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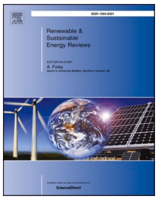

A critical review on ammonia as a fuel for internal combustion engines: Is it a viable option?

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ABSTRACT

Ammonia is considered an attractive alternative fuel for power generation in the context of global decarbonisation efforts. This study examines the advancements in ammonia combustion technology for spark ignition (SI) and compression ignition (CI) engines. An extensive analysis of the characteristics of ammonia (NH_3) combustion, a fuel free of carbon, is provided in this paper. Since ammonia burns similarly to fossil fuels and emits less CO_2, CO, NO_x, soot, and hydrocarbon (HC) pollutants, NH_3 is a desirable substitute fuel that can be stored and transported using existing commercial infrastructure. It also comes with productivity from renewable sources. However, unlike traditional hydrocarbon fuels, NH_3 exhibits unique combustion characteristics, highlighting the challenges of using it as a fuel for internal combustion (IC) engines. This paper critically reviews the challenges of NH_3 blended with diesel, biodiesel, dimethyl ether, and some other alternative fuels in IC engines. The literature reports mixed findings on this topic. Many studies have not demonstrated NH_3 as a substitute fuel for IC engines yet. In addition, ammonia's toxicity and unusual/complex combustion characteristics hinder its use as a fuel substitute in IC engines. Further research is required to overcome challenges associated with using NH_3 as a fuel for IC engines. This study identifies and discusses these challenges.

1. Introduction

Using fossil fuels to meet energy needs is not a viable long-term solution. Their dominance as the primary energy source is due to their low cost, which has resulted in a technological dependency. However, fossil fuels have significant drawbacks, including their limited availability and supply security concerns stemming from their high demand. Additional factors driving the push to move away from fossil fuels include their impact on climate change, which has caused a rise in global temperatures and various related environmental consequences. The primary greenhouse gas released in massive quantities is carbon dioxide, predominantly from burning fossil fuels. This has prompted the introduction of CO_2 taxes, raised the cost of fossil fuels, and potentially accelerated the adoption of alternative energy sources sooner than anticipated. Transitioning to renewable and alternative fuels will significantly reduce carbon emissions and contribute to a sustainable future.

The transportation sector, particularly road transport, is a significant contributor to global warming due to the direct emission of carbon dioxide (CO_2) and other greenhouse gases [1,2]. It also emits greenhouse gases indirectly, including carbon dioxide (CO_2), volatile organic compounds (VOCs), and nitrogen oxide (N_2O), as well as particulate matter (PM) and aerosols, which impact the atmosphere's oxidative capacity [3]. This is primarily due to the transportation sectors relies heavily on fossil fuels such as gasoline, diesel, petroleum gas, and natural gas [4,5].

For instance, the transportation industry in the United States uses around 94 % of the nation's petroleum supply [6]. Studies by Wallington et al. [6] and Skeie et al. [7] indicate that road transport accounts for

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16–17 % of anthropogenic CO_2 emissions globally, which equates to around 5 gigatons (Gt) out of the total 30 Gt of CO_2 emissions worldwide. Road transport is expected to sustain higher emission levels compared to other transportation sectors, such as aviation, shipping, and rail. This is because greenhouse gas emissions are directly proportional to fossil fuel consumption. As the population grows, automobile production increases, leading to a higher number of vehicles on the road. This trend reflects the association between the ability to travel comfortably and an improved quality of life [2,8].

The transportation industry is not only a major contributor to greenhouse gas emissions but also a major cause of the declining quality of the air in metropolitan areas, which poses a danger to public wellness and is anticipated to continue as the primary air pollution source in soon [9]. Furthermore, research by Nelson et al. [10] has established a strong link between adverse human health issues and exposure to vehicle-related air pollutant emissions. Therefore, the use of biofuels has been proposed as a solution to mitigate the rise in carbon emissions.

However, biofuels can have negative side effects, including the loss of carbon stocks, emissions from pesticide use, and deforestation. An alternative is ammonia, which emits no carbon and is comparable to propane in that it can be managed using current infrastructure and equipment. This has led to the consideration of finding fuel within the cycle of natural nitrogen, rather than the cycle of carbon, as a method to decrease greenhouse gas emissions. Ammonia was used as a fuel for vehicles during World War II. In 1942, the Belgian transport agency received word that the war would prevent diesel fuel from being available [11]. With a 30 % increase in bus passengers during wartime, engineers needed an alternative to diesel fuel. While coal gas was considered, its minimal energy level and the requirement for substantial quantities of storage made it impractical. Consequently, coal gas was blended with ammonia to fuel buses, with coal gas acting as a combustion promoter due to ammonia's reluctance to ignite.

After fossil fuels became widely available again, these buses were retired from service. Interest in ammonia as a fuel resurfaced when the U.S. military recognized that 65 % of the total tonnage needed for combat and transport operations during wartime consisted of fuels and lubricants [12]. To address this, the military explored alternative fuels and considered constructing mobile nuclear reactors to generate ammonia for their vehicles. This approach aimed to reduce transport expenses and enhance independence from third parties. While these movable reactors were intended to be operational by the 1980s, the plan was never realised for unknown reasons.

While alternative fuels were previously sought to reduce dependency on fossil oil and lower transport costs, today's primary concerns revolve around carbon emissions and their impact on climate change. The quest for alternative fuels, including ammonia, experienced a hiatus after the 1960s but has recently regained momentum as an intriguing area of research. The information provided has sparked the idea of exploring the feasibility of moving away from carbon-based fuels and instead harnessing fuels derived from the "natural" nitrogen cycle to power our vehicles without significant modifications to the designs of internal combustion engines.

The negative impacts of fossil fuels and greenhouse gases on climate change necessitate a transition to renewable energy sources to mitigate carbon dioxide emissions. In response to these global challenges, the 2015 Paris deal, an internationally enforceable climate change deal, established a structure to lower greenhouse gas emissions over the coming decades. Consequently, member states of the European Union have set a target to reduce greenhouse gas emissions by 55 % by 2030 [13]. Substitute carbon-free fuels, like hydrogen and ammonia, present promising avenues for replacing fossil fuels and curbing carbon dioxide emissions. However, a major challenge with hydrogen is its extremely low gas density requiring high-pressure storage which is unaffordable. Ammonia is one of the green fuels that is now receiving lot of attention as a possible substitute for fossil fuels, along with ethanol, methanol, and methyl ester [1,14–19]. Ammonia 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. Furthermore, ammonia is appealing for use in hydrogen-based fuel cells. Within ammonia, an alkaline fuel cell can be transformed into a combination of nitrogen and hydrogen by repurposing the heat produced directly by the fuel cell [20]. Nonetheless, there are technological hurdles to utilising ammonia effectively as a fuel for engines. These challenges include its high ignition temperature, slow flame propagation, corrosive nature, and toxicity.

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 °C 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 [10]. Due to its high flame speed and low ignition energy, hydrogen features 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 °C [20]. 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 [21].

Although the ignition temperature of ammonia is quite high at 650 °C, it shares similar qualities as a liquid fuel with propane (C_3H_8). Propane and ammonia have nearly the same octane values, boiling points, and densities [22]. Interestingly, the existing infrastructure for propane could potentially be adapted for transporting and storing ammonia, provided that all copper, brass, and rubber-based materials are swapped out for their mild steel and Teflon equivalents.

In general, cost and accessibility are the most crucial and fundamental considerations when selecting a mode of transportation. This implies that all approaches must be evaluated in terms of cost and the availability of the infrastructure required to transfer ammonia, depending on the ultimate location. Along with the previously listed factors, safety considerations should also be considered when selecting the best mode of transmission because failure to do so may result in irreversible harm to both people and the environment [23]. Regarding storage solutions, ammonia can be stored in pressurized tanks or refrigerated conditions, necessitating robust safety measures to prevent leaks and ensure integrity [23,24]. Implementing stringent safety protocols is crucial due to ammonia's toxicity and environmental impact [25]. Advances in energy storage technologies, including compressed gas, liquid, and solid-state storage, have increased their viability as energy carriers by making them eco-friendlier and more efficient [26].

Numerous studies and experiments are being conducted on ammonia as a potential combustion fuel. Liquid ammonia shares similar safety concerns as liquid propane, but it has the advantage of having very high autoignition resistance. The storage of ammunition may not present much more environmental risk because safety regulations are well-established. 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 [19]. This is because processing hydrogen requires more energy than producing and handling ammonia, both of which should be used as fuel. With the development of innovative techniques for generating hydrogen from renewable resources (such as wind, hydropower, and biomass gasification), ammonia is a carbon-free fuel that can also benefit from these technologies.

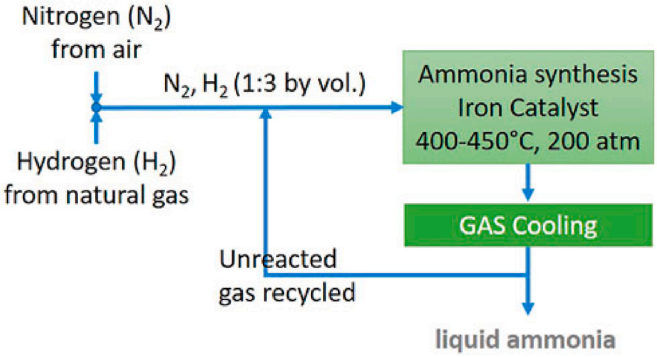

Fig. 1. Typical Haber-Bosch process schematic [28].

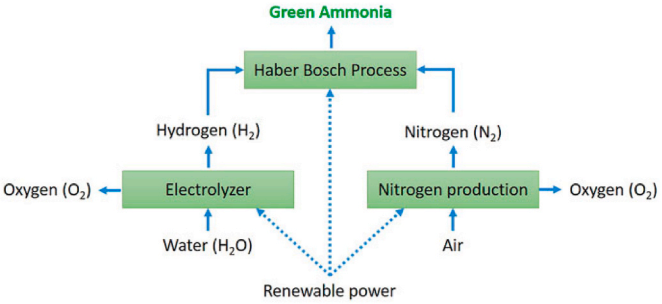

Fig. 2. Using the Haber-Bosch process with electrolysis of water to produce green ammonia [28]. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Moreover, ammonia can profit from these innovations and be used as a fuel that emits no carbon as new methods for creating hydrogen from renewable sources are discovered. Ammonia's direct use in combustion systems as a fuel is another option, particularly in IC engines. The possibility of ammonia as engine fuel is investigated in this study by reviewing the process of ammonia production, with a focus on innovative methods for producing green ammonia. It also describes the chemical and physical properties of ammonia fuel to identify its main advantages and disadvantages for utilise in IC engines. Finally, this paper presents a comprehensive review of the results of using ammonia as a fuel in both spark ignition (SI) and compression ignition (CI) engines, a topic that is virtually unavailable in the current literature.

2. Production of ammonia

Currently, roughly 70 % of globally produced ammonia comes from natural gas, while the remaining 30 % primarily relies on coal [19]. 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.

$$3H_2 + N_2 \rightarrow 2\,NH_3.$$

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 and 450 °C and pressures of 200 atm, with catalysts present. A schematic of a a standard Haber-Bosch procedure is shown in Fig. 1. Osmium, ruthenium, uranium, and iron are all suitable catalysts, with iron being the most 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 synthesis reactor is refilled [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 [29]. 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 [30].

The Claude process is a cost-effective approach for plant engineering. Hydrocarbons are partially oxidised to create CO and hydrogen. This reaction takes place in a muffling furnace at temperatures more than 1000 °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 "gray ammonia," which necessitates a substantial amount of energy (approximately 28–33 GJ/tNH_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 [31,32].

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 [33]. 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 7.8 % compound yearly growth rate, which might potentially decrease the reliance on fossil fuels for ammonia production [34].

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 Ha-ber-Bosch process.

2.1. First route: green sourced hydrogen combined with the Haber-Bosch Method

A technique for producing green ammonia comprises harnessing hydrogen derived from nitrogen obtained from the air separation unit (ASU) and renewable sources. These components are subsequently included in the Haber-Bosch method, utilising renewable electricity as the power source [1]. Water electrolysis is the most well-established method for creating hydrogen from renewable resources, although currently this method can only yield 4 % of hydrogen, primarily because of financial factors [35,36].

Fig. 2 is a diagram of the manufacture of green ammonia using electrolysis and the Haber-Bosch process. Electrolysis is the process of employing electric current to break water molecules into hydrogen and oxygen. Two electrodes and an electrolyte separate them in a water electrolysis cell. The electrolyte acts as a channel for moving the anions or cations, or chemical charges, that are generated between two electrodes. Depending on the kind of electrolyte utilised, there are four categories into which water electrolysis falls.

- Microbial electrolysis cells (MEC),
- Alkaline water electrolysis (AWE),
- Solid oxide electrolysis (SOE), and

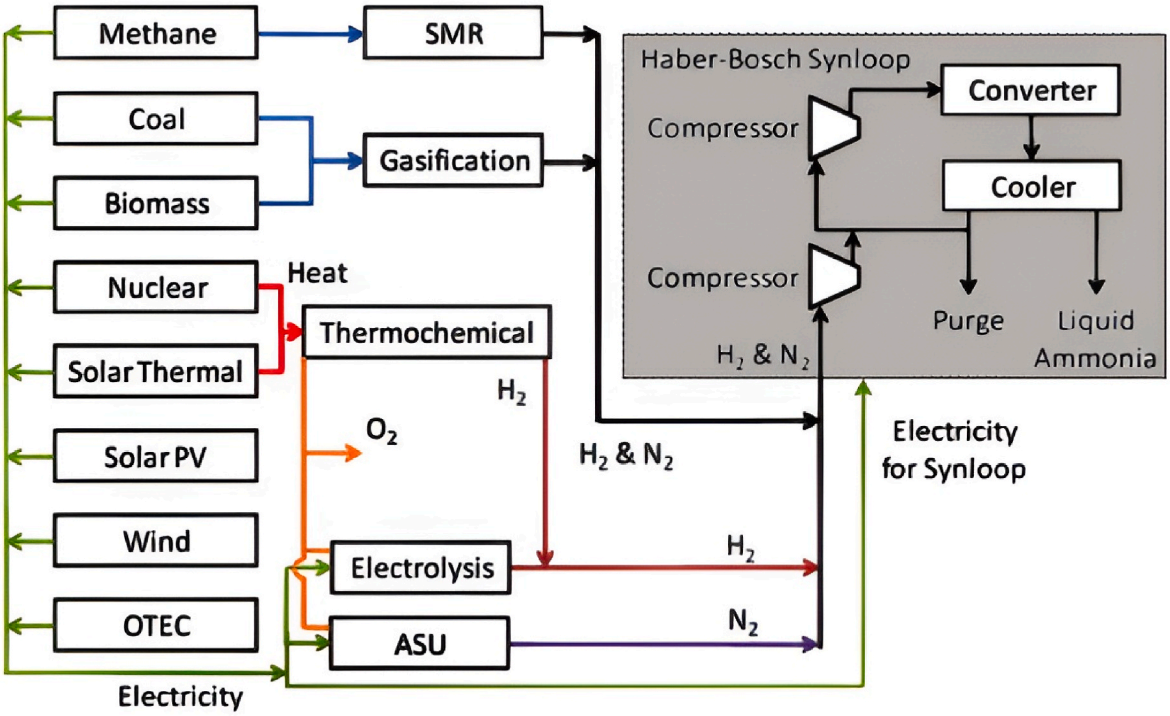

Fig. 3. Various approaches to integrating technologies with the HB-Synthesis loop [19].

- Proton exchange membrane (PEM) water electrolysis.

The electrolyser consists of the stack, where the process of water electrolysis occurs, as well as the other components of the plant. The components include the provision of electricity, hydrogen buffering, compression, water purification, and power, along with hydrogen processing [37]. The prevalent and economically feasible electrolysers are predominantly according to (Proton Exchange Membrane) PEM and AWE (Alkaline Water Electrolysis). These electrolysers are classified as low-temperature electrolysers since they function within the temperature range of 30 °C–80 °C. Solid oxide electrolyte (SOE) cells can perform high-temperature electrolysis within a temperature range of 800 to 1000 °C. Although still in the process of being developed, they have not yet been implemented on a large basis.

Microbial electrolysis cells are developing the technology of bioelectrochemistry used to generate hydrogen (H_2) from organic substances. MEC technology holds great promise for efficient energy generation in biorefineries for waste [8]. To facilitate the widespread use of electrolysis, researchers are currently focusing their efforts on addressing existing obstacles and transforming the technology from a specialized niche into a commonly used method. The primary objective is to reduce the expense associated with the production of green hydrogen using this method. By understanding the electrolyser systems' durability, cost, and performance trade-offs during expected dynamic functioning in the future that use carbon dioxide-free power from sources like solar, wind, and hydropower, a substantial cost reduction can be attained. Simultaneously, endeavours are focused on diminishing the initial investment required for the electrolyser unit (stack) and the remaining components of the facility.

Furthermore, activities related to research, development, and demonstration (RD&D) aim to enhance energy efficiency to achieve the conversion of electricity to hydrogen under various operating conditions. It is necessary to enhance our comprehension of the degradation mechanisms in stacks and electrolytic cells and devise mitigation strategies to extend stack operational life [38].

An alternative method for producing green hydrogen, which can be integrated with the Haber-Bosch method used to produce ammonia, is biomass gasification. This thermochemical process transforms biomass into hydrogen and several byproducts (CO, CO_2, CH_4, and N_2) without combustion. Conducted under sub-stoichiometric conditions, biomass gasification involves introducing an agent for gasification into the reactor, where it reacts with the biomass. While air is the most used gasification agent, other gases such as O_2, steam, or a combination a combination of these can be employed to increase the H_2 content and prevent N_2 dilution [39].

