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Review Article

Utilization of green ammonia as a hydrogen energy carrier for decarbonization in spark ignition engines

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HIGHLIGHTS

- Decarbonization of power generation and transportation sectors by ammonia fuelled SI engines.
- Review on green ammonia production, combustion, and utilization in spark ignition engines.
- Fuel enhancement and engine modifications improved combustion and performance characteristics.
- Unburned ammonia and NO_x emissions demand requirement for after-treatment systems.

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ABSTRACT

Rising concerns about the dependence of modern energy systems on fossil fuels have raised the requirement for green alternate fuels to pave the roadmap for a sustainable energy future with a carbon-free economy. Massive expectations of hydrogen as an enabler for decarbonization of the energy sector are limited by the lack of required infrastructure, whose implementation is affected by the issues related to the storage and distribution of hydrogen energy. Ammonia is an effective hydrogen energy carrier with a well-established and mature infrastructure for long-distance transportation and distribution. The possibility for green ammonia production from renewable energy sources has made it a suitable green alternate fuel for the decarbonization of the automotive and power generation sectors. In this work, engine characteristics for ammonia combustion in spark ignition engines have been reported with a detailed note on engines fuelled with pure ammonia as well as blends of ammonia with gasoline, hydrogen, and methane. Higher auto-ignition temperature, low flammability, and lower flame speed of ammonia have a detrimental effect on engine characteristics, and it could be addressed either by incorporating engine modifications or by enhancing the fuel quality. Literature shows that the increase in compression ratio from 9.4:1 to 11.5:1 improved the maximum power by 59% and the addition of 10% hydrogen in supercharged conditions improved the indicated efficiency by 37%. Challenges and strategies for the utilization of ammonia as combustible fuel in engines are discussed by considering the need for technical advancements as well as social acceptance. Energy efficiency for green ammonia production is also discussed with a due note on techniques for direct synthesis of ammonia from air and water.

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Introduction

The intensity of renewable energy sources (wind, solar, geothermal, etc.) varies from one geographic location to another and it is dispersed on the earth [1]. For instance, regions near the equator receive a higher intensity of direct normal solar radiations [2]. It has been a major challenge to transport renewable energy from regions of higher intensity to other regions as an energy vector and liquid fuels produced using renewable energy sources could be a possible solution for the storage and transportation of renewable energy [3]. Green hydrogen produced by water electrolysis (utilizing electricity from renewable energy sources) has gained a lot of attention recently as the future fuel but the challenges related to the storage and transportation of hydrogen have limited its implementation [4]. Ammonia has been identified as an energy vector for the green energy (zero-emission) cycle owing to its potential to serve as a hydrogen energy carrier for the storage and transportation of green hydrogen [5].

Energy storage techniques will play a key role in the transition from dependency on fossil fuels to renewable energy systems since the integration of renewable energy systems will raise the huge requirement for electricity storage to ensure a continuous supply of power to meet rising demand (considering intermittent power supply from wind turbines and solar panels) [6–8]. Various techniques for energy storage are deployed depending on the required storage capacity and restitution time for specific applications and it includes mechanical (ex: compressed air energy storage) [9], electrical (ex: capacitors) [10], electrochemical (ex: batteries) [11], thermal (ex: cryogenics) [12] and chemical storage systems (ex: fuels like gasoline, diesel, hydrogen, methane, ammonia, etc.) [13]. Energy storage for longer terms with larger quantities can be accomplished by chemical storage techniques since it has a lower levelized cost of energy storage, where energy generated by using renewable sources will be stored by converting it

into fuel (power-to-fuel) [14]. Wherein electricity produced by using solar or wind turbines will be employed for hydrogen generation by electrolysis method and the useful product (H_2) released from electrolysis will further react with nitrogen (air separation unit) to produce ammonia to act as an energy carrier [15]. The hydrogen produced can also react with carbon dioxide (from the carbon capture facility) to produce methane or methanol, which also falls under the Power-to-Fuel paradigm [16,17]. Fuels produced by following this process are called e-fuels and these will have a major role in future mobility, serving as a sustainable energy source [18]. Also, the need for decarbonization of transportation and power generation sectors uplifts the suitability of ammonia among these e-fuels as an effective power-to-x fuel, since it is carbon-free fuel and also a hydrogen energy carrier [19–21]. In recent years, there has been an increasing focus on ammonia as a liquid energy carrier for enabling easy transportation of hydrogen energy by cracking ammonia to hydrogen and nitrogen at end use [22–24]. The physico-chemical properties of hydrogen, methane, ammonia, and other fuels are listed in Table A1 in appendix A [25–29]. The development of facilities for green ammonia production accompanied by the feasibility for direct use of ammonia as a combustible fuel has broadened its range of applications specifically for power generation and transportation [30]. Extensive studies and reviews on ammonia oxidation chemistry are reported in the literature [31–34] owing to its fuel NO_x formation and widespread application as a reducing agent in selective catalytic reduction systems. Detailed kinetics for ammonia oxidation was proposed initially by Miller et al. [35] by performing computational studies in a variety of burner-stabilized and freely propagating flames (ammonia/oxygen and ammonia/hydrogen/oxygen) and the model (22 species and 98 reactions) predicted satisfactorily at lean and moderately rich conditions. The elementary reaction models and the understanding of ammonia oxidation have improved over the years and some of the recently developed reaction mechanisms with

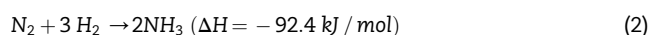
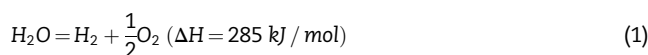
improved comprehensiveness and accuracy are as detailed in Table 1. A detailed review on the comparison of different reaction mechanisms and advances in the understanding of chemical kinetics for ammonia combustion was reported by Elbaz et al. [36], and interested readers may refer to the same.

Dias et al. [47] reported a literature study on the comparison of energy and economic costs for ammonia and hydrogen, produced by power-to-x techniques (chemical energy storage) from renewable energy sources and the results indicated that ammonia is a very good candidate for transportation, considering its higher density, and affordable storage and transportation. The synthesis, industry potential, utilization, and advantages of ammonia energy-based storage systems were discussed in literature reviews by Tawalbeh et al. [48], Cardoso et al. [49], Olabi et al. [50] and Chehade et al. [51]. The potential of ammonia as an alternative fuel for vehicular applications was reported in a literature study by Sonker et al. [52], where the authors detailed the direct (direct use as fuel in engines or fuel cells) and indirect (catalytic decomposition) employment of ammonia as a fuel with a note on green ammonia production, direct ammonia fuel cells, and electrolysis cost. The engine characteristics and techniques for utilization of ammonia as an alternate fuel in dual fuel compression ignition engines were reported in the literature studies by Kurien et al. [28] and Dimitriou et al. [27]. Chiong et al. [53] reviewed the advancements of ammonia combustion technologies in spark-ignition engines, compression ignition engines, and gas turbines by considering the optimization of operating parameters for improved performance. However, a detailed and specific technical review on the performance and combustion characteristics of ammonia fuelled spark-ignition engines is not reported previously in the literature, hence this study provides a detailed understanding of the engine characteristics and operating conditions for ammonia-fuelled engines in spark-ignited mode. In this work, a comprehensive literature study has been reported on state of the art for utilization of green ammonia as a combustible fuel in spark-ignition engines for power generation and transportation applications. The article is organized as follows; a brief discussion on the green ammonia production and direct synthesis of green ammonia from air and water is discussed in [Green ammonia production](#). Detailed literature survey on ammonia fuelled SI engines are discussed in [Ammonia combustion in spark ignition \(SI\) engines](#), where sub-sections details the engine characteristics of spark ignition engines fuelled with pure ammonia (3.1), ammonia/hydrogen fuel blends (3.2), ammonia/gasoline fuel blends (3.3) and ammonia/methane fuel blends (3.4). [Challenges and strategies for ammonia combustion in SI engines](#) covers the challenges and strategies for ammonia combustion in SI engines and the techno-economic aspects of green ammonia as

a fuel is discussed in [Techno-economic aspects of green ammonia as a fuel](#). The concluding remarks of this literature survey is discussed in [Conclusions and future scope](#) with a note on future directions for research on this topic.

Green ammonia production

Ammonia is a carbon-free fuel with a narrow flammability range and it is synthesized with the help of the Haber-Bosch process [54,55]. The energy required for the production of green ammonia by utilizing hydrogen from water electrolysis and nitrogen from the air separation unit was evaluated by Dias et al. [47], wherein the required energy output from fuel was considered to be 100 kWh for ease of calculations as shown in Fig. 1. Efficiency for the production of hydrogen by water electrolysis (i.e. output hydrogen energy by input electric energy) depends on the nature of the electrolyzer and studies by Connolly et al. have identified it to be 72.4% [56]. Around 27 kg of water and 138 kWh of renewable energy-based electricity is required for producing 100 kWh of hydrogen by endothermic water electrolysis as detailed in Fig. 1 and Equation (1). Green ammonia is produced by the Haber-Bosch process, where hydrogen (from water electrolysis) is combined with nitrogen (from air separation unit) at high temperature (400–600 deg. C) and pressure (200–400 atm) [51,57]. Around 125 kWh of hydrogen (i.e. 34 kg water) and 7 kWh of nitrogen is required for producing 100 kWh of pure ammonia (assuming that reactants are also pure [58]) with a total efficiency of 55% [59] as detailed in Fig. 1 and Equation (2).



Green ammonia synthesis from air and water

Direct synthesis of ammonia from air and water at atmospheric pressure and temperature conditions, bypassing stages for hydrogen production and nitrogen separation, is a significant challenge, and a synthesis route for the same was proposed by Lan et al. [60]. Electrochemical synthesis of ammonia at room temperature via protolysis of dinitrogen complex was first reported in 1985 by Picket et al. [61] and following that, there were reports on electrochemical synthesis of ammonia at 570 deg. C (atmospheric pressure) from hydrogen and nitrogen, with solid proton conducting oxide as electrolyte [62]. A schematic diagram for the electrochemical synthesis of green ammonia from air and water is detailed in

Table 1 – Overview of reaction mechanisms for ammonia oxidation.

