solar–hydrogen system allows emission-free, but expensive, hydrogen production. YIP et al. (2019), 96% of total hydrogen was produced from fossil fuels [24]. However, when fossil hydrocarbons are used, CO_2 is produced during reforming. To prevent its emission into the atmosphere, it must be captured and stored [1, 25].

2.2. Production of ammonia

Currently, roughly 70% of globally produced ammonia comes from natural gas, while the remaining 30% primarily relies on coal [17]. Therefore, the price of ammonia is influenced by the price of natural gas, which, in turn, affects food prices due to its predominant use as a fertilizer in agriculture. Currently, most of the ammonia available worldwide is produced by combining hydrogen and nitrogen over an iron oxide catalyst in the Haber-Bosch process. Gaseous nitrogen and hydrogen undergo a direct gas-phase reaction to initiate the ammonia's synthesis.

This reaction is an exothermic $\Delta H = -92.4$ kJ/mol and is reversible. The Haber-Bosch (H-B) process is the main way to produce ammonia. The reaction occurs at temperatures between 400–450°C and pressures of 200 atm, with catalysts present. A simplified schematic of a typical Haber-Bosch process is shown in Fig 2. Osmium, ruthenium, uranium, and iron are all suitable catalysts, with iron being the most commonly used, typically derived from magnetite. Through cooling and ensuing condensation, the ammonia is extracted from the product stream in the closed-loop H-B process. After mixing new feed with the unreacted synthesis gas, the ammonia a synthesis reactor is refilled [26].

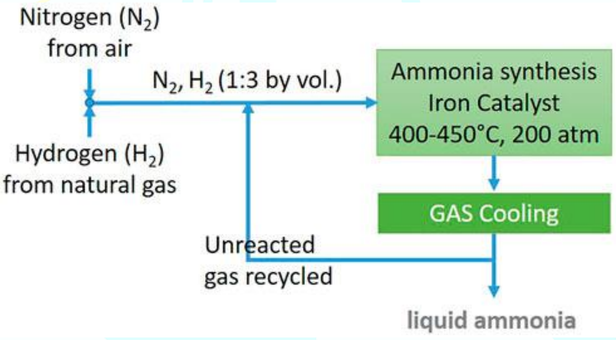

Fig 2. Typical Haber-Bosch process schematic [27]

In the last century, the Haber-Bosch Method has improved, reducing energy usage from around 100 GJ per ton of NH_3 in the 1930s to approximately 26 GJ per ton of NH_3 in 2020 [28]. Furthermore, there are alternative methods, such as Fauser, NEC, Claude, Casale, and Mont-Cenis, which vary in the apparatus used for synthesis as well as the pressure at which the reaction occurs. The nitrogen required for these processes is obtained by rectifying liquid air created using either the Linde or Claude methods [29].

The Claude process is a cost-effective approach for plant engineering. It involves partial oxidation of hydrocarbons to produce carbon monoxide and hydrogen. This reaction takes place in a muffling furnace at temperatures more than 1,000°C, using an appropriate amount of air and a nickel catalyst supported by magnesium oxide. Most of the coal-based ammonia manufacturing takes place in China. Currently, ammonia is predominantly derived from fossil fuels, known as "grey ammonia," which necessitates a substantial amount of energy (approximately 28-33 GJ/NH_3) and leads to significant CO_2 emissions (around 1.6 tCO_2/tNH_3, equivalent to roughly 1.8% of global CO_2 emissions). The main cause of these emissions is the hydrogen-producing process's energy- and carbon-intensive reforming procedure ([30, 31].

When carbon capture and storage (CCS) technology is employed in ammonia production, the resulting product is referred to as “blue ammonia”. Although technologies for CCS show potential in substantially mitigating CO_2 emissions from major point sources such as industrial and power generation plant facilities that utilise biomass or fossil fuels, they are not now viable for commercial use or cost-efficient [32]. Conversely, when all energy sources used to create ammonia are renewable, it is referred to as "green" ammonia. The worldwide green ammonia market is projected to have significant growth between 2021 and 2027, at a compound annual growth rate of 7.8%, which might potentially decrease the reliance on fossil fuels for ammonia production [33].