2.2. *Second route: ammonia synthesis by electrochemical method*

Ammonia's electrochemical synthesis has garnered significant attention in the 21st century due to its carbon emission-free nature and its optimal operating conditions requiring temperature and pressure of the atmosphere [40]. Unlike the highly unsustainable Haber-Bosch process, renewable energy sources such as hydropower, wind, or solar can power EAS. EAS primarily involves the electrochemical reduction of nitrogen (NRR) to produce NH_3, with water serving as the ultimate source of hydrogen.

Multiple modalities of this procedure are currently under active investigation.

1. The electrochemical nitrogen reduction reaction (eNRR) involves using an electrocatalyst to facilitate the direct addition of electrons and protons to the N_2 molecule.
2. Indirect or mediated nitrogen reduction reaction (NRR) processes include the reduction of a redox mediator, which then undergoes a series of events resulting in the formation of ammonia and the regeneration of the mediator. Recently, there has been a resurgence of interest in lithium-mediated electrochemical NRR due to its high level of reproducibility. This process begins with the electrochemical deposition of lithium, followed by two chemical reactions that include the splitting of dinitrogen and the addition of protons to generate ammonia [41].

Fig. 3 illustrates various sources utilised for ammonia generation. Steam methane reforming (SMR) is a process that uses methane to

Table 1
Characteristics of NH_3 and other hydrocarbon fuels during combustion [28].

Fuels	Heating valve [MJ/Kg]	Energy density [MJ/ m^3]	Density [kg/ m^3]	Octane [RON]	Flame velocity [m/s]	Flammability limits [Vol/%]	Minimum ignition energy
NH_3 cooled and liquefied	18.6	12.691 atm −33 ° c	682	>130	0.067	15–28	680
NH_3 compressed and liquefied		11.65 300 atm 25 ° c	626				
H_2 cooled and liquefied	120	8.51 atm −253 ° c	70.85	>130	3.25	4.7–75	−0.016
H_2 compressed and gasified		2.46300 atm 25 ° c	20.54				
Diesel n-dodecane	44.11	32.89 1 atm 25 ° c	745.7	<20	−0.80	0.43–0.6	−0.23
Gasoline iso- octane	44.34	n-octane 30.93 1 atm 25 ° c	n-octane 697.6	100	0.41	0.6–8	−0.14
Methanol	19.90	15.651 atm 25 ° c	786.3	108.7	0.56	6.7–36	0.14
Ethanol	26.84	21.071 atm 25 ° c	785.1	108.6	0.58	33–19	0.6

extract hydrogen from the hydrocarbon chain. On the other hand, gasification is a method used to convert coal and biomass into gas. Electricity sources can be used to power the electrolysis process, usually in conjunction with an Air Separation Unit (ASU) that supplies the Hoffman-Bosch synthesis loop (synloop) with hydrogen and nitrogen. The ammonia production methods using nuclear and solar energy involve the use of a heat source operating at high temperatures enabling the extraction of hydrogen through thermochemical reactions. Thermochemical processes offer superior efficiency and economic benefits compared to electrolysis, although a certain amount of electricity is still required to operate the ASU. The outcomes of these processes consist of oxygen and ammonia in their pure form.

Besides the methods mentioned earlier, ongoing studies in the scientific community explore various approaches to green ammonia synthesis.

- Nitric oxide electrochemical synthesis [42].
- Utilising photoelectrochemically produced hydrogen in the presence of intense sunshine for electrochemical production [43].
- Photo-electrochemical synthesis [44].
- Ammonia synthesis is achieved by utilising biomimetic catalysts and nitrogenase organisms, which creates a biotechnological pathway [45].

Currently, all these processes are at Technology Readiness Level (TRL) 1, indicating that they are in the early stages of development. Additional research and development endeavours are required before the implementation of large-scale industrial production.

In general, the future direction for ammonia manufacturing is increasingly focused on sustainable and decentralized production methods, driven by the need for environmental protection and energy efficiency. Traditional processes like the Haber-Bosch method are being challenged by innovative technologies that utilise renewable energy sources, aiming to reduce carbon emissions and enhance production efficiency. Therefore, key advancements and trends in ammonia production would be green ammonia production, electrified and decentralized systems and advanced catalytic methods [46–48]

Additionally, the 2021 IEA Ammonia Technology Roadmap examines three potential ammonia production scenarios and attempts to lower industrial emissions. More ammonia will be needed in the future, but with fewer emissions, according to the paper, since the demand for ammonia will rise due to a growing and more prosperous global population. Additionally, the research states that 1.3 % of CO_2 emissions from the energy system and almost 2 % of total final energy consumption are attributable to ammonia production [49].

3. Ammonia’s chemical and physical properties

3.1. *Properties of NH_3 chemical and physical*

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 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, respectively. The fuels’ density is measured in kg/m^3. 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 lowering its temperature to −33 °C while in air 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. In contrast, we analyse conventional fuels used in internal combustion engines (ICEs) such as diesel (n-dodecane) and petrol (iso- or n-octane), as well as alcohols like methanol and ethanol. These alcohols are low-carbon fuels that can be produced from renewable resources.

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 pressurized (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).

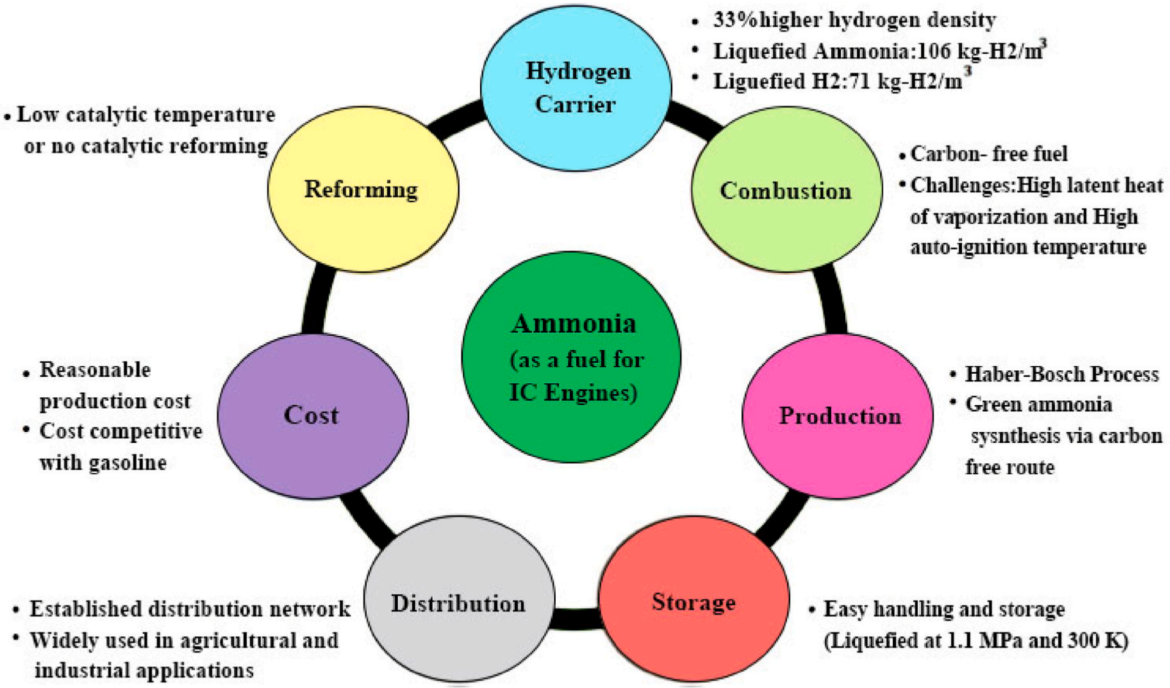

Fig. 4. Properties of ammonia as a fuel for IC engines [51].

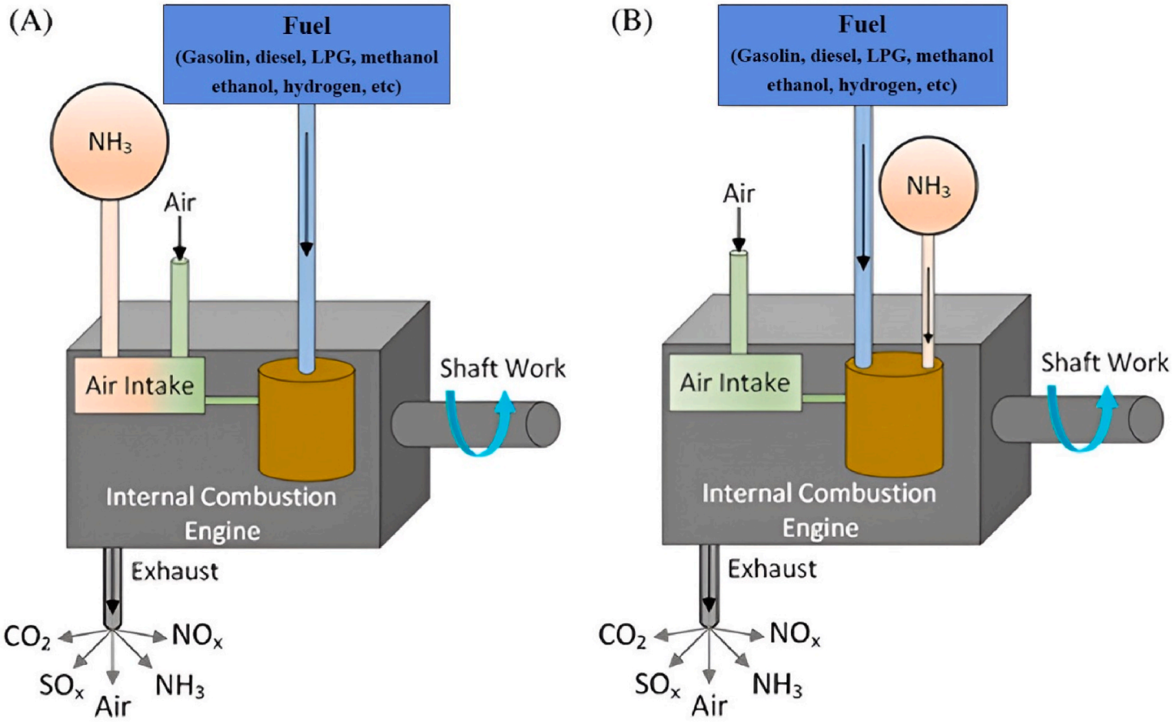

Fig. 5. Examples of internal combustion engines powered by ammonia-fuel blends are (A) an ammonia intake with fuel added separately and (B) an ammonia intake with air in the gas form [52].

3.1.1. *Main practical issues of combustion of NH_3*

The primary practical challenges associated with combustion systems using NH_3 as a fuel arises from its inadequate ignition quality (RON >130), which is characterised by a stoichiometric NH_3/air mixture with a low flame speed of about 7 cm/s and a high autoignition temperature of 924 K at standard conditions of pressure (P = 1 atm) and temperature (T = 298 K). The flame speed of this substance is approximately ten times slower than that of ordinary fuels and alcohols and one thousand times slower than that of H_2. In addition, NH_3 has a relatively high MIE (680 mJ) for minimal ignition energy and a restricted range of flammability (15 %–28 % by volume in air), which makes its combustion properties more complex compared to the other fuels mentioned in Table 1. Reiter and Kong could establish an effective engine running with a fuel composed of 95 % NH_3 while facing several obstacles. Fig. 4

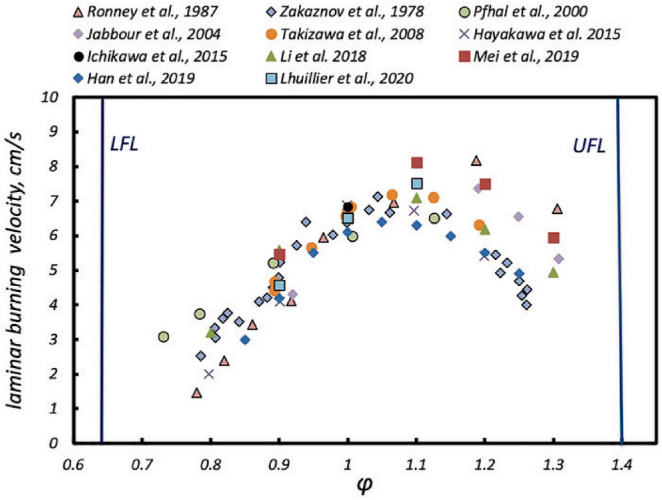

Fig. 6. NH_3/air laminar burning velocities at 298 K and 1 atm vs mixture equivalency ratio (φ) [28].

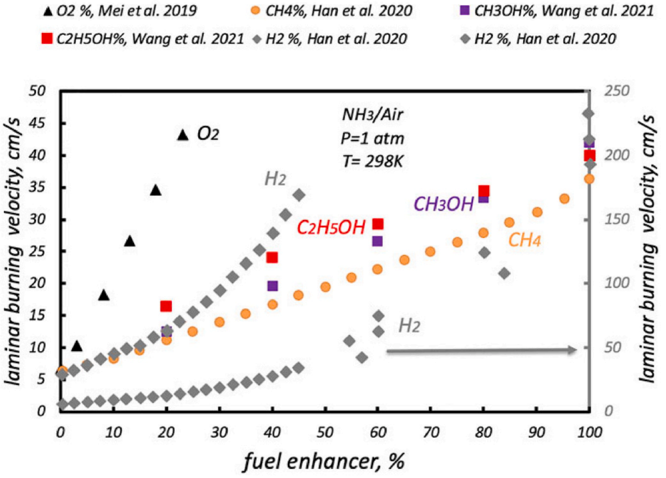

Fig. 7. SL in relation to the O_2 content or the fuel "enhancer" addition (stated as %) [28].

provides a full account of the NH_3 fuel share trend that has been examined by other researchers in earlier studies [50].

To address the challenging ignition characteristics of ammonia, a common approach is to blend it with conventional fuels like gasoline, diesel, LPG, CNG, ethanol, methanol, hydrogen, and other fuels that are commonly used in internal combustion engines. Internal combustion engines employ ammonia-fuel mixes, as seen in Fig. 5. The air intake manifold allows for the introduction of ammonia into the engine either in a gas mixed with air, or it can be independently injected it into the cylinder as a liquid, in addition to the fuel. Since traditional fuels ignite at lower temperatures, they elevate the cylinder temperature, aiding in the ignition of ammonia.

Ammonia-fuel blends can minimize the need for additional engine modifications or devices, facilitating a cost-effective transition to the hydrogen economy within internal combustion engines (Fig. 5A). Achieving optimal power output and minimal emissions entails careful adjustment of the ammonia, fuel, and air mixture, necessitating the design of specialized blenders and automatic control systems tailored for each conventional fuel (Fig. 5B) [52]. Introducing separate liquid phase injections of fuel and ammonia into the intake manifold allows for precise adjustment of flow rates, requiring the development of effective ammonia injectors to prevent ammonia slip. It is important to note that NH_3 possesses a high vaporization latent heat (1370 kJ/kg), significantly more than ethanol, liquid H_2, and gasoline. Injecting NH_3 into engines may lead to a sharp drop in combustion temperature sharply, potentially resulting in lower engine efficiency and incomplete combustion [53].

The high NH_3 RON value can be advantageous for SI engines, potentially allowing for higher compression ratios and increased engine efficiency [53]. However, precautions must be taken to mitigate NO_x emissions resulting from NH_3 oxidation, necessitating the implementation of primary or post-combustion techniques (Cornelius et al., 1996). Many of NH_3's characteristics stem from its molecular structure, including its trigonal pyramidal shape and covalent N-H bonds, which contribute to its lower reactivity compared to standard fuels in combustion systems [54].

Understanding NH_3 chemistry and NO_x formation routes is crucial for optimising system operating conditions and ensuring complete NH_3 conversion while minimizing NO_x emissions. The ignition delay periods, and laminar burning speed (SL) are important factors for gas turbines and internal combustion engines (ICEs). The experimental characterization of NH_3's SL has been conducted throughout the years about the equivalent ratio of the mixtures, as shown in Fig. 6 [55–59].

The speed of the laminar flame of NH_3/air mixtures at 298 K and 1 atm falls within the range of 1.4–8.23 cm/s for mixture equivalence ratios (φ) ranging from 0.7 to 1.3. When conditions change from fuel-lean to fuel-rich, the flame speed increases with φ, peaking at approximately φ = 1.1, with the highest values ranging between 6.3 and 8.2 cm/s. However, as φ increases more, it falls, with larger discrepancies observed for fuel-rich conditions. Increasing pressure from 1 to 5 atm results in a linear decrease in the laminar flame speed of NH_3/air mixtures. For example, at φ = 1, between 7 and 5 cm/s, the flame speed drops [57]. Such modest flame rates might restrict the direct application of NH_3 in internal combustion engines (ICEs), prompting the exploration of various strategies to enhance this crucial parameter.

Experimental studies have shown that preheating NH_3/air mixtures up to 448 K and 473 K increases the laminar flame speed, with a nearly linear relationship between flame speed and temperature. For stoichiometric NH_3/air mixtures, the flame speed can reach T = 448 K, up to 14 cm/s [55,59].

To improve NH_3 oxidation properties, common strategies involve the application of fuel additives, like H_2, CH_4, syngas, or other conventional or e-fuels. These enhancers can be added to NH_3 to enhance combustion properties, in line with decarbonisation strategies for energy production. Alternatively, modifying the environmental atmosphere to be O_2-enriched can also enhance NH_3 oxidation. H_2 can be produced directly through NH_3 partial catalysis techniques before injection into combustion systems. Additionally, plasma-assisted systems may offer further avenues to improve NH_3 oxidation features [53,59–63]. Recent studies have focused on H_2, CH_4, and alcohol as potential fuel enhancers for NH_3.