Mechanism	Species	Reactions	Experiment type	Mixtures
Konnov-Mech [37–39]	201	2300	Laminar burning velocity [39]	NH ₃ /N ₂ O/air
Shrestha-Mech [40,41]	125	1099	Laminar burning velocity [42]	NH ₃ /H ₂ /air
CEU–NH ₃ –Mech [43,44]	91	445	Laminar burning velocity [43,44]	NH ₃ /H ₂ /CO/CH ₄ /air
Okafor-Mech [45,46]	59	356	Laminar burning velocity [45,46]	NH ₃ /CH ₄ /air

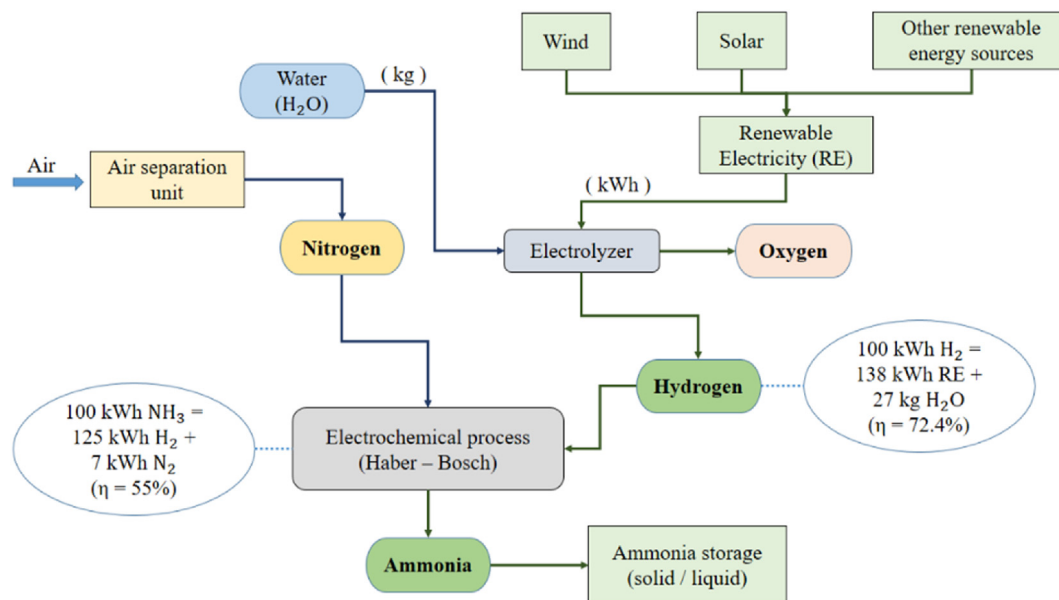


Fig. 1 – Energy efficiency for the production of green ammonia.

Fig. 2 [63]. Decomposition of ammonia takes place at ~ 500 deg. C [64] and hence low-temperature proton conducting materials are required for low-temperature synthesis of ammonia to avoid decomposition. Synthesis of ammonia from N_2 and H_2O at 20 deg. C in a solid polymer electrolyte cell with the ruthenium-based cathode, platinum-based anode, potassium hydroxide electrolyte, and Nafion membrane was reported by Kordali et al. [65], where the authors achieved an ammonia formation rate of $2.78 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1}$. The formation of potassium bicarbonate limits the direct use of air instead of nitrogen and there are concerns related to the chemical compatibility of the Nafion membrane [66]. Natural synthesis of ammonia at room temperature from air and water occurs in higher plants and the generated ammonia is directly utilized

as fertilizer by the plant, whereas imitating this natural phenomenon has been a major challenge for researchers [67,68].

Lan et al. reported the first study on the electrochemical synthesis of ammonia at room temperature with air and water as a precursor (instead of H_2 and N_2) in a membrane electrode assembly with Nafion 211 membrane (mixed NH_4^+/H^+ conducting) solid electrolyte and platinum electrodes (air at cathode and water at the anode), and they indicated an ammonia formation rate of $1 \times 10^{-5} \text{ mol m}^{-2} \text{ s}^{-1}$ at an applied voltage of 1.5 V [60]. Even though platinum-based catalysts are expensive for ammonia synthesis, the development of cobalt and nickel-based low-cost catalysts in the future can replace platinum for ammonia synthesis in atmospheric conditions [69,70]. Utilization of electricity produced from renewable

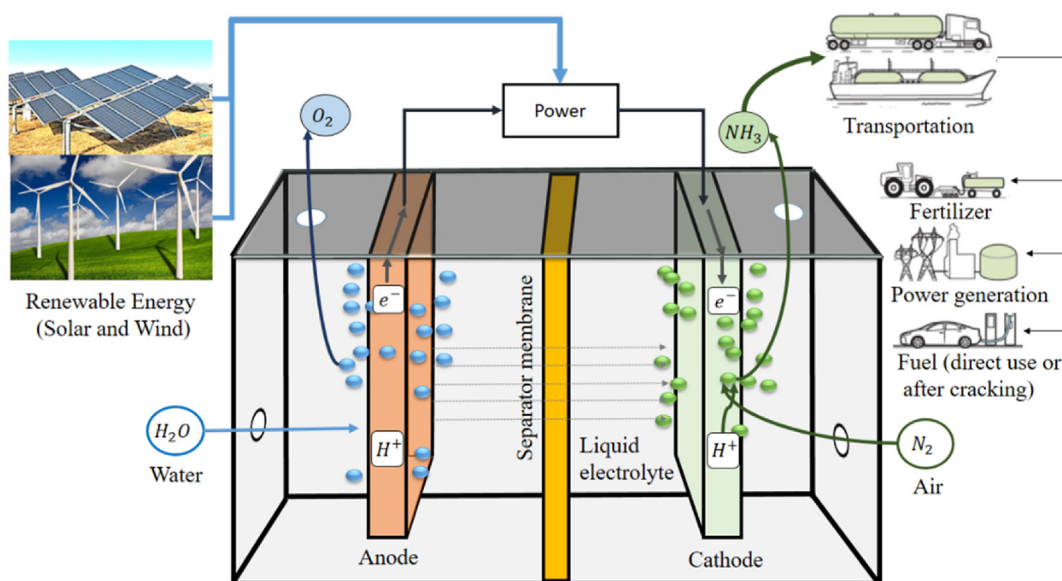


Fig. 2 – Schematic diagram for electrochemical synthesis of green ammonia.

energy sources like wind and solar for the electrochemical cell will enhance green ammonia production and will serve as a link between the ammonia industry and fossil fuels for the development of a sustainable energy future. Australia has positioned itself as a leader in the vision of the Ammonia economy, owing to the abundant availability of renewable (wind and solar) energy for green ammonia production, and the Australian renewable energy agency has announced initial funds (AU\$20 million) in 2018 to support the export of renewable technologies including shipping of ammonia [63].

Ammonia combustion in spark ignition (SI) engines

Hydrogen has gained a lot of popularity as a credible fuel, owing to its higher calorific value and zero carbon emissions [71,72]. However, the challenges faced due to the lack of reliable and efficient infrastructure for the storage and distribution of hydrogen, accompanied by the requirement for the development of novel compression/liquefaction technologies for storage, and leak detection systems for safety have limited its application [73–75]. Ammonia is a hydrogen energy carrier with a hydrogen content of 17.7% and liquid ammonia has a higher volumetric energy density as compared to liquid hydrogen [77,78]. Heat content in equal volumes of stoichiometric air-fuel mixtures for the case of ammonia-air is 80% of that of gasoline-air mixture owing to lower energy content (18 MJ/kg) and richer stoichiometric air-fuel ratio (6.06:1) for ammonia as compared to gasoline (LHV: 43.4 MJ/kg and A/F_{stoich} : 14.5:1) [79,80]. Hence the power produced by a normally aspirated ammonia-fuelled engine is expected not to exceed 80% of that produced by a gasoline (normally aspirated) engine. The performance of conventional engines while burning ammonia could be improved by incorporating developments in auxiliary equipment and controls with increased spark energy, compression ratio, engine supercharging, and fuel blending [81]. In 1933 Norsk hydro initiated studies on the utilization of ammonia as a hydrogen energy carrier in a hydrogen-fuelled IC engine, where onboard reforming of ammonia was used for hydrogen production. In Europe (1935), Ammonia Casale Limited performed the first studies on the practical use of ammonia as fuel on a limited scale and following that in 1942, a more extensive application of ammonia in motor buses was tried in Belgium following the Gazamo process, where a mixture of ammonia vapor and coal gas was supplied to the engine [82]. This program was taken up by the SNCV (Societe Nationale des Chemins de Fer Vicinaux), Belgium due to a shortage of hydrocarbon fuels after World War II, and the same was terminated when the fuel shortage issues were relieved [82]. The energy crisis in the 1960s and the requirement for mobile energy depot to reduce fuel tonnage for army operations had resulted in various studies exploring the possibilities of using ammonia as a fuel [83,84]. General Motors Research Laboratories performed studies in 1965 to explore the utilization of ammonia as a fuel for SI engines, with an objective to reduce the reliance of armed forces on hydrocarbon fuels by developing an energy depot concept where fuel will be produced onsite, utilizing energy from a mobile nuclear reactor [81]. Results of this study

indicated that the maximum engine power could be developed by adopting either of the two approaches, i.e., (a) addition of a supercharger, or (b) addition of a small amount of hydrogen with moderate supercharging and increased compression ratio [81]. Detailed history and progresses in the literature on ammonia combustion is detailed in Table 2.

