Progress in Energy and Combustion Science 69 (2018) 63–102

Contents lists available at ScienceDirect

Progress in Energy and Combustion Science

journal homepage: www.elsevier.com/locate/pecs

Ammonia for power

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ARTICLE INFO

Article history:
Received 22 December 2017
Accepted 27 July 2018

Keywords:
Ammonia
NH3
Power generation
Renewable energy storage

ABSTRACT

A potential enabler of a low carbon economy is the energy vector hydrogen. However, issues associated with hydrogen storage and distribution are currently a barrier for its implementation. Hence, other indirect storage media such as ammonia and methanol are currently being considered. Of these, ammonia is a carbon free carrier which offers high energy density; higher than compressed air. Hence, it is proposed that ammonia, with its established transportation network and high flexibility, could provide a practical next generation system for energy transportation, storage and use for power generation. Therefore, this review highlights previous influential studies and ongoing research to use this chemical as a viable energy vector for power applications, emphasizing the challenges that each of the reviewed technologies faces before implementation and commercial deployment is achieved at a larger scale. The review covers technologies such as ammonia in cycles either for power or CO_2 removal, fuel cells, reciprocating engines, gas turbines and propulsion technologies, with emphasis on the challenges of using the molecule and current understanding of the fundamental combustion patterns of ammonia blends.

Contents

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https://doi.org/10.1016/j.pecs.2018.07.001
0360-1285/

1. Introduction

Renewable energy is playing an increasingly important role in addressing some of the key challenges facing today's global society, such as the cost of energy, energy security and climate change. The exploitation of renewable energy looks set only to increase across the world as nations seek to meet their legislative and environmental obligations with respect to greenhouse gas emissions. There is broad agreement that energy storage is crucial for overcoming the inherent intermittency of renewable resources and increasing their share of generation capacity.

Thus, future energy systems require effective, affordable methods for energy storage. To date, a number of mechanical, electrical, thermal, and chemical approaches have been developed for storing electrical energy for utility-scale services. Storage solutions such as lithium batteries or redox cells [1–3] are unlikely to be able to provide the required capacity for grid-scale energy storage. Pumped hydro and methods such as compressed gas energy storage suffer from geological constraints to their deployment [4–6]. The only sufficiently flexible mechanism allowing large quantities of energy to be stored over long time periods at any location is chemical energy storage [7].

Chemical storage of energy can be considered via hydrogen or carbon-neutral hydrogen derivatives. One such example is ammonia, which has been identified as a sustainable fuel for mobile and remote applications. Similar to synthesised hydrogen, ammonia is a product that can be obtained either from fossil fuels, biomass or other renewable sources such as wind and photovoltaics, where excessive electrical supply can be converted into some non-electrical form of energy [1]. Some advantages of ammonia over hydrogen are its lower cost per unit of stored energy, i.e. over 182 days ammonia storage would cost 0.54 $/kg-$H_2$ compared to 14.95 $/kg-$H_2$ of pure hydrogen storage [8], higher volumetric energy density (7.1–2.9 MJ/L), easier and more widespread production, handling and distribution capacity, and better commercial viability. Ammonia produced by harvesting of renewable sources has the following properties [9–11],

1. It is itself carbon-free, has no direct greenhouse gas effect, and can be synthesized with an entirely carbon-free process from renewable power sources;
2. It has an energy density of 22.5 MJ/kg, comparable to that of fossil fuels (low-ranked coals have around 20 MJ/kg; natural gas has around 55 MJ/kg, LNG 54 MJ/kg, and hydrogen 142 MJ/kg);
3. It can easily be rendered liquid by compression to 0.8 MPa at atmospheric temperature; and,
4. An established, reliable infrastructure already exists for both ammonia storage and distribution (including pipeline, rail, road, ship); today around 180 million tons of NH_3 are produced and transported annually.

1.1. Interest in ammonia for power

Ammonia has recently started to receive attention internationally as a consequence of the primary benefits outlined in the previous section. For example, Japan has been looking for renewable alternatives for their energy consumption requirements over the last few decades, due to lack of natural energy resource. Hydrogen has been presented as an attractive solution that could meet their energy demands, accompanied by reduction in greenhouse gas emissions. However, Japan has clearly recognised the potential of ammonia to serve as the hydrogen carrying energy vector, and a 22-member consortium led by Tokyo Gas has been created to curate "Green Ammonia" promoted by the Cross-Ministerial Strategic Innovation Program (SIP) of Japan [12], seeking to demonstrate hydrogen, ammonia and hydrides as building blocks of a hydrogen economy, Fig. 1. The Japan Science and Technology Agency (JST) has announced the intentions of the consortium to develop a strategy for "forming an ammonia value chain" that promotes the leadership of the country in the production and use of the chemical worldwide. All consortium members have extensive knowledge of handling ammonia, with multimillion projects in progress or under consideration. For example, IHI Corporation and Tohoku University plan to invest $8.8 M in 2017 to set up a duel-fuel gas turbine that co-fires one part of ammonia to five parts of methane [13]; similarly, Chugoku Electric Power Company intends to conduct co-firing experiments with coal and ammonia (at 0.6%) at one of their power plants, paying $373,000 for the implementation of this project [14].

In the USA, the Advanced Research Project Agency-Energy (ARPA-E), subsidiary of the Department of Energy, has recently launched its "Renewable Energy to Fuels through Utilisation of Energy-Dense Liquids" (REFUEL) program, whose aim is to develop scalable technologies for converting electrical energy from renewable sources into energy-dense carbon-neutral liquid fuels (CNLFs) and back into electricity or hydrogen on demand, thereby accelerating the shift to domestically produced transportation fuels, improving American economic and energy security, and reducing energy emissions [16].

ARPA-E announced that grants totalling $32.7 M would be awarded to 16 REFUEL projects of which 13 are focusing on ammonia. From small scale ammonia synthesis using stranded wind en-

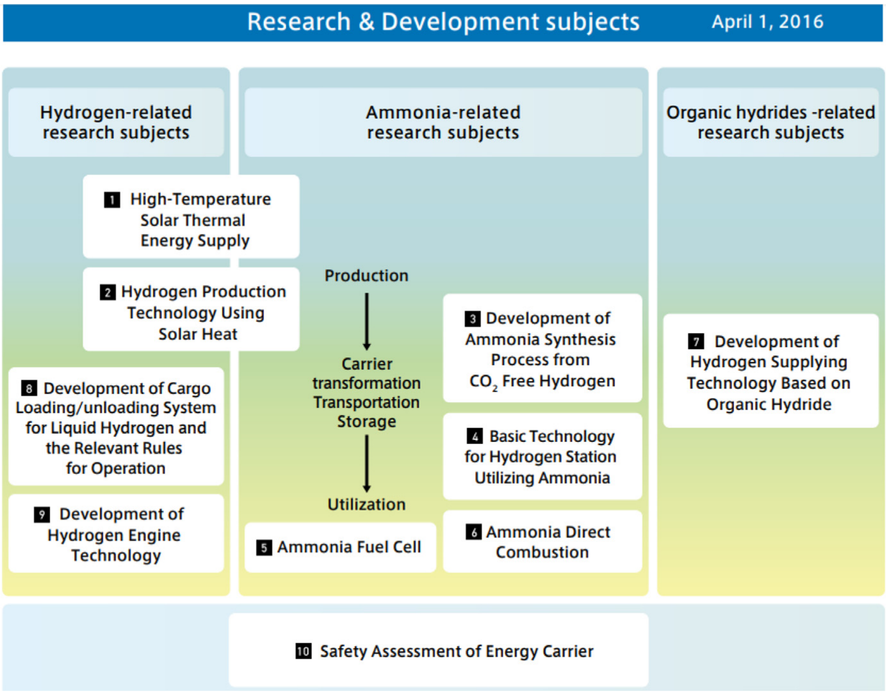


Fig. 1. SIP energy carriers' 10 focuses for R&D [15]. Courtesy of the Japan Science and Technology Agency (JTS).

ergy to improving the Haber–Bosch process, recognised academic institutions and large industrial enterprises are directly involved in this program [17]. Thus, commitment from the US Department of Energy to use ammonia as an energy vector and its further implementation in fuelling technologies to convert it back into hydrogen or energy are materialising through programs such as these. Significant work on the use of ammonia for future energy systems has been undertaken by other US institutions such as the Iowa State University and the University of Minnesota. The University of Minnesota [18] has pursued new methods for distributed ammonia synthesis whereby small plants are able to produce hydrogen from wind to manufacture ammonia for fertilizing applications and fuelling of internal combustion engines. The latter will run on a mixture of up to 50% ammonia with thermal reformers to improve combustion efficiency through partial decomposition of the molecule. This work is supported by recent analyses [19] that show the implementation of ammonia to US fuel light-duty vehicles (LDV) could potentially mitigate up to 30% of the cumulative CO_2 produced by LDV, eliminating up to 96% of carbon emissions from the sector by 2040 (718 Mt_{CO2} per year). Furthermore, these programs intend not only to develop new technologies but also formulate public policies that motivated governmental agencies could employ to encourage development and employment of such systems [18].

The UK has also shown strong interest in the use of ammonia as a chemical energy store. Works performed by Cardiff University, Siemens, Oxford University and UK Science and Technology Funding Council are underway to design and commission a first "Green Ammonia Decoupled" device that will show how energy from wind can be converted to ammonia for its storage and further release of energy via an internal combustion engine [20]. Similarly, Oxford University recently published an extended report entitled "Analysis of Islanded Ammonia-Based Energy Storage Systems" [21]. The work assessed different technologies available in the market and the potential economic implications of recovering stranded, renewable energy in various sites, i.e. islanded and non-islanded, through use of ammonia. The results demonstrated that ammonia is economically viable for islanded regions where both ammonia for energy storage and fertilizer are combined, Fig. 2. Although the current market is small and further development on the synthesis of carbon-free ammonia is needed for further expansion, the proposal shows that under the current scenario the use of ammonia for these means is feasible. Special emphasis on this point needs to be given to those small islands around the UK or other islanded nations where such systems can successfully and economically be deployed. Politics have also a role to play in the use of ammonia, which has found support from Parliament in the form of Lord Howell of Guilford, who recently wrote in 'Jpn Times' that ammonia will be a "revolutionary disruption coming to the energy sector," and suggests that using ammonia for energy storage will prove to be "a game-changer at least on the scale of the shale oil and gas revolution." Lord Howell of Guilford served as Secretary of State for Energy and for Transport during his thirty years as a British Member of Parliament, and he is now chairman of the House of Lords International Relations Committee [22].

In Australia a new chapter of the NH_3 fuel association has been recently opened, with industrial support from companies producing ammonia and hydrogen, hosted by Monash University. Representatives of the NH_3 chapter have discussed the interest that ammonia has spurred over the last year after a large conference in the US, emphasizing the need to start working closely with the hydrogen fuel community. The Australian chapter hopes to attract individuals and industries from Singapore, Malaysia and New Zealand to increase awareness of the chemical, boosting the profile of the use of ammonia for energy storage and power generation [23]. The promotion of these works has led to one of the biggest projects for the production of green ammonia from solar energy. Yara, the second biggest ammonia producer, has announced its intentions to build a demonstration plant that will produce ammonia from solar energy in Pilbara, Western Australia. Hydrogen, product of the electrolysis of water powered by solar energy, will be used for the Haber–Bosch process in these facilities. Although this is not the first project that uses solar energy to produce ammonia, this is by far the biggest company to commission such a system to date. The company believes that if the program is successful, "it could grow to a full replacement of our current natural gas consumption

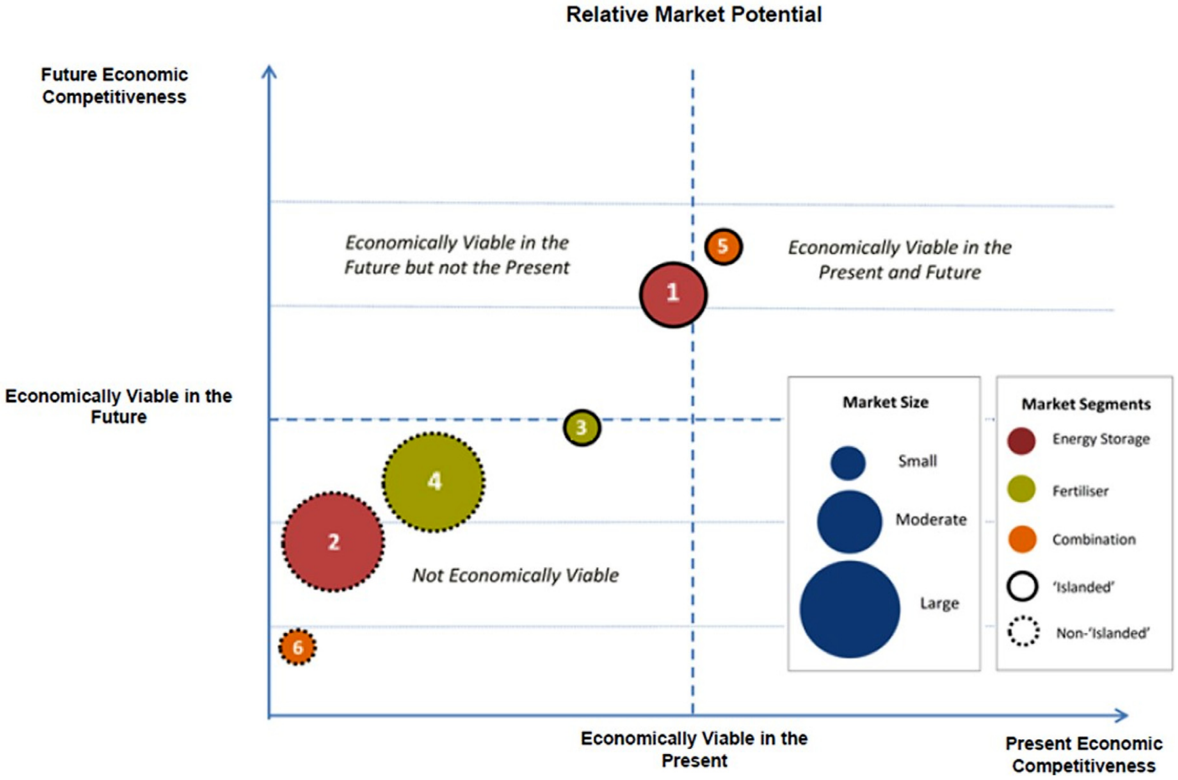


Fig. 2. Relative market potential of various market segments; 1) "Islanded" energy storage; 2) "Non-islanded" energy storage; 3) "Islanded" fertilizer; 4) "Non-islanded" fertilizer; 5) "Islanded" energy storage and fertilizer; 6) "Non-islanded" energy storage and fertilizer [21]. Courtesy of Prof. Bañares-Alcantara, Oxford University.

by producing hydrogen with a solar field. In the long-term future you could think about making it so big that it could be a multiple of the current ammonia production. And then you could think about integration of ammonia into the world market, but also in the world market of renewable fuel production" [24].

Among all mainland European nations, the Netherlands are leading the promotion of ammonia. The rationale for this fact is that the Netherlands possess a substantial quantity of renewable resources as a consequence of the high investment from government and industry. Therefore, ammonia appears as an energy carrier that has the potential to provide the country with enough energy for its current demand, whilst allowing producing companies to export any excess power. Companies including NUON, Gasunie, Statoil and OCI Nitrogen are assessing the conversion of one of the Magnum Power plant's three 440 MW gasifiers with the intention of using hydrogen, and eventually ammonia, in super batteries that will feed the station by 2023–2030 [25]. Simultaneously, producers, distributors and naval designers seek the progression of the technology in terms of storage in large ship containers that cannot only mobilise ammonia but also can use it for fuelling purposes. C-Job Naval and Proton Venture are part of a consortium that seeks funding opportunities to develop a new generation of super vessels capable to run on ammonia by 2040 [26].

Finally, and with a global interest in the use of ammonia for power, the International Energy Agency (IEA) has recently become a promoter of ammonia for a carbon-free future. The Renewable Energy Division [27] has recognised that ammonia can be used to tap into stranded energy produced from renewable sources (wind, solar, tidal, etc.), and then be used to redistribute hydrogen product from electrolysers connected to these systems. As evidenced in their study, ammonia is much less costly to store for a long time compared to hydrogen, i.e. 0.5 $/kg-$H_2$ for ammonia compared to 15 $/kg-$H_2$ for hydrogen over half a year, and at least three times less costly to ship on sea or land [28]. However, the concept is not directly competing with hydrogen, only with its mobility and storage. Cedric Philibert, Senior Energy Analyst at the IEA, reflects that the production of hydrogen from renewables dates from the 1960s, but it is only recently that the increasingly lower cost of renewables starts making these technologies competitive for production of the chemical, thus conversion into ammonia for distribution seems the most economically competitive alternative.

In this year's edition of the Energy Technology Perspectives 2017 - Catalysing Energy Technology Transformations [29], for the first time the EIA has featured ammonia in two major technology transformations. First, ammonia production is shown making a transition away from fossil fuel feedstocks and towards electrification, using hydrogen derived from electrolyzers. Secondly, following this assumption that sustainable ammonia will be widely available in the future, the IEA also classifies ammonia as an energy carrier, in the category of future electricity-based fuels (PtX synthetic fuels). The inclusion of this pair of technology transformations represents a major step towards broader acceptance of ammonia as an energy vector, from the perspectives of both technical feasibility and policy imperative.

Therefore, countries and international agencies have started raising the awareness of the potential of ammonia for storage of hydrogen, a rationale that has served to boost research in the area of its use as energy vector and potential fuel.