Fig. 7 illustrates the NH_3 laminar flame velocity as a function of the concentration of these fuel enhancers or for O_2-enriched environments in stoichiometric NH_3/O_2 flames. The O_2 concentration should be interpreted as a surplus compared to standard air conditions. The inclusion of H_2 as a "fuel enhancer" is depicted regarding both the main axis, where its concentration reaches up to 45 %, highlighting its distinctive characteristics, and the secondary axis, showcasing its significantly higher laminar flame speed compared to other pure "fuel" enhancers.

It's notable that the addition of H_2 or CH_4 [59], as well as CH_3OH or C_2H_5OH [63], notably enhances the laminar burning velocity of NH_3. For example, H_2 (rhombus), CH_4 (dot), and alcohols (squares) contribute almost equally to the increase in ammonia SL up to a relative concentration of 20 %. Beyond this threshold, CH_4 and alcohols exhibit a linear relationship between their concentration and the NH_3 laminar flame speed, while H_2 demonstrates an exponential increase. An efficient method to augment the NH_3 laminar flame velocity is evident in

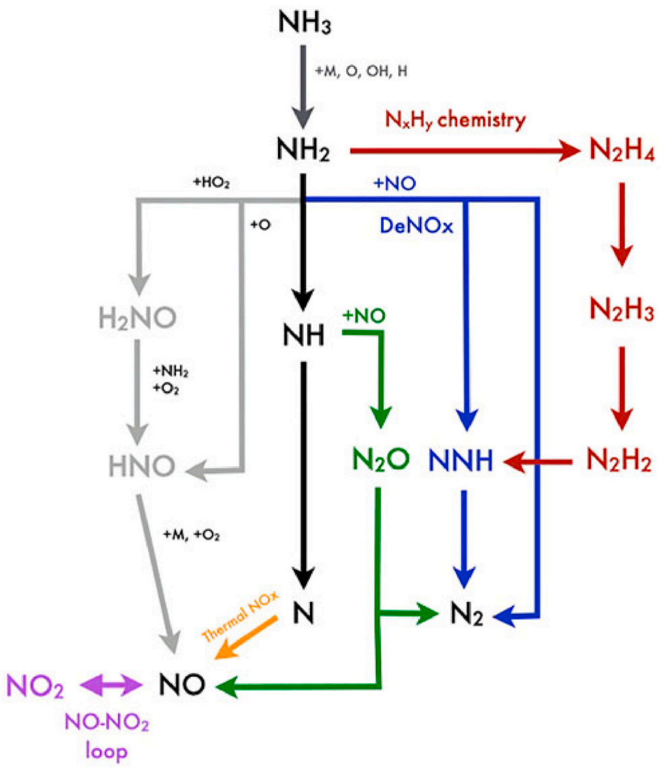

Fig. 8. Typical scheme for Chemical oxidation of NH_3, NO_x production pathways, the NO-NO_2 loop, $DeNO_x$, N_xH_y, and N_2O chemistry [28].

O_2-rich surroundings where SL experiences a prompt rise with increasing O_2 concentration [58], beginning with triangles, the basic "air" condition.

3.2. Chemical kinetic problems with NH_3 oxidation

As previously noted, comprehending NH_3 oxidation chemistry and identifying the fuel NO_x pathway are pivotal in defining the initial system operating parameters. The mechanisms are elucidated in the comprehensive depiction of NH_3 oxidation chemistry, illustrated in Fig. 8.

NH_3 can undergo dehydrogenation reactions to become NH_2 through the action of OH, H, and O radicals, or heat degradation (shown by the gray pathway). NH_2 radicals have the potential to combine and form N_2H_x species, particularly in fuel-rich or pyrolytic environments and at high pressures. Konnov and de Ruyck [64] proposed the route of N_2H_x, which involves the breakdown of N_2H_4 within shock tubes under fuel-rich conditions. They also identified a new pathway for NO_x generation with N_2H_3 radicals. Many writers have emphasised the significance of this pathway in predicting NH_3 laminar flame velocities, particularly under fuel-rich conditions [53,65–68].

At lower temperatures or higher pressures, NH_2 radicals have the alternative option to interact with HO_2 radicals, leading to the formation of H_2NO, as depicted in the light-gray pathway. Recent work by Stagni et al. [68] and Song et al. [69] has involved updates to the rate constant governing the reaction of H_2NO with O_2 to produce HNO and HO_2, particularly focusing on conditions of elevated pressure (up to 300 bar) with temperatures be-tween 450 and 925 K [68,69]. Subsequently, HNO radicals contribute to the NO generation, outlining a significant pathway for fuel NO formation.

Alternatively, NH_2 radicals can engage in $DeNO_x$ chemistry by reacting with NO through termination and branching reactions. Specifically, NH_2 reacts with NO to form N_2 and H_2O, or NNH and OH, termed the blue pathway, operating effectively within the temperature range of 1100 to 1400 K [70,71]. The laminar flame speed and ignition delay time are significantly influenced by the ratio of rate constants associated with $DeNO_x$ chemistry.

Subsequently, NNH undergoes decomposition to produce N_2 and H. This reaction holds considerable importance as it releases H radicals necessary to sustain the radical branching mechanisms of H_2 and O_2. However, due to its brief lifespan and tunnelling nature, modelling activities involving NNH can be quite complex. Another reaction of interest involves NNH reacting with O to produce NO and NH, which has garnered significant attention as an additional route for NO formation [64,72].

Over 1400 K in temperature, NH_2 radicals undergo rapid dehydrogenation to NH. This NH can then react with NO to produce N_2O, as described by the reaction $NH + NO = N_2O + H$, which was recently revised by Klippenstein et al., in 2011. Alternatively, the NH radicals can release N radicals, which can participate in the classical Zeldovich mechanism (orange pathway) at temperatures above 1600 K [73]. This mechanism involves reactions such as $O + N_2 = N + NO$, $N + O_2 = O + NO$, and $N + OH = H + NO$. At high pressures and temperatures, it is seen that the generation of NO_x decreases due to the reduction in radical concentration caused by third-body reactions ($H + OH + M = H_2O$, $H + O_2 + M = HO_2 + M$), which are required to keep the Zeldovich mechanism going. Nitrous oxide (N_2O), by its decomposition process $N_2O + M = N_2 + O + M$ at low pressures, acts as a reservoir for oxygen radicals. This, in turn, increases the pace of the reaction $H_2 + O = H + OH$. In conditions of high pressure or extremely lean fuel mixtures, this reaction undergoes a reverse process, which plays a crucial role in the N_2O production (Valera-Medina et al., 2015; [72]).

In contrast, at temperatures above 1650 K, N_2O is decomposed via the reaction $N_2O + H = N_2 + OH$, leading to the release of OH radicals and a reduction in the characteristic delay time for fuel ignition [74]. The NO-NO_2 loop, represented by the purple route, increases the conversion of unreactive HO_2 radicals into reactive OH radicals through the reaction $NO + HO_2 = NO_2 + OH$. This process enhances the overall reactivity of the mixture. Additionally, the loop recycles NO through the reaction $NO_2 + H = NO + OH$, further releasing more OH radicals.

The influence of N_2O and NO-NO_2 interactions on the characteristic chemical kinetics of fuel warrants meticulous examination in the context of exhaust gas recirculation (EGR) systems [74]. These systems reintroduce exhaust gases into the engine to regulate the temperature of the adiabatic flame, thereby limiting NO_x emissions to prescribed thresholds. Mathieu and Petersen [75] investigated NH_3 ignition delay times under high-pressure (30 bar) and high-temperature conditions using a shock tube. Their findings underscored the significance of pathways involving N_2O and NO_2 [75]. Zhang et al. [76] and Ahmed et al. [77] further elucidated the process of NO-NO_2 conversion, revealing a more intricate pathway that includes intermediate species such as HONO, HNO_2, $HONO_2$, and HNO_3.

A numerical study was carried out to contrast several detailed models with ignition delay periods published by Hayakawa et al.'s (2015) laminar flame data and Mathieu and Petersen's [75], in response to the increasing number of kinetic schemes established in the last ten years, as well as Duynslaegher et al. [78], for pressures as high as 5 atm. The primary discrepancies among these mechanisms were attributed to NO_x formation routes. Notably, key reactions such as $HNO + O_2 = HO_2 + NO$ and ammonia pyrolysis under fuel-rich conditions (e.g., $2NH_2 = NH_3 + NH$) were identified as essential steps for predicting NO emissions [64–69,71,76,79].

In addition, Zhang et al. [76] and Nakamura and Hasegawa [65] provided evidence of the importance of thermochemical parameters in predicting the behaviour of NH_3 weak flames and the time it takes for ignition to occur under high-pressure settings. Kovács et al. [79] conducted a study where they examined eight intricate kinetic models for the process of experimental data on the pyrolysis and oxidation of NH_3 [57,65,75,76,78]. They observed a substantial disparity among model predictions and emphasised the need to expand the validation process to

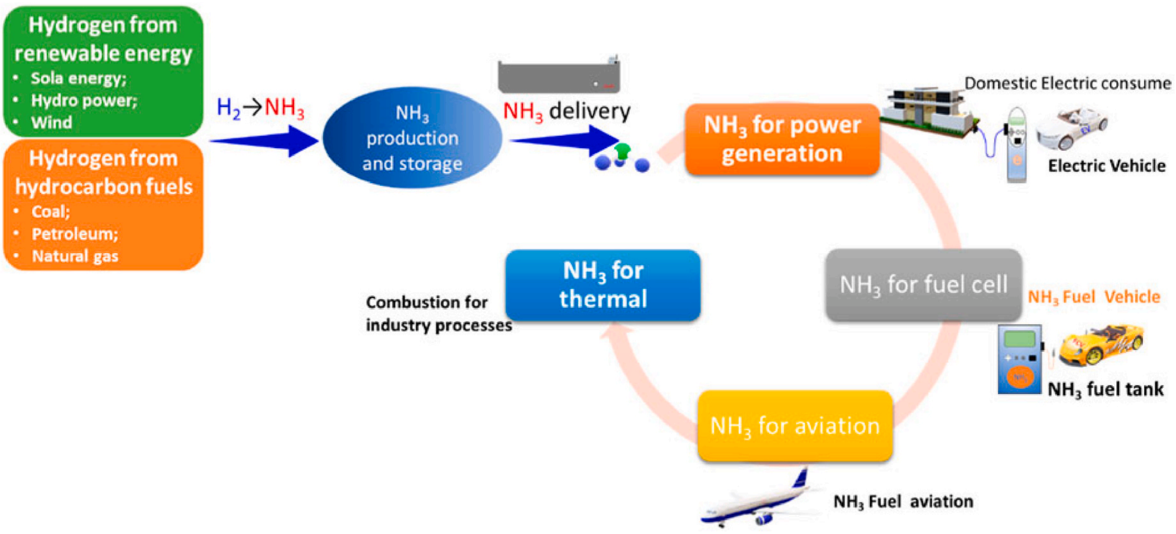

Fig. 9. Utilising NH_3 as a fuel system with almost minimal emissions [89].

include a broader NH_3 database.

After reviewing the recent developments in kinetic scheme development, it becomes evident that numerous challenges persist in NH_3 oxidation chemistry and NO formation pathways. These include substantial uncertainties in rate constants, variations in thermochemical parameters, the pronounced non-Arrhenius behaviour of NH_3 dehydrogenation reactions, and the need for accurate descriptions of pressure-dependent rates, particularly pertinent in high-pressure environments. Additionally, unresolved aspects such as the chemical pyrolysis of NH_3 and the N_xH_y route, the tunnelling characteristics of NNH responses, the significant impact of $DeNO_x$ chemistry on NO sensitivity, and the kinetics associated with the NO-NO_2 loop, N_2O, and H_2NO/HONO species remain unresolved. Furthermore, recent experimental investigations in engine applications have explored NH_3 blends with

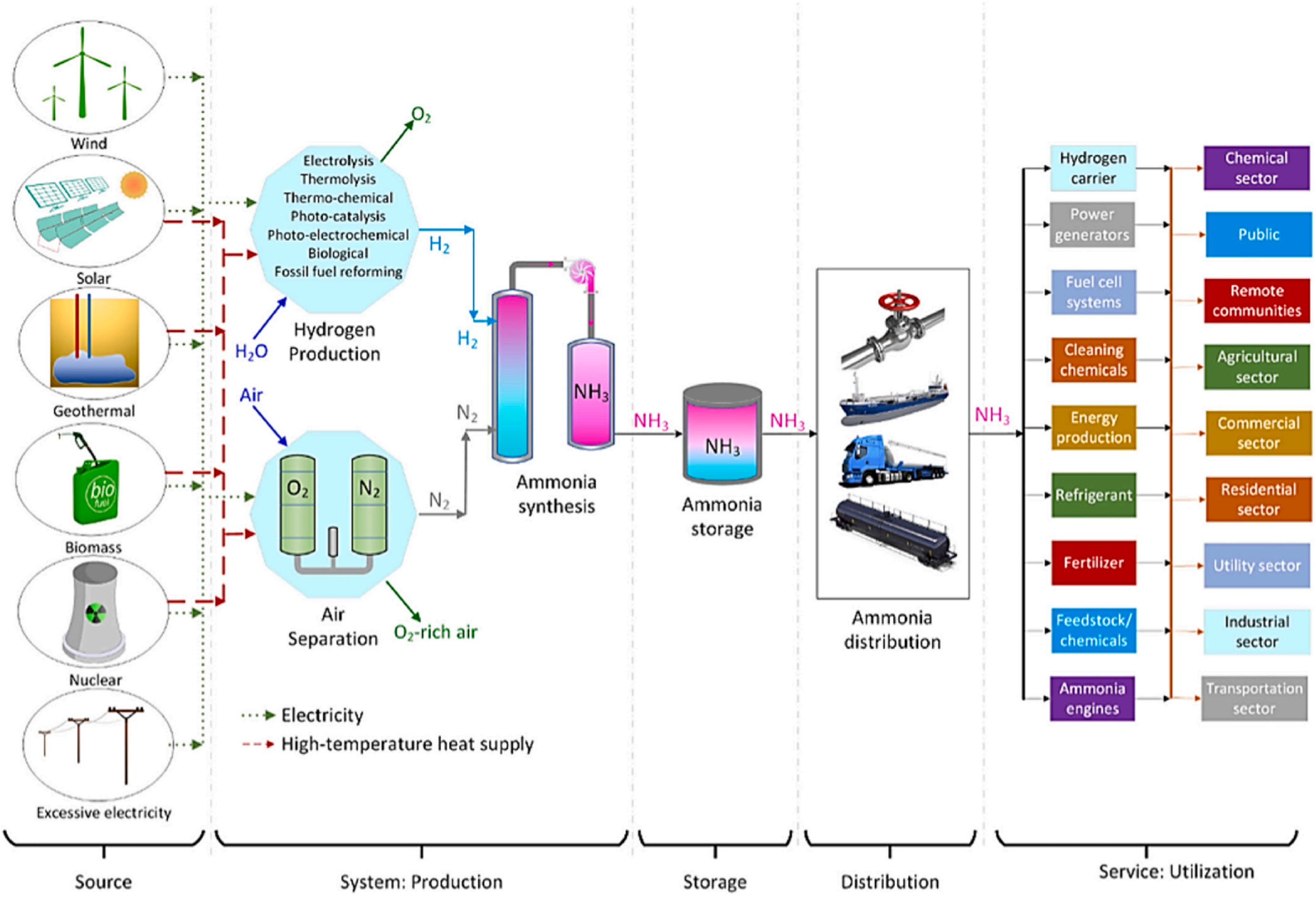

Fig. 10. An ammonia economic cycle from production to consumption [52].

Table 2
Comparison of the properties of ammonia and other fuels [104].

Fuel	Liquid H_2	Gaseous H_2	Natural gas	Ammonia	Propane	Gasoline	Methanol	Diesel
Formula	H_2	H_2	CH_4	NH_3	C_3H_8	C_8H_{18}	CH_3OH	$C_{12}H_{23}$
Storage method	Cryogenic liquid	Compressed gas	Compressed gas	Liquid	Liquid	Liquid	Liquid	Liquid
Lower heating value (MJ/kg)	120.1	120.1	38.1	18.8	45.8	42.5	19.7	43.5
Fuel density (kg/m3)	71.1	17.5	187.2	602.8	492.6	698.3	786.3	838.8
Storage temp ($^{\circ}C$)	−253	25	25	25	25	25	25	25
Storage pressure (Kpa)	102	24.821	24.821	1030	1020	101.3	101.3	101.3
Fuel volume (L)	131.5	534.4	157.5	99.2	49.8	37.9	72.5	
Fuel weight (kg)	9.4	9.4	29.5	59.8	24.5	26.4	57.0	14.8
Flame speed (m/s)	3.51	3.51	8.45	0.15	0.83	0.58	0.56	0.87
Energy density (MJ/m3)	8539	2101	7132	11333	86487	31074	9350	36403

various fuels such as NH_3/H_2, NH_3/CH_4, NH_3/diesel, NH_3/n-heptane, NH_3/DEE, and NH_3/CH_3OH and C_2H_5OH. These studies aim to enhance the ignition delay times of NH_3 and, laminar flame speed, offering promising strategies for optimisation [63,80–84].