There are two methods to generate green ammonia: The first approach, which has significant long-term potential, relies on the utilisation of the procedure of Haber-Bosch fuelled by green hydrogen produced from renewable resources. Furthermore, the full procedure is driven exclusively through electrical energy derived from renewables. The second pathway relies on ammonia produced electrochemically, thereby obviating the requirement for the Haber-Bosch process.

3. Chemical and Physical Properties

It has been established that ammonia is a transportable hydrogen carrier with a high density that is safe and suitable for application in transportation systems and energy production. This makes it well-suited to swiftly comply with environmental policies aimed at decarbonizing energy production chains. Unlike hydrogen, its main advantage lies in the existing storage and transportation infrastructures that have been developed over time for the delivery of ammonia as a chemical compound. However, despite these benefits, there are some significant drawbacks, particularly in combustion-based systems, due to the chemical and physical properties of NH_3. To highlight these problematic issues, the oxidation properties of ammonia are compared to those of common fuels for internal combustion engines (ICEs) in Table 1.

Table 1. Characteristics of NH_3 and other hydrocarbon fuels during combustion [34]

Fuels	**Heating valve [MJ/Kg]**	**Energy density [MJ/m³]**	**Density [kg/m³]**	**Octane [RON]**	**Flame velocity [m/s]**	**Flammability limits [Vol/%]**	**Minimum ignition energy [Mj]**
NH_3 cooled and liquefied	18.6	12.691 atm -33℃	682	>130	0.067	15-28	680
NH_3 compressed and liquefied		11.65 300 atm 25℃	626				
H_2 cooled and liquefied	120	8.51 atm -253℃	70.85	>130	3.25	4.7-75	-0.016
H_2 compressed and gasified		2.46300 atm 25℃	20.54				
Diesel n-dodecane	44.11	32.89 1 atm 25℃	745.7	<20	-0.80	0.43-0.6	-0.23
Gasoline iso-octane	44.34	n-octane 30.93 1 atm 25℃	n-octane 697.6	100	0.41	0.6-8	-0.14
Methanol	19.90	15.651 atm 25℃	786.3	108.7	0.56	6.7-36	0.14
Ethanol	26.84	21.071 atm 25℃	785.1	108.6	0.58	33-19	0.6

Table 1 presents relevant parameters for internal combustion engines (ICEs), including the lower heating value (LHV) of the fuel expressed in terms of both gravimetric and volumetric units, measured in MJ/kg and MJ/L, correspondingly. The fuels' density is measured in kg/m³. The other important fuel's characteristics include the minimum ignition energy (MIE), flammability constraints (vol%), flame velocity (m/s), and octane number, measured in MJ. NH_3 is assessed in its condensed state, either by cooling it to -33°C at atmospheric pressure or by pressurising it to 300 bar and 25°C, to facilitate direct comparison with liquid or hydrogen in the compressed form under the identical pressure of reference.

Out of the fuels that were examined, NH_3 has the lowest Lower Heating Value in MJ/kg. It is only equivalent to alcohols that have undergone partial oxidation. The energy content of H_2 is 120 kJ/kg, which is about three times more than that of petrol and diesel, which is approximately 44 MJ/kg when compared on a weight basis. H_2 has the lowest energy density when measured in terms of volume (MJ/L), regardless of whether it is in pressurised (2.46 MJ/L) or liquefied (8.5 MJ/L) states. This emphasises the primary issues associated with storing and transporting H_2. In addition to safety considerations, the compression efficiency of H_2 is remarkably high, with only 1.05 kWh/kg H_2 required to compress it from 20 to 300 atm. On the other hand, cryogenic liquefaction of H_2 at -253°C necessitates 2.88 kWh/kg. On the other hand, NH_3 possesses an energy density of 12.69 MJ/L in its cooled liquefied state and 11.65 MJ/L when liquefied through compression. The process of converting energy content from gravimetric to volumetric takes into consideration the density of the fuel, highlighting the fact that hydrogen has a very low density while ammonia (NH_3) is characterized by a high density of hydrogen (H_2).