1.2. Challenges for ammonia for power

A viable energy system based on ammonia faces four primary barriers:

1. Carbon-free synthesis of ammonia,
2. Power generation from small to utility-scale size,

3. Public acceptance through safe regulations and appropriate community engagement,
4. Economic viability for integration of technologies and green production of ammonia.

Current ammonia production methods are heavily reliant on fossil fuels and consequently, barrier (1) is a challenging area that still requires exhaustive research and will be treated as a separate topic. Barrier (2) above is also critical, since most developments to date have focused on improving small- to medium-scale devices such as reciprocating engines. However, power output from such units using ammonia is relatively modest, typically in the range of 0.1–1.0 MW. Here, one of the main challenges is the reduction of NOx emissions and unburned ammonia, contaminants that directly impact on climate change and are toxic to life, respectively. It is recognised that NO_2 can aggravate cardiovascular and respiratory diseases, with an estimate of 23,500 premature deaths per year only in the UK alone [30]. Although considerable research has been conducted understanding the formation process of this pollutant [31], its formation and consumption during combustion and post-combustion processes using ammonia are still at the core of the research agendas of various research groups. Similarly, toxicity of ammonia is one of the major impediments to deploy these technologies, as public perception is very formative and perception on the nuisance of its smell even at low concentrations is a critical barrier (3) that requires further studies, understanding and innovation. Thus, barrier (3) has played an important role even in small devices, restricting the deployment of reciprocating engines, i.e. in transport or small scale energy production. Therefore, any potential system based on ammonia needs to undergo health and safety impact analyses and a review of current legislations, as well as taking into account public and end-user perceptions and tolerability. Finally, the Economic viability (barrier 4) of such systems needs to be proved, encouraging investors to set the foundations of both industries and suppliers capable of delivering equipment and integrated systems that produce green ammonia for its use in power generation.

1.3. Significance of ammonia for power generation

A key step in the realisation of ammonia as a viable energy vector is releasing the stored energy at the power levels required for commercial or grid-scale applications. Existing fuel cells, cycles, reciprocating engines and gas-turbine technologies and the underpinning science have been developed for use with hydrocarbons or other fuel sources. Thus, the development of new devices and techniques that can utilise green ammonia would have the following advantages:

1. *Reducing emissions.* Being carbon free, ammonia offers the possibility of fuelling gas turbines, fuel cells and reciprocating engines without direct CO_2 emissions. If the energy (and raw materials) used to synthesise the ammonia come from renewable sources, the entire cycle can be made completely carbon-free. Although the transition from current fuel sources to ammonia will still produce carbon, a dual-fuel exchange strategy that includes carbon sources (i.e. methane, methanol) can potentially lead to an order-of-magnitude reduction of carbon emissions in the near term [32], ultimately leading to zero-carbon energy systems.
2. *Improving security of supply*. Ammonia can be synthesised from abundant raw materials, namely hydrogen (in water) and nitrogen (in air). Ammonia is already produced and transported in considerable volumes (∼180 Mtonnes/year [27]), and is therefore a practical and scalable fuel. With the capability of providing grid-scale energy storage, ammonia facilitates the increasing exploitation of renewable energy sources.
3. *Reducing costs of energy*. Large (grid) scale energy arbitrage can only be practically achieved by pumped hydro (in suitable dams/aquifers), compressed air energy storage (in suitable undergrounds cavities), and chemical energy storage (including ammonia). The capital costs of ammonia energy storage are comparable to or better than those for compressed air and pumped hydro but without the attendant geological constraints, and substantially lower than other challenger technologies such as electric batteries [33]. Considerable infrastructure already exists for the transportation and storage of ammonia, along with well-established safe handling procedures, and this reduces the need for investment in further infrastructure and training [34,35]. Although the economic inertia of using fossil fuels is entrenched globally, competitive scenarios can be created by using such a fuel source that can be traded and moved using existing infrastructure, build around liquid fuels [32].

These aspects require careful consideration, thus recognising urgent further research needs for the realisation of a carbon-free ammonia economy via storage of renewable energy.

At present, there is a range of existing mechanical, chemical, thermal and electrical technologies for storing electrical energy adaptable from small to large scale applications, Fig. 3. Of all these technologies, only Compressed Air Energy Storage (CAES), Pump Hydro and Chemical Energy Storage systems have enough commercial maturity and the ability to store energy for large scale applications over long periods of time. The first two suffer the limitation of site placement due to their geographic/geological requirements. Thus, chemical storage via hydrogen and/or derivatives (such as ammonia) and hydrocarbons present a viable option for practical energy storage in the near term. Bearing in mind a desire to reduce carbon emissions, then only hydrogen and ammonia remain as candidates to drive the storage of large quantities of energy with flexible relocation of resources with a reduction on CO_2 emissions. Finally, movement and storage of hydrogen has proved to be more complex than for ammonia, for which a fully developed infrastructure has existed over a century, thus positioning ammonia as a strong candidate to support the concept of flexible energy storage at the largest scale.

Regarding ammonia transition, ammonia can be used to support power and heating processing with other fuels, thus increasing its flexibility of usage. Ammonia blends have been assessed and compared to conventional and higher hydrocarbon fuels, Fig. 4. These blends were analysed in terms of their Wobbe Index and volumetric High Heating Value [36]. As observed, the Wobbe indexes of the ammonia blends fall very close to that of town gas (i.e. 31%CH_4, 49%H_2 and 20%CO_2) and likely similarly to other syngases. Hydrogen, with a higher Wobbe Index, is closer to ammonia than hydrocarbon based fuels with a similar volumetric high heating value, thus rendering conversion equipment simpler. Also, it is evident that the increase of hydrogen in the ammonia blends (from 0% to 75% in this comparative study [36]) does not show a greater increase in Wobbe Index, a point to be considered when developing distribution and combustion systems for ammonia-hydrogen blends, which on this basis could be well started from the precedent of town gas systems.

Recent Life Cycle Assessments (LCA) conducted by Bicer and Dincer [37] show how the use of ammonia for transportation and power production can have considerable advantages for the mitigation of environmental impacts such as global warming potential, abiotic depletion, etc. The study uses ammonia produced via wind energy-based water electrolysis using molten salt electrolytes. It was shown that vehicles reduce their greenhouse gas (GHG) emissions from 0.270 to 0.100 kg/km. Similarly, the production of 1 MJ of electricity using ammonia results in a reduction of CO_2 emissions from 0.130 to 0.083 kg CO_2 eq (with a time horizon of 500

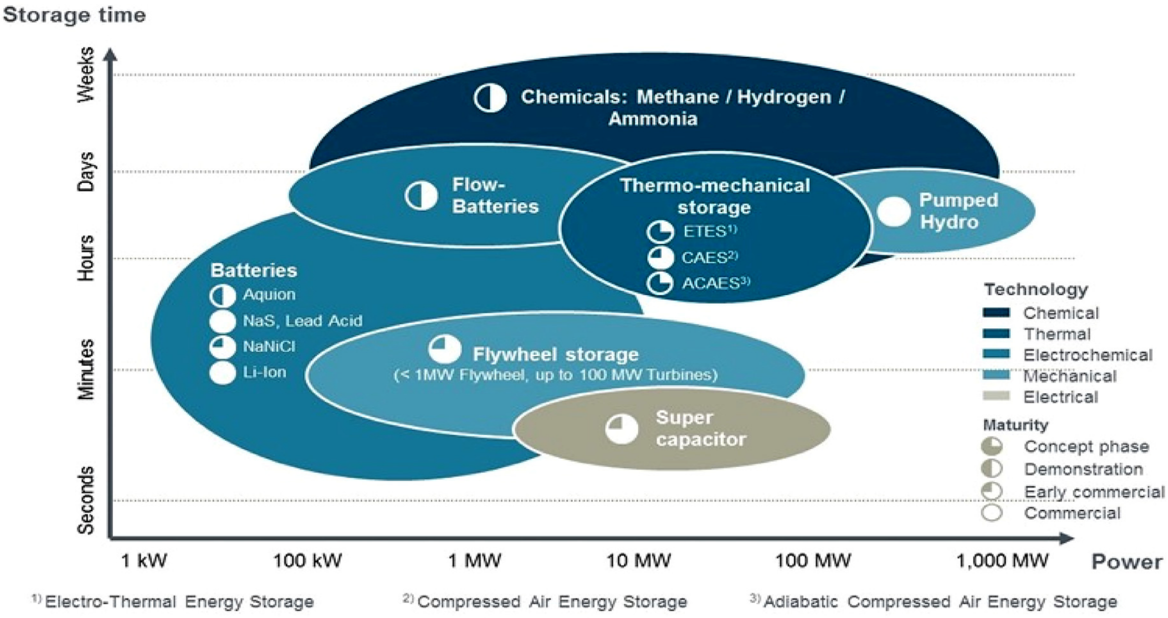


Fig. 3. Comparison between different storage technologies [7]. Courtesy of Dr Ian Wilkinson, Siemens.

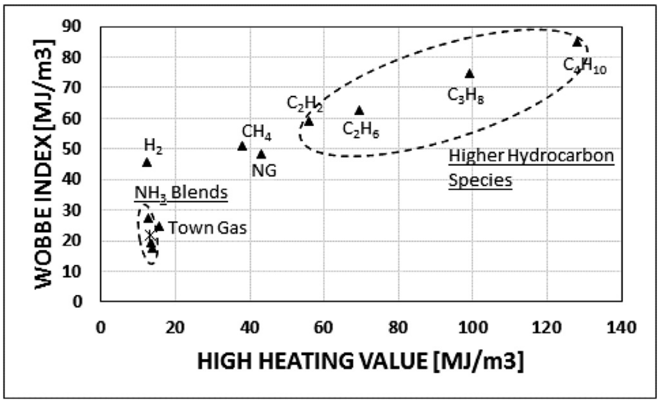


Fig. 4. Wobbe index v HHV of various fuels. Reprinted from [36] with permission from Int J Hydrogen Energy, Elsevier.

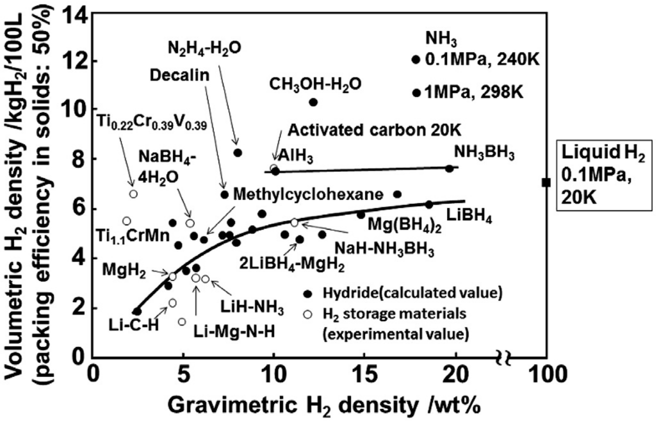


Fig. 5. Hydrogen densities in hydrogen carriers [40]. Courtesy of Prof. Yoshitsugu Kojima, Hiroshima University.

years, GWP500). For power generation, the main global warming potential in natural gas power plants is based on the combustion process (i.e. 97% production of GHGs), while in the ammonia power plant the majority of GHGs (i.e. 93%) is due to the production of ammonia, with only 6% of gases with global warming potential being produced by the combustion system. Although acidification (kg SO_2 eq/MJ) was two orders of magnitude greater for ammonia due to potential leaks, ozone layer depletion was half the value when compared to natural gas power systems, i.e. 2.74×10^{-9} and 5.92×10^{-9}, respectively. Therefore, the greater potential of ammonia for cleaner power can mitigate the production of unwanted GHG emissions and contaminants.

In discussing ammonia storage, comparison with pure hydrogen is always a point of contention. However, here the potential for introduction of ammonia is presented as a complementary enabler of the hydrogen economy, rather than a contender. Hence, the aim of current research groups is to enable the distribution and usage of hydrogen in a safer, more economically viable manner. There are indirect and direct hydrogen storage solutions, with the latter being direct ways to recover hydrogen after heating or pressurisation, while the former need various steps before hydrogen is recovered.

The best known direct solutions for hydrogen storage include metal and complex hydrides, whilst indirect solutions include steam reforming of hydrocarbons or methanol, hydrolysis of hydrides and decomposition of ammonia [38]. Organic hydrides such as methyl cyclohexane (MCH) have also emerged as serious candidates for storage of hydrogen. However, MCH also presents challenges, as it requires a complicated system for returning the base fuel toluene from the point of consumption to the point of production while carrying a low gravimetric mass of hydrogen [39]. Similarly, most current technologies for direct storage fall short for higher gravimetric hydrogen density, and in particular, for those that allow hydrogen desorption at sufficiently low temperatures at fast rates [38].

For indirect solutions, methanol and ammonia currently appear the most viable options, especially when related to full cells and distribution systems, although ammonia presents an extra advantage as it offers the possibility of truly carbon-free energy.

Recent investigations [40,41] have considered the development of new materials for hydrogen storage, Fig. 5. Ammonia possesses one of the highest gravimetric hydrogen densities (17.8 wt%) with the highest volumetric hydrogen densities (0.107 kg-H_2 /L), Fig. 5. Thus, efforts are focused on exploiting this quality to create new technologies for ammonia conversion into hydrogen. Some results demonstrate good feasibility for almost complete cracking of NH_3 into pure hydrogen [40], presenting the former as an enabler for a hydrogen economy.

Distribution of the fuel is also a critical parameter to consider. Transportation of ammonia is now a mature technology after over a century of development. Recent distribution methods have appeared to reduce complexity and the potential for toxic leaks. Metal amines are solid salts in which ammonia is attached to a metal ion. From these, hexa-ammine-magnesium chloride has been considered in some detail as an indirect hydrogen carrier since it has both high gravimetric and volumetric hydrogen content. Furthermore, it is prepared from magnesium chloride, which is abundant, inexpensive, binds ammonia reversibly, and can be considered safe [38]. This material can be also compacted into a dense material, which holds approximately 615 kg-NH_3/m^3, or 110 kg-H_2/m^3, almost the same volumetric ammonia content as that of liquid ammonia. Due to a much lower ammonia vapour pressure (200 Pa) and release rate at room temperature, it is actually possible to handle this material safely at ambient conditions. Thus, hexa-ammine-magnesium chloride ($Mg(NH_3)_6Cl_2$) and similar materials now present a commercially viable option to mitigate the toxicity and corrosivity that liquid ammonia presents, justifying further the distribution of hydrogen via ammonia [42], although current developments are based on applications such as NOx reduction.

Nevertheless, the use of hydrogen carriers other than ammonia are being investigated. Despite the fact that in most industrial sectors one solution among multiple options usually tends to achieve a position of dominance, here it is conjectured that two or more chemical storage technologies could co-exist for various shares in the market. Although this is rare in most circumstances, hydrogen carriers and ammonia can complement each other very well, hence instead of competing, together supporting the transition of a carbon free economy. Thus, for ammonia to contribute to this economic transition, new technologies need to be developed for its consumption while allowing recovery of hydrogen with increased efficiencies. This review, for that reason, presents various methods of conversion from ammonia to power which seek to reduce inefficiencies across the whole process of conversion, transport and recovery of hydrogen.

2. Background

2.1. General characteristics

Ammonia is a colourless gas with a sharp, penetrating odour. Its boiling point is 239.8 K, and its freezing point 195.5 K, with a density of 0.73 kg/m^3 and an auto-ignition temperature of 930 K (compared to methane, 859 K) under atmospheric conditions. With an octane number of ∼130, it has a high heat of vaporization (1371 kJ/kg compared to ∼271 kJ/kg of gasoline) and can be handled as a liquid in thermally insulated containers. The ammonia molecule has a trigonal pyramidal shape with the three hydrogen atoms and an unshared pair of electrons attached to the nitrogen atom. It is a polar molecule and is highly associated because of strong intermolecular hydrogen bonding. The dielectric constant of ammonia (22 at 239.2 K) is lower than that of water (81 at 298.2 K), so it is a better solvent for organic materials. However, its dielectric constant is still high enough to allow ammonia to act as a moderately good ionising solvent. Ammonia also self-ionises, although less so than water [43]. The combustion of ammonia is challenging, due primarily to its low reactivity, but yields nitrogen gas and water, with a stoichiometric Air Fuel Ratio (AFR) of 6.06 by weight,

$$4NH3 + 3O2 \rightarrow 2N2 + 6H2O + heat \quad (1)$$

Liquid ammonia is used extensively as a non-aqueous solvent. The alkali metals as well as the heavier alkaline-earth metals and even some inner transition metals dissolve in liquid ammonia.

It is transported and contained in tanks under modest pressure, similar to propane. Production of ammonia as a transport vector for renewable energy and its subsequent reconversion to hydrogen are energy intensive steps but the handling and shipping infrastructure including regulations for transportation are already in place. It is potentially hazardous to inhale. However, ammonia is readily detected by its odour, and being lighter than air it rapidly dilutes in a spill. The energy content of ammonia is 18.8 MJ/kg (LHV), while hydrogen's is 120 MJ/kg [43].

Ammonia is known to have an indirect impact on ozone depletion through the formation of nitrous compounds in the atmosphere. These are currently considered a negligible contribution to ozone depletion [44], but will need to be considered for large scale ammonia utilisation especially considering NOx production.

2.2. Health and safety

Although the H&S issues associated with the use of ammonia in electricity/power generation are minimal when compared to transportation, Table 1, several considerations need to be taken into account. In addition, the increase in risk management legislation, industrial cases of dangerous circumstances, and human injuries involving ammonia release [45] need to be taken into account.

The National Fire Protection Association (NFPA), USA, has classified ammonia as a toxic substance, thus making it a chemical of high risk for health [46]. However, due to its low reactivity, the hazards it presents from accidental combustion or explosions are much lower than other fuel gases and liquids, Fig. 6.