Pure ammonia combustion

Combustion of pure ammonia in single cylinder SI engine was initially attempted on military vehicular applications by Cornelius et al. [81] and the researchers achieved ignition in a single-cylinder engine (overhead valve engine; 8.573 cm bore, 7.66 cm stroke, and CR 9.4:1) with conventional ignition system (12V) by inducting gaseous ammonia. However, the results indicated poor performance for ammonia fuelled engine, as compared to gasoline with a maximum, indicated thermal efficiency of 21% (Gasoline: 38%) and it was attributed to poor utilization of ammonia fuel, which was evident from exhaust gas analysis where the unburned ammonia was observed to be in large quantities. Modifications in the engine system like increased spark energy, compression ratio, multiple ignitions, and fuel blending were identified as possible corrective actions to improve the ignitability and combustion of ammonia in the SI engine. The results of the experimental study indicated that the modified ignition system (high-performance coil, 1 Ohm resistor, and 13.6 V primary voltage) improved maximum power by 80%, and the increase in compression ratio from 9.4:1 to 11.5:1 improved maximum power by 59%. It was also observed that further increase in compression ratio to 15:1 and 18:1 had negligible effects on indicated power (at speeds below 2400 rpm [81]). The effect of ammonia combustion on nitric oxide emissions was experimentally evaluated (CFR single-cylinder engine; 8.25 cm bore, 11.43 cm stroke, CR 10:1 and 1800 rpm speed) by Sawyer et al. [86] since it is expected to have a rise in fuel bound NO_x emissions and the results indicated that lean combustion ($\phi < 0.9$) resulted in higher NO_x emissions. However the NO_x emissions were comparable for both ammonia and iso-octane fuelled engines at $\phi = 0.9$ and further for richer combustion ($\phi > 0.9$), the NO_x emissions were observed to reduce for ammonia-fuelled engine due to a reduction in peak cycle temperature for rich ammonia-air mixtures. Starkman et al. [108] performed theoretical (thermodynamic calculations) and experimental studies on characteristics of ammonia fuelled SI engine under contract to the Army material command R & D directorate in 1967 to expand the basic and applied knowledge in this field by comparison of fact to theory. Maximum indicated power output in ammonia fuelled engine is expected to be around 77% of that of a hydrocarbon-fuelled engine as per theoretical calculations and the experimental results showed indicated power close to 70% at a higher compression ratio as observed in Fig. 3 and the theoretical performance could be accomplished by partial decomposition of ammonia where fuel quality is enhanced by dissociated hydrogen fractions. The results of the comparative study on different alternative fuels (methanol, ethanol, ammonia, hydrogen, and iso-octane) for SI engine combustion by El-Emam et al., in 1985 indicated that the fuels regarded as non-conventional at that period would become increasingly important in the future with a

Table 2 – Literature on ammonia combustion in SI engines.

Ref.	Year	Engine	CR	Fuels used	Major observations
[84]	1965	–	–	–	Proposed ammonia as a fuel for army vehicles, via direct consumption from a fuel cell as energy depot fuel and performed conceptual design analysis.
[81]	1965	SI	9.4:1, 11.5:1 and 18:1	Ammonia and hydrogen	Ammonia fuelled spark-ignited engine could deliver equivalent performance like gasoline SI engine by (a) Using a supercharger or (b) Adding a small amount of hydrogen as an ignition promoter.
[85]	1966	SI	12.6:1	Ammonia and gasoline	An ammonia engine with a 12.6:1 compression ratio had peak pressure similar to that of a gasoline engine with a CR of 7.5:1.
[86]	1968	SI	10:1	Ammonia and iso-octane	A different mechanism for nitrogen oxide formation (in-part pyrolytic) as a combustion product from an ammonia fuelled engine was implied from experimental results.
[87]	1985	SI	6.5:1 to 16:1	Iso-octane, methanol, ethanol, hydrogen, and ammonia	Ammonia had the lowest peak temperature and indicated mean effective pressure compared to all other fuels at all operating conditions (CR: 6:1 to 16:1 and ϕ : 0.6 to 1.6).
[88]	2003	SI	7:1, 10:1 and 15:1	Ammonia	Numerical study on ammonia air combustion by using PREMIX (planar flame), TWOPNT (system of equations), and CHEMKIN (boundary value problem solver). The maximum laminar flame velocity was achieved at $\phi = 1.1$ and the maximum adiabatic flame temperature at $\phi = 1$.
[89]	2006	SI	8:1, 10:1 and 12:1	Ammonia and gasoline	An experimental study on gasoline-ammonia dual-fuelled SI engine and the results showed that the developed fuel mix map (for different loads, speeds, and compression ratios) could replace 50% of gasoline.
[90]	2008	SI	8:1, 10:1 and 12:1	Ammonia and gasoline	Fuel mix with 70% ammonia and 30% gasoline (on energy basis) was suggested for normally aspirated engines and a higher ammonia ratio can be operated in supercharged engines effectively.
[91]	2009	SI	10:1 and 9:1	Ammonia and gasoline	Emission results suggested to always use combustion promoter (gasoline) at low engine loads to tackle unburnt ammonia emissions and avoid lean operation for the effective functioning of catalytic converters.
[92]	2011	SI	6:1 to 14:1	Ammonia and hydrogen	10% (by vol.) of hydrogen in the NH_3/H_2 mixture resulted in higher efficiency and mean effective pressure. Increasing the compression ratio helped to compensate for intake air dilution. NO_x emission levels were the same for NH_3/H_2 case and the gasoline case.
[93]	2012	SI	10.7:1	Ammonia and hydrogen	The addition of hydrogen as a combustion promoter improves combustion velocity and minimum 6–10% hydrogen to ammonia energy ratio was suggested for ensuring engine stability with COV_{imep} less than 10%.
[94]	2013	SI	10.7:1	Ammonia and hydrogen	The practical minimum hydrogen to ammonia energy ratio for stable engine operation ($\text{COV}_{\text{imep}} < 10$) was observed to be in the range of 9–12% (full load) and 6–8% (half load) for all engine speeds.
[95]	2013	SI	7:1 to 15:1	Ammonia and hydrogen	Nitrogen oxide emissions with 80% NH_3 -20% H_2 gaseous fuel blend were comparable to that of gasoline due to lower flame temperatures.

[96]	2014	SI	10.4:1	Ammonia and gasoline	The solubility of ammonia in gasoline (for fuel blending) was enhanced by using ethanol as an emulsifier. It was observed that 18% of ammonia could be retained by using gasoline with 30% ethanol as compared to 4.5% in the case of pure gasoline without emulsifier.
[97]	2014	SI	10:1	Ammonia and gasoline	Application of ammonia dissociation catalyst (aluminum pellets with ruthenium coating for decomposing ammonia to hydrogen and nitrogen) along the ammonia fuel line before the injector improved the engine characteristics.
[98]	2014	SI	10:1	Ammonia and gasoline	Direct injection of gaseous ammonia. The lower peak pressure in the case of gasoline – ammonia fuelled engines was due to low flame speed and overall combustion temperature as compared to gasoline alone.
[99]	2014	SI	10.7:1	Ammonia and hydrogen	The ruthenium-based catalytic reactor was used for the dissociation of some amount of ammonia to produce hydrogen utilizing engine exhaust heat – which acts as a combustion promoter.
[100]	2015	SI	10.7:1	Ammonia and hydrogen	A cracking reactor for hydrogen generation from ammonia was developed (ruthenium catalyst based) with a generation capacity of 1.4 Nm ³ /h.
[101]	2015	SI	10.4:1	Gasoline, ammonia, and ethanol	Gasoline-ammonia composite liquid fuel blend with ethanol as an emulsifier; gasoline fuel blend with 12.9% NH ₃ and 20% C ₂ H ₅ OH was found to be optimum.
[102]	2019	SI	10.5:1	Ammonia and hydrogen	Utilization of hydrogen (10%) as a combustion promoter in fuel blend along with supercharged conditions exhibited indicated efficiency higher than 37%; indicating ammonia as a suitable fuel.
[103]	2019	SI	10.5:1	Ammonia, methane, and hydrogen	Comparative study on combustion characteristics of three fuel blends (NH ₃ /air, CH ₄ /air, and NH ₃ /H ₂ /air) at near stoichiometric lean operations. Higher intake pressures (>1 bar) were favorable for pure ammonia combustion.
[104]	2020	SI	10.5:1	Ammonia and hydrogen	The blending of the fuel mixture with 20% hydrogen improved the cyclic stability and exhibited performance comparable to conventional fuel.
[105]	2021	SI	9:1	Ammonia and hydrogen	Cold start performance of NH ₃ fuelled engine was evaluated; with auto thermal reforming for hydrogen generation and Cu-zeolite adsorber downstream for ammonia capture (which ensured ammonia-free emissions).
[106]	2021	SI	10.5:1	Natural gas and ammonia	Feasibility study on dual-fuel combustion with ammonia and natural gas; 0–50% ammonia split ratio; CO ₂ emissions reduced by 18–28% as compared to operation with natural gas; reduction in initial burn duration was observed with increase in air-fuel ratio and split ratio.
[107]	2022	SI	11.75:1	Ammonia and hydrogen	Partial dissociation of ammonia to hydrogen and nitrogen. The energy content of the mixture at intake and energy output reduced with ammonia cracking. However, combustion efficiency is enhanced owing to a reduction in unburned ammonia emissions.

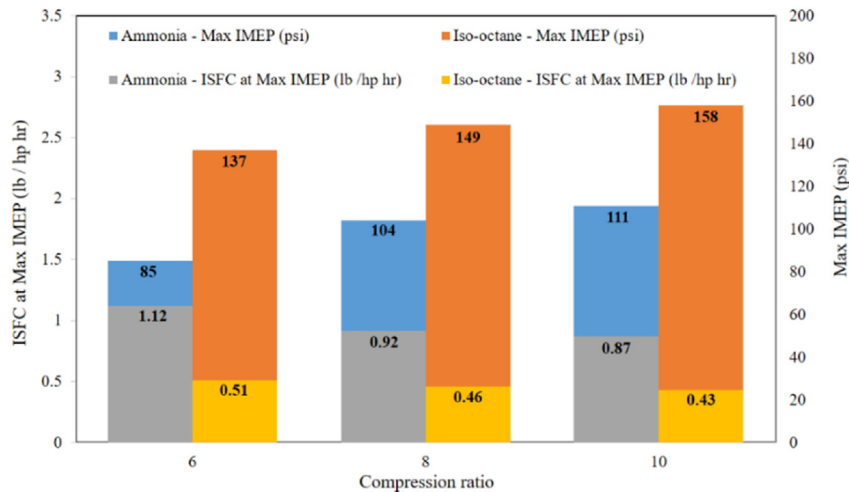
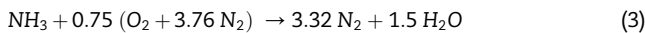


Fig. 3 – Comparative evaluation on the effect of compression ratio on the theoretical performance of SI engine fuelled with ammonia and iso-octane [108].

requirement for carbon-free fuels (ammonia and hydrogen) and highlighted the role of alcohol as a motor fuel for improved engine performance [87]. Ammonia had the lowest peak cylinder temperature, IMEP, and indicated thermal efficiency at all operating conditions (CR: 6:1 to 16:1 and ϕ : 0.6 to 1.6 at 1500 rpm), and the literature on ammonia combustion in SI engines had a long pause after this comparative study. The global equation for stoichiometric combustion of the ammonia-air mixture is detailed in equation (3).