4. Ammonia as a fuel

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 in combustion systems. NH_3 is a compelling high hydrogen density hydrogen carrier weighing 17.8 %, making it a viable carbon-free fuel. It offers several advantages: 1) it emits no CO_2, SO_x, or soot; 2) it can be produced from diverse sources like biomass, renewable energy, and fossil fuels; and 3) it can be transported and stored using existing infrastructure like pipes, trucks, ships, and gasoline tanks. These features make NH_3 an appealing contender for an alternate fuel [85–88]. Fig. 9 illustrates the synthesis of NH_3 from various energy sources, including nuclear energy, wind power, and fossil fuels with CCS. This method guarantees that NH_3 is completely free of CO_2 and can be recycled, demonstrating its promise as a viable carbon-free fuel.

Ammonia as a clean fuel and energy vector is increasingly recognized, making it a strong candidate for adoption in multiple applications. Ammonia presents a versatile solution for various sectors, particularly in energy generation including gas turbines, IC engines and Ammonia solid oxide (SO) fuel cells that are both alkaline and direct as well as maritime transport because of strict rules set by the International Maritime Organisation to reduce ship-related NO_x and SO_x emissions and to decrease CO_2 emissions by 50 % by 2050 [25]. Furthermore, ammonia has been shown to be a reliable, safe, accessible, and simple refrigerant for all cooling system functions, including air conditioning and dehumidification. According to Sanchuli et al. [90], working fluids based on ammonia also performed better than other parts of the adsorption refrigeration cooling system.

The viability of NH_3 as a carbon-neutral fuel, thanks to its favourable characteristics for storage and transportation, has been proven, and its prospective uses in automotive engines. However, significant challenges remain in ensuring NH_3's alternative fuel capabilities with exceptional performance, durability, and reliability. It is essential to optimise the combustion properties of ammonia and reduce pollutant emissions, requiring a precise determination of combustion characteristics when using NH_3 as fuel. Fig. 10 illustrates the ammonia economy: from manufacturing to consumption.

The limited understanding of NH_3 combustion characteristics, methods for enhancing combustion, and the limitation of NH_3 as a fuel is due to the optimisation of NO_x production. A comprehensive comprehension of the combustion and emission properties of pure NH_3 and its fuel mixes is of utmost importance. This understanding is expected to enable NH_3 to serve as a power source for vehicles, to generate electricity, and provide industrial heating in future energy systems, due to its appropriate combustion qualities [88].

Due to its poor combustion characteristics, few researchers have attempted to use ammonia in compression-ignition engines. Notably, Gray et al. achieved ammonia combustion only with an intake gas temperature greater than 423 K and a compression ratio of 35:1 [92]. Pearsall et al. conducted experiments at a compression ratio of 30:1; however, they could ignite ammonia fuel in compression-ignition engines [93].

Due to ammonia's poor combustion performance, Pearsall et al. modified a spark ignition engine to study pure ammonia fuel effects at 1800 rpm and ratios of compression: 12:1, 16:1, and 18:1. At an 18:1 ratio, peak ignition pressure increased by 100 psi compared to 16:1, but fuel consumption did not change significantly. However, at 12:1, fuel consumption increased by 6 %. Notably, spark plugs were significantly damaged at the 18:1 compression ratio [94]. Li et al. studied ammonia combustion under oxygen-enriched conditions, testing oxygen levels from 21 % to 30 %. They found that ammonia's combustion properties improved significantly with higher oxygen levels, reaching a maximum combustion rate of 38.6 cm/s at 30 % oxygen, which is 2.6 times higher than at 21 % oxygen. However, combustion under oxygen-enriched conditions tends to produce more NO_2 than NO [56].

4.1. Ammonia in engines

Taking environmental issues, the potential application of ammonia (NH_3) as a low-carbon fuel and energy carrier presents significant environmental consequences that warrant careful consideration. While ammonia offers benefits in reducing carbon emissions, its toxic nature and the risks associated with its handling and use can lead to adverse environmental impacts, particularly in the event of spills or accidents. Furthermore, unplanned releases of ammonia can have immediate detrimental effects on both aquatic and terrestrial ecosystems, affecting various receptor species and human health [95,96]. The combustion of ammonia can lead to the formation of nitrogen-based pollutants, including N_2O and NO, which pose serious environmental risks [97,98].

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 [11,20,99]. Ammonia's use as a fuel began in 1943 in Belgium during a diesel fuel shortage in World War II [100]. In the 1960s, researchers further explored ammonia's potential in ICE, providing initial guidance on its application [93,101–103].

Starkman et al. [100] conducted an experiment on a spark ignition CFR engine, where they adjusted the compression ratio within the range of 6:1 to 10:1. They used ammonia from a high-pressure container, which was stored in a heated water bath. For efficient combustion of anhydrous ammonia in a spark ignition (SI) engine, it must be introduced as vapour and partially decompose it into nitrogen and hydrogen. Four to five percent of the weight must be decomposed as a minimum. Fuel was heated electrically and directed through a stainless-steel catalyst chamber to break down ammonia. The chamber included an active iron catalyst in pellet form. It is shown that the brake-specific fuel consumption (BSFC) at maximum engine power output increased by a factor of two because of the lower energy content of ammonia. The ammonia achieved a peak nitric oxide (NO) concentration of

Table 3
Comparing the coverage of the present review paper with review papers published in the domain of the fuelling an internal combustion engine (ICE) with ammonia.

Various NH_3 blends in CI engine				Effects on the behaviour of CI engines			Various NH_3 blends in SI engine		Effects on the behaviour of SI engines			References
Diesel	Biodiesel	DME	H_2	Performance	Pollution	Combustion	H_2	Others	Performance	Pollution	Combustion	Ref
✓	×	✓	×	×	✓	✓	✓	✓	×	✓	✓	[94]
✓	×	✓	×	×	×	✓	✓	✓	×	×	✓	[115]
×	×	×	×	×	×	×	✓	✓	×	✓	✓	[88]
✓	✓	✓	✓	✓	✓	×	✓	✓	✓	✓	×	[116]
✓	✓	×	✓	✓	✓	✓	×	×	×	×	×	[117]
✓	✓	×	×	✓	✓	×	×	×	×	×	×	[118]
×	×	×	×	×	×	×	✓	✓	×	✓	✓	[89]
✓	✓	×	×	×	✓	×	×	×	×	×	×	[119]
✓	✓	✓	✓	✓	✓	✓	×	×	×	×	×	[112]
✓	✓	✓	✓	×	✓	×	✓	✓	×	✓	×	[28]
×	×	×	×	×	×	×	✓	✓	×	✓	×	[120]
✓	✓	✓	✓	✓	✓	✓	×	×	×	×	×	[51]
✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	This review

√: included × : Not included.

approximately 4800 ppm, but iso-octane only reached about 3400 ppm. Ammonia produced a maximum of 3000 parts per million (ppm) of NO, whereas iso-octane produced 500 ppm of NO. Some properties of ammonia and other fuels, such as propane, gasoline, diesel, and natural gas, are summarised in Table 2. These properties can help compare engine performance when using different fuels.

Gray et al. [92] performed studies on a1CFR1 engine utilising a CI method, where liquid ammonia was injected directly into the cylinder. Successful autoignition required a 35:1 compression ratio, 150 °C intake air temperature, and a jacket. Early injection timing and high vaporization rate suggested a close-to-homogeneous air-fuel mixture during ignition. Various auxiliary fuels were explored to reduce the need for a high compression ratio, with fuels having a satisfactory cetane number deemed suitable as pilot injection fuels for ammonia. Oil samples showed no composition or property changes at 40-h intervals, with oil deterioration after 120 h less than that of a gasoline engine.

Pearsall and Garabedian [93] attempted direct injection of liquid ammonia, raising the compression ratio to 30:1, but found it unsuccessful. A tiny pilot injection of diesel fuel was used to induce compression ignition after ammonia was added to the induction system. Results indicated that ammonia preferred operation closer to stoichiometric, achieving power outputs exceeding diesel-only operation by up to 32 %. No. 1 diesel (50 CN) outperformed No. 2 diesel (44 cetane number), and military engine fuel (38 cetane number) is preferred because of its superior igniting properties. An increase in pilot fuel quantity is directly correlated with higher output and reduced fuel consumption.

Grannell et al. [105] experimented using a spark ignition CFR engine to evaluate different ratios of gaseous ammonia and petrol mixtures to achieve circumstances without knocking. Results indicated the need for 100 % gasoline at idle and a 70 % ammonia/30 % gasoline mixture at wide-open throttle conditions. Ammonia's high ignition temperature could allow for a higher compression ratio. Despite its resistance to autoignition, investigating ammonia combustion in diesel engines, dominant in heavy-duty transportation and power generation, is worthwhile. Reiter and Kong [106] successfully operated a multi-cylinder diesel engine by employing ammonia as the primary fuel in their chemical kinetics study of ammonia/hydrocarbon systems while employing pilot diesel for ignition. They conducted tests using different ratios and reported the fuel efficiency and gaseous emissions (CO_2, HC, NO_x) based on volume.

NH_3 serves as a reliable hydrogen carrier, facilitated by onboard systems for NH_3 cracking or dissociation [51]. Gill et al. [107] 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 decrease greenhouse gas emissions.

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 [108]. High-pressure common rail direct injection systems have been developed for methanol, ammonia, and more low-viscosity fuels [109]. For spark ignition engines, a higher compression ratio takes advantage of ammonia's high-octane number while compensates for its low laminar flame speed [110]. To enhance the ammonia burning rate, H_2 is added, and a dissociation catalyst facilitates onboard H_2 generation by ammonia cracking [111]. To stop hydrogen backfiring in SI engines, spark plug materials are modified [112].

Generally, the key issues associated with ammonia as a fuel in modern engines are combustion challenges, emission concerns and technological solution. Since the ammonia combustion process has poor chemical kinetics, the high ignition temperature and the low flame front propagation speed are the two biggest challenges in this path. Due to all these problems, this fuel must be used in combination with other fuels that burn easier.

Also, mixed combustion or blending ammonia with hydrogen or methane can enhance combustion stability and efficiency. In other words, despite these advancements, the inherent limitations of ammonia combustion suggest it may not serve as a universal solution for modern engines, necessitating further research and development to address these challenges. Because of the reduction in activation energy and the increase in variety provided by active particles in the reaction system, the limit of flame extinction can be exceeded by plasma-assisted combustion. and burn at lower temperatures while lowering NO_x emissions [113]. Technologies such as plasma-assisted combustion and oxygen-enriched combustion are being explored to improve ammonia's combustion characteristics [113,114].

Despite considerable attention from the scientific community and the business sector, practical applications of ammonia-fuelled internal combustion engines remain limited. Recent research has focused on analysing ICE performance, emissions, and combustion using various fuel mixtures, including diesel oil, biodiesel, methanol, hydrogen, ammonia, or their combinations. Table 3 compares this review with previous ones on ammonia's use as an ICE fuel. This paper is the first comprehensive review of the effects of incorporating ammonia and its mixtures with other fuels on ICE behaviour, discussing opportunities and limitations thoroughly.

4.1.1. Ammonia in compression ignition (CI) engines

Ammonia combustion presents difficulties in compression-ignition engines because of its poor reactivity, making positive ignition a more suitable option for its use. Nevertheless, the marine shipping industry's growing fascination with ammonia as a fuel stems from its predominant utilisation of compression ignition engines. Researchers are now

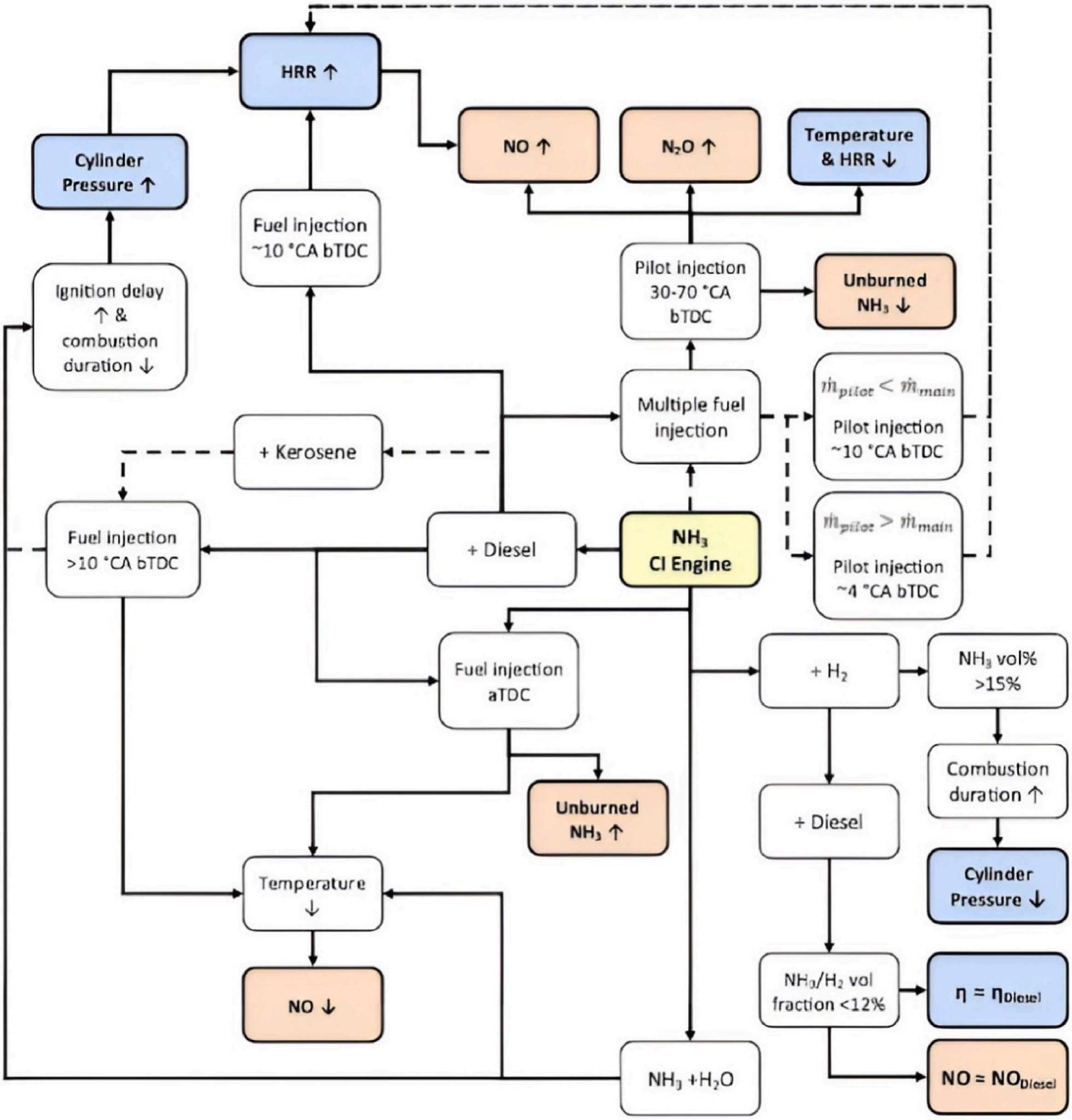

Fig. 11. Modifications to CI engine settings to allow for NH_3 operations [91].

exploring different methods to combust ammonia in compression ignition engines, either by using pure ammonia or in combination with another fuel. The exploration of ammonia in diesel engines began in the late 1960s as part of the US Army Energy Depot program. Gray et al. [92] conducted an experiment where they burnt pure ammonia in a CFR engine. They could achieve an intake temperature of 423 K and a compression ratio of up to 35:1. The high compression ratio and ammonia's relatively modest reactivity produced a pressure peak of around 150 bar. One possible explanation for this would be a homogenous charge combustion process. By using a diesel fuel pilot as the ignition source, the compression ratio was reduced to 15.2:1.

Recent literature supports dual-fuel mode combustion, prompting studies to optimise NH_3/diesel-fuelled engine performance and reduce GHG emissions without sacrificing efficiency. Researchers are addressing challenges in CI and SI engines running on ammonia as fuel, though the current focus leans towards SI engines due to ammonia's compatibility. CI engines have greater thermal efficiency (η: 45–55 %) and compression ratios (CR: 14–25), compared to SI engines (CR: 8–12, η: 28–42 %), and are prevalent in power generation [121]. Their yearly installed capacity is roughly an order of magnitude greater compared to SI engines. In addition to producing electricity, the shipping sector is a significant fossil fuel user, consuming about 330 million metrics tons per year [122,123].

Heavy fuel oil (HFO), high in sulphur, propels vessels for maritime cargo, directly contributing to sulphur oxide (SO_x) emissions upon combustion. Stricter International Maritime Organisation (IMO) regulations have reduced sulphur content in ship fuel from 3.5 wt % to 0.5 wt %, aiming to cut annual SO_x emissions by ~8.5 million metric tons. Consequently, attention has shifted to ammonia-fuelled CI engines, with researchers and maritime companies focusing on this option [50,106,124]. Unlike SI engines, CI engine combustion involves four distinct stages [125], with the presence of NH_3 influencing the reaction in each stage. Schönborn et al. [121] estimated a minimum Compression Ratio (CR) of 27 required to ignite pure ammonia in CI engines.

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 [124]. According to research by Lamas and Rodriguez [126], at 40 ∘CA aTDC, fuel injection profiles using parabolic technology produced the biggest reduction in NO_x (about 75 %) as compared to the triangle and rectangle profiles (approximately 65 %). 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 [124]. Despite an increasing trend in NO_x and N_2O emissions with injections from 0 to 10 ∘CA bTDC, Pyrc et al. [127] investigated the use of an ammonia solution ($NH_3 + H_2O$) in a CI engine, using standard diesel as the standard. Engine heat release using the water ammonia solution (WAS) increased by 12 J/$\lnsim$CA at full load, resulting in a ~3 % increase in brake thermal efficiency (BTE) due to prolonged combustion duration and increased ignition delay. NO_x 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 [124,128].