4. Carbon-free fuels in IC engines

Combustion processes in various industries contribute significantly to CO_2 emissions. To ensure the objective of achieving zero-carbon emissions is attained, it is imperative to decrease CO_2 emissions by employing carbon-free fuels such as NH_3 and H_2 in combustion systems.

4.1. Hydrogen-Powered Engines

Hydrogen may be utilized as a fuel in internal combustion engines; however, the combustion structure of the fuel can be altered with modest engine changes. The usage of hydrogen in an internal combustion engine is similar to that in other types of motors. In different investigations on the use of internal combustion gasoline engines within the automobile industry [35], hydrogen enters the combustion chamber of the motor via injection or carburetor frameworks from the premixed complex.

Hydrogen has considerable potential in applications to power spark ignition engines and to achieve good performance. Some beneficial properties of hydrogen, such as fast flame propagation, low ignition energy, and a wide operating range, allow for optimization and improvement of the combustion process. This makes it possible, among other things, to limit the emission of harmful components to only NOx [36]. Hydrogen in SI engines can be used in one of the following ways [36, 37]:

1- Manifold induction—Low-temperature hydrogen is injected into the manifold through a valve-controlled duct.

2- Direct introduction—A cryogenic cylinder is used to store hydrogen. A pump circulates liquid hydrogen to a heat exchanger to vaporize it. Then, cold hydrogen is injected into the engine. By using cold hydrogen, pre-ignition is avoided and NOx formation in the combustion process is reduced.

3- Hydrogen addition to gasoline: In this method, a mixture of hydrogen and petrol is introduced into the combustion chamber of an internal combustion engine. There, the compressed mixture is ignited by a spark.

Hydrogen fuel, when mixed with air, forms a combustible mixture. It can be burned in a conventional spark ignition engine with an equivalence ratio below the flammability limit of a gasoline–air mixture. The resulting ultra-lean combustion produces low flame temperatures. This directly leads to lower heat transfer to the walls and higher engine efficiency. This is an important advantage of hydrogen-powered SI engines. Hydrogen-powered engines have lower unwanted emissions compared to hydrocarbon-fueled engines. Previous studies have shown that the main pollutants in hydrogen engines are NOx as well as PM. NOx emissions from hydrogen-fueled ICEs are higher than from petrol-fueled ICEs due to the high combustion temperature. Due to the higher combustion temperatures, high NOx emissions occur especially when the engine is operating in the stoichiometric fuel-to-air ratio range. Reducing the air-fuel ratio decreases the combustion temperature and NOx emissions.

Moreover, there are several reasons for using hydrogen as a fuel additive in compression ignition (CI) internal combustion engines [38]. The injection of small amounts of hydrogen into a CI internal combustion engine improves the homogeneity of mixing in the diesel spray stream. This is largely due to the high diffusivity of hydrogen. As a result, the combustible mixture is more thoroughly mixed with air [2]. As such, the formation of hydrocarbons, carbon monoxide, and carbon dioxide during combustion can be almost eliminated. Only the partial combustion of lubricating oil can produce trace amounts of these compounds in the combustion chamber [38]. Also, in hydrogen-fueled CI engines, an injector is used to inject high-pressure hydrogen into the cylinder. Therefore, not only is the design of the engine structure important but that of the injector because the injection nozzle controls how pressurized hydrogen is injected into the combustion chamber [38]. Compression ignition engines cannot be operated with hydrogen as a standalone fuel the compression temperature is insufficient for initiating combustion due to the higher autoignition temperature required [39]. Therefore, burning hydrogen in a CI engine requires the aid of a spark plug or a glow plug. With a dual-fuel engine, the main fuel (hydrogen) is injected into the intake air or carburetor. Combustion is initiated by the diesel fuel acting as an ignition source. The amount of pilot fuel can be 10–30% of the total fuel, with the rest of the energy provided by the main fuel (hydrogen).