Ammonia started gaining research interest in the first decade of the 21st century owing to environmental concerns and the requirement for carbon-free fuels. Liu et al. [88] performed numerical studies to evaluate the combustion characteristics of ammonia-air mixtures using PREMIX flame code for elevated conditions in an SI engine at different compression ratios (1,7,10 and 15) and equivalence ratios (0.5–1.5). The maximum laminar burning velocity for the ammonia-air mixture was observed to occur at an equivalence ratio of 1.1 and as expected the laminar burning velocity increased with an increase in compression ratio, however, the peak value of laminar velocity occurred at an equivalence ratio of 1.1 for all compression ratios. Nitric oxide mole fractions were observed to be higher (4500–5500 ppm) at lean ($\phi = 0.8$) and stoichiometric ($\phi = 1$) conditions for ammonia-air mixture, whereas it was observed to be lower (1500 ppm) in the richer mixture ($\phi = 1.2$) due to the lack of oxygen. Lhullier et al. [103] recently evaluated the combustion characteristics of pure ammonia in a modern SI engine (77 mm bore, 85.8 mm stroke, and CR 10.5:1 at 1500 rpm and MBT spark timing) at different intake pressures and equivalence ratios. The authors could achieve stable engine operation with good cyclic stability and minimal cyclic variations ($\text{COV}_{\text{IMEP}} < 5$) for all equivalence ratios (0.9, 1, and 1.1) when the intake pressure was 1 and 1.2 bar. Pressure rise and heat release rate for ammonia based combustion was lower than that of pure methane combustion as observed in Fig. 4.

Flame initiation duration (SIT to CA10) for pure ammonia was observed to be very long (~36–42 CAD) as compared to

other combustion phases (combustion duration~25 to 32 CAD) and the combustion duration for pure ammonia was approximately 10 CAD longer than that of lean methane. Near-stoichiometric lean conditions were reported as optimum operating conditions for better performance and lower nitrogen-based emissions. However, blending ammonia with superior-quality fuels will enhance the combustion characteristics and ensures a wider range of operating points as compared to that of pure ammonia operation. Mounaim Rouselle et al. [109] evaluated the operating limits of a GDI spark-ignition engine fuelled with neat ammonia and they could operate the engine at low load (idle speed – 650 rpm) with neat ammonia and the addition of 10% hydrogen in ammonia fuel mixture ensured operation at all conditions considered in the work (Speed: 650–2000 rpm; $\phi = 0.9$ to 1.1; CR: 10.5:1 and intake pressure = 0.65–1 bar). The slow combustion speed of ammonia-air mixtures hindered the operation with neat ammonia at 2000 rpm. Mounaim-Rouselle et al. [110] reported the first study on neat ammonia combustion in spark-assisted compression ignition (SACI) engine at a wide range of operating conditions (CR: 14 to 17; speed: 650–2000 rpm; $\phi = 0.9$ to 1.1 and intake pressure: minimum to 1 bar) and the results were compared with neat ammonia operation in GDI spark ignition engine (CR: 10.5:1). Results of the experimental study indicated that increasing the compression ratio will facilitate ammonia combustion in spark assisted compression ignition engine without incorporating any modifications in the design of combustion chamber, and the operating range at low loads could be further extended by improving the flame propagation duration (blending with hydrogen fractions). Higher compression ratio in SACI engines resulted in higher unburned NH_3 emissions as compared to GDI SI engine, owing to the higher volume of ammonia trapped in crevices, however, N_2O emissions didn't exceed 50 ppm.

Ammonia and hydrogen fuel blends

The stoichiometric reaction for ammonia-hydrogen combustion is as detailed in Equation (4) and α_{H} represents the

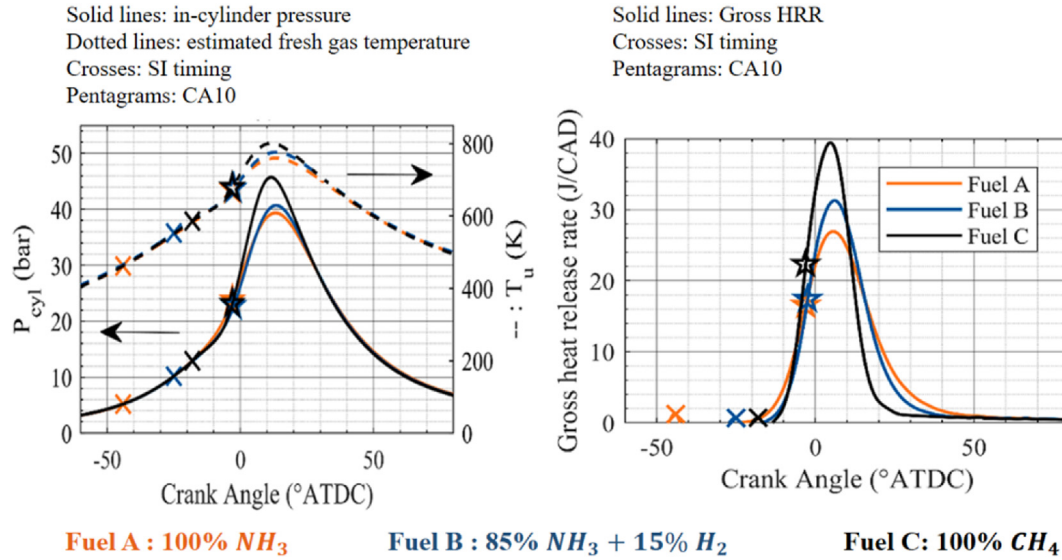
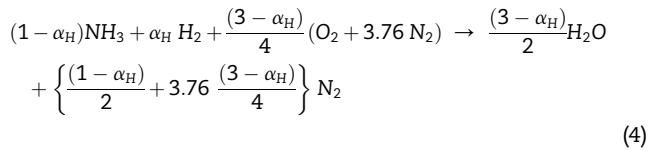


Fig. 4 – In-cylinder pressure, estimated fresh gas temperature, and gross heat release rate for pure ammonia, ammonia/hydrogen, and pure methane combustion in a modern SI engine with intake pressure of 1 bar at 1500 rpm ($\phi = 1$) [103].

hydrogen molar fraction [89]. Morch et al. [92] performed experimental studies to confirm the suitability of ammonia/hydrogen fuel mixtures in SI engine (82.6 mm bore; 114.3 mm stroke and 612.5 cc displacement volume) by increasing the volume percentage of hydrogen from 0 to 100% in NH_3/H_2 fuel mixtures for a range of compression ratio from 6.23 to 13.58 with excess air ratio (EAR) varying from leanest possible to rich side of stoichiometric. Indicated efficiency and IMEP were observed to be lower for the fuel mixtures with a higher share of hydrogen due to higher intake air dilution and maximum indicated efficiency was observed at the leaner side of stoichiometric ($EAR > 1$), whereas max IMEP was observed at richer side of stoichiometric ($EAR < 1$). Increasing the compression ratio will compensate the effect of intake air dilution and ensures similar power output like gasoline fuelled engine. IMEP increased to a maximum of 725 kPa with increase in compression ratio to 13.58 with 10% of hydrogen in the NH_3/H_2 fuel mixture.



Morch et al. also developed a fuel supply system for ammonia, where a metal ammonia complex was used for ammonia storage and exhaust heat was utilized for the desorption of ammonia from the ammine complex, however, the results indicated that external heating (electrical heating) or higher exhaust temperatures (excess fuel supply) would be required for better utilization of stored ammonia [92]. NOx emissions increased with the increasing share of hydrogen in the fuel mixture due to higher combustion temperature resulting in thermal NOx and the highest NOx emissions were observed at EAR in the range of 1.1–1.4 as evident from Fig. 5. However, fuel-bound NOx emissions dominates in the case of fuel mixture with lower hydrogen shares and it was concluded

from the results that total NOx emissions (1000–5500 ppm) from ammonia/hydrogen-fuelled engines are similar to that of gasoline-fuelled engines irrespective of the differences in NOx formation mechanisms [92,111,112]. Nitrogen-based emissions from ammonia/hydrogen-fuelled engines were studied in detail by Westlye et al. [95] by performing experiments in a single-cylinder SI engine (82.6 mm bore; 114.3 mm stroke and 612.5 cc displacement volume) with a constant fuel mixture of 80% NH_3 + 20% H_2 at different excess air ratios and spark timings. At optimal ignition conditions (MBT spark timing of 15 CAD BTDC), NO formation peaks around 1.1 EAR for gasoline combustion as a result of tradeoff between oxygen availability and combustion temperature indicating thermal NOx formation, and a similar trend was observed in the case of ammonia/hydrogen combustion with a peak of NO emissions at 1.2 EAR and MBT spark timing of 30 CAD BTDC as observed in Fig. 6. A second peak for NO emissions was observed at leaner combustion (1.35 EAR) indicating the formation of fuel-bound NOx emissions at low-temperature conditions and the magnitude of NO emissions for NH_3/H_2 combustion were comparable to that of gasoline combustion at close to stoichiometric lean conditions due to lower flame temperature as evident from Fig. 6. Frigo and Gentili [93,94] modified an SI engine (72 mm bore; 62 mm stroke and CR: 10.7:1) to accommodate a simple electronic fuel injection system for ammonia and hydrogen fuel injection by incorporating electro-injectors along the intake manifold and experimental studies were performed at different engine speeds (2500–5500 rpm) to identify minimal hydrogen to ammonia energy ratio (HAER) for stable engine operation. The experimental results indicated that the minimal hydrogen to ammonia energy ratio for stable engine operation ($COV_{imep} < 10\%$) is 7% at full load and 11% at half load conditions.