4.1.1.1. Ammonia and diesel. Using ammonia alone in CI engines necessitates high compression ratios (CR), leading to its application as a supplementary fuel that operates in dual-fuel mode with a tiny quantity of diesel or biodiesel without significant engine modifications [50]. Reiter and Kong [106] explored injecting gaseous ammonia into the intake manifold to examine its effects on emissions and combustion characteristics. They varied ammonia/diesel ratios to maintain constant power within the 40 %–60 % operating range, optimising fuel efficiency. Experimental findings revealed that NO emissions increased significantly when ammonia contributed over 60 % of the total energy, while soot emissions decreased with higher ammonia ratios. The study confirmed successful engine operation with 95 % energy from ammonia, albeit with increased unburned NH_3 due to incomplete combustion. However, reasonable efficiency can be attained with 80 % of the total energy from ammonia.

Lee and Song [129] proposed a novel combustion strategy for reducing NO emissions in CI engines using ammonia. Parametric research validated this strategy, evaluating engine characteristics based on ammonia dose, timing of the start of injection (SOI), and NO emissions. Findings indicated that NO production strongly correlates with SOI timing rather than engine load, with a reduction from 8500 ppm to 3040 ppm achieved by adjusting SOI timing. Yousefi et al. [43] studied the impact of ammonia energy fraction on engine performance and emissions, revealing a 58.8 % decrease in NO_x emissions with a 40 % increase in ammonia energy. However, this led to increased N_2O emissions, which have a higher greenhouse effect. Fig. 11 illustrates general modifications to CI engine settings to enable NH_3 operation.

Li et al. [130] evaluated combustion parameters and emissions in a dual-fuel diesel engine with two systems for injecting ammonia, high-pressure direct and low-pressure indirect. Outcomes showed increased maximum energy replacement, reaching 97 %, with the high-pressure system. The low-pressure mode exhibited greater thermal efficiency as shown; however, the high-pressure mode reduced unburned NH_3 emissions. Reiter & Kong [50] investigated the combustion of diesel and NH_3 in a CI engine and discovered that in comparison to pure diesel, engine brake torque rose by 20 ft-lb at a 50 % ammonia input power percentage. Wang et al. [131] utilised catalytic NH_3 decomposition in CI engines, achieving similar brake thermal efficiency (BTE) to Ultra-Low Sulphur Diesel (ULSD) engines irrespective of H_2/NH_3 volume fraction variation. As the H_2/NH_3 volume fraction increased, HC and CO decreased by ~7.5 %, while NO emissions remained comparable to ULSD engines, although NO_2 was slightly higher [132].

Yousefi et al.'s study (2022) examined the effects of a heavy-duty common rail dual-fuel engine's diesel injection strategy and ammonia/diesel ratio. Regulating ammonia energy fraction via port fuel injection led to reduced diffusive diesel combustion, resulting in lower in-cylinder pressure peaks and prolonged combustion. With a maximum NH_3 energy fraction of 40 %, NO_x emissions decreased by up to 58 %, while optimising the diesel injection strategy maintained indicated thermal efficiency (ITE) nearly constant with a 12 % reduction in greenhouse gas emissions. The blending of hydrogen with diesel in CI engines was investigated by Ghazal [133] and Jafarmadar [134] using numerical simulations. The findings indicated that raising the amount of hydrogen led to enhanced performance, reduced emissions, and shortened ignition lag. Additionally, it was noted that the energy efficiency decreased as the hydrogen proportion grew.

Nadimi et al. [135] investigated the possibility of substituting diesel with an engine that runs on a combination of ammonia and diesel. They discovered that ammonia could replace up to 84.2 % of the energy provided by diesel, resulting in reduced carbon emissions. However, they also observed that the engine emitted significant amounts of nitrogen oxides and ammonia. Kuta et al. [136] conducted a study on the emissions and after-treatment of a dual-fuel CI ammonia engine using $V_2O_5/SiO_2–TiO_2$ SCR. They achieved a substantial reduction in nitrogen oxides, but the issue of ammonia emissions remained unresolved [135,137]. Zhang et al.'s study (2023) looked at a two-stroke low-speed engine with a dual direct injection system that could inject diesel and ammonia. They found that by optimising the timing of diesel injection, they could enhance the engine's thermal efficiency by promoting faster combustion of ammonia. Additionally, this optimisation resulted in reduced NO_x emissions.

Gray et al. [92] demonstrated the successful combustion of liquid ammonia and diesel through direct injection at compression ratios ranging from 30:1 to 15.2:1 in a CFR engine. Heating the intake air and injectors was crucial to prevent freezing due to ammonia's high heat of vaporization and low boiling point. Injection of ammonia vapour into the air-intake with direct diesel injection showed improved pressure output compared to direct ammonia injection, albeit with reduced volumetric efficiency. Pearsall [138] successfully implemented this strategy in a V2 supercharged diesel engine with a compression ratio of 18.6:1. Ammonia/diesel operation resulted in a 32 % increase in indicated power and 13 % higher indicated thermal efficiency than pure diesel operation [139]. Newhall [140] supported these findings theoretically, showing that ammonia/diesel operation outperformed pure diesel operation in power and thermal efficiency. They also noted that cylinder head temperature positively impacted performance and that fuel consumption was optimal at lower speeds due to ammonia's slow flame propagation rate. Throttle operation of ammonia/diesel was found to be impractical.

A numerical study by Hoseinpour et al. [141] examined the effects of different EGR rates (0 %, 10 %, and 20 %) and inlet charge temperatures (330K, 360K, and 390K) on the emission characteristics and combustion of an ammonia/diesel dual-fuel engine running at high load while considering various ammonia energy shares. Converge software was used to do simulations of computational fluid dynamics (CFD). The findings indicated that the settings of 390K, 40 % NH_3, and EGR20 produced the best CO_2 reduction, which was about 30 %. According to the results, there is a significant decrease in NO_2 of around 65 % when compared to diesel at 20 % NH_3, 360K, and EGR20. The results also demonstrated that the reduction of NH_3 peaks at higher temperatures, approaching a 50 % drop.

4.1.1.2. Ammonia and biodiesel. Several studies have investigated the application of NH_3 combined with alternate fuels in CI engines. Reiter and Kong [106] examined using methyl ester of soybean oil as a catalyst for igniting ammonia in combustion, finding no significant performance or emission differences when replacing biodiesel with diesel. Tay et al.

[142] conducted a computational analysis on the use of kerosene, either blended with diesel or as a substitute for diesel, to advance ignition onset and enhance NH_3 combustion. Lin et al. [143] observed increased PM emissions with excessive biodiesel content in diesel blends, potentially due to heightened soluble organic fraction in the exhaust. Similarly, a 15 % increase in mean PM emission was observed with a 50 % biodiesel-50 % diesel blend, which was attributed to poor nebulisation due to the blend's higher cetane number and viscosity compared to pure diesel [144].

Chang et al. [145] demonstrated that emulsified fuels offer a potential NO_x–PM trade-off, achieving a reduction of 36–53 % in PAH toxicity and a 39–49 % reduction in total PAH. Their findings suggest that using a fuel blend comprising 50 % biodiesel and 25 % ABE solution leads to decreased aromatic content in diesel fuels and more complete combustion due to increased oxygenation. Lee et al. [146], by altering an H_2/O_2 mixture's intake rate, found that as the biodiesel mix increased, both total mass and total BaPeq decreased, attributing it to improved combustion performance and reduced fuel PAH content. They also found that employing biodiesel combined with water containing ethanol effectively reduces sulphur content, thereby mitigating SOF formation and reducing nucleation mode PM emissions.

Nadimi et al. [137] found that replacing a higher proportion of biodiesel with ammonia resulted in significant reductions in CO_2, CO, and HC emissions. The lowest emissions occurred at the highest ammonia energy contribution (AEC = 69.4 %), with CO_2 dropping to 510 g/kWh and CO decreasing by 30.1 g/kWh. However, NO emissions increased with higher ammonia flow due to the nitrogen content in NH_3. Ammonia also altered the combustion mode from diffusion to premixed combustion, increasing the heat release rate's maximum and decreasing the diffusion combustion phase.

According to Sivasubramanian et al. [147], using an 80/20 blend of biodiesel (BD) and NH_3 in an engine resulted in a reduction of emissions of smoke, CO, and HC by around 25 % under full load conditions. The engine using BD/NH_3 exhibited slightly greater NO_x emissions compared to diesel but lower emissions than the biodiesel engine. Lin and Lin [148] observed reduced emissions of CO and NO_x for the blend of NH_3 and biodiesel compared to diesel, with lower emissions for engine speeds below 1800 rpm.

Damanik et al. [149] reviewed diesel engine performance and exhaust emissions with biodiesel blends, highlighting nano additives' potential to improve efficiency and reduce emissions. Abedin et al. [150] discussed internal combustion engine energy balance, presenting different approaches and case studies with alternative fuels. In a subsequent study, Abedin et al. [151] analysed three biodiesel introduction methods: blend, fumigation, and emulsion, finding varied effects on engine performance and emissions, with thermal efficiency increasing in the emulsion mode but decreasing in blend and fumigation strategies.

Abdelrazek et al. [152] conducted a numerical study comparing soybean biodiesel and diesel fuel in a diesel engine with direct injection, noting lower carbon monoxide and hydrocarbon emissions but higher nitrogen oxides and carbon dioxide emissions with biodiesel. They also reported increased brake-specific fuel consumption and decreased brake thermal efficiency. Selvan et al. [153] assessed biodiesel blends in a diesel engine, finding higher efficiency with algae oil (AO10D) and similar emissions across load ranges. Thiyagarajan et al. [154] explored hydrogen addition to biodiesel in CI engines, observing enhanced performance and reduced emissions, except for increased nitrogen oxides.

4.1.1.3. Ammonia and dimethyl ether. Researchers investigated the characteristics of CI engines using various mixtures of ammonia and dimethyl ether (DME) as fuel due to their miscible properties [111,155,156]. DME, with its high cetane number, low ignition temperature, and higher LHV compared to ammonia, offers advantages and can be made using renewable resources. Additionally, DME's similar vapour pressure to ammonia and its commercial use in refrigeration enhance its feasibility as an alternative fuel. Different ratios of ammonia/DME mixtures were studied, including 80 %, 60 %, and 40 % DME, compared to 100 % DME, utilising high-pressure pumps and injectors for fuel delivery [157]. High cycle-to-cycle variations and engine performance deterioration were noted with a 60 % ammonia fuel mixture, leading to elevated emissions of CO and HC because of the significant ignition delay [155]. Despite higher NO_x emissions compared to dimethyl ether 100 %, all emissions remained within the 7.5 g/kWh EPA small output engine limits, with notably low soot emissions (<0.002 g/kWh) under all conditions.

Exhaust gas temperature decreased with a higher ammonia share due to ammonia's high latent heat, aligning energy costs of ammonia-DME blends with diesel and renewable energy sources, thus lowering the carbon footprint. In-cylinder pressure and heat release rate histories revealed longer ignition delay at medium loads because ammonia is resistant to auto-ignition, while differences were less pronounced at low loads. Dimethyl ether (DME)/NH_3 mixtures have been injected as NH_3 is miscible with DME, showing potential for further exploration [156].

Ryu et al.'s investigation (2014b) involved the direct injection of DME and DME/NH_3 mixtures (with NH_3 concentrations of 40 % and 60 %) into a compression-ignition engine, revealing worsened performance and higher cyclic variability with increased NH_3 percentage. Combustion prolongation and lower NH_3 combustion temperature led to elevated CO and HC emissions across loading conditions. Despite fuel injection method improvements, exhaust emissions remained unaffected, indicating the necessity for post-exhaust treatment. Gross & Kong (2011) showed that using a 40 % volume fraction of NH_3 resulted in a ~5 J/∘CA increase in engine heat release rate (HRR) compared to engines using pure DME. The NO emissions were comparable between pure DME and engines using a mixture of 40 % NH_3 and 60 % DME. However, using pilot injection increased the cylinder pressure and heat release rate. The emissions of NO_x and CO were unaffected by the dual injection; however, the amount of unburned NH_3 fell by approximately 30 % when the pilot injection was increased.

Kong et al. [158] examined the influence of DME injection time on the performance of single-fuel and ammonia dual-fuel operations. The release of hydrocarbons (HC) and carbon monoxide (CO) was enhanced because of decreased combustion temperatures caused by delayed injection timings near the top dead centre (TDC). Nevertheless, although a single DME operation led to a reduction in NO_x emissions, the dual-fuel instance experienced an increase in NO_x emissions due to the presence of fuel-bound nitrogen. Zacha-rakis-Jutz [159] investigated a DME-ammonia CI engine, examining the effects of different energy share ratios. The results showed that when the ratio of DME to ammonia changed from 80/20 to 40/60, there was a notable need for the DME injection timing to be significantly advanced. Taghavifar et al. [160] found through numerical analysis that hydrogen systems in CI engines yielded the maximum power output and minimum suggested specific fuel consumption.

4.1.1.4. Ammonia and hydrogen. Boretti et al. [161] 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. Pochet et al. [162] 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.

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,

Table 4
Different NH_3 blends' performances in CI engines.

Tested fuel	Baseline	Engine type	Operation conditions	Key findings	references
Diesel /Ammonia	Diesel + NH_3 (05 %–95 %)	John Deere 4045 Model Multi-cylinder Four-stroke Turbocharged engine CR 16:1	Engine speed (1000 rpm). Full load.	BSFC ↑ 380 g/kWh. Brake power ↑ 15 kW. CO ↑ 60 g/kWh. NO ≈ NO diesel.	Reiter & Kong [50]
	Water with NOE - 7F -natural organic enzyme - 7F + diesel	QC495 diesel generator Four-cylinder Direct-injection Water-cooled	75 % total torque load. 125 Nm.	BSFC ↑ 5.82–13.8 %. BTE ↑ 4.75–5.88. PM ↓ 31.1–61.4 %.	Lin et al. [166]
	Diesel + NH3 (0 and 50 %)	Single-cylinder Two-stroke Low speed engine Direct injection CR 13.8	Engine speed 375 rpm. Pressure 135 Kpa. Ammonia injection duration (−6 to −12).	ITE ↑ Soot and CO↓ NO_x↑	Zhang et al. [167]
	Diesel, Diesel (40 %–60 %) + NH_3 (40 %–60 %)	John Deere 4045 Four-cylinder Four-stroke Turbocharged Direct injection CR 17.6:1	Engine speed (1000 rpm). Engine load (5 %–100 %).	CO_2 ↓ NO_x ↓ for less than 40 % Ignition delay ↑ Peak cylinder pressure ↓	Reiter & Kong [106]
	Diesel + NH_3	Single-cylinder Four-stroke CR 35:1	Engine speed (1000 rpm). Engine load 500 bar. SOI 4 to −24 ∘CA aTDC.	No ↓ 8500 ppm to 3040 ppm.	Lee and Song [129]
	Diesel, Diesel (10 %–30 %) + NH_3 (70 %–90 %)	Single-cylinder Four-stroke naturally aspirated CR 17.5:1	Engine speed (1000 rpm). Engine load (1.3 bar). Low- and high-pressure injection dual-fuel mode.	Indicated thermal efficiency ↑ NO_x ↓	Li et al. [130]
	Diesel + NH_3 (17 %–70 %)	Lifan C186F Single-cylinder Four-stroke Air-cooled CR 16.5:1	Engine speed (1500 rpm). Engine load (20 %–100 %). Different ammonia load contribution (ALC) (10 %–96.5 %). Different biodiesel load contribution (BLC) (10 % and 3.5 %).	CO_2, CO, and particulate matter (PM) emissions ↓ NO_x ↑ (14800 ppm).	Nadimi et al. [135]
	Diesel + NH_3 (0-13LPM)	Single-cylinder Four-stroke Naturally aspirated CR 18.5:1	Engine speed (1362 rpm). Engine torque (10–42 nm). Injection timing (8, 10 and 13).	NO_x ↓ by a factor of 1.7. N_2O ↓ by a factor of 4.	Niki et al. [124]
	Diesel + NH_3	MAN, D2840LE model Multi-cylinder Four-stroke turbocharged Direct injection	Engine speed (1500 rpm). Different Strategies of Ammonia Injection.	NO_x ↓ up to 78.2 %.	Lamas and Rodriguez [126]
	Diesel, Diesel + NH_4OH (0–16 %)	Andoria Type S320 Single-cylinder Four-stroke Naturally aspirated CR 17:1	Engine speed (1000 rpm). Engine load (35 %, 60 % and 100 %).	NO_x ↓ 56 %. CO ↑ 76 %. CO_2↑ 10 %.	Pyrc et al. [127]
	Diesel + NH_3 (0 %–40 %)	Caterpillar 3401 Single-cylinder Four-stroke Heavy-duty CR 16.25:1	Engine speed 910 rpm. BMEP 8.1 bar. SODI -14 to −27 ∘CA aTDC. EODI ∘CA aTDC.	NO_x ↓ by 58.8 %. Advanced SODI reduced the N_2O and GHG emissions. The thermal efficiency of dual mode (i.e., ITE = 37.85 %) w slightly lower than that of diesel-only mode (ITE = 38.53 %).	Yousefi et al. [43]
	Diesel + NH_3 (40 %–90 %)	Dual-fuel mode (ADDF) CR 16.25:1	Engine speed (910 rpm). BMEP (8.1 bar). Constant injection duration (CID). Constant injection rate (CIR)	Combustion temperature ↑ and NO_x ↑ in the CIR mode. Engine pressure, HRR, and ITE ↑ while NH_3 is less than 0.9.	Deng et al. [168]
	NH_3 40 %, 50 % and 60 %	Hatz 1B30 Single-cylinder Four-stroke Air-cooled CR 17.5:1	Engine speed (1500 rpm). Ammonia injection timing (−80 to 2.5 ∘CA aTDC).	The maximum NO_x and lowest N_2O for the operating points with the highest combustion efficiency. Combustion Efficiency ↑ for 40 %and50 %.	Bjørgen et al. [169]
	Diesel + Ammonia (5, 10, and 15 LPM)	Multi-cylinder Four-stroke Water-cooled Naturally aspirated	Engine speed (1000 rpm–3000 rpm)	Exhaust gas temperature ↓ BSFC ↓ BTE ↑ CO ↓ and CO_2 ↓	Arivalagan et al. [170]
Biodiesel /Ammonia	Diesel, B100, B(90 %) + NH_3(10 %), B(80 %) + NH_3(20 %)	Single-cylinder Four-stroke Water-cooled CR 18:1	Constant engine speed (1600 rpm). Engine load (0–100 %).	Smoke ↓ ~25 %. NO_x ↓ ~100 ppm. CO ↓ ~40 %.	Sivasubramanian et al. [147]