Human exposure limits of ammonia depend on the legislation and exposure time. The limit is set between 25 and 50 ppm with dangerous consequences for exposure to concentrations above 300 ppm. For instance, the UK Health and Safety Executive (HSE), establishes an 8 hrs Time-Weighted Average (TWA) of 25 ppm, whilst its short-term exposure limit (STEL) is 35 ppm, compared to a 20 ppm TWA and 50 ppm STEL for Europe [47,48]. Table 2 provides some exposure guidance according to the NFPA. The variances clearly show that there is a need for research establishing more accurate values for industries and a variety of potential users. Interestingly, CO concentrations of 35 ppm TWA are recommended by the Occupational Safety and Health Administration (OSHA) [49].

A further set of recommendations for industrial interests is given by the Environmental Protection Agency (EPA), USA, and is known as Acute Exposure Guideline Levels (AEGL), which is used for ammonia. There are 3 categories, Table 3 [50].

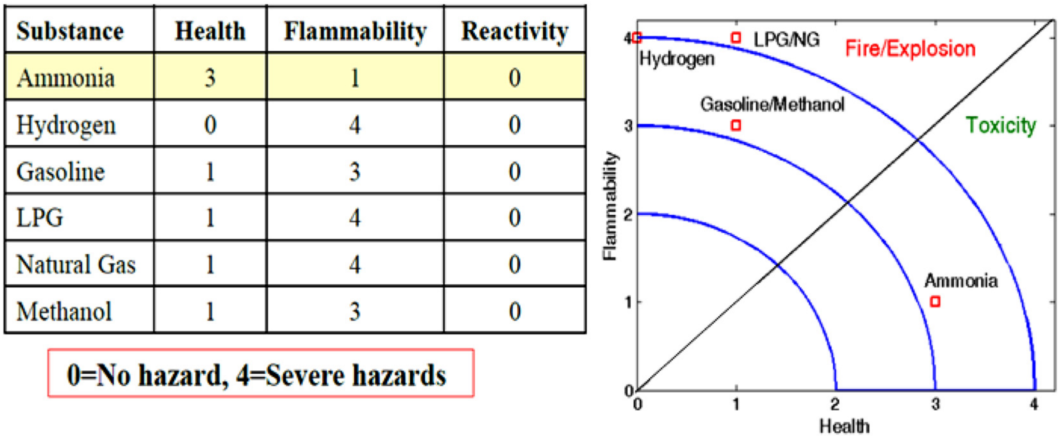
AEGL-1 is the airborne concentration above which it is predicted that the general population, including susceptible individuals, could experience notable discomfort, irritation, or certain asymptomatic, non-sensory effects. However, the effects are not disabling, and are transient and reversible upon cessation of exposure.

AEGL-2 is the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape.

AEGL-3 is the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience life-threatening health effects or death.

Table 1
Comparison between ammonia in transportation and electricity/power generation [46]. Courtesy of NH3 fuel association.

	Transportation	Electricity generation
Safety	Very Critical	Not as critical
Cracking	Cracking reactors heavy/expensive	Easily done
Storage tank weight	Critical	Not an issue
Storage tank robustness	Need to be “indestructible”	Existing storage tanks are suitable
Distribution	Complicated	Relatively simple
Start up	Problematic	Not many start ups
Operational	Pumps operated by non-professionals	Delivered/handled by professionals



Substance	Health	Flammability	Reactivity
Ammonia	3	1	0
Hydrogen	0	4	0
Gasoline	1	3	0
LPG	1	4	0
Natural Gas	1	4	0
Methanol	1	3	0

0=No hazard, 4=Severe hazards

Fig. 6. Toxicity and Fire/Explosion comparison of different fuels [46]. Courtesy of NH3 fuel association.

Table 2
Exposure guidance [46]. Courtesy of NH3 fuel association.

Effect	Ammonia concentration in air (by volume)
Readily detectable odor	20–50 ppm
No impairment of health for prolonged exposure	50–100 ppm
Severe irritation of eyes, ears, nose and throat. No lasting effect on short exposure	400–700 ppm
Dangerous, less than ½ hours of exposure may be fatal	2000–3000 ppm
Serious edema, strangulation, asphyxia, rapidly fatal	5000–10000 ppm

Table 3
EPA AEGL guideline [50].

Ammonia 7664–41–7 (Final) Expressed in PPM					
	10 min	30 min	60 min	4 h	8 h
AEGL 1	30	30	30	30	30
AEGL 2	220	220	160	110	110
AEGL 3	2700	1600	1100	550	390

According to some key points in the Compendium of Chemical Hazards of ammonia from the Health Protection Agency (UK) [51], ammonia has the following characteristics:

Fire

- Anhydrous ammonia is non-flammable. Ammonia vapour in air is flammable and may explode when ignited
- Chemically stable under normal conditions
- Emits poisonous fumes when heated to decomposition
- Use fine water spray and liquid-tight protective clothing with breathing apparatus

Health

- Exposure by any route may be dangerous
- Secondary contamination may occur
- CHIP Classification: toxic and corrosive
- Acute inhalation may result in irritation of eyes and nose with a sore throat, cough, chest tightness, headache and confusion
- Acute ingestion of ammonia solutions may result in burns to the mouth and throat
- Acute skin exposure may result in deep burns
- Acute eye exposure may cause inflammation, lacrimation and photophobia
- Chronic inhalation has been associated with increased cough, phlegm production, wheeze and asthma
- Ammonia is not considered to be carcinogenic to humans
- Ammonia is not considered to be a human reproductive or developmental toxicant
- Environment
- Dangerous for the environment
- Inform Environment Agency of substantial release incidents

Even though it is toxic for humans and most invertebrates (but not for fertilising purposes), ammonia is lighter than air, thus allowing leakages to move quickly through the rising plume whilst reducing exposure. However, it is usually released in ‘flashing’ liquid form, resulting in a dense aerosol cloud which cools as it evaporates –hence atmospheric dispersion models refer to low-lying, cold, droplet laden dispersion, which possesses greater risks [52]. Although it can be carried away due to its low density, eddy transport of agents and large/small scale wind variations could occur [53]. Ammonia can spread in a V-Pattern through buildings tracking wind; moisture and vegetation can also cause ammonia to become more turbulent, rolling rather than laying out in a defined pattern. Dry, windy and warm weather diffuses ammonia to the

Fig. 7. Explosions and cracks in cylinder by build-up pressure, respectively [54]. Courtesy of NH3 fuel association.

atmosphere faster than humid, cool and low wind conditions. High pressure inversions and humidity may cause the vapour to bounce and return to ground level before completely diffusing. Therefore, guidelines recommend always to have a refuge point upwind from the point of storage/use of ammonia, taking into consideration the larger scales. Moreover, although toxic, NH_3 becomes perceptible at very low, safe concentrations and is not carcinogenic.

Ammonia is also corrosive when mixed with water as pH rapidly increases to 11.6. The corrosiveness of ammonia will mix with body fluids like sweat and respiratory tract moisture to cause irritation. The environmental threat increases when NH_3 goes into a live body of water.

2.3. Fire/Explosions

Explosions with the sudden release of ammonia have been documented, Fig. 7. The build-up of pressure due to the boiling of the saturated liquid inside the container due to an external heat source can produce situations where the cylinder is unable to retain its structural integrity, resulting in rupture and release of the contained gas. If sparks or a heat source are presented the likelihood of explosion increases, with potentially catastrophic scenarios. These phenomena are known as BLEVEs (Boiling Liquid Evaporating Vapour Explosions). Although this has only been documented in large industrial facilities and for large containers, care is required when handling ammonia. Ammonia has a flammability limit that ranges from ~18 to 28% fuel mole fraction, Fig. 8. Therefore, dilution systems are needed to avoid this range when hot surfaces or combustion devices are in use nearby. The likelihood and severity of ammonia combustion hazards are mitigated somewhat by the fuel's slow reaction characteristics, particularly its relatively high ignition energy (2–3 orders of magnitude higher than common hydrocarbons) and low laminar burning rate more than four times less than methane (<0.010 m/s).

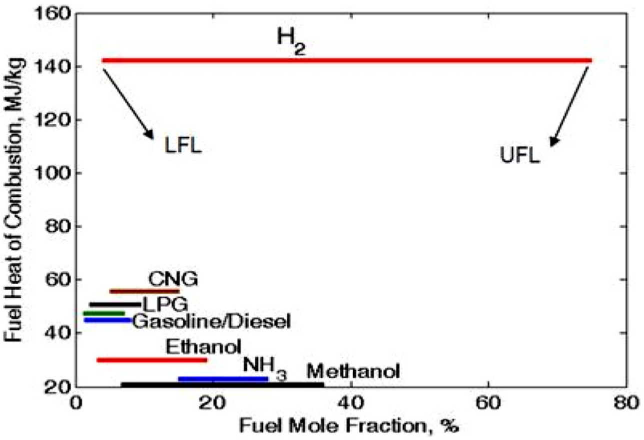


Fig. 8. Low and upper flammability limits of various substances [46]. Courtesy of NH3 fuel association.

2.4. Corrosive nature of ammonia

An important parameter to consider when selecting a chemical for power applications either as a working fluid or fuel is to recognise the impact of the former on materials required for pipelines and structural components, thus increasing the complexity of some systems and potential applicability of such chemical. In the case of ammonia, the benefits of greater versatility than hydrogen get slightly blurred as NH_3 is incompatible with various industrial materials. NH_3 is corrosive to copper, brass and zinc alloys, forming a greenish/blue colour corrosion. NH_3 should not be mixed with bromine, chlorine, iodine and hypochlorites as ammonia is an alkaline reducing agent and reacts with acids, halogens, and oxidizing agents. Cole–Parmer [55] have produced a comprehensive but not exhaustive list of compatibility results between ammonia and various industrial materials, Table 4. Thus, careful material selection needs to be performed when considering ammonia for power generation.

2.5. Current position of ammonia for power

2.5.1. Production process

Historically, ammonia has been manufactured as a fertilizer to enhance food production via the well-established Haber–Bosch process. Approximately 97% of nitrogen fertilizers are derived from ammonia [56]. In the latter, high purity (99.99%) hydrogen and nitrogen are typically reacted together at a temperature between 623.2 and 823.2 K at pressures between 10 to 25 MPa in the presence of a catalytic material [9]. The hydrogen is mainly sourced from hydrocarbons - obtained from steam reforming of methane and partial oxidation of coal - resulting in a highly carbon intensive process [57]. The production of ammonia consumes an esti-

Table 4
Material compatibilities of ammonia as in [55], Chemical Compatibility Database Copyright © Cole-Parmer. A: excellent; B: good- minor effect, slight corrosion or discoloration; C: fair- moderate effect, not recommended for continuous use, with softening or loss of strength, swelling may occur; D: severe- not recommended; N/A: information not available. Courtesy of © Cole-Parmer.

ABS plastic	D	CPVC	A	Polycarbonate	D
Acetal (Delrin ®)	D	EPDM	A	PEEK	A
Aluminium	A	Epoxy	A	Polypropylene	A
Brass	D	Fluorocarbon (FKM)	D	Polyurethane	D
Bronze	D	Hastelloy-C ®	B	PPS (Ryton ®)	A
Buna N (Nitrile)	B	Hypalon ®	D	PTFE	A
Carbon graphite	A	Hytrel ®	D	PVC	A
Carbon Steel	B	Kalrez	A	PVDF (Kynar ®)	A
Carpenter 20	A	Kel-F ®	A	Silicone	C
Cast iron	A	LDPE	B	Stainless Steel 304	A
Ceramic Al2O3	N/A	Natural Rubber	D	Stainless Steel 316	A
Ceramic magnet	N/A	Neoprene	A	Titanium	C
ChemRaz (FFKM)	B	NORYL ®	B	Tygon ®	A
Copper	D	Nylon	A	Viton ®	D

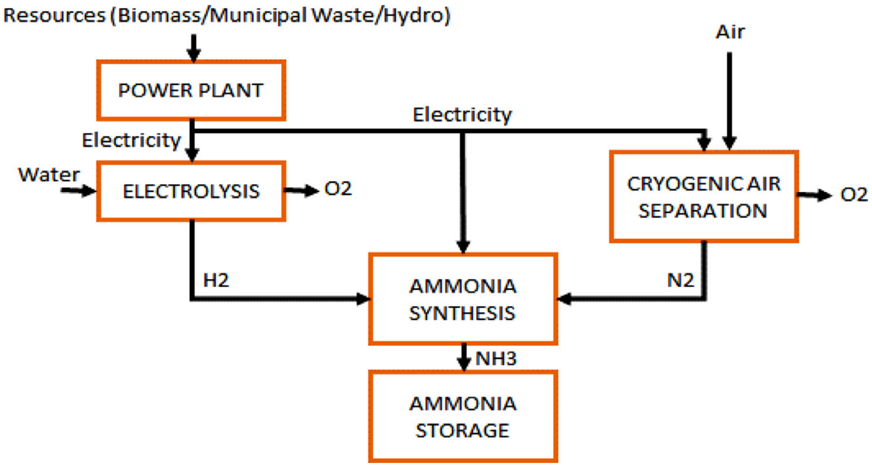


Fig. 9. Ammonia production via hydrogen electrolysis and H-B process. Reprinted from [59] with permission from J Cleaner Production, Elsevier.

mated 1.8%–3.0% of all global energy [56], mainly via fossil fuels, making it one of the single largest producers of carbon dioxide. Moreover, the production process generates vast quantities of NOx that through Best Available Techniques need to be removed via Selective non-catalytic reduction, thus increasing cost of operation [56]. Therefore, new technologies seek to produce hydrogen from carbon-free sources such as electrolysis of water using sustainable energy, thus mitigating the excessive production of carbon emissions while increasing flexibility of production and recovery of stranded sources internationally. Recent energy studies [58] conducted using data obtained from the facility at Leuna, Germany, determined that the use of water electrolysis and pressure swing adsorption (PSA) to develop decentralised Haber–Bosch processes are feasible options as potentially competitive systems for the production of ammonia, which can be employed for energy storage. Currently, ammonia production from electrolysed hydrogen accounts for approximately 0.5% of global ammonia production [9]. However, the greatest limitation to this process are the economics, which are continually being improved through studies that have been conducted to show the considerable potential for the production of hydrogen and ammonia via electrolysis product of sustainable sources, Fig. 9, with companies already investigating the development of industrial facilities to pursue the reduction of GHGs while improving feedstock and resilience of these ammonia production methods. Nuclear power has also been considered [59], although initial Life Cycle Assessments show their detrimental impact on various aspects related to confinement and disposal of radioactive material, Fig. 10, thus making renewable sources the most promising alternative for the near to intermediate future.

As stated, current ammonia production (brown ammonia) is mainly produced through reformation of hydrogen from natural gas [60], thus producing an annual global total of ~290Mt of CO_2, approximately 1% of carbon dioxide emissions. Unless these emissions are captured and stored or utilised, the sustainability of any new cycle running on brown ammonia is significantly detrimentally affected. Therefore, it is highly desirable for the hydrogen obtained for the production of ammonia to be obtained from alternative sustainable sources such as wind, biomass gasification, solar. Recent research has been undertaken to determine energy requirements from various renewable technologies to produce green ammonia [60], showing that the use of biomass can potentially produce higher CO_2 emissions but at lower power requirements (although these processes may be carbon neutral), while other sources such as wind/solar can have negligible carbon emissions with reduced power consumption compared to fossil reformation, i.e. 14.248 kW/kg_{NH3} for green ammonia compared to 17.113 kW/kg_{NH3} for brown ammonia, hence demonstrating that ammonia can be produced via renewables to increase the sustainable, greener nature of new power cycles.

2.5.2. Market

The consensus among analysts is that there is a high degree of uncertainty regarding the future outlook for the grid-scale energy

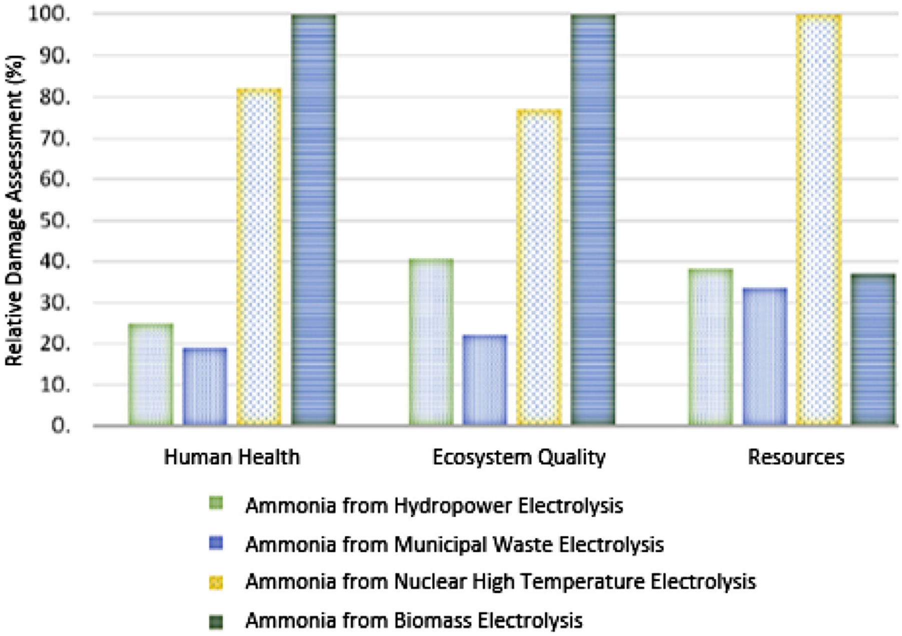


Fig. 10. Damage assessment for different ammonia production sources. Reprinted from [59] with permission from J Cleaner Production, Elsevier.

storage market because of the lack of established storage technologies and the uncertainty concerning government subsidies and regulatory frameworks to incentivise markets around the world. However, a number of analysts have attempted to estimate the size of the worldwide energy storage market: the Energy Research Partnership [61] concluded the global market could be worth in excess of $600bn over the coming 10–12 years while Navigant Research estimate global investment in energy storage would total $68bn between 2014 and 2024, and be worth over 15$bn/yr by 2024 [62].