Lhullier et al. [102,104] evaluated the performance, combustion, and emission characteristics of a supercharged modern SI engine (CR: 10.5:1; 77 mm bore and 85.8 mm stroke) fuelled with gaseous ammonia/hydrogen blends with an

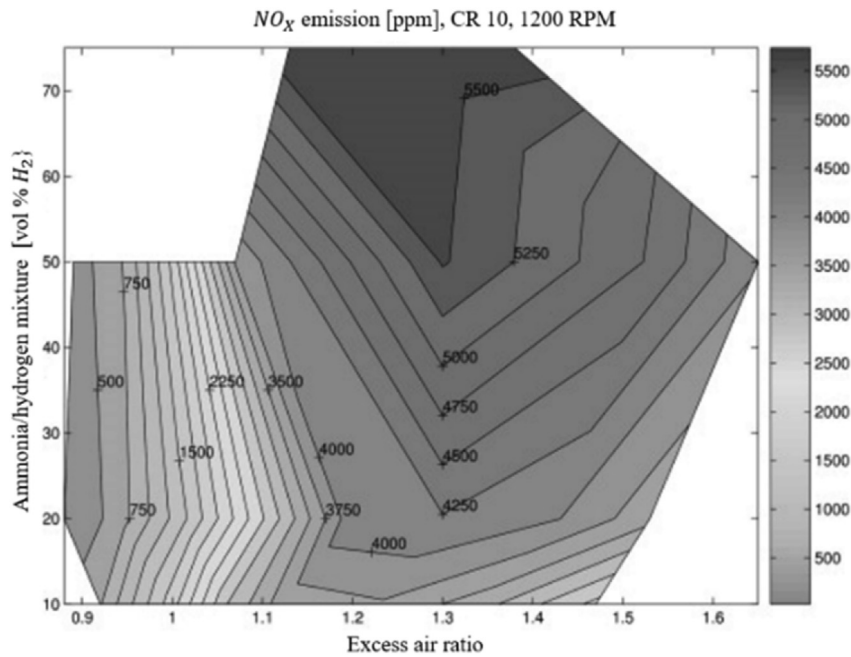


Fig. 5 – (a) Effect of hydrogen substitution and excess air ratio (EAR) on NO_x emissions of a SI engine fuelled with ammonia/hydrogen at 10 CR and 1200 rpm [92].

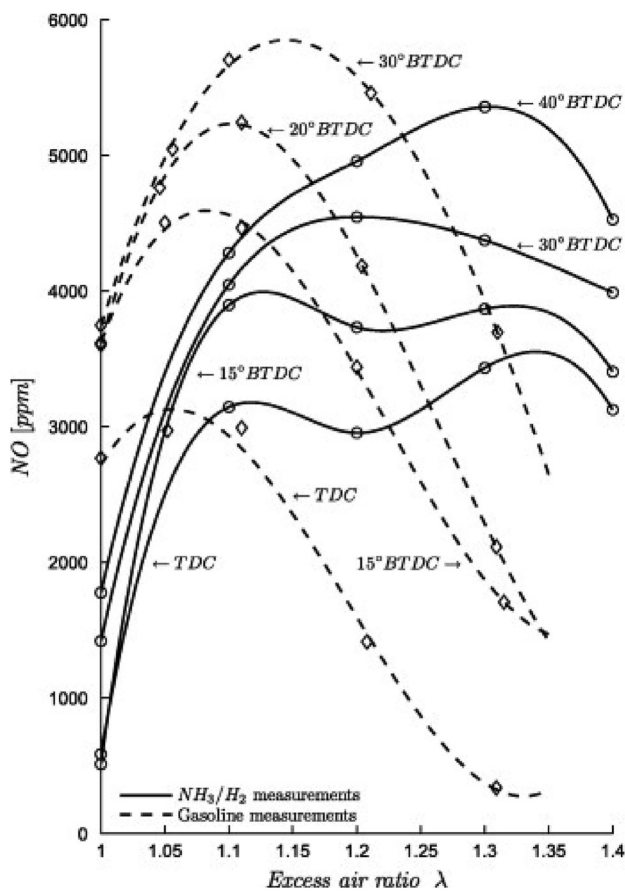


Fig. 6 – NO emissions from ammonia/hydrogen fuelled (80% NH₃ + 20% H₂) and gasoline fuelled SI engine (1000 rpm) at different excess air ratios and spark timing [95].

increasing share of hydrogen (0–60%) at different engine loads (intake pressure: 0.1 and 0.12 MPa) and equivalence ratios (0.6–1.2) at a constant speed of 1500 rpm. Maximum IMEP values were achieved for near stoichiometric lean fuel mixtures with low to moderate hydrogen fractions, and for hydrogen-rich mixtures, IMEP was lower due to higher wall heat losses as seen in Fig. 7 (a). Spark timings were advanced for ammonia-air fuel mixtures for maximum net IMEP and with the increase in hydrogen fraction it was retarded accordingly based on IMEP values as shown in Fig. 7 (b) and the location of peak in-cylinder pressure was constantly phased in the cycle for all fuel mixtures indicating max IMEP. Increasing levels of hydrogen in the fuel mixture had a greater effect on flame initiation duration due to the rise in turbulent flame speeds and favorable thermodynamic conditions. The results of the study indicated that fuel blends with higher hydrogen share (>20%) had lower efficiency due to heat losses and gaseous ammonia blends with hydrogen share up to 20% had the best work output and efficiency [104].

Michikawuchi et al. [113] (Toyota Motor Corp) developed an ammonia-burning internal combustion engine in 2009, which utilized exhaust heat for reforming some amount of ammonia to hydrogen and this hydrogen was stored in the hydrogen storing alloy for feeding the same with ammonia gas to the combustion chamber for enhanced combustion of the fuel mixture. Koike et al. [114] developed an auto-thermal-cracker for onboard thermal reforming of ammonia to hydrogen and the authors could achieve stable combustion without auxiliary hydrogen supply at high loads and it was reported that fuel blends with 40% hydrogen and 60% ammonia on an energy basis would ensure comparable flame velocity like gasoline. However, the decomposition yield of the cracker is difficult to control while directing the entire ammonia stream and will lead to an unstable fuel mixture either consisting of

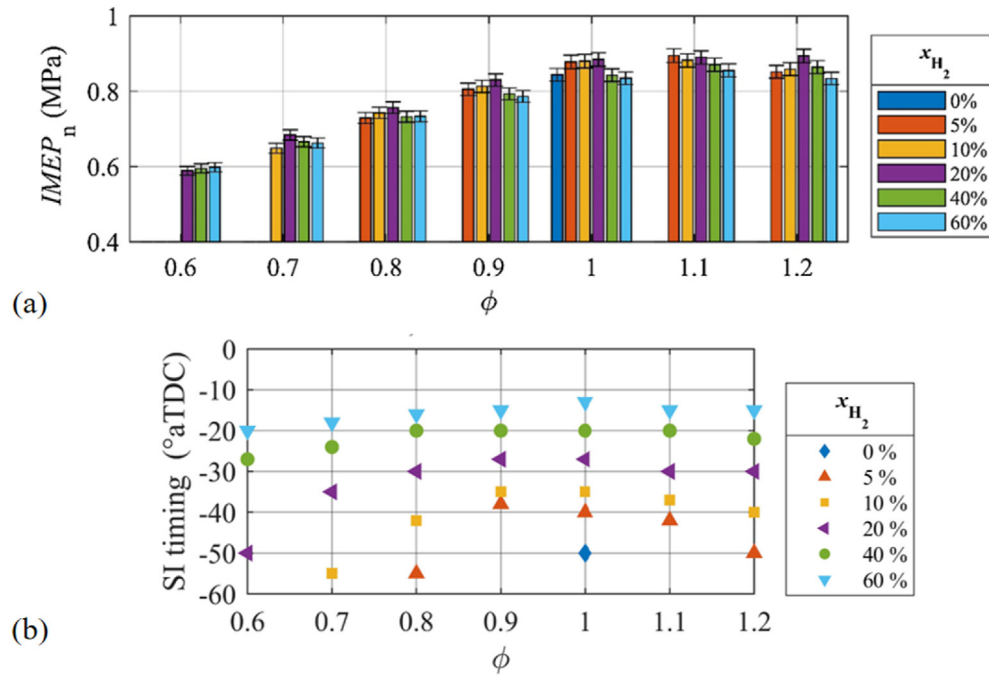
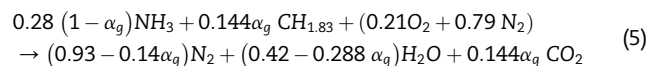


Fig. 7 – Effect of hydrogen enrichment on (a) Net Indicated Mean Effective Pressure (IMEP), (b) spark ignition timing, and (c) Cylinder pressure traces of ammonia-fuelled SI engine operating at an intake pressure of 0.12 MPa and an engine speed of 1500 rpm [104].

uncracked ammonia or fully cracked ammonia (75% hydrogen + 25% nitrogen mixture) which affects the engine operating characteristics (pre-ignition and backlash) [108,115]. Koike et al. [105] evaluated the cold start performance of ammonia fuelled SI engine fitted with an auto thermal reforming unit in the engine head for ammonia cracking and a three-way catalyst with an ammonia adsorber (Cu-zeolite catalyst) unit for controlling ammonia emissions, and ammonia-free emissions were achieved during cold start with less than 10% hydrogen fuel ratio.

Ammonia and gasoline fuel blends

Utilization of gasoline as a combustion promoter in ammonia fuelled engine will ensure fuel flexibility and also provide a scope for replacing gasoline with ammonia as principal fuel to a practical extent without using external thermal crackers, based on the commercial availability of ammonia. The stoichiometric reaction for gasoline-ammonia combustion is as detailed in Equation (5) and α_g represents the gasoline fraction [89].