Similarly to SI engines, nitrogen oxides (NOx) are a major problem in hydrogen-operated dual-fuel CI engines. EGR is effective in reducing NOx emissions due to the dilution effect, which reduces the oxygen concentration in the intake charge. However, volumetric efficiency significantly decreases as EGR increases. Compared to a dual-fuel hydrogen propulsion system without EGR, an approximately 15% decrease in volumetric efficiency is observed [40]. In addition, the use of EGR in hydrogen dual-fuel operations can increase particulate emissions. The effect of a bi-fuel engine using hydrogen and EGR is to produce smoke levels similar to those of a CI ICE. At the same time, the use of EGR increases the emissions of unburned HC, CO, and CO_2. Another way to reduce NOx emissions is to introduce liquid water into the combustion chamber. It can also prevent knocking combustion and premature ignition when burning hydrogen. The action of water has a similar effect to the dilution of exhaust gases by EGR, causing cooling of the charge and reducing the combustion rate. However, water injection into the intake manifold results in reduced volumetric efficiency of the engine [39].

4.2.Ammonia-powered engines

The use of liquid ammonia as a fuel for internal combustion engines faces significant technical challenges due to its low flame speed, high autoignition resistance, and corrosivity [41]; [15]; [42]. Ammonia's use as a fuel began in 1943 in Belgium during a diesel fuel shortage in World War II [43]. In the 1960s, researchers further explored ammonia's potential in ICE, providing initial guidance on its application [44]; [45]; [46]; [47]. Some properties of ammonia and hydrogen, are summarized in Table 2. These properties can help compare engine performance when using different fuels.

NH_3 serves as a reliable hydrogen carrier, facilitated by onboard systems for NH_3 cracking or dissociation [48]. Gill et al. (2012) conducted experiments replacing 3% of the intake air with gaseous or dissociated NH_3, as well as pure hydrogen, in direct-injection diesel engines, to analyse their combustion and emissions. Ammonia is being considered a viable option in large internal combustion engines used for power generation and marine transportation to reduce greenhouse gas emissions[49].

Table 2. Comparison of the Properties of ammonia and hydrogen

Fuel	Liquid H_2	Gaseous H_2	Ammonia
Formula	H_2	H_2	NH_3
Storage method	Cryogenic liquid	Compressed gas	Liquid
Lower heating value (MJ/kg)	120.1	120.1	18.8
Fuel density (kg/m3)	71.1	17.5	602.8
Storage temp (℃)	-253	25	25
Storage pressure (Kpa)	102	24.821	1030
Fuel volume (L)	131.5	534.4	99.2
Fuel weight (kg)	9.4	9.4	59.8
Flame speed (m/s)	3.51	3.51	0.15
Energy density (MJ/m3)	8539	2101	11333

Modifications are required for engines to run on NH_3, such as introducing a supply system like LPG and an 8-bar fuel tank for port fuel injection, often equipped with a heated vaporiser [50]. High-pressure common rail direct injection systems have been developed for methanol, ammonia, and more low-viscosity fuels [51]. For spark-ignition engines, a higher compression ratio takes advantage of ammonia's high-octane number while compensates for its low laminar flame speed [52]. To enhance the ammonia burning rate, H_2 is added, and a dissociation catalyst facilitates onboard H_2 generation by ammonia cracking [53]. To stop hydrogen backfiring in spark-ignition engines, spark plug materials are modified [54]. Recent literature supports dual-fuel mode combustion, prompting studies to optimise NH_3/diesel-fuelled engine performance and reduce GHG emissions without sacrificing efficiency.