Hence, since ammonia is a disruptive energy storage technology that can be realised using existing processes for the synthesis and storage of ammonia, it can then benefit from the economic predictions previously stated, as it has the potential to be brought to market both relatively quickly and in significant volume. Generally, the ammonia market is estimated at $91–225bn per year [63]. Therefore its production for either power or agriculture will permit more flexible energy options worldwide. It is difficult to estimate the effect of a reliable decoupling mechanism on the energy mix as a whole. However it is possible to estimate the effect of a percentage swing to the renewables away from the combined gas power generation. The economic cost to society of a 1% swing would be around $1.5bn a year worldwide, thus showing highly profitable profiles for interested companies working on the topic.

For these scenarios to happen, capital costs for ammonia technologies need to be competitive against other forms of energy storage. Estimates of the capital costs ($/kW) for ammonia energy storage (between 1350 and 1590 $/kW [29]) indicate it will be competitive compared to battery storage technologies such as Li-ion, NaS and VREDOX (between 850 and 3,660 $/kW [64]), but with the advantage of considerably cheaper (~2(O)) capacity costs inherent in a liquid fuel. Furthermore, it is not constrained by local geology in the same way as compressed air or pumped hydro.

However, a number of competing technologies are also under intensive development, including compressed air, thermal, and electrochemical (battery) storage, and so predicting with confidence penetration into this uncertain market is challenging.

2.5.3. Distribution

Anhydrous (without water) ammonia is distributed across the world via pipelines, railroads, barges, ships, road trailers and storage deports. Long term experience of ammonia distribution from the first quarter of the first century has facilitated the global deployment of ammonia, ensuring that well established distribution networks exist across the world.

In the USA, the NuStar Line (3070 km long) transports ammonia from Mississippi into the heart of the corn-belt region of the central and northern States of the Union, where it can be distributed still further via the Magellan line (~1900 km long). Both lines deliver approximately 2.9 million tons of ammonia per year [65]. In Eastern Europe, a pipeline runs from TogliattiAzot's plant (Tolyatti, Samara) to Odessa in the Black Sea and is one of the largest (~2400 km long) with a capacity of 3 million tons per year [66].

Western Europe alone transports around 1.5 million tonnes of ammonia by railway every year. Pipeline transport of liquid ammonia in the European Union is not as significant as in the US and in Russia. Only relatively short pipeline systems are in operation. Greater quantities are transported using insulated tank cars capable of storing up to 126,800 litres [67]. When pipeline or railway connections are not possible, then large barges, road trailers, nurse tanks and even bottles are used to transport ammonia across regions. Therefore, vast infrastructure exists to support the concept of using ammonia for distribution of stored energy.

3. Ammonia for power

Grid-connected energy storage is widely accepted as an enabler for further deployment of renewables. As energy networks incorporate more decentralised power generation, storage is also likely to play a significant role in load balancing and strengthening distribution grids. Significant renewable resources are often found in isolated geographies or locations with no grid access. Examples include the wind resources in the mid-West of the US and the north of the United Kingdom (e.g. the Orkneys or Hebrides), and Photovoltaic resources in Africa, the Middle East and Australia. The cost of a conventional distribution grid connection can be a significant barrier to exploiting such resources. Ammonia, on the other hand, is competitive against a variety of transmission systems, Fig. 11 [68]. Therefore, the viability of ammonia as an energy carrier rests on the overall conversion efficiency of the process, including

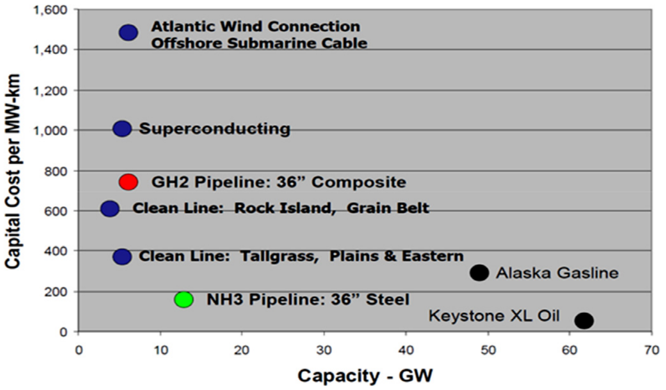


Fig. 11. Cost / capacity comparison for selected power transmission methods. Reprinted from [68] with permission from ASME.

the ability to convert it at the necessary power levels at the point of consumption with minimal environmental impact.

3.1. Initial attempts to use ammonia for power

The industrial revolution brought an endless number of patents and new devices for power and transportation, with most utilising steam as the preferred working fluid. This was not always the case, with some inventors seeking competitive advantage through the development of new, more complex systems. Sir Goldsworthy Gurney - pioneer of the use of oxygen and hydrogen for lighting and transportation devices - built upon, amongst others the work of Trevithick's steam carriage, to develop what was probably the first ammonia gas locomotive, which required little change from an ordinary steam engine [69]. However, resistance from others with vested interests opposed the new invention and he faced competition from steam railways, which was backed by large financial and political capital. Similarly, there were attempts to replace horse drawn street-cars in New Orleans with ammonia powered engines, although these lost out to electrification projects [70]. Hence it was not until the 20th century that transport solutions based on ammonia were developed.

The first part of the 20th century also saw the development of what became known as the Haber–Bosch process, where atmospheric nitrogen is fixed to industrially produced ammonia. It is named after its inventors, Fritz Haber and Carl Bosch, who obtained the Nobel Prize for this work. The production of ammonia in this way revolutionized farming by introducing a cheap and readily available fertilizer, and it is estimated that half the world's population increase is due to the use of fertilizers produced via the Haber-Bosch (HB) process [71]. Nitrogen fixed from air played a pivotal role in armament production in Germany in World War I and II for production of ammonium nitrate which has also been used as a transport fuel where diesel and petrol were not available. For instance due diesel shortages in Belgium during World War II, engineers adapted approximately 100 buses to run on liquid ammonia. Although this experiment only lasted until carbon-based fuels were available again, the use of ammonia with a small amount of coal gas demonstrated that NH_3 could be used as power generation fuel [72]. Moreover, further works would follow to use ammonia as working fluid in advanced cycles, thus wide spreading the chemical for power generation purposes.

3.2. Ammonia power cycles

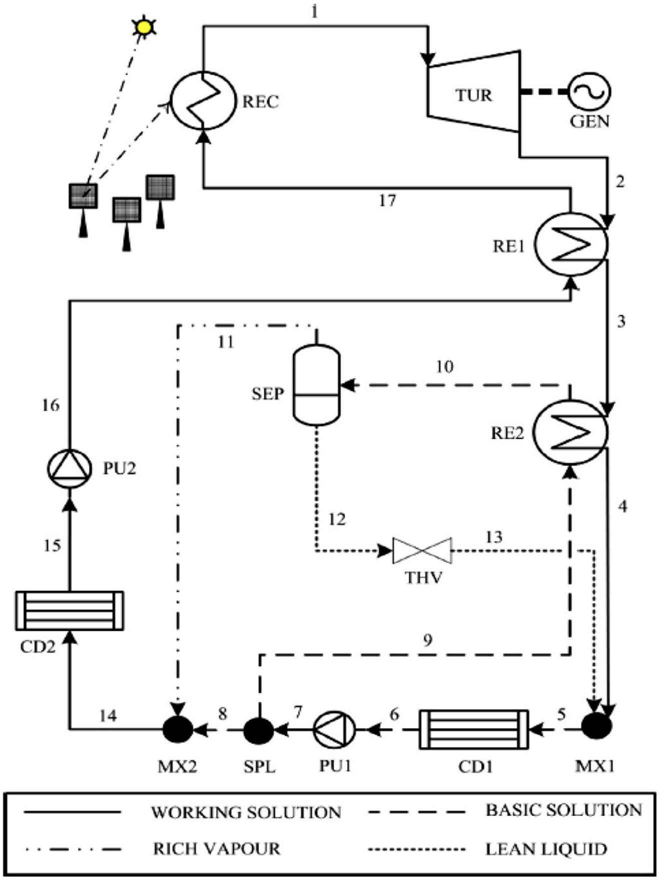


Fig. 12. Kalina cycle with central solar receiver. Reprinted from [76] with permission from J Energy Conversion and Management, Elsevier.

Although ammonia as a working fluid or carbon dioxide scrubber material in power cycles is not directly linked to the use of the chemical for energy storage, utilisation of NH_3 into these cycles can present an opportunity to initially recover the chemical for storage, use it as working fluid and finally employ it for release of energy via fuel cells, engines, rockets or other technologies, increasing overall system efficiency. Thus, a comprehensive review of the literature on the use of ammonia in power cycles is presented to complement the various uses of ammonia for power.

3.2.1. As working fluid in power cycles

In 1984, Alexander Kalina developed a cycle to be used as a bottoming cycle instead of the Rankine cycle in Combined Cycle (CC) power plants and demonstrated that the cycle can reach higher efficiencies than the Rankine cycle for heat recovery [73]. The essence of the cycle is the use of an ammonia-water mixture whose change in composition affects the thermodynamics and transport properties of the mixture. Since the boiling temperature of ammonia is lower than water it can then be used for low grade heat recovery. Moreover, designs for steam turbines can still be used with such a mixture due to the close molecular weight between water and ammonia [74]. The use of the Kalina Cycle (KC) with this ammonia-water working fluid can bring up to 20% enhancement compared to other cycles [75]. Therefore, it has been used for recovery of renewable energies produced from sources such as geothermal applications, coal-fired steam plants, triple cycles, gas turbine modular helium reactor heat recovery, solar plants (Fig. 12), etc. [74,76] and even conventional power applications such as diesel engines [77].

Related work has suggested that mixtures of 84% ammonia – 16% water (in mass fraction) can produce superior thermodynamic and economic benefits [78]. It has been recognised that combinations of the cycle with mixtures between 78% to 82% of ammonia concentration can provide the best operating conditions in such a cycle [75], with some authors even suggesting concentrations as low as 50% for especial geothermal applications [79]. Therefore, the importance of ammonia in the performance of the cycle is clear, allowing researchers to explore its properties and concentration changes through the cycle to unveil problems such as irreversibilities that can lead to potential design improvements [75]. More recent studies have been concentrated on improvements to the cycle, especially for geothermal applications [80,81].

The use of the cycle at higher temperatures is questionable due to the nitridation effect, resulting from thermal decomposition of ammonia, that can potentially corrode equipment [79]. However, further work by Kalina and other researchers has demonstrated its successful usage at higher temperatures under industrial conditions [76]. Therefore, research groups have also sought to evaluate the use of ammonia-water mixtures for energy recovery from high energy devices such as concentrated solar power plants. However, such studies concluded that the use of the cycle was more expensive than the use of state-or-the-art steam Rankine cycles, presenting a difference of ~20% cost per MWh^{-1} [76]. Further studies have sought improvements of systems with both high temperature and pressure inlets ($> 773\,K$, $> 10\,MPa$). New numerical designs based on the number of recuperators through the cycle, turbine outlet pressure, separator inlet temperature and the separator inlet ammonia mass fraction played an important factor to maximise cycle efficiency up to 31.47% with an ammonia concentration of 80% [82].

When the KC is integrated to other cycles such as the Rankine, the system can be operated in various ways to provide power in non-heating seasons and power plus heat during the winter, thus allowing operation as either a Kalina cycle or an ammonia-water Rankine cycle (AWRC) [83]. Studies on these cycles have shown that increasing the ammonia mass fraction increases the total exergy destruction cost rate as well as unit cost of electricity produced by the turbine, showing the benefits of using an ammonia-water mixture [74].

Ammonia is also considered a good refrigerant, with high potential for future use in domestic applications in addition to its current large industrial use, i.e. in breweries and warehouses [84]. Due to its low Global Warming Potential –relative heat trapped by the gas compared to CO_2- (GWP < 1 based on a 100 year time horizon), high critical pressure and low Cp, some commentators believe ammonia could become one of the most used refrigerants of the future for small scale devices, especially if advances in mixture can be combined with revolutionary heat exchanger designs at microscale level [84–88]. Furthermore, recent studies have used the KC for power generation in combination with ammonia-water absorption refrigeration to cogenerate power and cooling. The use of throttling valves, evaporators and removal of expansible working fluid for cooling provided 14–49% higher efficiencies with 3.6–70 times higher generated cooling quantities, showing that high ammonia mass fractions produce better performance and lower costs [89]. A similar study has been conducted with a Brayton-Rankine combined cycles to integrate ammonia-water refrigeration [90]. The study placed a particular emphasis on the effect of the ammonia condenser temperature on the plant performance between summer and winter, i.e. from 313 to 278 K. Results showed an increase in Coefficient of Performance (COP) and cooling efficiency, with a net power output increase of ~400 kW. This is a consequence of the air leaving the evaporator of the system at cooler temperatures. Low grade heating sources have also been studied through numerical and parametric analyses, showing that combination of power and cooling provide higher exergy efficiencies (available useful power) and net power outputs [91].

Cooling and power generation can also be combined to produce water heating through the use of ammonia-water mixtures, as demonstrated numerically by Mohammadi et al. [92] who proposed a plant capable of producing 30 kW power employing 8 kW cooling with efficiencies above 67%. Similar studies have been conducted to determine energy and exergy values for solar driven systems [93], optimization of three-stage (Brayton, Rankine and Kalina) combined cycle power systems [94] and flue-gas energy recovery from devices such as gas turbines, internal combustion engines and high temperature fuel cells [95]. The cycle can also be combined with energy solutions such as gasification and solid fuel cells, thus achieving high efficiencies $> 58\%$ with alternative energy sources [96]. The results demonstrate that the use of ammonia-water cycles can not only increase efficiency, but also provide versatility of operation at medium power outputs.

Versatility of ammonia and its properties allow the chemical to be used also as an organic fluid for power generation in Organic Rankine Cycles (ORC). Due to its properties, it has been compared to other fluids such as R245fa, R236ea, isobutene, isopentane, pentane, toluene to support energy production from the conversion of renewable energy [97,98]. During some of the tests conducted to develop Ocean Thermal Energy Conversion (OTEC) systems, which are essentially technologies based on platforms that generate energy through temperature differential to drive heat engines, the use of ammonia as the working fluid has showed a higher work capacity than other organic working fluids [97]. Therefore, the use of ammonia in these technologies has increased over the years. It must be noted that although ammonia has the properties to allow production of vapour to run turbines at low temperature differentials [98], the technology is still controversial in the sea due to the toxic properties of NH_3 to water living organisms.

Some futuristic designs have also considered the use of water and/or ammonia heat transfer cycles for smaller systems such as lightweight space radiators [99]. Due to the heavy reliability on radiator subsystems in space, increased efficiency coupled with reduced mass is of strategic importance in space thermal systems. Thus, this research showed that after evaluating various working fluids, the most promising design would be a carbon composite heat pipe with a working fluid of liquid water or ammonia and triangular fans.

3.2.2. *Carbon capture and storage*

One way to increase energy efficiency is by improving combustion processes that use fossil fuels. Thermal efficiencies have been increased as a consequence of new materials and designs that allow higher temperature combustion systems. These new properties have established fundamental concepts for more advanced techniques that not only increase combustion efficiency but also are capable of ensuring low carbon dioxide emissions as part of the global commitment to tackle climate change.

One of these techniques is the use of carbon capture and storage (CCS) systems via post-combustion capture. The concept is based on recovering CO_2 at the end of the gas turbine, once that power has been produced using conventional fuels [100–103]. For this aim amine scrubbing is the main process in which aqueous solutions of alkyl amines are used to react with carbon dioxide to capture it from exhaust gases. Aqueous monoethanolamine (MEA) is the most commonly used amine for scrubbing CO_2 [104]. The stable and reliable properties of monoethanolamine derive from its primary amine and primary alcohol composition. Thus, it has been assessed for its use in fossil power plants to reduce carbon footprint. Since the CO_2 process is reversible, up to 80% of the emissions can be captured but through a highly energy intensive process [105]. Another challenge for this technology is the low reaction temperature needed to increase the chemical reaction efficiency - since the CO_2 is released at elevated temperatures - resulting in the requirement for flue gases cooling before scrubbing.