(continued on next page)

Table 4 (*continued*)

Tested fuel	Baseline	Engine type	Operation conditions	Key findings	references
	Soybean oil at a molar ratio of 1:6	Homogenizing machine (T50 IKA Inc. In Germany). Direct-injection Four-stroke Water-cooled	1000–2000 rpm Inlet air temperature = 25 °C Brake torque = 98 Nm.	BSFC ↑ ~0.03 kg/kWh. CO ↑ ~50 ppm (2000 rpm). NO ↑ ~60 ppm (2000 rpm).	Lin et al. [148]
	Diesel Diesel + Ammonia-enriched biogas (10, 20 and 30 LPM)	Kirloskar Single-cylinder Four-stroke Water-cooled CR 17.5:1	Engine speed (1500 rpm) Engine loads (25 %,50 %,75 %, and100 %)	BSFC ↓ and BTE ↑ CO ↓ and HC ↓	Ramar et al. [171]
	Biodiesel	Single-cylinder Four-stroke Lifan diesel engine C186F	Full load 3500 rpm 6.4 kw Compression ratio 16.5:1.	CO_2 510 g/kWh CO, and HC↓ NO ↑, CO ↓ 30.1 g/kWh The SOC is delayed by a higher ammonia contribution to the engine load. For pure biodiesel, BTE dropped from 31.8 to 29.4. Peak of the HRR ↑	Nadimi et al. [137]
	10 % Soybean biodiesel 20 % Soybean biodiesel 50 % Soybean biodiesel	NM260L, Mitsubishi Single-cylinder Direct-injection Water-cooled	Four modes: 5 kW, 7 kW, 10 kW.	BSFC↑0.80–0.99 %, BTE↑0.13–0.20 % BSFC↑1.33–1.67 %, BTE↑0.31–0.39 % BSFC↑5.006.40 %, BTE↑0.41–1.80 %.	Tsai et al. [144]
	Microalgae biodiesel (% 40-%60) NH_3(0–40 %) H_2(0–20 %)	Kirloskar Engine Single-cylinder Four-stroke Water-cooled CR 17.5:1 RCCI combustion	Constant speed (1500 rpm). Engine load (%20-%100).	BTE 8.42 %↑ HC 16.8 % ↓, CO 15.06 % ↓, smoke 26.8 % ↓ BSEC 13.28 % ↓	Elumalai et al. [172]
	Diesel (50 % and 100 %) + biodiesel (50 % and 100 %) + NH_3 (99.5–100 %) or (6 and 3LPM)	Four-stroke Single-cylinder Direct injection CR 12:1–22:1	Variable engine load (0–100 %).	Peak in-cylinder pressures and HRR ↑ CO ↓ by 11 %, CO_2 and HC ↓ BTE of diesel ↑ from 31.1 % to 34.8 % via NH_3 at 6 LPM, NO_x ↓ via NH_3 supplementation.	Jayabal et al. [173]
DME /Ammonia	DME 60 % ammonia	Yanmar L70V Single-cylinder Direct-injection diesel engine	DME vol% = 60 % 2500 rpm. Brake effective mean pressure = 0.32 MPa. SOI = 160 ∘CA bTDC.	HRR ↑ ~ 5J/∘CA. NO ↑ 3 g/kWh. CO ↑ 10 g/kWh HC ↑	Ryu et al. [174]
	DME 20 %, 40 %, 60 % NH_3	Compression-ignition (diesel)	0.14–0.32 Mpa BMEP. 1900 rpm and 2500 rpm.	Energy ratio ↑ 80/20 to 40/60. CO ↑ CO_2↑	Zacharakis-Jutz [159]
	20 % NH_3/80 % Dimethyl Ether (DME); 40 % NH_3/60 % DME	Yanmar L70 V Single-cylinder Direct-injection diesel engine	DME vol% = 60 % 2200 rpm. Brake torque = 6.47 Nm. SOI = 30 ∘CA bTDC Compression ratio 20:1.	HRR ↓ ~3J/∘CA. $\dot{m}$pilot ≈ $\dot{m}$main, HRR ↑ ~20 J/∘CA (DME80 vol%). CO, HC and NO_x↑	Gross & Kong [156]
	DME	John Deere Four-cylinder, 4.5 litter	3480 rpm.	NO_x ↓ CO ↑ CO_2↑	Kong ET AL [158].
H_2/ ammonia	Diesel		H_2vol%~11 %. 1500 rpm. Indicated mean effective pressure = 4 bar.	$\eta H_2/NH_3 \approx \eta$diesel. HC and CO ↓ ~7.5 %. NO_2 was marginally higher than ULSD engine. NH_3 wt.% ↑, ignition delay ↑, combustion duration ↑	Wang et al. [131]
	Diesel 100NH_3, NH_3(60 %–95 %) + H_2(5 %–40 %)	Medium speed engine Single-cylinder Four-stroke CR 15.5:1	Constant engine speed (800 rpm). Air intake temperature (280-520k). Air intake pressure (1–3 bar). Equivalence ratio (0.4–1).	NO_x ↓ with the NH_3 + H_2, laminar flame velocity of ammonia ↑ with the NH_3+H_2.	Wang et al. [175]
	Diesel 100NH_3, 100H_2, 1–2 % NH_3 + 75 % H_2 + 23–24 % N_2	Single-cylinder Four-stroke CR 15.5:1	Engine speed (1500 rpm). IMEP (3 and 5 bar).	NO_x ↑ CO_2 ↓ 15 %. BSFC ↑ Combustion efficiency ↓	Gill et al. [107]
	Diesel + hydrogen-ammonia (0–94 %)	YANMAR L100V model Single-cylinder Four-stroke Air-cooled CR 23:1 HCCI engine	Equivalence ratio (0.1–0.6), intake temperature (50–240 °C) Exhaust Gas (0–100 %) Recirculation Variable load	NO_x ↓ 580 ppm for hydrogen 50 ppm 75 % IMEP ↓ before 50 %vol ammonia at IMEPs at 4.5 and 5.0 bar, 95 % combustion efficiency.	Pochet et al. [164]
	Diesel + NH_3+ H_2 (5 % and 10 %)	MAN, D2840LE model Multi-cylinder Four-stroke Direct-injection	Variable load (50 %–100 %).	NO_x ↓ ~60 % at 43.2 ∘CA aTDC. NH_3 ↑ NO_x > 3. NO_x↑ 18.3 %. CO_2, CO and HC↓	Lamas & Rodriguez [165]

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Table 4 (*continued*)

Tested fuel	Baseline	Engine type	Operation conditions	Key findings	references
		16V-710G3	900 rpm. 85 kw. 415 nm.	NO_x, CO, HC, and PM ↓ SO_x ↓ 53 %. CO_2↓ 53 %, from 0.905 kg/kW-h to 0.425 kg/kW h.	Hogerwaard & Dincer [163]
	Diesel + H_2+NH_3	HDT Multi-cylinder Four-stroke Turbocharger CR 18:1	Engine speed (1200-200 rpm). BMEP 25 bar.	Fuel conversion efficiencies ↑ 45 %. Substantial NOx needs a proper after treatment.	Boretti [161]
	Diesel + NH_3 (0 %–65 %) + H_2 (35 %–100 %)	PSA DW10 model Single-cylinder HCCI CR 16:1	Constant engine speed, Engine load (1–1.5 bar). Intake temperatures ranging (428–473 K). Different EGR percentage.	NO_x 1000–3500 ppm. The production of significant N_2O quantities under 1400 K.	Pochet et al. [162]
	Diesel + hydrogen (5-10-20 LPM) + Ammonia (5-10LPM)	TV model Single-cylinder Four-stroke Water-cooled CR 17.5:1	Constant Engine speed. Variable engine load (25 %–100 %).	BTE ↑ across all engine brake powers. NO_x ↓ and vibration ↓ with ammonia + hydrogen.	Anderson et al. [176]

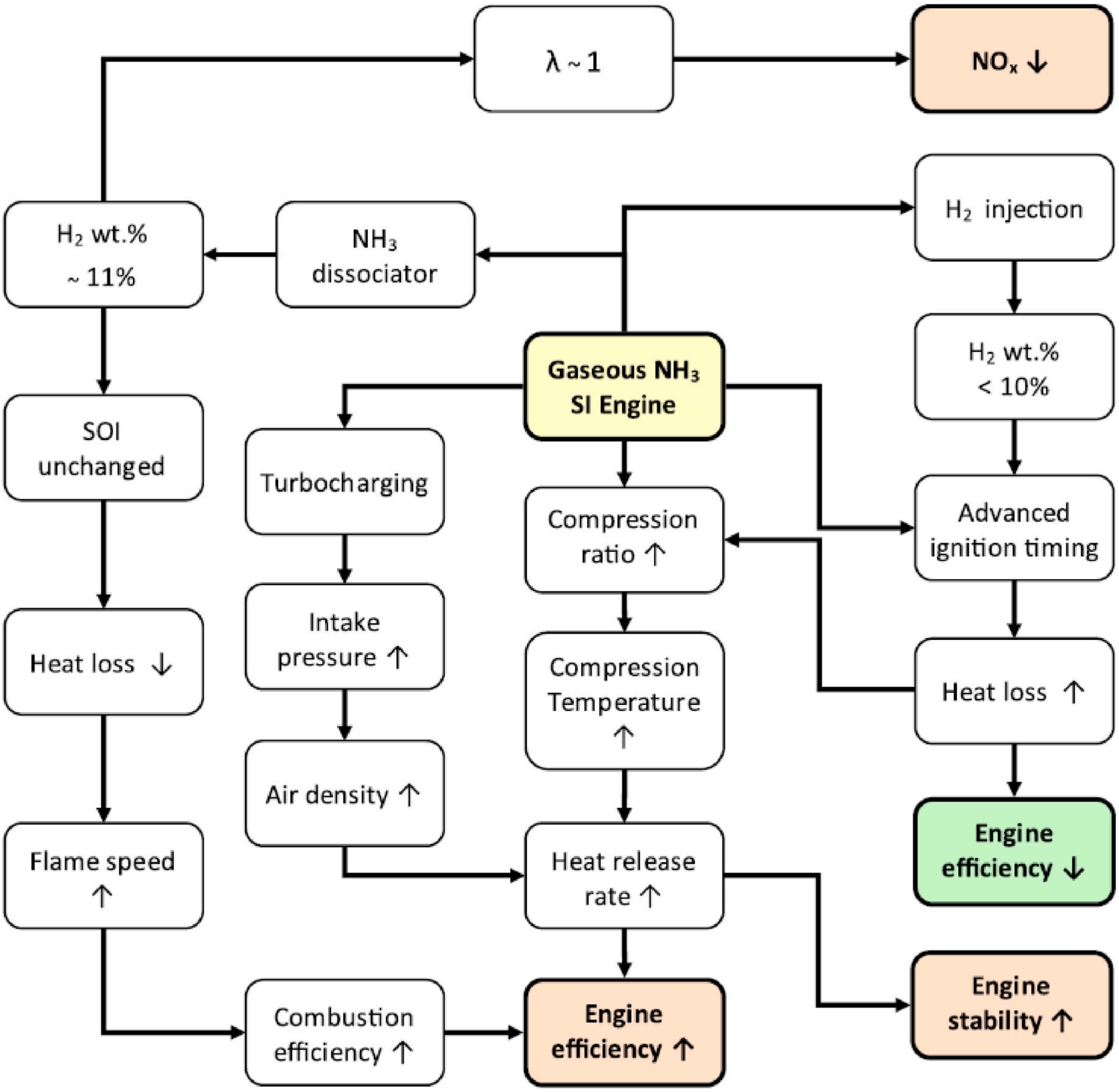

Fig. 12. Modifications to SI engine specifications to allow for gaseous NH_3 and NH_3/H_2 operations [91].

which requires an increase in intake temperature and pressure. Hydrogen combustion produces radicals that promote ammonia autoignition, 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 [162].

Hogerwaard & Dincer [163] 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. Gill et al. [107] investigated gaseous dissociated NH_3, H_2, and NH_3 combustion in a CI engine, noting lower BSFC for a 75/1/24H_2/NH_3/N_2 blend compared to neat NH_3, suggesting better fuel efficiency. Pochet et al. [164] 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. Lamas & Rodriguez [165] studied the injection of ammonia in diesel/hydrogen engines, achieving an optimal decrease of NO_x (around 60 %) at 43.2 ∘CA aTDC, with NO_x decreasing significantly with a higher proportion of ammonia. The performance of the dual-fuel CI engine fuelling with diesel-ammonia, biodiesel-ammonia, DME-ammonia, and H_2-ammonia is summarised in Table 4.

4.1.2. Ammonia in spark ignition (SI) engines

Various organisations such as Green Transportation Technology Group, Savia Coalition, and Biogas International have shown interest in using NH_3 to fuel internal combustion engines [177]. Early attempts at NH_3-fuelled spark ignition engines date back to the late 1960s for military purposes to achieve fuel independence [178]. In a study [110], researchers investigated NH_3's impact on a 48 kW, 4-cylinder spark ignition engine, finding initial power and speed reductions. However, adding small amounts of hydrogen increased power output by up to 20 kW and extended the speed range to 3200 rpm. Further enhancements were made by boosting the compression ratio, enabling a power output of 40 kW at 4000 rpm.

Cornelius and colleagues (1966) investigated the gaseous NH_3 combustion in a SI engine by injecting vaporised NH_3 into the intake manifold. Despite advanced ignition timing, NH_3 engines showed an ITE about 12 % lower than gasoline engines at 2400 rpm. Increasing compression ratios to 18 allowed NH_3 engines to reach 4000 rpm, with turbocharging providing output power comparable to gasoline engines. This study suggests that optimising engine parameters can enhance NH_3 engine stability, addressing concerns about its performance in SI engines [179].

Lhuillier et al. [55] investigated the performance of a neat gaseous NH_3 spark ignition engine, demonstrating stable operation with COVIMEP <3 % for Pin ≥ 1 bar and $0.9 < \phi < 1.1$, achieved by advancing SOI to ~40 ∘CA bTDC. With increased Pin, NO_x emissions rose by ~500 ppm for $\phi \leq 1$ [180]. Reducing unburned NH_3 emissions involved blending NH_3 with H_2. Engine parameters, including SOI timing and intake pressure, significantly influenced NH_3 SI engine performance, which can be further enhanced by dissociating NH_3 to create in situ hydrogen, improving flame stability and speed.

Sawyer et al. [102] utilised a dissociator to decompose NH_3 into N_2 and H_2, with up to 25 % decomposition. Mixing NH_3 with the H_2 generated at 5 % volume led to variations in cylinder pressure, with NH_3/H_2-fuelled engines exhibiting higher pressures than Iso-Octane-fuelled engines for $\phi < 0.8$. Conversely, Starkman et al. [101] found NH_3/H_2 engines with CR 10 had lower IMEP and efficiencies than Iso-Octane engines. Cornelius et al. [178] demonstrated that adding 0 %–3 % H_2 extended the operational range of NH_3 engines between 2400 and 4000 rpm at CR = 9.4, with ITE comparable to gasoline engines. To separate NH_3, Ryu et al. [174] used hot exhaust gas.

Injecting NH_3 separately into the combustion chamber improved engine brake power by approximately 0.2 kW compared to gasoline/NH_3 blending injection. While NH_3 slip and CO emissions decreased by 2.5 and 8 g/kWh, respectively, NO_x emissions decreased by about 25 g/kWh. Comotti and Frigo [181] introduced a Hydrogen Generation System (HGS) for NH_3 dissociation, maintaining brake thermal efficiency (BTE) at around 28 % even at 3000 rpm, unlike gasoline engines. The NH_3/H_2 engine exhibited significantly lower NO_x emissions, averaging 1000 ppm less than gasoline engines. (See Fig. 12).

Ezzat and Dincer [182] investigated the thermodynamic benefits of a system for the dissociation of liquid ammonia, revealing increased engine power with a rising mass fraction of NH_3 but declining energy and exergy efficiency due to increased irreversibility. Vehicles powered by dissociated NH_3 showed a 30 % increase in energy efficiency at max traction power compared to those using NH_3 in fuel cells. Another proposed system for vehicles by Ezzat and Dincer employed onboard hydrogen production using an ammonia electrolyte cell (AEC) and waste heat recovery with a thermoelectric generator (TEG), attaining a combined energy efficiency of 31.1 % and an exergy efficiency of 28.94 %. Overall, vehicles equipped with NH_3 dissociators demonstrated the highest energy efficiency and fuel performance among the analysed systems.