Various injection techniques for NH_3 CI engines have been investigated recently. Advanced pilot injection, while reducing NH_3 slip, led to increased N_2O and NO_x emissions. Engine heat release rate (HRR) decreased significantly with advanced pilot injections due to early combustion onset. Retarded post-injection reduced HRR moderately [55]. According to research by Lamas and Rodriguez (2019), at 40 ◦CA aTDC, fuel injection profiles using parabolic technology produced the biggest reduction in NOx (about 75%) as compared to the triangle and rectangle profiles (approximately 65%)[56]. Prolonged injection duration produced a worse reduction of NO_x, while retarded fuel injection drastically reduced NO emissions because of the expansion stroke's heat loss.

Late fuel injection strategies are expected to decrease fuel efficiency, while advanced injection at 10–18 ◦CA bTDC appears more practical [55]. Despite an increasing trend in NOx and N_2O emissions with injections from 0 to 10 ◦CA bTDC, Pyrc et al. (2021) investigated the use of an ammonia solution (NH_3 + H_2O) in a CI engine, with conventional diesel as the baseline[57]. Engine heat release using the water ammonia solution (WAS) increased by 12 J/≲CA at full load, resulting in a ~3% increase in brake thermal efficiency (BTE) due to prolonged combustion duration and increased ignition delay. NOx emissions were 520 ppm lower for the diesel/WAS engine than for diesel, attributed to the lower combustion temperature. Late fuel injection may reduce fuel efficiency, while advanced injection at 10–18 ◦CA bTDC is more practical. While N_2O and NO_x emissions raise the CA bTDC injection from 0 to 10◦. further advances could drastically reduce NO_x [55]; [58].

4.3.Ammonia-hydrogen blend in IC engines

Boretti et al. (2012) proposed a new heavy-duty engine design for ammonia-hydrogen dual fuel combustion, integrating a jet pre-ignition chamber with a secondary hydrogen injector and a glow plug alongside the main ammonia and hydrogen injectors. Simulation using GT-POWER was constrained by the absence of models for such dual fuel combustion, and limited experimental data hindered result accuracy[59]. Pochet et al. (2017) investigated ammonia in addition to hydrogen HCCI engines, identifying achievable energy ratios and their impact on performance and emissions. They found minimal impact on the resistance to auto-ignition until the ammonia content reached 60%, with 100% hydrogen combustion requiring an intake temperature close to TDC of 427 K[60].

Combustion efficiency decreases with a higher proportion of ammonia in comparison to 100% hydrogen combustion due to increased ignition delay from lower temperature inside the cylinder, which requires an increase in intake temperature and pressure. Hydrogen combustion produces radicals that promote ammonia auto-ignition, intertwining their combustion processes. Ammonia-hydrogen combustion's longer duration helps counter hydrogen's ringing behaviour in HCCI engines, as shown experimentally with all operational areas in the safe region when ammonia is present in the fuel mixture compared to pure hydrogen [60].

Hogerwaard & Dincer (2016) found that the NH_3/diesel engine with H_2 assistance had just a little bit higher efficiency and exergy destruction rates compared to neat diesel[61]. Gill et al. (2012) investigated gaseous dissociated NH_3, H_2, and NH_3 combustion in a CI engine, noting lower BSFC for a 75/1/24 $H_2/NH_3/N_2$ blend compared to neat NH_3, suggesting better fuel efficiency[49]. Pochet et al. (2020) discovered that adding around 15% ammonia by volume in combination with hydrogen resulted in a significant increase in resistance to autoignition, with slower pressure and temperature rises as ammonia loading increased[62]. Lamas & Rodriguez (2017) studied the injection of ammonia in diesel/hydrogen engines, achieving an optimal decrease of NOx (around 60%) at 43.2 ◦CA aTDC, with NOx decreasing significantly with a higher proportion of ammonia[63]. The performance of the dual-fuel engine fuelling with H_2-ammonia is summarised in Table 3.