Grannel et al. [89,90] performed experimental studies in a single-cylinder cooperative fuel research engine (83.4 mm bore and 114.3 mm stroke) to identify the fuel mix limits for gasoline and ammonia fuel mixture to achieve knock-free combustion with minimal roughness at all loads since the higher share of ammonia is limited by excessive roughness and higher share of gasoline is limited by MBT (Maximum

Brake Torque) knock limit. The roughness limit was identified from COV_{IMEP} (smooth firing $COV_{IMEP} \leq 3\%$) and the knock was identified from the pressure signal where knock signal amplitude greater than 50 kPa indicates excessive knock. Spark timing has to be retarded away from MBT timing with an increase in load for the case of gasoline combustion and higher loads are limited by spark timing at TDC or higher exhaust gas temperature (>900 deg. C). However, with 43% ammonia substitution, researchers achieved MBT spark timing without knock at IMEP of 700 kPa (with CR: 9:1 and 1000 rpm), and the same was identified as the upper fuel mix limit for knock-free combustion with gasoline-ammonia fuel mixture at considered operating conditions. The lower fuel mix limit (rough limit) for gasoline-ammonia mixtures was observed to be 18% gasoline/82% ammonia and the reported fuel mix limits for different operating conditions are as detailed in Table 3. Rough limit fuel mix was observed to have a strong dependence on load since it extended close to 90% ammonia substitution with an increase in load from 200 kPa to 1200 kPa (CR: 12:1) and it had a weak dependence on compression ratio due to long ignition delay for ammonia which placed MBT spark timing (50 deg or more) at points where the effect of compression ratio was negligible. Knocking always occurs near peak pressure ($\pm 20^\circ$ window) range where compression ratio and load have a strong effect on compressed charge density and hence will have a strong dependence on the upper fuel mix limit. A crossover between the knock limit and rough limit (i.e., the required gasoline share at the rough limit is more than the permitted one for the knock limit) was observed to occur at higher compression ratios (14:1 and 16:1) and hence based on trends, upper

Table 3 – Operating conditions and fuel mix limits for gasoline-ammonia combustion [89,90].

Operating condition (CFR engine; VCR; 83.4 mm bore; 114.3 mm stroke, and 625 cubic cm displacement volume)	Upper fuel mix limit or Knock limit (Limited by 50 kPa knock pressure signal)	Lower fuel mix limit or Rough limit (Limited by $COV_{IMEP} \leq 3$)
CR: 8:1 Speed: 1600 rpm $IMEP_n$: 550 kPa	87% gasoline + 13% ammonia	37% gasoline + 63% ammonia
CR: 9:1 Speed: 1000 rpm $IMEP_n$: 700 kPa	57% gasoline + 43% ammonia	18% gasoline + 82% ammonia
CR: 12:1 Speed: 1600 rpm $IMEP_n$: 260 kPa	58% gasoline + 42% ammonia	53% gasoline + 47% ammonia

compression ratio (12:1) limit was set for gasoline/ammonia fuelled SI engines. Engine out ammonia emissions were higher for 100% ammonia operation (24,000 ppm) and substitution of gasoline by 6% and 13.5% reduced these emissions to 15,000 ppm and 12,000 ppm, respectively, hence it is recommended to have a combustion promoter for minimal unburned ammonia emissions and acceptable combustion efficiency [91]. Hydrocarbon emissions reduced significantly as the ammonia content in the fuel mixture increased by more than 70% and slightly lower NO emissions were observed for 100% ammonia combustion (1700–2500 ppm) as compared to gasoline (iso-octane) combustion (2300–3000 ppm).

Ryu et al. [98] worked on the direct injection of gaseous ammonia in a SI engine (CFR engine; CR: 10:1; 82.5 mm bore; 114.3 mm stroke; 1800 rpm speed) by developing a direct injection system (fuel line heating controller, pressure regulator, and standard solenoid valve injector) for improving volumetric efficiency alongside gasoline port injection for combustion enhancement. Gasoline was used to sustain the idling operation with a baseline power of 0.6 kW and further higher loads were achieved by introducing ammonia and all experiments were performed at constant spark timing of 30 CAD BTDC. Advancing the ammonia injection timing from 270 to 370 CAD BTDC increased the engine power output at a specific injection duration and an increase in power output

(1.25 kW–2.75 kW) was observed by increasing the ammonia injection duration from 8.75 to 23 ms. Gasoline-ammonia combustion indicated lower peak cylinder pressure as compared to gasoline-only operation as shown in Fig. 8 (a), owing to the slow flame speed and low flame temperature of ammonia resulting in reduced peak combustion temperature and some amount of after burning. Direct injection of ammonia also enhanced combustion intensity by encompassing strong turbulence in the inducted gasoline air mixture before the spark and hence the combustion duration was observed to reduce from 113 CAD to 92 CAD, with an increase in load from 0.6 kW to 2.75 kW by ammonia introduction as evident from mass fraction burned curves in Fig. 8 (b). The formation of fuel-bound NO_x emissions resulted in higher NO_x emissions at higher load points due to increased ammonia share and the unburned ammonia emissions also increased with load due to increased ammonia supply [98]. However, the operation of a selective catalytic reduction (SCR) system could be benefited from ammonia slip, and in SCR systems, the NO_x emissions are reduced to nitrogen by ammonia in the presence of a catalyst and further studies would be required to characterize and validate the system efficiency.

Ryu et al. [97] also developed an ammonia dissociation catalyst (2% ruthenium on alumina pellets) for the

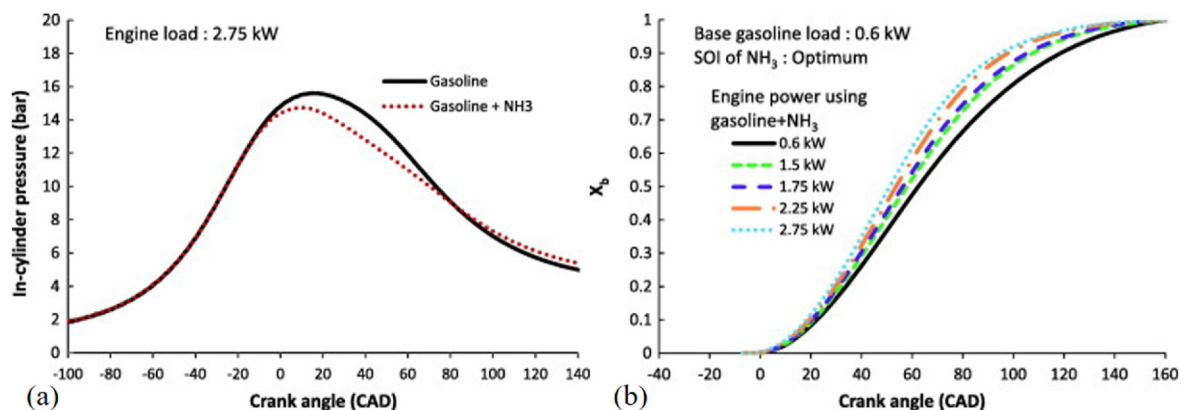
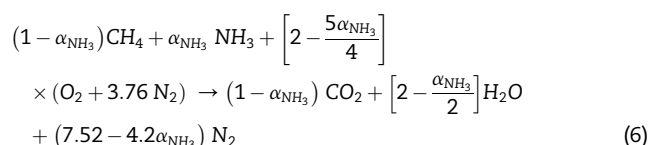


Fig. 8 – (a) In-cylinder pressure traces for gasoline and gasoline + ammonia combustion at 2.75 kW load and (b) History of MFB for gasoline (0.6 kW) and gasoline + ammonia (1.5 kW–2.75 kW) combustion in a spark ignited CFR engine with direct injection of gaseous ammonia at 1800 rpm [98].

decomposition of ammonia to hydrogen and nitrogen, and the developed catalyst assembly was installed in the ammonia supply line before the ammonia injector in the gaseous ammonia direct injection engine. Combustion characteristics of the engine for gasoline/ammonia combustion with and without catalyst assembly were evaluated for different injection durations (9.5 ms–23 ms) and injection timings (320 and 370 CAD BTDC) with constant spark timing (10 CAD BTDC), gasoline injection timing (310 CAD BTDC) and gasoline supply (27.5 g/min) which is required for idle operation (0.6 kW). Gasoline combustion exhibited higher peak pressure as compared to gasoline/ammonia combustion due to the slow flame speed of ammonia resulting in longer combustion durations and the introduction of ammonia dissociation catalyst assembly in gasoline/ammonia combustion resulted in higher peak pressure and HRR than gasoline case owing to the enhanced combustion by the presence of hydrogen in the fuel mixture. The presence of ammonia dissociation catalyst will reduce fuel-bound NOx emissions and will increase thermal NOx emissions at the same time due to hydrogen-enhanced combustion resulting in higher temperatures. BSNOx emissions were lower for gasoline/ammonia combustion with the catalyst at low injection durations due to better decomposition of ammonia prior to combustion and the short residence time during higher injection durations caused an increasing trend in BSNOx emissions. Reduction in the exhaust energy consumed by ammonia dissociation reaction resulted in lower exhaust gas temperatures for the case of gasoline/ammonia combustion with catalyst and BSNH₃ emissions were also reduced greatly by 70–80%. Haputhanthri et al. [96,101] worked on the development of composite ammonia-gasoline fuel blends with the aid of an emulsifier to improve solubility and the results showed that 30% volume of ethanol in gasoline could retain 17.35% volume of ammonia in the liquid phase. Experimental studies were performed in a four-cylinder SI engine (CR: 10.4:1; 88 mm bore and 98 mm stroke) to identify the optimum composite fuel blend (ammonia + gasoline + ethanol) and the results indicated that gasoline fuel blend with 20% ethanol and 12.9% ammonia exhibited best engine performance at all engine speeds and was also observed to be ideal for existing SI engines [101,116].

Ammonia and methane fuel blends

The global reaction for the combustion of stoichiometric mixtures of CH₄/NH₃/air is detailed in Equation (6), where α_{NH_3} is the molar fraction of ammonia in the air-fuel mixture [117].