4.1.2.1. Ammonia and hydrogen.

H_2 is commonly used to enhance the combustion performance of ammonia SI engines, with benefits including increased turbulence flame velocity and shorter combustion duration. However, excessive H_2 addition can lead to drawbacks such as reduced turbulent flame speed due to preferential diffusion effects, potentially causing local flame extinction and wrinkling. While peak heat release rate (HRR) remains unaffected, the turbulent flame speed can decrease by approximately 16.7 % with excessive H_2 addition [55].

Comotti and Frigo [181] demonstrated in a practical engine test that an engine speed of at least 3000 rpm is required for an H_2 mass fraction of around 22 % to maintain the efficiency of the NH_3/H_2 engine is comparable to that of the engine running solely on petrol. When the NH_3/H_2 engine's speed dropped below 3000 rpm, its efficiency sharply decreases. Additionally, employing hydrogen as an additive in the spark ignition engine raises concerns about increasing N_2O emissions [183]. It was demonstrated that during fuel-lean combustion, N_2O emissions rose by almost 50 % as the H_2 vol percentage rose by 12.5 % [183]. The sharp rise in N_2O is most likely caused by increased NO emissions during fuel-lean operation, which encourages the synthesis of N_2O by the reaction of NH (imidogen) + NO → N_2O + H. Compared to CO_2, N_2O is around 300 times more detrimental to the climate [184]. Therefore, reducing N_2O emissions into the surrounding air is the difficult challenge for the ammonia/hydrogen spark ignition engine.

NH_3/H_2 engines can also be enabled by injection of ammonia and hydrogen into the SI engine's intake manifold independently, in addition to dissociating NH_3 into N_2 and H_2. In an experimental engine, NH_3 and H_2 were injected using an electro-injector. From 2500 to 5000 rpm, it was shown that the BTE of ammonia/hydrogen mixing was 3–4 % lower than that of the gasoline engine [108]. Separate NH_3 and H_2 injection techniques were also used by Mørch et al. [185]. According to reports, a good power response might still be obtained by combining ammonia with around 5 % hydrogen [186]. In comparison to a pure gasoline engine, the engine's ITE rose by 0.5 % when the hydrogen was raised to about 10 % [187]. However, when the hydrogen content was raised to around 20 %, NO_x emissions of about 750 ppm were generated, indicating the necessity of SCR at the exhaust gases in these circumstances.

Westlye et al. [188] found that an NH_3/H_2 engine's NO_x emissions increased by over 2000 parts per million when fuel injection was advanced by 40∘CA for lambda (λ) > 1. Nitrous oxide (N_2O) dropped by 50 ppm, whereas NO_2 rose by around 100 ppm. When start of injection was advanced to 40 ∘CA bTDC, slip NH_3 stayed the same. Additionally, it was discovered that when CR rose from 7 to 15 for $\lambda > 1$ operation, NO, NO_2, and NH_3 slip increased by 1000 ppm, 25 ppm, and 1500 ppm, respectively. Cardiff University's Green Ammonia demonstration at the

Rutherford Appleton Laboratory was another advancement that made use of independent injection [91].

Cardiff University's Green Ammonia demonstration at the Rutherford Appleton Laboratory was another advancement that made use of independent injection [91]. According to the findings, methane may be replaced by 30 % (vol) hydrogen injected into an ammonia mixture to produce up to 16 kW of power at 1500 rpm. The combustion was found to be inefficient despite NO_x emissions being below 20 ppm, necessitating more improvement in terms of time, equivalency ratio, and injection technique. To guarantee stable engine operation, spark ignition timing for an independent hydrogen supply system needs to be delayed by an additional 10 to 15 CA (in comparison to a gasoline engine). This results in less residual expansion and higher heat loss than gasoline engines [108]. If the hydrogen mass fraction is raised to around 11 % (like the NH_3 dissociation system), it should be possible for the independent H_2 supply system to provide engine performance that is equivalent to that of the NH_3 dissociation system. NH_3 dissociation technique significantly reduced NO_x emissions in comparison to gasoline engines. This occurred as a result of the engine running close to stoichiometric, where NO emissions are significantly reduced [189].

Advanced SOI was needed for an independent mechanism for supplying H_2 in order to guarantee steady engine running. The SI engine that used a separate H_2 supply system had a lower thermal NO because of the significant heat loss caused by advanced SOI [188]. However, the dissociated NH_3 was not mixed with gasoline in investigations that used the PFI approach [55,108]. Therefore, it is impossible to directly compare the two fuel induction methods. Although a gasoline/ammonia spark ignition engine without a dissociation system produced more engine power, the fuel economy of a DI gasoline/NH_3/H_2 engine was reduced by an average of 10 MJ/kWh in comparison to a pure gasoline engine [155]. To get comparable fuel efficiency to a pure gasoline engine, the DI gasoline/NH_3/H_2 engine needed ammonia injection for around 22 MS.

According to Ryu et al. [155], there was no direct comparison of emissions between the pure gasoline engine and the DI gasoline/NH_3/H_2 engine. The NH_3/H_2 thermal efficiency of the PFI engine is likewise worse than that of the clean petrol engine [108]. However, there was no direct comparison of NH_3/H_2 emissions with the clean petrol engine. Since the gasoline/air combination does not mix with the NH_3/H_2 fuel spray prior to entering the combustion chamber, the fuel mixture in the DI NH_3 engine is expected to be heterogeneous, with combustion predominantly taking place in a non-premixed manner, however a direct comparison is not practical. Nevertheless, the fuel mixture and air for PFI injection are mixed prior to entering the combustion chamber. As a result, the combustion mode is mostly premixed, and the response time scale is probably shorter.

Lhuillier et al. [190] investigated how the addition of hydrogen affected the performance and emissions of a spark ignition engine that was powered by ammonia. The H_2 volume content ranged from 5 % to 15 % at different equivalent ratios and input pressures. Over the whole engine map, satisfactory combustion stability was made possible by the employment of hydrogen as a combustion enhancer. The ideal H_2 concentration to boost combustion efficiency without sacrificing exhaust emissions was determined to be 10 %. Lean, almost stoichiometric conditions produced the highest efficiency results. The same results were emphasised in Frigo and Gentili [108], who found that further charge dilution causes a considerable rise in NO_x and NH_3 at the exhaust without increases in combustion efficiency. In a single-cylinder SI engine, Lhuillier et al. [55] conducted a thorough examination of the usage of NH_3/H_2 blends with varying equivalency ratios and H_2 volume concentrations up to 60 %.

New information on operating limitations in ammonia-fuelled gasoline direct injection (GDI) SI engines is presented in a recent study by Mounaïm-Rousselle et al. [191]. This information is particularly useful for determining the lowest load limit that may be achieved when pure ammonia is used to fuel the engine. However, by mixing ammonia with less than 10 % hydrogen, they increased the working restrictions. The ammonia-fuelled engine can create substantial NO_x emissions even though it doesn't produce carbon-based pollutants. However, their findings indicate that NO_x emissions can be greatly reduced by up to 40 % when 10 % H_2 is added to ammonia.

Using a 0.612-L displacement CFR engine with a sustained fuel composition of 20 vol% hydrogen and 80 vol% ammonia, Westlye et al. [188] tested the NO_x emission characteristics of the hydrogen/ammonia fuelled engine at 7, 11, and 15 compression ratios. According to experiments, the ammonia escape phenomenon is significantly influenced by the size of the compression ratio; the higher the compression ratio, the more obvious the ammonia escape phenomenon is; the ignition time affects the production of N_2O from ammonia combustion; a later ignition time will cause a temperature rise, which will promote the formation of N_2O; and the MBT (maximum brake torque) ignition time will result in very low N_2O emissions. The amount of NO_x produced by burning hydrogen combined with ammonia is comparable to that of burning traditional fossil fuels, even though the mechanisms behind NO_x formation are different. Therefore, ternary catalysts or selective catalytic reduction (SCR) may be used to efficiently clean up the NO_x emissions from ammonia-blended hydrogen engines. These methods have been widely used thus far [1,50].

By examining the unstretched laminar combustion rate of NH_3/H_2 blend and the flame reaction to stretching, Lee et al. [192] demonstrated that a rise in the hydrogen share efficiently boosted the laminar combustion rate of ammonia; Moreover, replacing ammonia with hydrogen negatively impacts combustion emissions, leading to higher NO_x (a harmful air pollutant) and N_2O (a greenhouse gas) formation, which exacerbates environmental pollution. However, when ammonia-hydrogen mixtures undergo combustion in fuel-rich conditions—where the fuel-to-oxidant ratio exceeds the stoichiometric requirement—NO_x and N_2O emissions are considerably lower compared to fuel-lean combustion scenarios.

4.1.2.2. Ammonia with other alternate fuels. Blending ammonia with other fuels offers a promising method to enhance its reactivity, as highlighted by previous studies [193]. Grannell et al. [179] explored the blending of gasoline with ammonia in SI engines, considering factors like speed, load, and compression ratio (CR) to identify optimal blending ratios for satisfactory engine performance. Their research concluded that a fixed gasoline/NH_3 ratio isn't universally effective across all engine operating conditions. However, a later study by Ryu et al. [155] suggested that a gasoline/NH_3 ratio ranging from 2 to 7.3 could ensure stable engine performance across varying power outputs. Another avenue for improving NH_3 SI engine performance is the addition of oxygenated fuels, as investigated by Yapicioglu and Dincer [194]. Their experiments aimed to utilise ammonia injections to mitigate carbon emissions, revealing a reduction in CO_2 emissions when ammonia was introduced into the gasoline engine. However, this also resulted in a notable decrease in engine energy and exergy efficiency.

Haputhanthri et al. [195] conducted an experiment in which they combined NH_3 with gasoline and either ethanol or methanol as additional fuels. This increased the engine speed to 3500 rpm, leading to a noticeable rise in engine braking torque by approximately 10 Nm. Increasing the methanol concentration to 30 % resulted in a slight torque increase at engine speeds ranging from 2000 to 2500 rpm. Fuels with a high ammonia concentration, containing up to 20 % ethanol, performed better than the standard fuels, especially at engine speeds above 3500 rpm [196].

CH_4 is a commonly used additive to aid NH_3 combustion, owing to its prevalence in natural gas (NG). Researchers found that increasing the CH_4 volume fraction by 15 % reduced the highest rate of heat release (HRR) of NH_3 premixed flame by about 40 % [55], mainly due to an extended combustion duration of around 10 °C as the CH_4 volume fraction reached 15 %. However, a higher CH_4 weight percentage is

Table 5
Performances of various NH_3 blends in SI engine.

Tested Fuel	Baseline	Engine performances	Operation conditions	Key findings	References
	$NH_3 + H_2$ (6 %–8 %)	Lombardini LGW 523 Multi-cylinder Four-stroke Water-cooled CR 10.7:1	Engine speed (2500–5000 rpm). Full load.	BTE ↓ by ~2.5 % regardless of engine speed. BP ↓ by ~3 kW (3500 rpm). NO_x ↓ at full load by 1000 ppm.	Frigo and Gentili [108]
	$NH_3 + H_2$ (5 %–100 %)	CFR-engine	Engine speed (1200 rpm). Variable compression ratio (varied 6.23 to 13.58). BMEP (250–300 kPa).	ITE ↑ by 0.5 % as CR ↑ by 2.6. NO_x ↓(5500 ppm) while H_2/NH_3(70/30) and CR = 8.9.	Mørch et al. [185]
	80 vol% NH_3/20 vol% H_2	0.612L engine CFR engine	Engine speed 1000 rpm. Excess air ration 1–1.4. CR (7–15). Full throttle.	NO ↓ 1500 ppm as SOI advanced to 30 ∘CA bTDC. NO_2 ↑ by ~100 ppm, N_2O ↓ by ~50 ppm as SOI advanced by 40 ∘CA.	Westlye et al. [188]
	100 % NH_3 B5 %, NH_3 + 15 %H_2, 100 %CH_4	PSA EP6DT Four-cylinder Four-stroke CR 10.5:1	Engine speed (1500 rpm). Intake pressure (0.8–1.2 bar). Equivalence ratio (0.9–1.1).	By modest amounts of hydrogen. Performance and stability ↑	Lhuillier et al. [180]
	$NH_3 + H_2$ (0 %–20 %)	Optical engine Single-cylinder Four-valve CR 13:1	Constant engine speed (1000 rpm). Different Spark timing (−4 to −40).	Premixed H_2 generates a lover COPVIMEP. Flame propagation with $\chi < 10$ % is more susceptible to temperature than flame propagation with $\chi > 12.5$ %. Ignition delay ↓ and combustion duration ↓ by increase in H_2 ratio. The maximum ITE at 7.5 % of H_2 fraction.	Li et al. [202]
	$NH_3 + H_2$ (7 %–70 %)	UIT-85 model Single-cylinder Four-stroke VCR engine	Engine speed (600 rpm). Engine load Maximum at WOT. CR 8:1 and10:1.	As the percentage of H_2 grows, NO emission rises for both CR, lowering ID. The ideal H_2 fraction was 12 % in energy, lowering SEC.	Pyrc et al. (2024)
	100 % NH_3	CFR engine Single-cylinder Four-stroke CR 4.5–15	Engine speed 1100 rpm. Compression ratio 4.5–15. Intake pressure 0.5–1.5 bar.	N_2O ↓, an improvement in ITE's optimal. Equivalency ratio of 1.25 (NH_3/NO_x). Combustion efficiency greater than 95 %.	Jespersen et al. [203]
	PFI, neat NH_3	Two-stroke, EX340EF Marine engine (diesel engine adopted to SI)	Condition of 75 % load according to the BS ISO 8178–4:2020 standard.	Compared to CI operation, there was a 2.9 % increase in ITE and a drop in the ignition minimum energy level of 75 mJ NO_x.	Yin et al. [204]
	$NH_3 + H_2$	Kirloskar TV1 model Single-cylinder, Water-cooled, CR (10:1 to17:1)	Engine speed (1440 and 1800 rpm). Variable compression ratio (14,15 and 16). Ignition timings (18°CA bTDC to 32 °CA bTDC).	BP and BTE ↑ when the CR was raised from 14 to 16 °CA 10–90, and EGT ↓ Knock combustion and NO_x ↑	Dinesh and Kumar [205]
	Pure NH_3 NH_3–H_2 blending (84 %–98 %)	Four-cylinder Four-valve DI CR 15:1	Engine speed (1000,1200,1300 rpm). BMEP (0.23–0.94 MPa).	BMEP ↑, ITE ↑ by 2.1 %. At a BMEP of 0.94 MPa, pure ammonia combustion produces a 33.7 %. BTE ↓ by 33.7 %. The engine's load range ↑ by adding hydrogen (2–6 %). Efficiency ↓ at 35.8 % with hydrogen blending at a BMEP of 0.63 MPa.	Zhu et al. [206]
	DIofNH$_3$, PFI of H_2 5 % in energy fraction	DI engine, Supercharged	Ammonia was injected directly into the cylinder and hydrogen was supplied into the intake port.	H_2 enhanced ITE, increased combustion efficiency, and COVIMEP <5 % Brake thermal efficiency (BTE) increased by 4.7 % when unburned NH_3 was decreased by 25 % and hydrogen was added.	Lee et al. [207]
Gasoline/NH_3	Gasoline, 70 %NH_3/30 %gasoline	Multi-cylinder Four-stroke CR 8:1	Engine speed 1600 rpm IMEP ~550 kPa.	Gasoline power% > 40 %, combustion duration ↓ 10°CA. Gasoline power% <30 %, COVIMEP>5 %, η↓5 %. Gasoline power%<30 %, COVIMEP>5 %, η~30 %.	Grannell et al. [179]
	Gasoline + NH_3	Yanmar L70V model Four-stroke Air-cooled Natural aspiration	Engine speed (900 rpm). Engine load 0.6 kW.	Total power ↑ by altering the ammonia injection. Fuel consumption ↓, engine power ↑ CO, HC, and NO_x emissions ↓	Ryu et al. [174]
	Gaseous NH_3	UIT-85 model Single cylinder four-stroke Water-cooled CR10:1	Engine speed (1800 rpm). Ammonia injection temperature (40–217 °C). Ammonia injection duration (8.75–26 ms). Ammonia injection timing (270–370 deg BTDC).	CO ↓, NO_x ↑ Engine efficiency ↑, and SEC ↓ The catalyst was very effective at low to medium flow rates.	Ryu et al. [155]

(*continued on next page*)

Table 5 (*continued*)