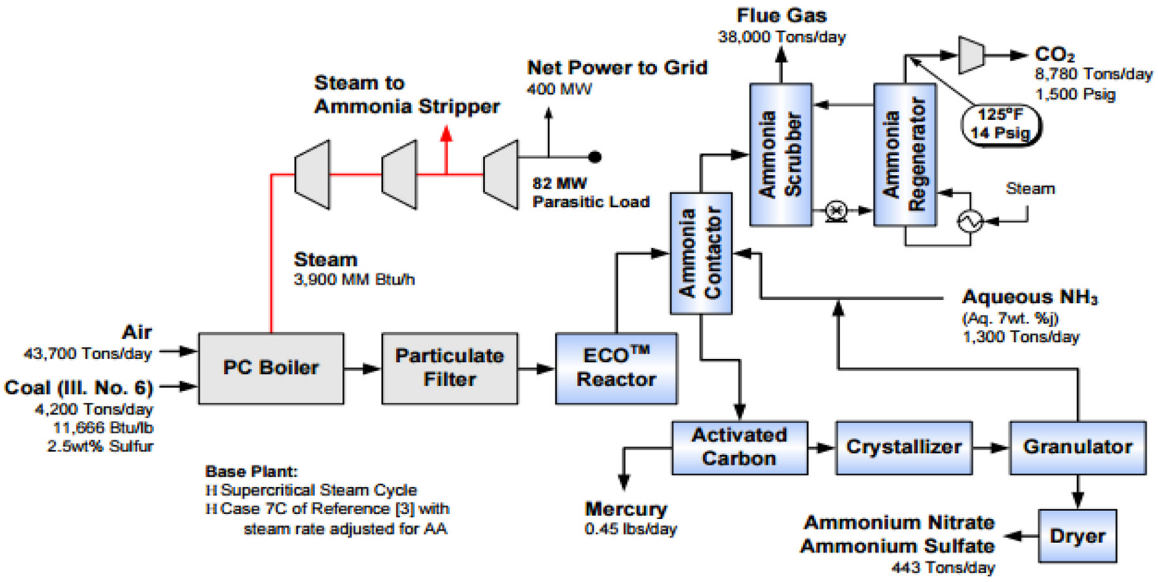


Fig. 13. Power plant with aqueous ammonia multi-pollutant control system [106]. Courtesy of NETL, USA.

One way in which capture efficiency can be increased is by using a low cost solvent capable of lowering the energy requirements for regeneration whilst allowing higher CO_2 loading capacity than that of MEA. Ciferno et al. [106] suggested the use of aqueous ammonia as an alternative solvent, potentially increasing the CO_2 capacity and lowering parasitic loads by 15%, with a decrease of net power plant heat rate of 15% compared to MEA, Fig. 13. Moreover, other compounds such as SOx, NOx and mercury could also be removed along with ammonia, making it an attractive chemical for multi-pollutant capture in power plants [107]. Aqueous ammonia does not present the problem of absorbent degradation caused by sulphur and oxygen in the flue gas, while MEA is susceptible to this degradation [108]. Finally, MEA has a maximum absorption of 0.36 kg_{CO2}/kg_{MEA} with a removal efficiency of 90% compared to 0.9 kg_{CO2}/kg_{NH3} and an absorption efficiency between 95% to 98% for aqueous ammonia [109].

As amines share many material compatibilities with ammonia, retrofitting an MEA scrubber for an ammonia system would be of relatively low cost. Another benefit is the low cost of the ammonia process compared to MEA, which is only ~70% (67.3$/tonne v 86.4$/tonne) of the price of the latter in an ammonia market with a decreasing cost trend, a consequence of the increased production of ammonia from developing countries [110].

Although the use of ammonia as a carbon capture solvent is possible [111], there are challenges before industrial deployment of this technology. For example, the temperature of the flue gas has to be lowered for CO_2 absorption with ammonia that could vaporize in the absorption towers, causing health and safety issues. Equally, NH_3 reactions with CO_2 depend on pressure, pH and temperature, making the application of ammonia carbon capture more flexible but potentially more difficult to control than MEA processes. However, it is recognised that good progress can be achieved with even further potential of improvement employing ammonia-based systems [110].

3.3. *Fuel cells*

Recently, researchers have proposed a way of making it easier and cheaper to run hydrogen fuel-cell vehicles by filling them with ammonia. The ammonia can be stored easily in tanks similar to those found in gasoline filling stations and then cracked using relatively cheap sodium or lithium catalysts rather than the current expensive transition metal catalyst systems [112,113]. At the recent ARPA-E's Summit [114], Director Grigorii Soloveichik presented his vision for future transportation using hybrid vehicles that combine plug-in batteries and fuel cells. He presented the different driving ranges of various sustainable fuels, emphasizing the potential of ammonia. In terms of energy density, liquid ammonia contains 15.6 MJ/L, which is 70% more than liquid hydrogen (9.1 MJ/L at cryogenic temperature) or almost three times more than compressed hydrogen (5.6 MJ/L at 70 MPa). In terms of driving range, a 60.6 L fuel tank of ammonia provides a driving range of 756 km, almost twice the range of the same volume of liquid hydrogen (417 km) and three times the range of the same volume of compressed hydrogen (254 km) [114].

Fuel cells (FC) using ammonia have also been studied extensively for stationary power generation and as power sources for transport. Although most cells developed to-date are based on hydrogen as fuel, it is recognised that the storage of hydrogen for such purposes is still challenging and expensive. Thus, chemical storage of hydrogen in other liquid fuels could provide a solution for high density chemical energy storage. Methanol, ethanol, n-octane, ammonia and methane are potential candidates to supply H_2 to these fuel cells. Therefore, the concept of integrated fuel processor and fuel cell (FP-FC) has gained considerable attention in the last decade.

Investigations using ammonia, which undergoes thermal cracking within a high temperature fuel cell to produce hydrogen and nitrogen at the anode [116], have shown that the maximum amount of work that can be obtained from ammonia is ~0.33 MJ/mol_{NH3}, although if the work is calculated in terms of the H_2 that can be obtained from the cracking of ammonia, the maximum value is 0.22 $MJ/mol_{CrackedH2}$, a value that is similar to other more conventional fuels, i.e. methane, n-octane, methanol, etc. [117]. Thus, ammonia can be used indirectly to produce the required hydrogen for energy production in fuel cells, as the ammonia is cracked by the anode within the cell and thus there is no need for a fore-line ammonia reformer [115], Fig. 14. Therefore, ammonia, as a well-established fuel with decades of synthesis, handling and utilisation expertise across the world, started attracting significant attention as fuel for fuel cells during the last decade [118–123].

Moreover, ammonia fuel cells can also be used to recover waste energy from low temperature process streams. Zhu et al. [124] re-

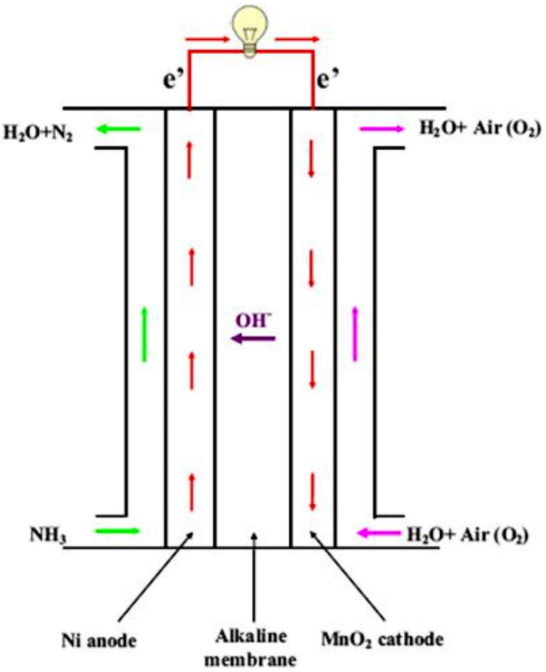


Fig. 14. Direct ammonia alkaline anion-exchange membrane fuel cell. Reprinted from [115] with permission from Electrochem Solid State Lett, IEEE.

ported that low-grade thermal energy can be converted into electricity using ammonia regenerative batteries. The batteries were assessed at different solution concentrations, flow rates, cell pairs and circuit connections to study their performance, which reached a 5% energy efficiency relative to the Carnot efficiency. As in other fuel cells, current could be increased using stacked cells, showing that the technology could be a promising option for future waste recovery.

Therefore, this review highlights the considerable evolution of fuel cells technology over the past decade, suggesting that further developments are highly likely and that fuel cell will remain a plausible option for the use of ammonia for power applications.

Fuel cells are categorized according to their operating conditions and electrolyte material, with six major systems as follow [125],

- Alkaline FC
- Phosphoric Acid FC
- Solid Oxide FC (SOFC)
- Molten Carbonate FC
- Proton Exchange/Polymer Electrolyte Membrane (PEM) FC
- Direct Methanol FC

Another category that could fit into the molten systems is Molten Hydroxides [126].

3.3.1. Solid oxide FC

The relatively small size of FCs make them good candidates for small scale energy production, i.e. distributed energy systems such as family homes, mobile applications such as cars and small commercial vehicles, small industrial processes, etc. For example, vehicular applications of ammonia based fuel cells are currently studied by many research groups with a view to developing new automotive units via Solid Oxide FCs. Energy produced by various electrolytes has been studied, finding that proton-conducting electrolytes (SOFC–H^+) have superior efficiencies to ion-conducting electrolytes (SOFC–O) [127–129]. This is confirmed in [130] where SOFC are shown to have significant advantages on combination of environment-friendly power generation with fuel flexibility.

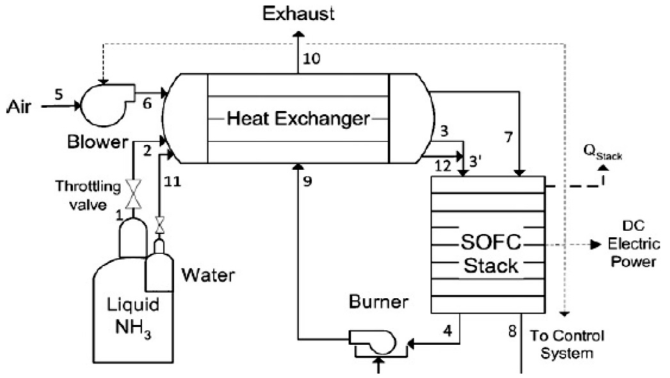


Fig. 15. Configuration of the introduced ammonia-fuelled portable SOFC system. Reprinted from [118] with permission from J Power Sources, Elsevier.

For the use of combined heat and power applications in automotive systems, Fig. 15, it has also been recognised that SOFC–H^+ systems can reach efficiencies in the range of 40–60% and exergies of 60–90% based on the conditions of operation. Moreover, reduction in cost, size and operating temperature demonstrate that the technology has a future in transportation [131]. However, loss of the exergy in SOFCs remains a significant technological challenge and the efficiencies are highly dependent on temperature variations [116], requiring further research in this topic to make the technology competitive to other ammonia-based systems.

The advantages of FCs have allowed some researchers to integrate FCs in other energy production units creating hybrid systems that produce energy in the ~kW range. For example, simulations of a system using solid oxide fuel cells and a Stirling engine for a bottoming cycle in a power plant were conducted using ammonia as main fuel [132]. It was found that the simplest design was achieved using ammonia as it can be directly fed into the fuel cell unlike other potential fuels such as natural gas, DME, ethanol and methanol which required fore-line reforming. It was found that it was sufficient to preheat NH_3 to the desired inlet temperature of 923 K with no requirement for desulphurisation or pre-reformer reactors. However, the efficiency of the total hybrid cycle using ammonia was the lowest (57.9%) due to the higher mass fuel flow rates, lack of reformers to increase operating temperature and less energy for the bottoming cycle. Similarly, the reduction of inlet temperature showed minimum changes using ammonia compared to all the other fuels. The results for the solid oxide fuel cell using ammonia were similar to those from other sources that showed efficiencies ~50% [116]. Other studies carried out by Wei and En-ke [133] demonstrated that the use of ammonia to fuel SOFC provides more sustainable energy production than the use of gasoline, diesel and even hydrogen in a driving range of 100 km.

Other researchers have also worked in improving the performance of ammonia based fuel cells using various materials and film configurations to increase currency at lower degradation rates. Liu et al. [134] used Scandia-stabilized Zirconia (SSZ) based thin films to obtain high power output performance from ammonia, showing that ammonia generated higher power densities than hydrogen based FCs at particular temperatures (973 and 1023 K). Similar work was performed by Zhang et al. [135] and Ma et al. [136] who demonstrated that at 1073–1123 K Yttria-stabilised Zirconia (YSZ) thin films running on ammonia had a comparable performance to those obtained from using hydrogen as a fuel, with the cell fuelled by ammonia displaying the same electrolyte resistance but a slightly larger interfacial polarization resistance [136]. Moreover, Fuerte et al. [137] demonstrated that such a cell has an internal resistance that behaves independent of the used fuel and that only slight differences exist in polarization resistance and

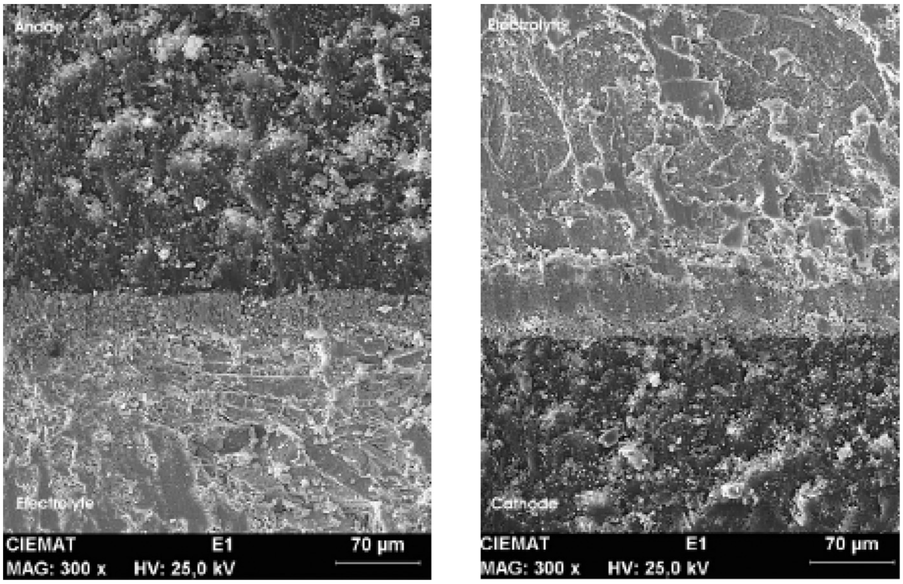


Fig. 16. SEM micrographs of a cross-section of an YSZ tested cell. Left) Anode/electrolyte and, right) electrolyte/cathode. Reprinted from [137] with permission from J Power Sources, Elsevier.

low current density at 973 K, probably due to a slower ammonia decomposition at this temperature. Experiments demonstrated that no severe changes or deterioration to cell performance were observed after long operation periods, Fig. 16. Other researchers [138] carried out experiments with a fuel cell that incorporated nickel and a doubly doped barium-cerate electrolyte and an anode of europium doped barium cerate. The activity of the fuel cell was reported to be superior to other catalysts, with results that suggested that ammonia could be used as a fuel at temperatures as low as 723 K.

Xie et al. [139] reported the development of a number of different electrolytes amongst which $BaCe_{0.9}Nd_{0.1}O_{3-\delta}$ (BCNO) powders were deposited as a thin layer on NiO-BCNO anodes with $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ used as cathodes. These cells were tested with ammonia and hydrogen and their results showed good performance with ammonia, with a power density of 3150 W/m^2 compared to 3350 W/m^2 produced when using H_2, and both producing voltages of ~0.95 V. Similar work has been carried out by other institutions using other ceramic composites [140–143] and ammonia blends [144] demonstrating that efficiencies of the fuel cell can increase up to 30% depending on the blend's lower heating value as well as material properties.

Some studies have developed thermo-electrochemical analyses using 2D Computation Fluid Dynamics (CFD) models in order to determine the performance of ammonia-fuelled SOFCs. The studies considered reactions and heat and mass transfer, finding that the decomposition of ammonia greatly increases at high temperatures above 970 K and has a significant impact on the electrical output of the fuel cell. Moreover, inlet temperatures were found to influence the performance of the device, with higher temperatures decreasing the electrolyte Nernst potential. Although a higher inlet temperature is desirable to achieve higher electric outputs, the results suggest that careful consideration is required to determine the inlet temperature into the system. The simulations carried out suggested that a decrease in operating potential can increase fuel utilization considerably by reducing negative temperature gradients and that a reduction in inlet gas velocity was an effective method to reduce the temperature gradient produced by the decrease in ammonia decomposition. Further analyses on SOFC technology can be found in the comprehensive review by Afif et al. [125].

Most recent achievements have been attained using SOFCs. Kyoto University announced a new device able to produce power outputs of one kilowatt. The device attained “direct current power generation efficiency” in excess of 50% and reached 1,000 hours of continuous operation [145]. Although the report claims that this is the most powerful device of its type, the longevity of the device is also of note. The group has been working with nickel based materials [146], and zirconia, which although inferior to gadolinia at the time, was taken forward probably as a consequence of its durability. This fuel cell uses direct supply of ammonia, demonstrating that the power generated from ammonia was at the same level as the one using hydrogen. Previous studies performed by the group tested different types of ammonia SOFCs, thus providing further data for this development [147]. Kyoto University also announced the use of auto-thermal cracking devices to modulate the power production of these fuel cells, demonstrating the possibility of high-speed activation without using external heating of NH_3-based SOFC.