In a practical engine test, Comotti and Frigo (2015) showed that for H_2 mass fraction of ~22%, an engine speed of at least 3000 RPM is needed to ensure that the NH_3/H_2 engine efficiency remains competitive with that of the neat gasoline engine. Efficiency for the NH_3/H_2 engine declined drastically as engine speed fell below 3000 RPM. Furthermore, increased N_2O emissions are another concern when using H_2 as an additive in the SI engine [64]. It was shown that N_2O emissions increased by ~50% as H_2 vol fraction increased by 12.5% under the fuel-lean combustion [64]. The drastic increase in N_2O is presumably due to the increased NO emission in fuel-lean operation that promotes N_2O formation via $NH + NO \rightarrow N_2O + H$. N_2O is nearly 300 times more harmful to the climate than CO_2 [65]. Thus, the challenging task for the NH_3/H_2 SI engine is to minimise N_2O emissions into the ambient air.

Apart from dissociating the NH_3 into N_2 and H_2, another way of enabling NH_3/H2 engine can be by injecting the NH_3 and H_2 separately into the intake manifold of the SI engine. An electro-injector was used for NH_3 and H_2 injection in an experimental engine. It was demonstrated that the BTE of NH_3/H_2 blending was 3–4% lower than the gasoline engine from 2500 to 5000 RPM [50]. Mørch et al. (2011) also utilised separate NH_3 and H_2 injection methods[66]. It was reported that blending ammonia with ~5 vol% hydrogen could still lead to a good power response [67]. By elevating the hydrogen to ~10 vol%, the engine ITE increased by 0.5% as compared to a neat gasoline engine [68]. Nonetheless, NOx emissions of ~750 ppm were produced when hydrogen content was increased to ~20 vol%, thus suggesting the need for SCR at the exhaust gases under these conditions. Westlye et al. (2013) found that NOx emissions of an NH_3/H_2 engine increased by ~2000 ppm as fuel injection was advanced by

40◦CA for lambda (λ) > 1. NO_2 increased by ~100 ppm while nitrous oxide (N_2O) decreased by 50 ppm. Slip NH_3 remained unchanged as SOI was advanced to 40 ◦CA bTDC[69]. Moreover, it was also found that NO, NO_2, and NH_3 slip increased by 1000 ppm, 25 ppm, 1500 ppm, respectively as CR increased from 7 to 15 for $\lambda > 1$ operation. Another development that used separate injection was presented by Cardiff University through the development of their Green Ammonia demonstrator at the Rutherford Appleton Laboratory [70]. The results showed that an injection of 30% (vol) hydrogen in an ammonia mixture could enable the replacement of methane for the production of power up to 16 kW at 1,500 RPM. Although NOx emissions were below 20 ppm, it was observed that the combustion was still inefficient, thus requiring further development in terms of timing, equivalence ratio, and injection strategy. For a separate H_2 supply system, spark ignition timing must be retarded by another 10–15 ◦CA (compared to a gasoline engine) to ensure stable engine operation, thus resulting in higher heat loss and less residual expansion than gasoline engines [50]. It is expected that the separate H_2 supply system can deliver comparable engine performances with the NH_3 dissociation system if the H_2 mass fraction is increased to ~11% (resembling that of the NH_3 dissociation system). Emission-wise, NH_3 dissociation technology led to considerable NOx reduction when compared with the gasoline engine. This was because the engine was operating near stoichiometric where NO emission is considerably low [71]. For a separate H_2 supply system, advanced SOI was required to ensure stable engine operation. Owing to the substantial heat loss incurred by advanced SOI, thermal NO was reduced in the SI engine that employed a separate H_2 supply system [69]. In contrast, studies that utilized the PFI technique [50] did not blend the dissociated NH_3 with gasoline [72]. Hence, direct comparisons between both fuel induction techniques are not possible. As compared to a neat gasoline engine, the fuel efficiency of DI gasoline/ NH_3/H_2 engine was lowered by an average of 10 MJ/kWh as compared to gasoline/ NH_3 SI engine without dissociation system [73], despite higher engine power was generated by the latter. Ammonia injection for ~22 MS was required for the DI gasoline/ NH_3/H_2 engine to achieve similar fuel efficiency with a neat gasoline engine. No direct emissions comparison between the DI gasoline/ NH_3/H_2 engine and the neat gasoline engine was performed [53]. For the PFI engine, the thermal efficiency of the NH_3/H_2 is also lower than the neat gasoline engine [50]. Nonetheless, no direct emission assessment between NH_3/H_2 and the neat gasoline engine was performed. Although a reasonable comparison cannot be performed, it is expected that the fuel mixture in the DI NH_3 engine would be heterogeneous and the combustion would be predominantly non-premixed because the gasoline/air was not mixed with NH_3/H_2 fuel spray before entering the combustion chamber. However, the fuel mixture and air for PFI injection are mixed before entering the combustion chamber. Hence, the reaction time scale is likely to be shorter, and the combustion mode is primarily premixed.