The upgradation of biogas to biomethane has gained a lot of research focus in recent years and the utilization of biogas/biomethane as a combustible fuel in SI engines has been reported in previous studies [118–123]. Ammonia-methane combustion in spark-ignition engines are not well explored and very limited studies have reported the engine

characteristics of ammonia-methane fuelled SI engine. Oh et al. [106] evaluated the feasibility of natural gas/ammonia dual-fuel combustion in a six-cylinder marine engine (123 mm bore; 155 mm stroke and CR: 10.5:1) by substituting natural gas with ammonia close to a 50% split ratio at different excess air ratios ($\lambda = 1.2$ to 1.5) by maintaining constant engine load (250 Nm) and speed (840 rpm). A significant reduction in carbon dioxide emissions was observed with an increase in ammonia split ratio and air-fuel ratio owing to the substitution of hydrocarbon-based fuel by ammonia and a moderated deterioration in combustion characteristics was observed as indicated by the increase in COV_{imep} and $\lambda = 1.5$ was identified as the upper limit of air-fuel ratio for ammonia-methane combustion owing to the rapid decline in combustion stability accompanied by poor emission characteristics. The peak pressure reduced with an increase in split ratio as evident from Fig. 9 (a) indicating a reduction in temperature hence it could be concluded that the rise in NOx emissions was caused by fuel bound NOx and not thermal NOx. NOx emissions increased with an increase in ammonia split ratio and got saturated at 40% ammonia substitution. Laminar flame speed of the fuel mixture reduces with an increase in ammonia split ratio and this will result in an increase in initial burn duration (spark timing to CA10, i.e., 10% mass fraction burned) as seen in Fig. 9 (b), indicating the delay in the development of initial flame kernel due to slow laminar flame speed [106]. Okafor et al. [46] evaluated the laminar burning velocity of premixed NH₃/CH₄/air mixtures by experimental (cylindrical constant volume chamber; 410 mm length and 270 mm diameter) and numerical approach (ANSYS Chemkin-Pro) and the results indicated that the unstretched laminar burning velocity decreased with increase in ammonia concentration due to the influence of preheating zone thickness [124] and zeldovich number [125]. A detailed reaction mechanism (Okafor reaction mechanism [46] with 5 elements, 59 species, and 356 reactions) based on CH₄/NH₃ oxidation kinetics was developed by the addition of important N/H chemistry from Tian's mechanism [126] to GRI Mech 3.0 [127] and the simulation results showed that the developed model could predict the burning velocity of ammonia/air flames and ammonia/methane/air flames satisfactorily for various ammonia heat fractions (0–0.3) and equivalence ratios (0.8–1.3). Further an optimized reduced reaction mechanism with 5 elements, 42 species and 130 reactions for CH₄–NH₃–air flames was proposed by Okafor et al. [45] and the simulation results indicated that the proposed reaction mechanism predicted the species concentration and laminar flame speed with high fidelity. Kurien et al. [128] performed experimental investigations on ammonia/methane combustion in gaseous fuelled SI engine by increasing the ammonia fuel share from 0 to 60% at constant engine load of 8 Nm (Lambda:1, speed:1500 rpm and BMEP:1.52 bar) and the results indicated that the cycle to cycle combustion variations (COV_{imep}) increased to 14.8% at 60% ammonia share as shown in Fig. 9 (c), indicating the lower operating load limits at specified operating conditions. However the COV_{imep} was observed to decrease from 14.8% to 4.3% when the engine load was increased from 8 Nm to 16 Nm with 60% ammonia share, owing to the rise in flame speed and in-cylinder temperature with engine load.

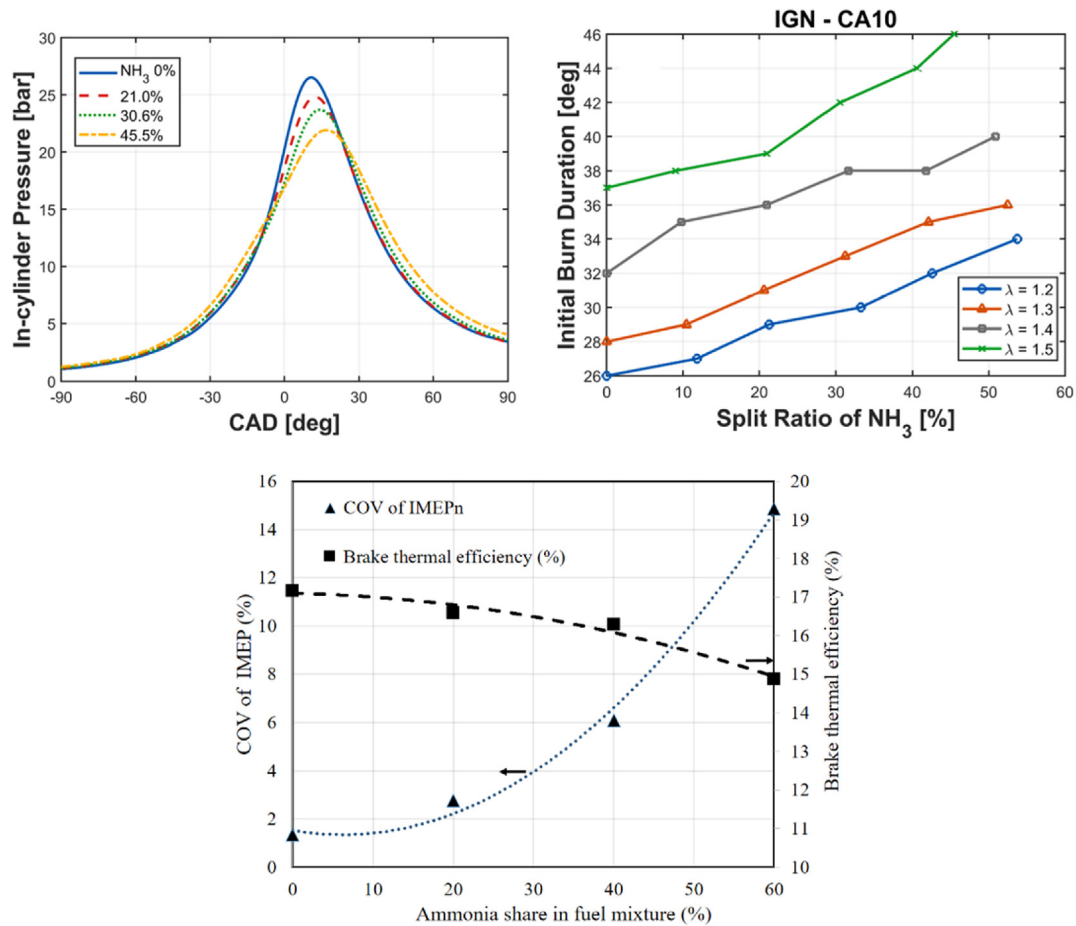


Fig. 9 – (a) In-cylinder pressure traces for various split ratios at $\lambda = 1.5$, (b) initial burn duration for different air-fuel ratios and split ratios of ammonia in a 6-cylinder marine SI engine fuelled with methane and ammonia at 250 Nm load and 840 rpm speed [106] and (c) effect of ammonia fuel share on brake thermal efficiency and COVimep of ammonia/methane fuelled SI engine at 8 Nm (BMEP 1.5 bar) engine load and 1500 rpm engine speed.

Challenges and strategies for ammonia combustion in SI engines

Ammonia undergoes one-step oxidation with air to produce water and nitrogen as detailed in Equation no. 3 and the combustion characteristics of ammonia play a major role in the consideration of ammonia as a fuel [129–131]. The physico-chemical properties of hydrogen, methane, ammonia, and other fuels are listed in Table A1 in appendix A [25–28]. However narrow flammability range of ammonia ensures less explosive risk as compared to hydrogen [132,133]. Reaction rates are slow in the case of ammonia combustion due to slow laminar flame speed and it limits the engine operation at high regimes [78]. Heat losses from the flame to walls will be lower in the case of ammonia owing to a longer flame quenching distance (7 mm) [134] as compared to methane and hydrogen at stoichiometric conditions [135,136]. Higher auto-ignition temperature, high minimum ignition energy, and slow flame speed of ammonia is a limiting factor

and it could be addressed by introducing strategies like higher spark energy, compression ratio, supercharging, and blending with superior quality fuels as shown in Fig. 10. Social acceptance will be a major challenge for the utilization of ammonia as fuel at commercial levels and the pungent odor released by ammonia even at very low concentrations like 5 ppm will create a perception of ammonia being highly toxic (25 ppm threshold limit value and >300 ppm immediately dangerous to life or health) [137,138], however, ammonia is not considered as carcinogenic unlike gasoline, which has carcinogenic substances [139]. A risk assessment study by Duijm et al. indicated that the risks associated with the accidental leak of ammonia are comparable to that of LPG [140] and a similar conclusion was reported by Quest Consultants Inc. (Quantitative risk analysis) that the risks and hazards with handling and utilization of anhydrous ammonia are comparable to that of gasoline and LPG [140,141]. The strong odor of ammonia also features as a self-alarms property for leak detection and helps the initiation of mitigation measures at the very initial stage and avoids chances for catastrophic failure [142].

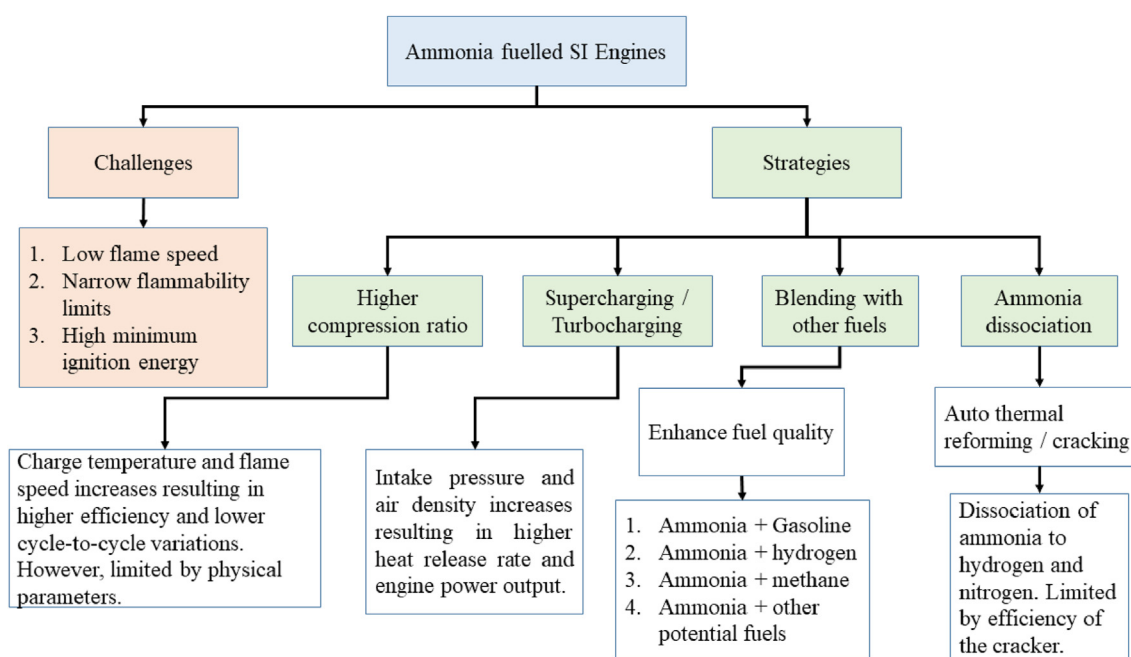


Fig. 10 – Challenges and strategies for ammonia fuelled SI engines.