Tested Fuel	Baseline	Engine performances	Operation conditions	Key findings	References
	70 % ammonia and 30 % gasoline	IRMAN P03602 portable gasoline generator	3.65 Kw. Compression ratio 7:1. 3000 rpm.	Engine energy↓35.7 %–28.74 %. Exergy↓ 44.85 %–36.4 %. CO_2 ↓ 2.535 g/s to 2.4916 g/s.	Yapicioglu and Dincer [194]
	Gasoline + NH_3 (0 %–30 %)	BYD Ltd model Four-cylinder Four-stroke CR 15.5:1 PFI	Engine speed (2000 rpm). Throttle opening degree (%) 10 (low load), 20 (high load). IMEP 0.84 MPa.	Combustion temperature ↓, concentration of reactive radicals ↓, de-NOx reactions ↑. NOx emissions initially ↑ with increasing NH_3 blending ratio but eventually↓ followed a decreasing trend.	Liu et al. [208]
	Gasoline/NH_3/H_2	BP ↑ ~0.2 kW. Brake Specific Energy Consumption. (BSEC) ↓ ~5 MJ/kWh.	611 cm^3 of displacement and 0.72 bore/stroke 1800 rpm, CR = 10 $\dot{m}$gasoline = 27.5 g/min NH_3 injected 270–370 bTDC. $\dot{m}$ammonia = 3.75–13.85 g/min	NO_x ↓ ~25 g/kWh. ($\dot{m}$ammonia = 7.2 g/min) NH_3 slip ↓ 83 %. ($\dot{m}$ammonia = 7.2 g/min)	Ryu et al. [111]
Methanol /gasoline/ NH_3	Ethanol + Gasoline + NH_3	Four-cylinder Four-stroke CR 10.4:1	NH_3 vol% ~23 %. Engine speed >3500 rpm. 6750 rpm.	Brake torque ↑ Brake effective mean pressure ↑ Ammonia 3.7 %vol in the case of binary NH_3/gasoline blends to 30 %v in ternary blends with 30 %vol of methanol.	Haputhanthri et al. [209]
	CH_4 + NH_3 + H_2(2.5,5and10 %),	Single-cylinder four-stroke CR 10.7 (VCR)	Engine speed (1250–4000 rpm). IMEP (2.3–11 bar). PFI (6 bar). Variable compression ratio (10.7–23).	Optimal CR 14:1 optimal for NH_3–H_2 combustion. 30 % faster combustion via tumble motion results in greater laminar flame rates ↑ by raising in-cylinder temperature.	Novella et al. [210]
Ethanol/ gasoline/ NH_3	Ethanol /Gasoline (Ethanol 10 vol%)	GDI single-cylinder engine PSA EP6DT	NH_3 vol% ~6 %. Engine speed >3500 rpm.	Brake torque ↑ Brake effective mean pressure ↑	Haputhanthri et al. [195]
	Gasoline + NH_3 (0 %–10 %) + Ethanol (0 %–10 %)	KIA Cerato model CR 10.5:1	Engine speed (1000–7000 rpm). Maximum power (92 kW).	NO_x ↓ ~50 %. SFC ↑ 3 %, CO ↑ 30 % and HC ↑ 21 %.	Salek et al. [201]
NH_3/ Methanol Ethanol /Gasoline	Gasoline + 30 vol% Ethanol or Methanol + 17.35 vol% NH_3	GDI single-cylinder engine PSA EP6DT	Torque by approximately 10 Nm, speed> 3500 rpm.	At $H_2$12.5 %vol under fuel-lean combustion, N_2O emissions ↑ ~50 %.	Haputhanthri et al. [209]
NH_3/H_2/air	Equivalence ratio hydrogen between 5 and 15 % by volume.	One litter, six-cylinder turbocharged Spark-ignited PSA EP6DT	Compression ratio 10.5:1. Engine speed 1500 rpm.	NO_x and NH_3 ↑ with additional charge dilution, but combustion efficiency does not increase. Increased intake pressure and the hydrogen proportion can exacerbate the impacts of very high NO_x emissions in lean conditions, which can reach 6000 ppmvw.	Lhuillieret al. [190]
	Gasoline + NH_3 (0–80 %) + H_2	Lombardini LGW 523 Fur-stroke Twin-cylinder Water-cooled MPI CR 10.7:1	Engine speed (2500–5000 rpm). Full load.	At full load, minimum hydrogen-to-ammonia energy ratio is around 7 %, while 11 % at half load (COVimep< 10 %) pollutant emission 1700 ppm at full load and 3000 rpm.	Frigo et al. [108]
NH_3/Methane /Air	CH_4/NH_3 CH_4/H_2 100 % NH_3, 85 % NH_3/15 % H_2, and 100 % CH_4	Single-cylinder Four-stroke, CR10.5 Four-cylinder four stroke PSA four-valves GDI engine	Compression ratio10.5:1 Engine speed1500 rpm Engine speed 1500 rpm by varying intake pressure	Reducing the CO_2 effect of methane on the combustion duration As the combinations get richer, NO_x emissions drop to less than 1000 ppm. Extremely high NO_x emissions of up to 6000 ppm are seen in lean circumstances.	Lhuillier et al. [99] Lhuillier et al. [180]
NH_3/natural gas	Natural gas 50 % NH_3-50 % CNG	Single-cylinder SI engine	Engine speed 840 rpm with low load. Torque 250 Nm. Stroke (mm) 155. Compression ratio 10.5.	With a 50 % volume fraction of ammonia and a lambda value of 1.5, 28 % of CO_2 is removed, which worsens emission characteristics and combustion efficiency.	Oh et al. [199]
	Blending ratios from 0 to 90 % in natural gas	TBD620. Single-cylinder diesel engine.	146 kW. Engine speed 1800 rpm.	Engine dynamics rapidly deteriorate as the ammonia blending percentage in natural gas rises. NO_x ↓ CO_2 and HC, CO, CH_2O, N_2O, and NO_2 ↑ The finest is premixed 40 % natural gas and 60 % ammonia.	Wang et al. [200]
	CH_4+ NH_3 (0 % -%20)	Multi-cylinders Four-stroke Turbocharged CR10.5	Engine speed (1100 rpm). Engine load (1000 Nm). Various ignition timing.	Rise in the NH_3 energy component results in a drop in pressure and an increase in ID. Increased NO_x necessitates the use of an SCR aftertreatment system.	Oh et al. [211]

necessary to enhance flame speed. Studies indicated that a CH_4 mass fraction of approximately 40 % boosted NH_3 flame speed by about 30 % [197]. Although H_2 can be conveniently derived from NH_3 dissociation, maintaining an H_2 weight percentage of around 10 % significantly improved engine performance. However, further increases in the H_2 mass fraction required engine parameter optimisation to counteract the reduced turbulent flame speed.

In their research, the scholars investigated a gasoline direct injection (GDI) single-cylinder engine's performance fuelled by a gaseous ammonia-air mixture, adjusting intake pressure while keeping the engine running at a constant 1500 rpm. With a wide throttle opening, they successfully proved the pure ammonia combustion feasibility. Pressure increases improved stability, and the inclusion of hydrogen was required to maintain acceptable cycle-to-cycle variability under partial load conditions. When using pure ammonia as a reference, engine performance at full load was comparable to that of methane, achieving an efficiency of approximately 36 %. The literature suggests that combining ammonia with a combustion enhancer is necessary for optimal engine operation across the load spectrum. Hydrogen emerges as the prime candidate for enhancing engine performance, albeit challenges in storage and transportation undermine its reliability in a dual-fuel setup.

Kumar et al. [198] conducted an extensive study, examining the laminar combustion rate of ammonia/hydrogen blends across a range of ammonia percentages (0–80 %) for both rich (1.1) and lean (0.5) fuel mixtures. Their findings revealed that NH_3/H_2/air combinations with high ammonia content (>50 % energy) exhibited deviations from predicted results due to the influence of free radical OH, as observed in Tian and Konnov's detailed combustion mechanism. Meanwhile, Frigo and Gentili [108] utilised hydrogen produced through onboard catalytic reforming of ammonia to enhance ammonia combustion in a 4-stroke, 2-cylinder SI engine. Nevertheless, the engine's performance experienced a decline in comparison to the original gasoline setup, primarily due to the dilution of intake air and the decreased speed at which the flame propagated in combinations of ammonia, hydrogen, and air.

As an alternative to hydrogen, natural gas emerges as a feasible option for sustaining NH_3 combustion, given its historical use as a primary fuel in engines with large bores. Combining natural gas with ammonia signifies a move towards decarbonisation. Oh et al. [199] examined the effects of natural gas-ammonia mixtures on heavy duty, 6-cylinder SI engine originally designed for use with compressed natural gas (CNG). Their trials involved supplying the engine with a fuel blend of 50 % NH_3 (ammonia) and 50 % CNG (compressed natural gas) while operating under partial load and low-speed conditions. Substituting CNG with ammonia resulted in a significant 28 % reduction in CO_2 emissions. However, limitations arose due to challenges in maintaining combustion stability at low NH_3 burning velocities, restricting charge dilution, and allowing only a maximum equivalence ratio of 1.5.

A study explored the impact of blending ammonia with premixed natural gas on engine combustion and emissions through simulation. Ten different ammonia blending ratios, ranging from 0 % to 90 %, were examined. Findings indicated that as the ammonia proportion in the natural gas blend increases engine performance gradually declines. The optimal fuel consumption rate occurs at a mixing ratio of 60 % ammonia. As the amount of ammonia rises, there is an increase in unburned ammonia within the piston ring gap, leading to significant reductions in CO_2 and NO_x emissions. However, emissions of soot, HC, CO, CH_2O, N_2O, and NO_2 tend to increase with higher levels of ammonia blending [200].

Lhuillier et al. [99] presented diverse findings on methane's impact on combustion duration in ammonia-fuelled spark ignition engines. They varied the CH_4 concentration from 5 % to 15 % across different equivalence ratios to assess its potential as a combustion enhancer. Methane marginally accelerated combustion under rich conditions ($\phi = 1.1$) but had minimal effect at stoichiometric levels and slowed burning velocity in lean conditions ($\phi = 0.9$). Additionally, ammonia was explored as a supplementary fuel in mixtures containing alcohol and gasoline to mitigate CO_2 emissions. Better spark timing and increased intake pressure, which offset power loss associated with lower energy density, were made possible by its high-octane number. Ryu et al. [174] investigated NH_3 direct injection in a dual-fuel spark ignition engine, maintaining gasoline power output while adjusting ammonia injection to enhance total power. Compared to pure gasoline operation, the dual-fuel mode showed similar brake-specific energy consumption but resulted in higher NO_x emissions.

Salek et al. [201] conducted a numerical investigation into the effects of injecting 10 % ammonia on engine dynamics and emissions at various engine speeds using AVL BOOST software. Their findings revealed a noteworthy decrease of 50 K in in-cylinder temperature with the ammonia injection, leading to a substantial 50 % reduction in NO_x emissions across all engine speeds. Additionally, after the ammonia injection, the minimum fuel octane number needed to avoid knocking down fell, suggesting a potential impact on engine performance. However, despite these benefits, the injection of ammonia resulted in adverse effects, including decreased brake-specific fuel consumption (BSFC) and increased hydrocarbon (HC) and carbon monoxide (CO) emissions. In summary, various NH_3 blends in spark ignition engine performances done with different studies and researchers are reported in Table 5.

Table 6

An analysis of the combustion properties of several fuels following their combination with ammonia. (In comparison to engines that solely use gasoline in the "Type" column.) [94].

Type	Combustion effects	Emission effects
Hydrogen	Enhanced engine power and cycle thermal efficiency	NO_x and NO carbon emissions are equivalent to those from fossil fuels.
Natural gas		CO_2 decreases, NO_x and NH_3 rise.
Gasoline	Peak pressure drops as engine power rises.	CO declines, NO_x and NH_3 rises
Diesel	Torque rises dramatically.	CO_2 and HC decline (ammonia doping ratio less than 70 %)
DME	Limited maximum engine load	HC, CO, and NO_x rise

Table 6 and Fig. 13 illustrate the effects of varying quantities of ammonia on the combustion efficiency and emission characteristics of different fuel mixtures.

The findings from the current study and Table 6 suggest that ammonia can improve combustion performance when used as a combustion enhancer in fuel blends. With higher ammonia proportions, there's a decrease in carbonaceous emissions (HC, CO, and CO_2), except for DME, where they increase alongside ammonia, though NO_x emissions also rise. Ammonia and hydrogen fuel blends offer several advantages, including the following.

- Comparing ammonia to other blended fuels, blending ammonia with hydrogen can improve its combustion characteristics without having a major detrimental impact.
- Because hydrogen and ammonia both have greater octane numbers, they can burn at higher compression ratios. This improves the power output and thermal engine efficiency.
- The combustion of these fuel blends theoretically does not result in the emission of additional carbon-containing substances.
- The primary pollutant emitted from these mixed fuels is NO_x, which is emitted at quantities comparable to those resulting from the burning of fossil fuels. However, NO_x emissions can be effectively reduced using SCR technology or ternary catalysts, which are widely employed.

5. Conclusions

Addressing the urgent need to curb greenhouse gas emissions presents a significant hurdle for the transportation sector, despite strides toward electrification. Transitioning from combustion to electric propulsion poses numerous challenges that must be tackled. While electric propulsion competes with internal combustion engines, it cannot fully replace them. Green ammonia emerges as a promising alternative due to its carbon-free nature, relatively high energy density, and ease of storage and transportation. Past limitations on the widespread adoption of ammonia stem from safety and efficiency concerns arising from its chemical and physical properties. Ammonia's toxicity and suboptimal/complex/difficult combustion characteristics hinder its direct use as a fuel substitute, particularly in internal combustion engines.

Ammonia needs to be regarded as a true green fuel, its production methods must align with environmentally friendly practices. Currently,

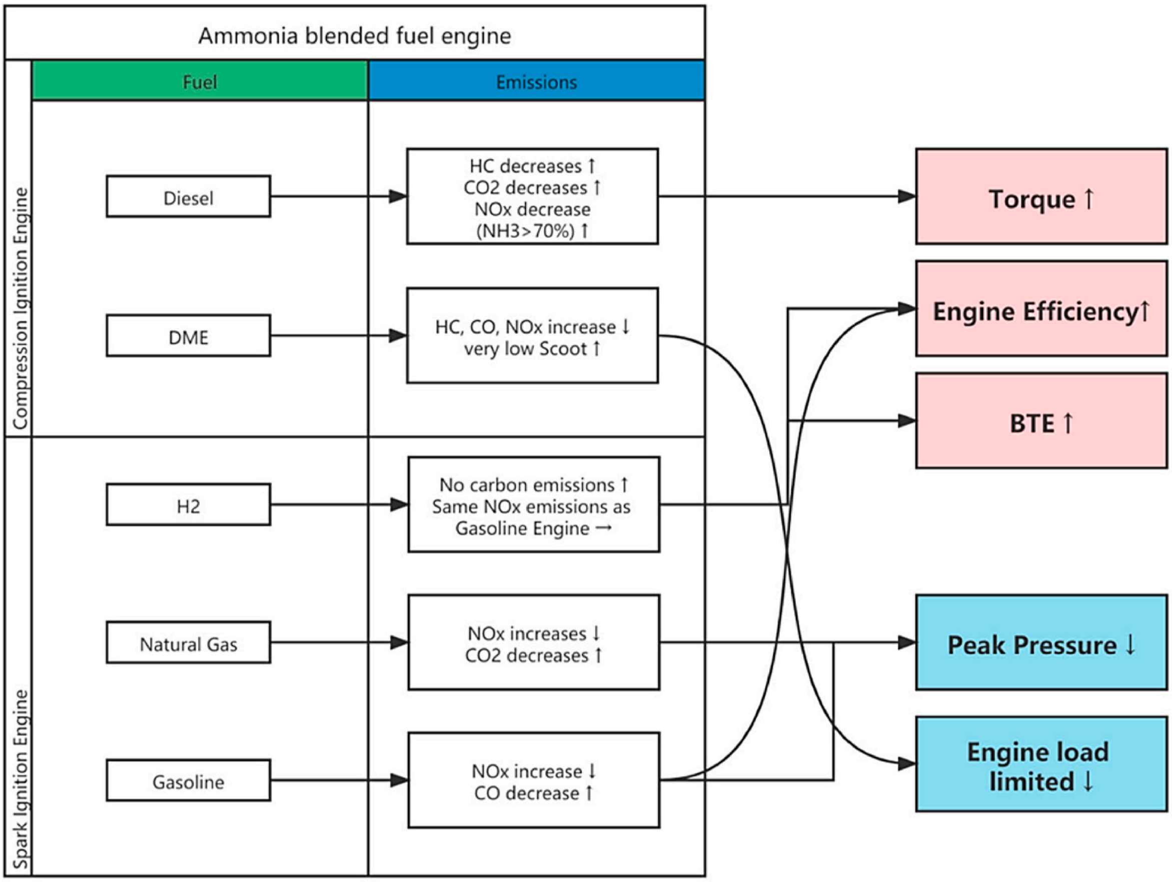

Fig. 13. An overview of the impacts of various mixed fuels [94].

Haber-Bosch, which uses nitrogen and hydrogen gases, is the process used in industrial ammonia synthesis. Extensive research has focused on using ammonia-based fuel, leading to the development of detailed kinetic schemes for combustion optimisation. Both CI and SI engine technologies have been explored for ammonia combustion. Hydrogen (H_2) emerges as a primary additive to enhance ammonia combustion in SI engines, introduced either using a separate H_2 supply system or ammonia breaking. Achieving comparable performance to neat gasoline engines typically requires a H_2 mass fraction of around 10 %. However, further optimisation may be necessary for H_2 mass fractions exceeding 10 %, as this can lead to challenges such as reduced turbulent flame speed due to preferential diffusion effects.

For compression-ignition engines, there's been a recurring suggestion to delay ammonia injection timing, aiming to reduce NO emissions, yet this often results in higher levels of unburned NH_3 emissions. While aqueous ammonia could enhance engine heat release rate and emissions, it also intensifies engine noise due to rapid heat release during premixing combustion. Optimal timing adjustments and mass flow via multiple injection methods offer promise in enhancing the HRR of CI engines and lowering N_2-based emissions. However, further investigation is required to assess emissions like N_2O and NO_2 during fuel-lean operation. This review underscores the potential for enhancing NH_3 combustion and emissions through combustion technology innovations. Coupled with advances in renewable-based ammonia production, this positions ammonia as a pivotal component in future energy landscapes.

The review explores the various methods for hydrogen and ammonia production and their integration into diesel engines, highlighting their both advantages and drawbacks. Ammonia, akin to hydrogen, is commonly introduced into diesel engines via the intake manifold, a method favoured for its simplicity. Its application in liquid and gaseous forms, particularly through dual-mode injection, offers flexibility. Introducing ammonia into the engine notably curbs pollutant emissions, with variations observed in CO, CO_2, NO_x, 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 NO_x 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 NO_x and HC emissions.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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