In a study by Lhuillier et al. (2019), the authors investigated the influence of hydrogen addition on the performance and emissions of an ammonia-fueled SI engine. The H_2 volume content varied from 5% to 15% at different equivalent ratios and intake pressures. The use of hydrogen as a combustion enhancer allowed acceptable combustion stability over the whole engine map. 10% H_2 concentration was found as the optimum to increase combustion efficiency without compromising exhaust emissions. The best efficiency results were achieved at lean, near stoichiometric conditions. Further charge dilution results in a significant increase in NO_x and NH_3 at the exhaust without combustion efficiency improvements[74]. Similar findings were highlighted in Frigo and Gentili (2013). Lhuillier et al. (2020) performed an extensive investigation on the use of NH_3/ H_2 blends with different equivalence ratios and H2 volume concentrations up to 60% in a single-cylinder spark-ignition engine[50, 72]. The recent paper carried out by Mounaïm-Rousselle et.al. (2021) provides new information on operation limits in ammonia-fueled gasoline direct injection (GDI) SI engines, especially to find the lowest possible load limit when the engine is fed with pure ammonia. However, they extended the operating limitations by adding less than 10% of hydrogen to ammonia. Although the ammonia-fueled engine does not produce carbon-based emissions, it can emit high NOx emissions. However, their results show that adding 10% of H_2 to ammonia significantly decreases NOx emissions by up to 40%[75].

Zhu et al. (2024) studied the combustion of ammonia within a spark-ignition engine with a compression ratio of 15:1. The findings suggest that efficient pure ammonia combustion occurs at low engine speeds (1000 r/min) and high brake mean effective pressure (BMEP exceeding 0.6 MPa). Pure ammonia combustion achieves a brake thermal efficiency of 33.7% at a BMEP of 0.94 MPa. Introducing hydrogen at an energy ratio of 2–16% expands the engine's load range. With hydrogen blending, the efficiency rises to 35.8% at a BMEP of 0.63 MPa. The research on NOx emissions reveals that, under specific operating conditions, there is a reduction reaction between unburned ammonia and NOx, leading to a decrease in NOx emissions as BMEP increases. This study can offer support for the application of ammonia engines[76].

Lee et al. (2024) studied the extension of the operable range of ammonia-fueled spark ignition engine by hydrogen addition was mainly discussed. Ammonia was injected directly into the cylinder, and hydrogen was supplied into the intake port. The result showed that the operable range of ammonia-fueled combustion with hydrogen addition could be extended from 0.2 to 1.4 MPa with relatively stable combustion, i.e., CoV of gIMEP <5 %, except for one case. Moreover, under the BMEP 1 MPa load condition, hydrogen addition improved brake thermal efficiency (BTE) by 4.7 % and unburned ammonia was also reduced by 25 %[77].