3.3.2. Alkaline FC

Alkaline FC have also been studied over the years, with works that go back to the 1960s [125]. Experimental trials [148] have demonstrated that in contrast to acid PEM fuel cells, alkaline FC can tolerate ammonia. Because of the simplicity of the conversion reaction and the absence of carbon monoxide and carbon dioxide, hydrogen produced by ammonia cracking is ideal to fuel alkaline fuel cells. Thus, new programs of development have started in various parts of the world. Specifically, The Alkammonia Project aims to test the efficiency of alkaline ammonia-fed fuel cells in providing power in remote areas for telecom base stations, usually powered by diesel engines [149]. These types of projects are assessed by groups such as Cox et al [150] who recently carried out Life Cycle Assessments for Alkaline Fuel Cells (AFCs) fuelled with cracked ammonia including all the components of these devices and comparing them to diesel engines, Fig. 17. The results suggest that recycling of components can have a relatively small impact on costs, but further research is required on improving cell lifetime, power density and fuel consumption. It should be emphasized that the results are highly dependent upon the source of ammonia used (either reforming, electrolysing, partial oxidation or biomass gasification). Studies like these are extremely scarce,

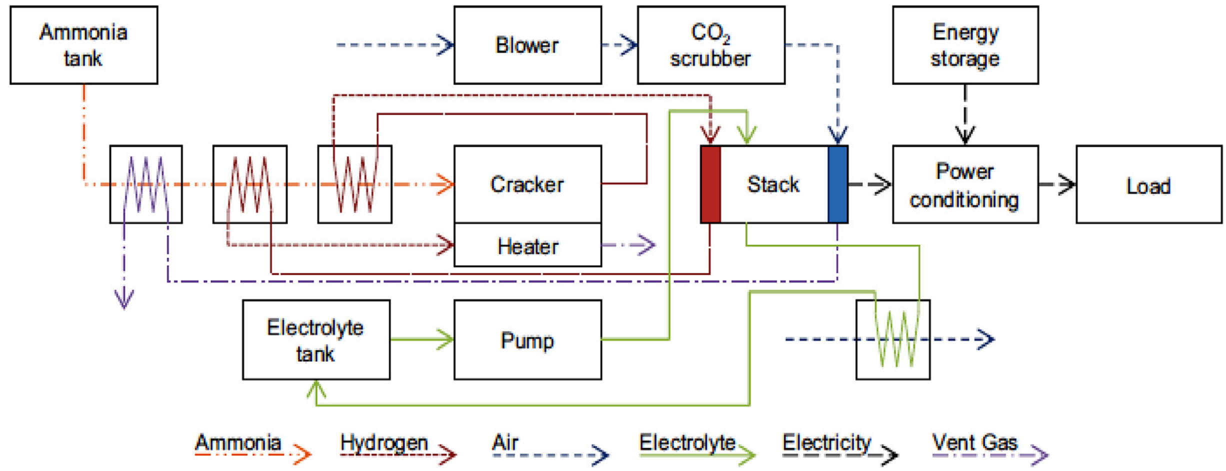


Fig. 17. Alkammonia system schematic. Reprinted from [150] with permission from J Power Sources, Elsevier.

making them now a priority to move forward in the deployment of large scale projects using ammonia. Some other developments have been presented through the years, with specific emphasis on using alkaline fuel cells for transport applications. The work done by the group of Kordesch et al. and the Argonne National Laboratory [151] has led to the development of AFCs capable of being implemented in cars such as the Silver Volt, where high efficiency (99.99% conversion) cracking devices are employed to fed the former, allowing a 386 km range with only 80 L of ammonia.

Other research has allowed the use of alkaline media to directly electro-oxidize in AFCs some chemical compounds that are high-energy density chemical hydrogen storage fuels such as boron based materials, one in particular containing ammonia is ammonia borane (AB), material that has a standard theoretical potential of 1.615 V, higher than other fuel cell fuels. Nickel based carbon-supported electrocatalysts such as Ni_3Co/C are showing their potential and greater stability compared to platinum or palladium, especially when it comes to use AB oxidation. Thus, the use of Alkaline Fuel Cells has also an important role to play in progressing to a hydrogen through ammonia economy, especially since costs are lower to other technologies such as PEM [152].

3.3.3. Molten hydroxide FC

Direct ammonia-fuelled molten hydroxide fuel cells [126] have recently received fair attention for the use of ammonia. The successful electrochemical oxidation of ammonia using these devices was confirmed, with constant reactions maintained at 473–493 K using flows of 97% ammonia purity over Pt electrodes. Although the feasibility of direct ammonia fuelled FCs was confirmed, these systems still require further development due to their low performance when compared to more mature technologies. Further research performed by Lomocso et al. [153] and Assumpcao et al. [154] suggest that the use of other materials such as Iridium in combination with Pt could considerably increase the performance of these devices, although this simultaneously increases their cost.

3.3.4. Proton exchange membrane FC

The use of Proton Exchange Membrane (PEM) FCs has gained considerable interest in the generation of small scale power (~5 kW) over the last decade. These systems require a clean hydrogen source. Since production of hydrogen from reforming processes is complex, ammonia has been presented as a potential alternative due to the null existence of carbon molecules that can poison the anodes of the fuel cell [155]. For fuel cells, ammonia needs to be almost completely decomposed ($>$ 99.5%) at around atmospheric pressure, a process that requires high temperatures for both thermodynamic and kinetic reasons. Studies of the reactions that occur between ammonia and hydrogen using different catalytic materials have received considerable attention. The reactions that occurs between 793 and 963 K using $Ni\text{-}Pt/Al_2O_3$ were evaluated by Chellappa et al [155], who found that the activation energy for the conversion is much higher than reported previously, emphasizing that a rate expression that is first-order with respect to ammonia provide good predictions at high temperatures and pressures, with inhibition probably caused by the existing hydrogen in the reaction. Other materials such as ammonia-borane are continuously presented as the closest option for delivery of hydrogen from ammonia decomposition to automotive power fuel cells [156–159]. Various methods for decomposition of ammonia have also been documented and patented to obtain pure hydrogen influxes for PEM fuel cells. These vary from micro-reactors consisting of an array of alternative catalytic plate channels [160], multi-stage fixed bed membrane reactors (MSFBMR) [161], micro-reformers capable of using conventional fuels for heat transfer improvement to dissociate ammonia intro hydrogen [162], etc. Light metal imides (i.e. lithium imide, Li_2NH) have also demonstrated their effectiveness to decompose almost completely ammonia into hydrogen, enabling the development of prototypes that can operate at temperatures from 773 to 863 K, Fig. 18 [163].

Unfortunately, ammonia residuals can have a detrimental effect on PEM FCs, as the compound contaminates the membrane array, inherently reducing efficiency [164,165]. As suggested by Uribe et al. [164] ammonium ions (NH_4^+), the product of ammonia with protons occupy charge sites in the PEM causing decrease of overall proton conductivity. Zhang et al. [165] proved that some of this contamination can be reversed, although permanent damage is observed on the membranes. Halseid et al. [166] showed that concentrations as low as 1 ppm of ammonia can significantly reduce the efficiency of PEM FCs in a relatively short period of time. Thus, although the technology is readily available with considerable potential for small powering applications, care needs to be taken to avoid contamination from un-decomposed ammonia, subject that requires the study of further materials to increase resistance and durability.

3.4. Combustion based technologies

3.4.1. Reciprocating engines

As previously depicted, ammonia can also be used as fuel for internal combustion engines (ICE) and for compression or spark ignition units. Similar to other alternative fuels such as ethanol, methanol, hydrogen and gasoline/diesel blends, the high octane of

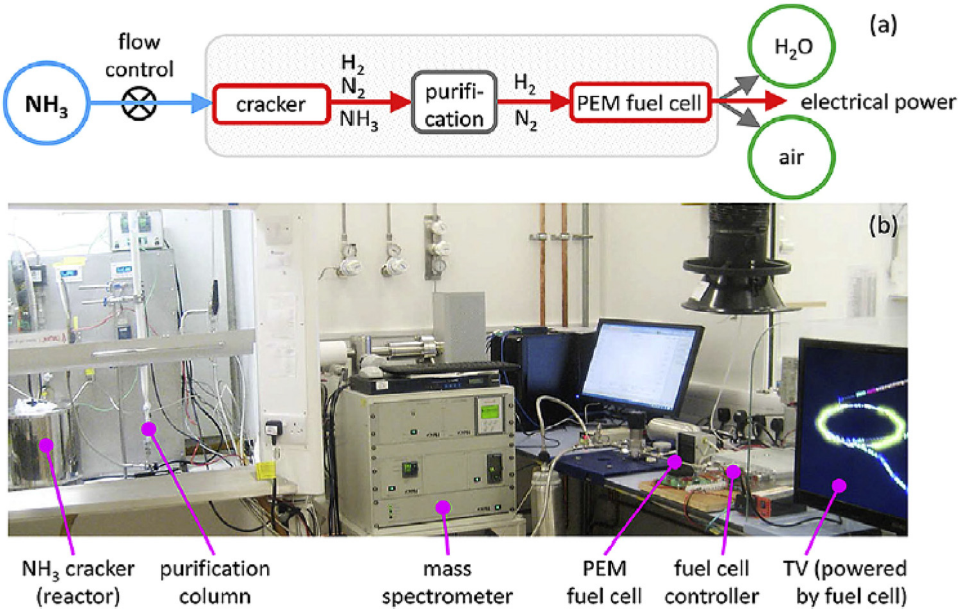


Fig. 18. a) Experimental setup for a cracker using metal imides and b) System overview. Reprinted from [163] with permission from J Power Sources, Elsevier.

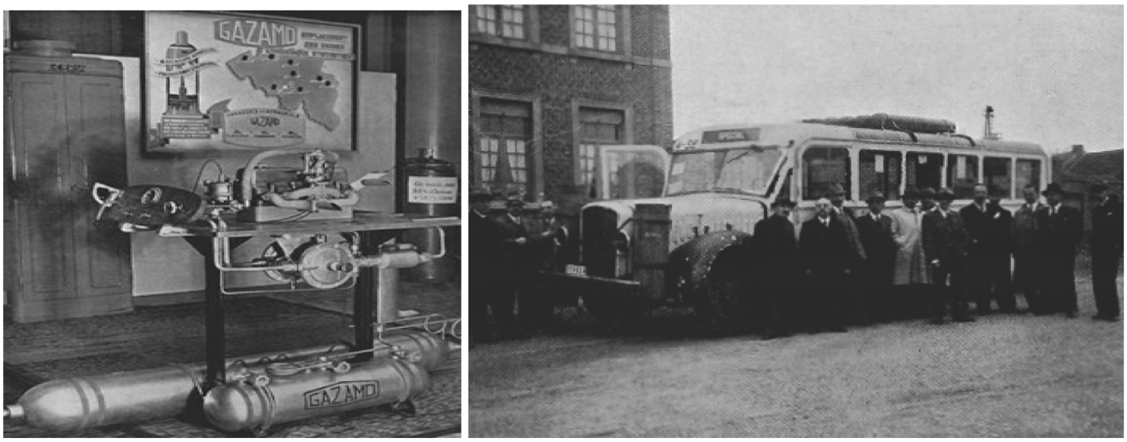


Fig. 19. Gazamo system and ammonia-equipped motor bus, respectively [168]. Courtesy of the Energy Institute.

ammonia (~130) can improve combustion properties and reduce undesirable effects such as knocking [167]. However, it must be recognised that due to the corrosive nature of ammonia, components made out of brass or copper must be removed from the system in order to avoid operability issues.

The use of ammonia as vehicular fuel for motorised applications goes back as far as 1822 with a proposal from Sir Goldsworthy Gurney [69] where he developed an engine to drive a small locomotive. However, it was not until 1905 that the first small scale motor was developed by Ammonia Casale Ltd., who took out patents in Italy in 1935 and 1936 [168]. As early as 1933, Norsk Hydro operated an internal combustion engine vehicle on hydrogen produced from on-board reforming of ammonia [169]. Other devices followed with minor success. During World War II the scarcity of fossil fuels in some regions led to the search for alternative fuels for use in public transportation. The lack of diesel in Belgium in 1942 led to the consideration of first compressed coal gas, and then ammonia. Ammonia Casale was commissioned to implement their new patent based on a process that employed compressed gas and ammonia to replace diesel in the Belgian bus service. The so-called Gazamo process, Fig. 19, was implemented in ~100 vehicles and continued until diesel fuel became plentiful again [168].

In the 1960s, further developments ensued in the quest for alternative fuels for IC-Engines, driven by new environmental legislations and early signs of the energy crisis which would impact on Western economies the following decade. Development work on spark ignition reciprocating engines, fuelled by ammonia, was undertaken for military applications, as conventional engines had been shown to perform poorly with pure ammonia. In order to improve performance, propositions included increasing spark energy, compression ratio, supercharging the engine and adding hydrogen into the fuel through dissociation of NH_3 [170–172]. These developments showed that ammonia needed to be vaporised with at least 4–5% (by weight) H_2 for good performance.

Use of IC engines also received considerable attention during this period [173–175]. Ammonia vapour and liquid ammonia were studied in diesel and spark ignition engines respectively, at high compression ratios. Although the tests at 30:1 compression ratio using the spark ignition engine were unsuccessful, the results using ammonia vapour and diesel (for ignition purposes) generated optimism for the success of using ammonia as fuel in IC engines. Perhaps surprisingly, very little research and development was undertaken during the 1970–80s in this field. The literature concerning development of ammonia based engines is very sparse during this period, with the exception of the AMC GREMLIN at the University of Tennessee in 1974 [176]. The field experienced a revival in the 1990s, followed by a considerable increase in publications from 2004 onwards, with the first ammonia conference in the USA.

Commercially, ammonia fuelled ICEs have attracted the attention of various companies and countries around the world as a promising technology that could contribute to a sustainable future. For example, Boothroyd [177] recently proposed the use of ammonia storage from stranded energy resources in rural areas to power large scale manufacture near cities for Australia. Since ammonia distribution is still conducted in Australia by trucks, it has been proposed to replace long distance trucks by a fleet of ammonia-inflated airships. Similarly, Leighty [178] proposed the use of stranded, renewable energy sources in Alaska to produce ammonia that can be used as fuel for ICE/Fuel Cells/GTs for on-demand energy production and transportation.

Analyses of the feasibility of ammonia as a sustainable fuel in internal combustion engines based on thermodynamic performance, system effectiveness, driving range, fuel tank compactness and cost of driving have also been performed [10,11]. Not surprisingly, the studies concluded that to make ammonia a viable fuel in ICEs, ammonia needs to be mixed with other fuels as combustion promoters due to ammonia's low flame speed and high resistance to auto-ignition. This was confirmed from previous studies where a dual-fuel approach was usually chosen to implement ammonia combustion in IC engines [179,180]. These works and others carried by Liu et al. [181] showed that ammonia fuelled engines have low power losses, no more corrosion and no more lubricant consumption than conventional fuels.

Thus, due to the high interest in developing this technology, patents and commercially available units for transportation are under test evaluation for commercial release in the near future. A good reference to previous ammonia patents dating back to 1937 can be found in a patent submitted by Caterpillar Inc. in 2008 for an engine fuelled using ammonia [182]. Specific to this particular patent, ammonia has been used as primary fuel with electrical supplements to the mechanical power to drive a new power system capable of providing good combustion efficiency. The publication *Ammonia Energy* has recognised other stakeholders in the development of ammonia fuelled engines, separating them into three categories [183]:

1) Spark Ignition carbon based dual fuels, i.e. Biogas International (Italy), the Savia Coalition (Italy), Green Transportation Technology Group (South Korea), Xiamen University (China), etc.
2) Compression Ignition carbon based dual fuels such as Sturman Industries (USA), Hydrofuel Inc (Canada) and Iowa State University (USA)
3) Hydrogen doped ammonia engines, i.e. Toyota (Japan), Siemens (UK), etc.

3.4.1.1. Ammonia blending with carbon based fuels. As previously presented, doping ammonia with other fuels has been considered one of the best solutions to improve ammonia combustion in ICEs. It has been demonstrated [184,185] that high performance can be achieved using ammonia/gasoline fuelling, a three-way catalytic converter capable of cleaning emissions under stoichiometric and rich conditions over short and long distances [186]. Replacement of diesel with diesel/ammonia has also been attempted [187] showing promising results with modification to current diesel engines. Some of the results demonstrated that peak engine torque could be achieved by using different combinations of diesel and ammonia, with a monotonic CO_2 reduction for the same torque output for systematic NH_3 increase. Additionally, lower NOx emissions were measured for ammonia fuel mixes not exceeding 60% NH_3 [188]. Combinations such as gasoline/ammonia and ethanol/ammonia [189], ammonium nitrate/ammonia [190] and even pure oxygen using 100% ammonia [191] have been also attempted, showing that these fuel mixtures can provide elevated power outputs under stable conditions, although mainly conditioned by the NOx emissions product of the combustion process.

Direct gaseous ammonia injection has also been assessed in recent studies by Ryu [192] who showed a high correlation between the timing and duration of the injection of ammonia in a spark-ignition-engine. It was noted that the injection timing should be in the range of 320 to 370 BTDC for gasoline-ammonia fuel mixes. Due to slow flame-speed propagation of NH_3, the engine efficiencies were observed to be lower than the baseline performance. Finally, it was found that the emissions were slightly reduced for some species, i.e. carbon monoxide, though accompanied with an increase in NOx and NH_3, as expected. Similar work has focused on blends of ammonia with commercially available emulsifiers such as ethanol or methanol that can enhance solubility of the blend [193]. Results proved that pure, liquid phase gasoline is capable of dissolving only 4.5% (vol) of ammonia at 345 kPa and 286.65 K, while the use of 10%(vol) of ethanol or methanol increased the solubility of ammonia to 11% (vol). Further studies showed that gasoline with 30% ethanol or methanol can retain up to 17.35%(vol) ammonia [194]. At higher engine speeds, better engine performances in terms of increased torque and power output were observed for ammonia rich fuels compared to those for pure gasoline fuels. Thus, it was concluded that hydrogen can be stored as an ammonia-gasoline fuel blend and successfully recovered without major modification to the existing infrastructure of the engine [195].

One of the most interesting new concepts for ammonia fuelled engine technology is the AmVeh, Fig. 20, developed by the Korean Institute for Energy Research (KIER), which is to convert existing vehicle fleets into 70% NH_3-30% gasoline vehicles [196]. The developers have converted an LPG-gasoline unit by adding a control system and removing the corrodible, copper containing metals - specifically the so-called 'yellow metal' high zinc brass. If the system was installed across 20% of the current Korean fleets, the country could reduce CO_2 emissions by 10 million tons annually, thus aiding their future targets on climate change mitigation.