Techno-economic aspects of green ammonia as a fuel

Ammonia has gained a lot of attention as a potential future fuel and the feasibility for the production of green ammonia from renewable energy sources has made it a competent green alternate fuel [143]. Ammonia has a higher octane rating with 17.8 wt% hydrogen content and it can be cracked thermally to produce hydrogen and, thus making it an effective hydrogen energy carrier for stationary and mobile applications [144,145]. Ammonia is a safer fuel as compared to hydrogen since it has a narrow flammability range, which reduces the risk of explosion and ammonia dissipates rapidly into the atmosphere owing to its lower density, and the pungent odor from ammonia makes a self-alarming factor for leak detection. The intermittent availability of wind and solar energies could be better utilized for renewable energy future by storing renewable energy in the form of chemical fuels which enables easy storage and transportation (short and long distances). Storage and transportation of liquid hydrogen are limited due to various challenges including higher energy expended for the liquefaction process accompanied with higher boil-off losses during transportation. The energy required for liquefaction of hydrogen in a plant with capacity of 200 tonne-hydrogen per day is estimated to be 30 MJ/kg-H₂ and hydrogen tanker trucks will consume 3% of the energy they are carrying during long distance transportation [114]. The utilization of hydrogen energy carriers has been regarded as the most viable technical option for the transportation of hydrogen energy and ammonia with 17.8 wt% hydrogen content has been identified as a suitable hydrogen energy carrier with well-established mature infrastructure for storage and transportation [146,147].

Ammonia has a manufacturing capacity of 230 million tonnes (Mt) per year and it is the second most highly produced chemical with applications in fertilizers, explosives, and other chemical commodities [148]. About 80% of the ammonia produced is used for fertilizer applications and synthesis of ammonia is performed by following the Haber-Bosch process which consumes 30–60 GJ of energy per tonne of ammonia produced [149] and it can be transported via established pipelines for reducing the energy loss during long distance transportation. Zamfirescu et al. [150] performed a comparative study on the costs associated with a hydrogen-fuelled IC engine (Ford focus prototype) and its ammonia-fuelled version. The results highlighted that the ammonia-fuelled engine can be operated with a lower storage tank volume at lower storage pressure and the driving cost for ammonia fuelled vehicle will be less than that of a hydrogen-fuelled vehicle as shown in Fig. 11 owing to 4 times better compactness in ammonia storage as compared to that of hydrogen storage. While considering the future scope for electrolytic production of green ammonia and the associated capital expenses/operational expenses, the levelized cost of ammonia is expected to reduce by 163 USD/t_{ammonia} in 2040 (310 USD/t_{ammonia}) as compared to 2019 (473 USD/t_{ammonia}) [151,152].

Conclusions and future scope

Green ammonia as a hydrogen energy carrier will play a key role in the storage and transportation of location-specific renewable energy (wind and solar energies) since it has a higher volumetric energy density (15.6 MJ/L) than high-pressure compressed hydrogen (5.6 MJ/L at 70 MPa) and it can be liquefied at low pressure (10 bar) and also has an

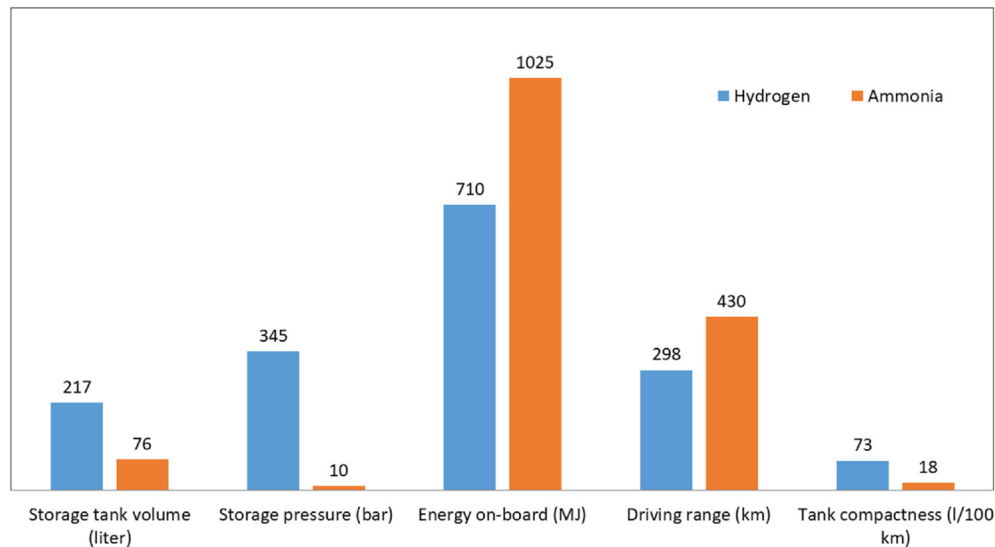


Fig. 11 – Comparative analysis of the variation in techno-economic aspects with the conversion of hydrogen-fuelled Ford Focus prototype to ammonia fuel mode [150].

established network for transportation and distribution globally by pipeline and bulk carrier. In this work, a detailed literature survey has been conducted to develop an understanding of the challenges and strategies for the combustion of green ammonia in spark ignition engines. Direct combustion of ammonia as a single fuel in SI engines is limited by its lower flame speed and high minimum ignition energy, which results in poor engine performance. Poor utilization of ammonia fuel in engines could be addressed by adopting the following strategies like increased spark energy, compression ratio, multiple ignitions, and blending with superior quality fuels like hydrogen, gasoline, and methane. An increment in maximum power by 59% was observed with an increase in compression ratio from 9.4:1 to 11.5:1 and modifying the ignition system with a high-performance coil improved maximum power by 80%. The blending of ammonia with 10% vol. of hydrogen was observed to improve the indicated efficiency, indicated mean effective pressure, and NO_x emissions, and a further increase in hydrogen share had a detrimental effect on engine characteristics owing to higher heat losses and intake air dilution, which could be compensated by increasing the compression ratio. The total NO_x emissions from hydrogen/ammonia-fuelled engines are comparable to that of gasoline-fuelled engines with the dominance of fuel-bound NO_x at lower hydrogen shares and thermal NO_x at higher hydrogen shares. Onboard reforming of ammonia to produce hydrogen with the help of catalytic crackers will reduce the complexity of including auxiliary hydrogen supply, however, it is quite challenging to control the decomposition yield of cracker or dissociation catalyst to ensure a stable fuel mixture and is dependent on the efficiency of the catalytic or thermal reforming unit. Better fuel flexibility could be attained by using gasoline as a combustion promoter with ammonia and a lower fuel mix limit (limited by cycle-to-cycle variations) for gasoline in fuel blend was observed to be 18% (i.e. 82% ammonia) with scope for further extension close to 90% ammonia with increase in load and

upper fuel mix limit (limited by knock) for gasoline was observed to be 57% (i.e. 43% ammonia) at 700 kPa IMEP_n (1000 rpm and 9:1 CR). A reduction in hydrocarbon emissions with comparable levels of total NO_x emissions could be achieved by replacing gasoline with ammonia. The requirement of combustion promoter for ammonia combustion is inversely related to engine speed/load and the recommended compression ratio for gasoline/ammonia fuelled engines is 10:1, due to a smaller margin of operation (knock and roughness) at higher compression ratios. Direct injection of gaseous ammonia will enhance combustion intensity by encompassing strong turbulence in the inducted gasoline-air mixture and the optimal injection timing for gaseous ammonia was observed to be 320 CAD BTDC (low loads) and 370 CAD BTDC (high loads). Ammonia-methane combustion in spark-ignition engines is not well explored and the recent growth of the biogas up-gradation sector has increased the scope for utilization of green ammonia and biomethane fuel blends in SI engines for transportation and power generation. The upper limit of excess air ratio for ammonia-methane combustion is identified to be 1.5 (due to a decline in combustion stability) and the laminar flame speed of the fuel mixture will reduce with the increasing share of ammonia.

Presently, there are limited research works covering ammonia-fuelled spark-ignition engines and very few research groups have explored ammonia combustion. Ammonia has a major role to play as a hydrogen energy carrier in the establishment of a hydrogen economy and the development of green ammonia/green hydrogen production plants has gained positive growth recently. Major countries have announced policies and grants for the development of cost-effective and advanced technologies for green ammonia production, considering the ease for storage and transportation of hydrogen energy in the form of green ammonia by utilizing its well-established infrastructure. The limited literature on ammonia combustion is a major challenge for the establishment of the ammonia fuelled engine cycle and

there is a rising demand for further exploration in this area. Future directions for research include the identification of operating limits for ammonia combustion, optimal ammonia fuel blends with bio-methane or green hydrogen, fuel injection strategies, reformer unit with a robust catalyst for partial dissociation of NH_3 , and the requirement of engine modifications and suitable emission control systems downstream. The social acceptance of ammonia as a fuel and energy carrier is also a crucial challenge and it could be only addressed by improving state-of-the-art literature for ammonia combustion accompanied by the development of standard protocols and procedures with aid of inter-governmental policies.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ijhydene.2023.04.073>.

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