Vin et al. (2024) proposed the Groove Diversion-Assist Ignition (GDAI) combustion system, which can effectively control the temperature, fuel distribution, and flow rate in the spark plug region near the top dead center and finally achieve the spark ignition of pure ammonia without any change in compression ratio and scavenging temperature. The results show that enhancing the initial temperature can alleviate the requirement for spark ignition energy, and a minimum energy level of 75 mJ remains necessary for effective spark ignition of ammonia. Furthermore, the utilization of spark ignition of ammonia fuel can achieve a maximum thermal efficiency of 51.32%, representing a 2.8% increase in overall thermal efficiency compared to the diesel mode. Additionally, the application of ammonia fuel can relieve the NOx emissions compared to diesel fuel, which provides a new and effective utilization way for the application of ammonia fuel on the marine engine[78].

Jespersen et al. (2024) made a comprehensive effort to understand and optimize the spark ignition system to mitigate the need for an ignition improver, and all experiments have been performed with 100 % neat ammonia. The emission of N2O is critical to minimize, as it is a strong greenhouse gas. It was measured to be between 20 and 80 ppm and appeared to be related to post-oxidation reactions of ammonia released from crevices during expansion. Advancing the ignition timing has proved to be an efficient handle for balancing the emissions of NH3 and NOx. These emissions will be reduced to H2O and N2 in an SCR catalyst if they are correctly balanced. Fortunately, advancing ignition timing also minimizes the formation of N2O[79].

Westlye et al. (2013) conducted tests on a 0.612-L displacement CFR engine with a maintained fuel composition of 80 vol% ammonia and 20 vol% hydrogen in a series of experiments at 7, 11, and 15 compression ratios to investigate the NOx emission characteristics of the ammonia/hydrogen fueled engine. Experiments show that the size of the compression ratio has a significant effect on the ammonia escape phenomenon; the higher the compression ratio, the more obvious the ammonia escape phenomenon; the production of N_2O from ammonia combustion is affected by the ignition time; a later ignition time will lead to a temperature rise, thus promoting the formation of N_2O; concerning the MBT (maximum brake torque) ignition time, the N_2O emission will be very low; N_2O emissions are very low at MBT ignition time[69]. Despite the different principles of NOx generation, the NOx production from ammonia-blended hydrogen combustion is close to that of conventional fossil fuels. Hence, the NOx emissions from ammonia- hydrogen engines can be effectively cleaned up by using SCR (selective catalytic reduction) or ternary catalysts, which have been widely adopted so far [9].

Lee et al. (2008) investigated the unstretched laminar combustion rate of ammonia mixed with hydrogen and the flame response to stretching and showed that the laminar combustion rate of ammonia was effectively increased as the hydrogen share increased; furthermore, hydrogen substitution worsens the combustion emissions of ammonia fuel, making it more inclined to produce NOx (an air pollutant) and N_2O (which is a greenhouse gas), increasing the level of environmental pollution, although when ammonia/hydrogen mixtures are burned under fuel-rich conditions (fuel-rich refers to combustion situations where the ratio of fuel to oxidant in the combustion mixture is greater than the theoretical equivalent ratio), NOx and N_2O emissions are significantly lower than those from combustion under fuel-poor conditions[80].

5. Conclusions

The impact of using hydrogen (H_2) as a blending fuel with NH_3 on combustion and emission characteristics was reviewed. H_2-based carbon-free fuel has a high combustion speed and broad flammability range, whereas NH_3 combustion, is characterized by a low flame speed and temperature, high ignition energy, and narrow flammability range. Therefore, H_2 is considered an ideal promoter for improving NH_3 combustion. Low-emission fuels (LEFs), including H_2 and NH_3, are expected to approach the net-zero.

Introducing ammonia into the engine notably curbs pollutant emissions, with variations observed in CO, CO_2, NOx, and HC levels contingent upon its concentration. While ammonia reduces carbon content and subsequent CO and CO_2 emissions, higher hydrogen atom presence elevates HC and NOx emissions. The addition of hydrogen, however, impairs engine performance due to slower flame speed, a limitation mitigated by the incorporation of ammonia in gaseous and nanoparticle forms, which effectively lowering NOx and HC emissions.

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