Numerical simulations of co-fuelling reciprocating engines with ammonia have also been conducted to determine best operating conditions of industrial and transportation engines. Zhong et al. [197] used CFD analyses to model compression ratios, air inlet temperatures and air/fuel ratios using ammonia with n-heptane. The results demonstrated that compression ratios of 16:1 and inlet air temperatures of 800 K allow ignition of ammonia blends through compression. Moreover, it was shown that as n-heptane increases, the ignition temperature required reduces from 800 to 360 K. A very comprehensive compilation of data has been gathered by Dincer et al. [198] with regards to co-fuelling ammonia blends for diesel locomotives using integrated heat recovery, hydrogen production and emission reduction subsystems. Economic considerations such as carbon-tax rates and fuel costs were considered. Further work has compared a conventional diesel-electric locomotive through energy and exergy efficiency, fuel consumption and environmental impacts. Results showed that a blend with 50% of fuel energy supplied by ammonia can improve heat recovery with a slight increase in energy and exergy efficiencies. Moreover, there is a considerable reduction of greenhouse gases of up to 53% with pollutant production (NOx, CO, particulate matter, hydrocarbons) below the standards required by 2012–2014 [35].

Dimethyl ether (DME) fuels were also assessed using liquid ammonia–DME mixtures in a compression-ignition engine with a direct-injection strategy. The cost analysis showed a comparable

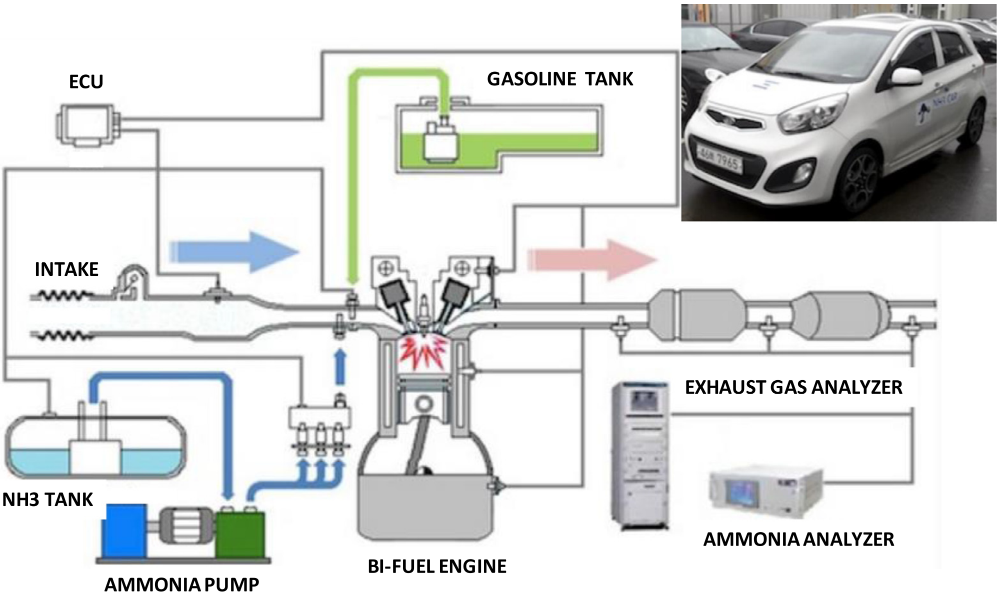


Fig. 20. AmVeh car (top right). Ammonia based engine for transportation in South Korea [196]. Courtesy of NH3 Fuel Association.

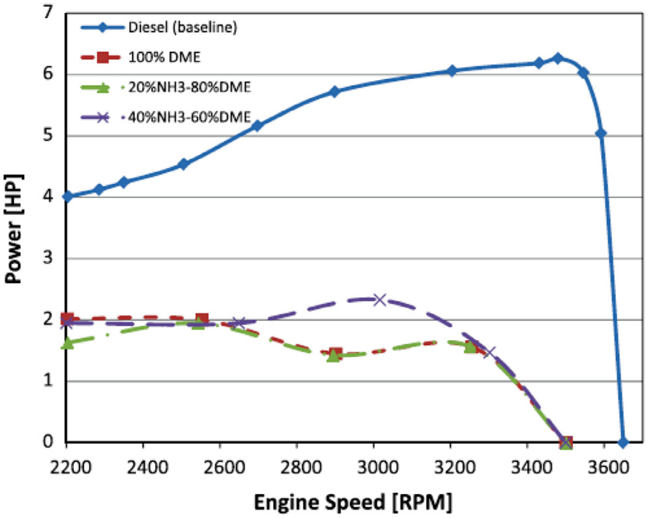


Fig. 21. Range of test conditions using different fuel mixtures. Reprinted from [199] with permission from FUEL, Elsevier.

fuel energy cost to diesel fuel with ammonia/DME, although the inclusion of ammonia in the fuel mixture was shown to increase CO, HC and NO_x emissions, with lower power outputs, Fig. 21 [199]. Although injection strategies were developed to enable the use of ammonia-DME in direct-injection compression-ignition engines [200], the corresponding engine performance was also linked to increased CO, HC and NO_x emissions, thus suggesting that post-exhaust treatment would be required for these systems.

As for all combustion systems, emissions from ammonia combustion play a crucial role in deployment; thus dedicated research has focussed in this area. Further investigations [201] depicted gasoline–ammonia combustion in a spark-ignition engine in terms of the combustion characteristics and exhaust emissions with direct injection. CO emissions were found to decrease but emissions of NO_x and hydrocarbons were increased with ammonia, as expected due to the high nitrogen content of the ammonia molecule. Notwithstanding the emissions challenges, however, direct injection of gaseous ammonia with carbonaceous fuels was proven to be feasible in engine combustion.

3.4.1.2. Ammonia and hydrogen. Of particular interest is the use of hydrogen in the ammonia blends, as the molecule can be recovered through splitting of ammonia, with the previously stated improvements in combustion performance. Studies show that ammonia can be blended with hydrogen at levels as low as 5% H_2 [202], still providing good power response. Higher doping ratios have also been deployed [203], showing, for example, that 10% hydrogen addition provided optimum efficiency and effective power, Fig. 22. High NOx emissions were present under lean conditions, thus suggesting the need for selective catalytic reduction (SCR) of exhaust gases under these conditions.

Further studies of reciprocating engines have also been extended to more commercial applications in Italy, where implementation of ammonia ICE technology has been performed by DESTEC in Pisa [204,205], showing good results for the conversion of a Lombardi 505 cm^3 gasoline engine into a hydrogen/ammonia system for waste collection buses. Liquid ammonia contains 1.7 times as much hydrogen as liquid hydrogen itself [206]. Thus, studies performed by Koike et al demonstrated that an ammonia tank (1 MPa) contains 2.5 times as much energy as a hydrogen tank (at 70 MPa) by volume, i.e. a hydrogen tank of 770 L (350 kg) could be replaced by an ammonia tank of 315 L (172 kg). Further analyses on storage capacity systems demonstrated the superior performance of ammonia storage capacity for transportation purposes [167], Table 5. Consequently, the smaller tanks required for liquid ammonia were presented as a commercial opportunity for the local Region of Tuscany [204].

The only mechanical modification to the engine required the addition of electro-injectors for hydrogen and ammonia to the intake manifold [207]. One of the main features of these devices was the development of a new patented device capable of cracking ammonia into hydrogen and nitrogen at the concentration required for the engine [206]. The experimental results confirmed the need to dope the ammonia blend with hydrogen and that observed brake power was less than that for gasoline as a consequence of the poor heating value of the mixture. The maximum observed NOx emission was 0.003 g/kJ at half load and 4500 rpm, without catalytic reduction [207]. Similar thermal ammonia reformers have

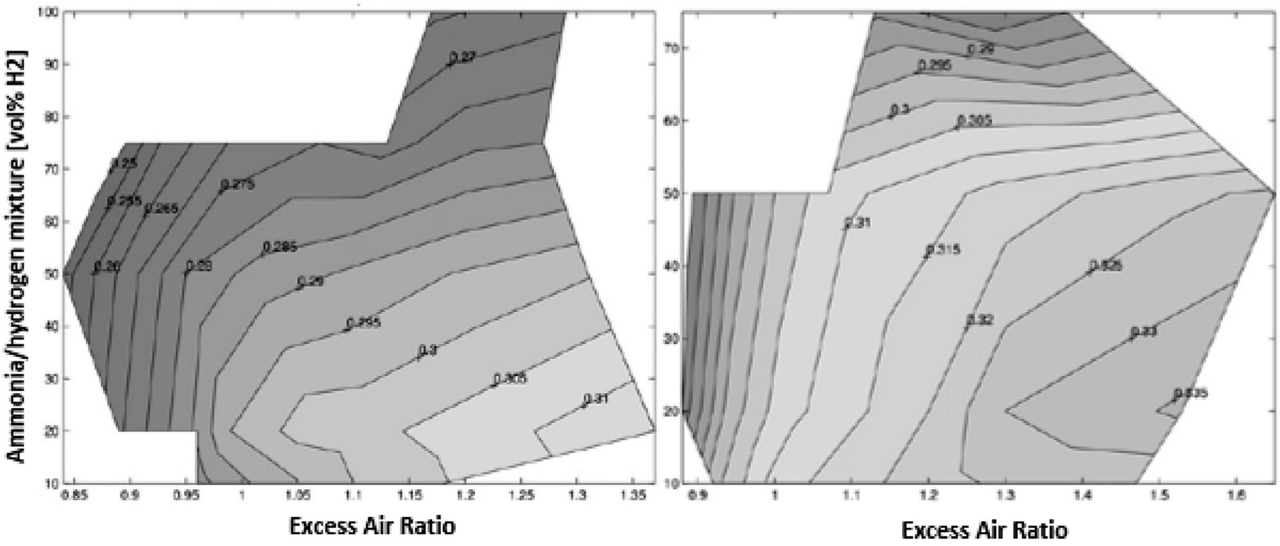


Fig. 22. Performance plots. Plots showing the indicated efficiency versus excess air ratio and the ammonia/hydrogen mixtures at 6.23 Compression Ratio (CR) and 10 CR, respectively. Measurements conducted at 1200 RPM. Operability ranges can be presented using these plots. Reprinted from [203] with permission from FUEL, Elsevier.

Table 5
Status of storage capacity. Data from [167].

	Compressed H_2 (70 MPa)	Liquified NH_3 (1 MPa)
Gravimetric – capacity (wt%) – energy density (MJ/kg)	3.5 - 4.2	70 - 13
Volumetric – capacity (kg/L) – energy density (MJ/L)	0.024 - 2.9	0.380 - 7.1

been also evaluated by other research groups to obtain hydrogen to increase the reactivity of an ammonia fuel blend [167], showing that a 40% hydrogen fraction improves combustion properties close to those observed for gasoline.

Recent studies [208] evaluate the implementation of hybrid systems. Developments show two systems using ammonia-hydrogen fuel for either an internal combustion engine or a combination of an ICE with PEM fuel cells to power a vehicle, Fig. 23. The study was performed with and without dissociation of ammonia. The results from the theoretical study show that the amount of exergy that is recovered using ammonia dissociation (i.e. hydrogen) are considerable, i.e. 16.4% and 13.1% for the ICE and the ICE-PEM systems respectively, consequence of the added hydrogen coming from the dissociation unit. Thus, the use of hydrogen from cracked ammonia is highly beneficial when compared to pure ammonia injection. It must be emphasized that integration of heat recovery for dissociation units played an important role in improving these systems, concept that can be expanded to other combustion technologies to increase efficiency while minimizing exergy destruction.

Regarding emissions, research groups have investigated mechanisms governing the nitrogen based emissions in a NH_3/H_2 fuelled SI-engine [209]. Applications with flue gases exhaust treatment showed lower levels than legally required when a SCR catalyst was used to eliminate all NO_x emissions. Gill et al. [210] compared the combustion and emissions characteristics of using H_2, NH_3 and dissociated NH_3 as a dual fuelling approach with diesel fuel in a compression-ignition engine. The study showed that pure NH_3 performed better than dissociated NH_3 at high load in terms of engine stability and brake thermal efficiency -possibly a consequence of increased heat loss from the combustion chamber, changes to combustion characteristics and changes to the efficiency of H_2 combustion under different loads and concentrations-, while at low loads the fuels behaved similarly, although it should be noted that using dissociated NH_3 was found to have lower exhaust NH_3 emissions and significantly low N_2O formation compared to un-dissociated NH_3 addition. Other advanced technologies such as Homogeneous Charge Compression Ignition (HCCI) have also been used to determine their impact on the performance and reduction of emissions while using hydrogen-ammonia blends [211]. Trials were expanded to the use of Exhaust Gas Recirculation (EGR) which showed a considerable decrease of NOx consequence of reduced oxygen available for combustion. However, it was also recognised that the production of N_2O increases at low temperatures, thus suggesting that operation using HCCI fuelled with ammonia-hydrogen blends is feasible and low polluting as long as combustion temperatures are above 1400 K while using EGR for NOx mitigation.

In terms of emissions, all modern combustion vehicles are now required to operate SCR catalyst systems and/or fuel additive systems to reduce nitrogen oxides to N_2 gas. Interestingly, these systems work through the addition of chemicals that decompose to ammonia, and ammonia then reduces the NOx within the gas flow according to the following equations;

$$4NO(g)+4NH_3(g)+O_2(g) \rightarrow 4N_2(g)+6H_2O(l) \tag{2}$$

$$2NO_2(g)+4NH_3(g)+O_2(g) \rightarrow 3N_2(g)+6H_2O(l) \tag{3}$$

$$NO_2(g)+NO(g)+2NH_3(g) \rightarrow 2N_2(g)+3H_2O(l) \tag{4}$$

Therefore, NOx emissions from ammonia fuelled combustion devices may be mitigated in a similar fashion. However, it should be noted that for devices fuelled by ammonia a ready reservoir of ammonia for NOx reduction will exist and therefore it may be possible to design ammonia fuelled systems that do not require secondary exhaust clean-up or high cost catalyst systems to achieve emission free exhaust. Furthermore, ammonia combustion is often improved through preheating or partial decomposition of the ammonia prior to combustion and it may be possible to parasitically use the waste heat from exhaust systems to pre-heat or decompose ammonia while simultaneously removing NOx pollutants.

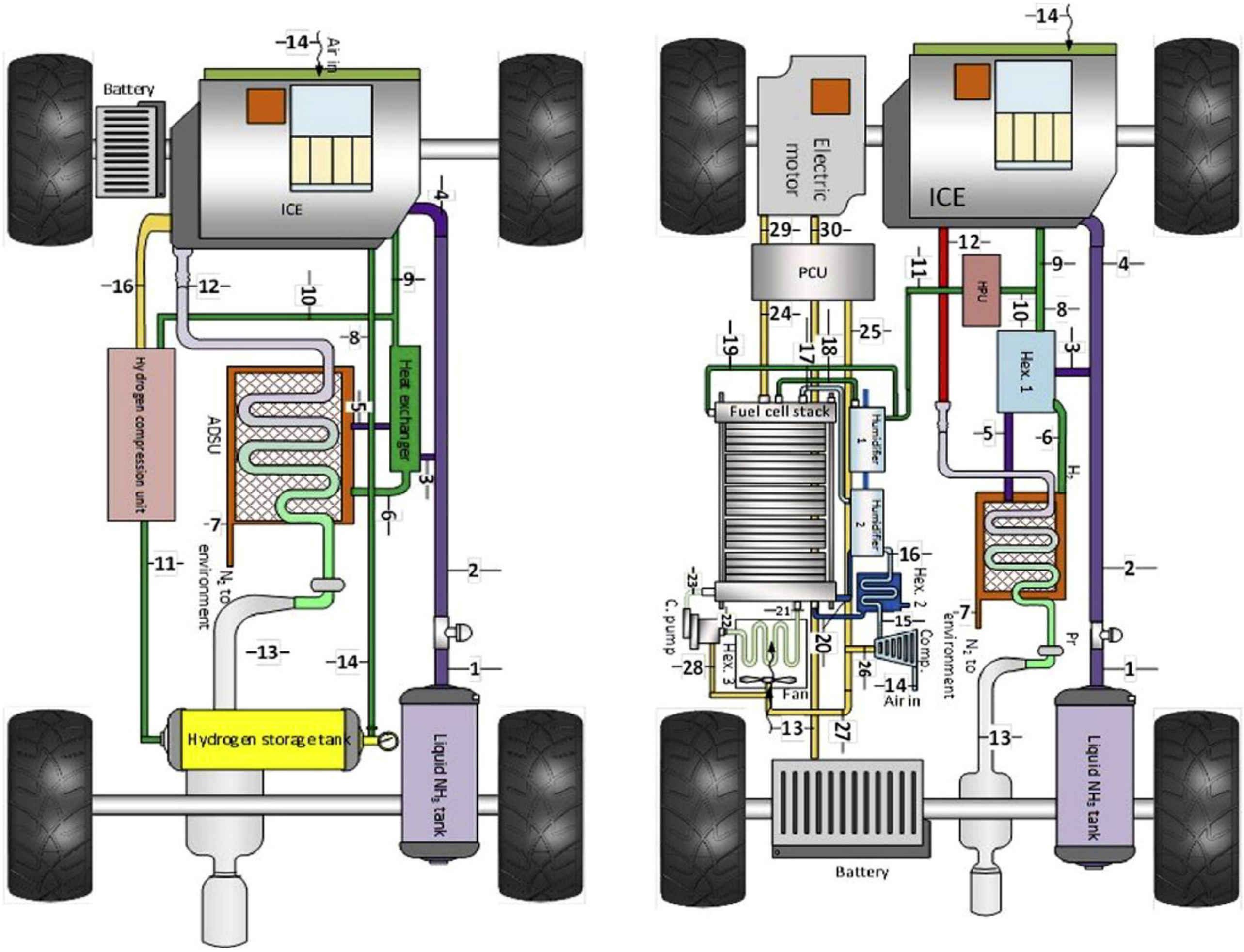


Fig. 23. Schematic diagrams of ICE's without (left) and with (right) PEM fuel cells. Reprinted from [208] with permission from Int J Hydrogen Energy, Elsevier.

In summary, clearly further research developing internal combustion technologies fuelled by ammonia is necessary. There is now increasing interest in these systems and considerable competition to produce the first commercially viable devices. However, as described previously, the challenge of reducing further NOx and unburned ammonia remains at the heart of this research and technological field.

3.4.2. Gas turbines

The gas turbine is another power-generating device which offers the potential benefits through ammonia fuelling described earlier. Hence, a gas-turbine combustor that burns a combination of NH_3 and other fuels with controlled emissions and combustion characteristics is highly desirable. Studies that have contributed to improving understanding of ammonia fuel blends for gas turbine power generation are summarised in this section. It is noted that this is an immature field, with relatively few publications concerning the development of ammonia gas turbines.

Early research on the development of ammonia fuelled gas turbine combustion systems was undertaken during the 1960's [212–214]. Those studies demonstrated that ammonia's ignition energy was considerably higher compared to fossil fuels due to the low reactivity of ammonia. Moreover, at stoichiometric conditions, the quenching distance for ammonia-air (6.7 mm) was 3.5 greater than for propane, with ammonia burning at narrower equivalence ratio ranges [213]. However, it was also found that dissociation of ammonia could produce faster flames, which could attain similar properties to some common hydrocarbons. Thus, it was concluded that 28% dissociated NH_3 could be used as a substitute fuel in gas turbine combustion systems sized for hydrocarbon fuels. Further experiments demonstrated that the fundamental problem with ammonia-air as a turbine fuel is the relatively slow chemical reaction rate, giving a laminar burning velocity of ~0.06–0.08 m/s [215]. As air flow is reduced to allow sufficient residence time for the reaction to progress, diminished Reynolds number effects lead to reduced turbulence and hence less effective mixing, which in turn decreases combustion efficiency [214]. Other studies have been conducted to demonstrate the concept of using ammonia as an engine fuel, with success in terms of power production that unfortunately fell short in terms of emissions performance for NOx [216,217].

In the 1960's, Solar and UC Berkeley investigated a 250HP T-350 (Technical Report DA-44-009-AMC-824(T)) single can ammonia burner turbine [46]. Performance of the engine using vapour NH_3 was found to be similar to JP-4. Initially, using ammonia injection at 2.35 times that of hydrocarbons provided cooler turbine inlet temperatures at similar power conditions. However, when turbine inlet temperatures were matched to those of hydrocarbons, ammonia provided 10–20% increase power with high efficiencies. In 1991, the Italian power generator ENEL undertook a research program that included ammonia for power generation. Their conclusions led to positive power production performance that was compromised by the high emission of NOx [218]. Grcar et al. [219] combined experimental and modelling investigations of ammonia chemistry in a hot combustion environment below adia-

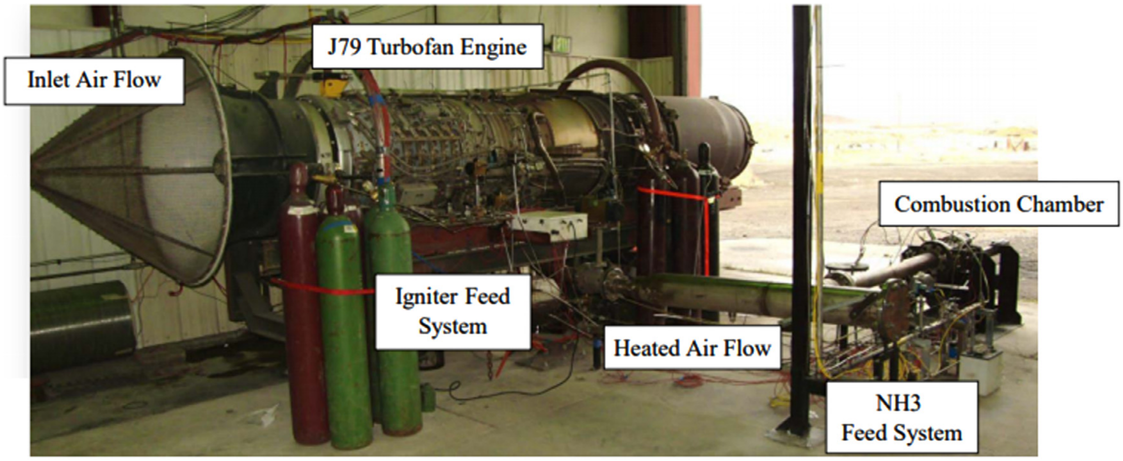


Fig. 24. Test rig, SPG Advanced Propulsion and Energy [46]. Courtesy of NH3 fuel association.

batic flame temperatures. The final products of NH_3 oxidation remained sensitive to mixing even at temperatures below those of self-sustaining flames. At these low temperatures, NH_3 oxidation occurred in a premixed reaction zone, as sufficiently high temperatures led to the development of a non-premixed reaction zone that produces significantly less NO than the equivalent premixed system developed, effect potentially caused by the recombination of ammonia with NOx products and the absence of OH radicals essential for the production of emissions.

More recently, a number of different approaches have been pursued to use ammonia as a flexible fuel in gas turbines, with most of them finding that emissions are the main limitation of such technologies [220]. SPG Advanced Propulsion and Energy [46,220] is one of the few companies claiming to be close to development of commercial systems, Fig. 24. They have presented series of papers that have summarised the main challenges for the development of a reliable technology. These are: a) Lower flame temperatures and slower kinetics of NH_3; b) unstable combustion; c) reliable ammonia vaporization to improve efficiency; d) pre-cracking of the molecule required to increase flame speed and burning ratios.

Swirl stabilised combustion of ammonia with other molecules has briefly been analysed at the University of Iowa by Meyer et al. [221] in a 40 kW burner, with nozzles, swirl stabilisers and a self-sustained heat exchanger. Stabilisation was achieved using different swirlers with different concentrations of ammonia, hydrogen and methane. For those experiments where ammonia and hydrogen were mixed, it was found that the use of a flame holder increased the combustion efficiency, with a demonstrable reduction in NO_X emissions, possibly as a consequence of recombination of species (NOx and unburned ammonia).

The Fukishima Renewable Energy Institute (FREA), has developed fuel flexible platforms to burn liquid NH_3 produced from renewable sources, i.e. wind and solar, in combination with kerosene in a 50 kW micro-gas turbine, Fig. 25. Diffusion combustion has been employed in the prototype by-fuel combustor due to its flame stability and it has been demonstrated that the equipment can be run using ammonia-kerosene blends at different concentrations.

The gas turbine was started with kerosene that was replaced by ammonia and an output power of 17 and 21 kW was achieved with 38% and 30% replacement of kerosene by supplying NH_3, respectively. However, the production of NO_X increased considerably based on the amount of ammonia injected, reaching levels up to 600 ppmV. The NOx emissions challenge for ammonia fuelled turbines has been investigated since the first development of the technology. Currently, the best solution is the use of selective catalytic converters (SCR) to reduce the emissions produced by a micro-gas turbine up to levels of 10 ppmV [222–224]. Further works on this system have been performed using other blends such as ammonia-methane blends, and the implementation of rich-lean combustion systems for NOx reduction has also been demonstrated with good performance and the reduction of emissions to half of those measured without this combustion technique [225]. Other findings [226] show that additions of hydrogen can improve flame stability and mitigate even further NOx production, encouraging the use of ammonia for power generation at low nitrogen oxide concentrations.

Other potential beneficiaries of the research undertaken include the steel industry where ammonia is available as a waste product which could be considered as fuel to be used in co-fired low-pressure furnaces, for example. Co-firing could be achieved using ammonia and methane/hydrogen to support power production of high energy intensive industries. With that aim, groups at Cardiff University (UK) and Tohoku (Japan) are currently investigating the development of new gas turbine combustion systems capable of providing large power quantities with low emission rates. The work at Tohoku has determined the exhaust gas compositions of a particular burner under atmospheric pressure and fuel lean conditions. It has been demonstrated that as the equivalence ratio increases towards stoichiometry, unburnt species such as NH_3, CO and total hydrocarbons decrease in contrast to NO_x and that the burner achieves combustion efficiencies above 97% for ammonia-mixing-ratios below 50%. It has been reported that it was difficult to achieve low emissions and high combustion efficiency in a single-stage combustor, and hence a two-stage combustion system has been conceptualised and demonstrated, with studies suggesting lower NOx and unburnt gas species emissions while maintaining high combustion efficiencies [227].

Valera-Medina et al. [228,229] presented a series of studies using a generic swirl burner that was fuelled using ammonia and hydrogen/methane at different concentrations. The results showed the complexity in stabilizing premixed ammonia blends, identifying a particular pattern of oxygen consumption that was followed by flame speed reduction, retarding the combustion process and eventually pushing the flame back into the combustion chamber with an inherent aeration. Also, it was recognised that the use of hydrogen injection required a new injection strategy to ensure stable combustion, as premixing eventually led to early flashback. NOx and CO were considerably lower at high equivalence ratios > 1.10, depicting a region of chemically reactive balance between methane/hydrogen and ammonia combustion, with recombination of NOx emissions with unburned ammonia, increasing OH

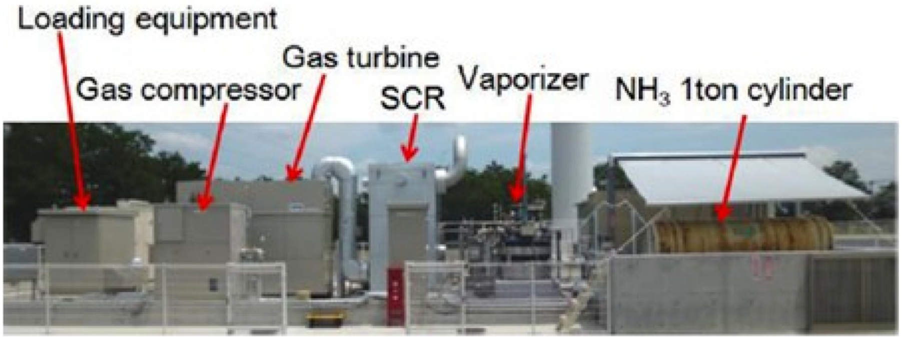


Fig. 25. Photo of the experimental facility of NH_3-air and NH_3–CH_4-air combustion gas turbine power generation [222]. Courtesy of NH3 fuel association.

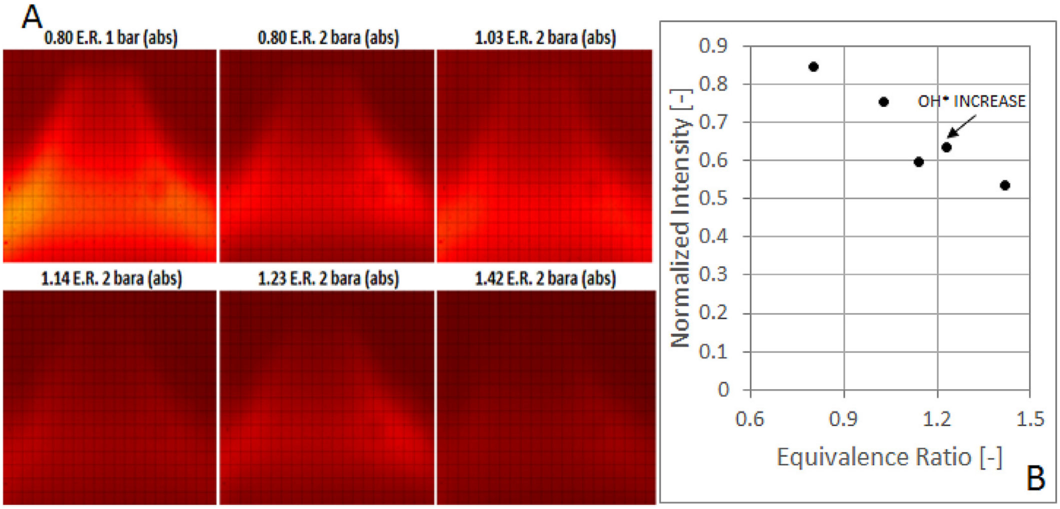


Fig. 26. A) OH* chemiluminescence, mean values out of 200 images. B) Normalized intensity of mean values at 0.84 E.R. at 0.1 MPa (absolute). Reprinted from [228] with permission from applied energy, Elsevier.

radicals, Fig. 26, topic that is still under debate across the scientific community.

Xiao et al. [230] have also produced data to determine the potential of using ammonia/methane and ammonia/hydrogen [231] blends for power generation. Results showed that the use of ammonia at high pressures as those found in industrial devices can mitigate the production of NOx by increasing the recombination of species and compacting the flame front. Moreover, there seems to be a trend in terms of the production of OH radicals at high equivalence ratios, denoting the recombination of emissions with NH_2 radicals in the post-flame zone, leading to the formation of nitrogen molecules, suggesting scenarios where ammonia gas turbines can become a feasible, reliable and environmental possibility.

Companies such as NUON have also started ambitious programs to develop their capabilities in terms of ammonia fired systems. The most notable is the “Power-to-Ammonia” program in which NUON collaborates with TU Delft, Proton Ventures, OCI Nitrogen, AkzoNobel, ISPT and the University of Twente [232,233]. The NUON project perceives ammonia as a “superbattery” that stores excess renewable power at large scale over long periods. The new Magnum-plant in Eemshaven, officially opened in 2013, is proposed to be converted into a green ammonia fuelled facility instead of a coal plant, thus reducing CO_2 emissions considerably [234,235]. Similarly, multinational companies such as Siemens have established R&D roadmaps to position green ammonia and hydrogen produced from renewables as energy vectors of the future, using the chemical in either transport, processes or large power generation, Fig. 27.

It has recently been announced [236] that Chugoku Electric Power Company has conducted a series of trials at its Mizushima power plant in July 2017, where ammonia was added to the 155 MW coal-fired plant at a rate of 450 kg/hr. The company confirmed that the addition of the ammonia did not cause the plant’s power efficiency to reduce. On the basis of energy content, the ammonia added represented 0.6–0.8% of total fuel. At this ratio, a decrease in carbon dioxide emissions was observed. The Chugoku demonstration has been the first where ammonia has been burned in a commercial power plant in Japan.

Research into the use of ammonia for large power generation in support of decarbonising high carbon-producing processes is still ongoing. Of particular interest are the ill-defined kinetic processes that occur at high power outputs using various blends of ammonia with gases such as methane and hydrogen. More specifically, at equivalence ratios between 1.05 to 1.25 an increase in reactivity and overproduction of OH species has been observed, suggesting recombination of molecules that require further understanding and research to reduce the time to deployment of ammonia power generation at a commercial scale.

3.4.3. Propulsion

Pioneering studies were undertaken during the middle of the 20th century by NASA, who identified through their XLR-99 program the need for “combustor enhancers”, i.e. hydrogen, kerosene, fossil fuels, etc. during start-up and idle for their propulsion engine [190]. According to some documents and “in field” research [176], Reaction Motors, the company that took over the XLR-99 program, decided to use ammonia on their Viking engine (XLR-10).

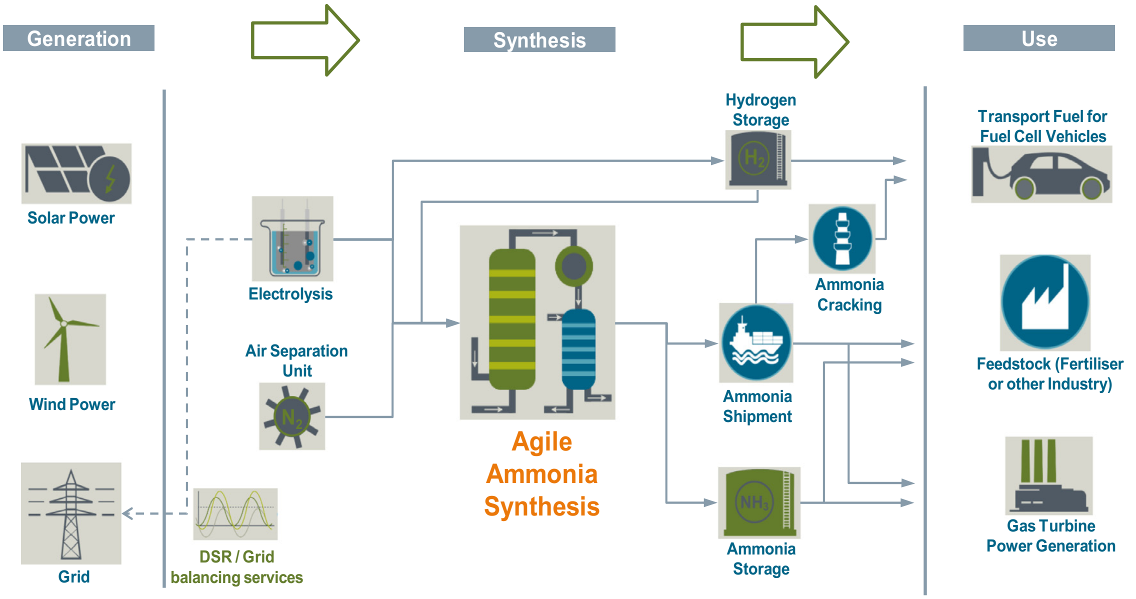


Fig. 27. Green ammonia [7]. Courtesy of Dr Ian Wilkinson, Siemens.

The rationale behind the use of ammonia and liquid oxygen (LOX) was the need for a stable fuel with good volumetric energy density, easy to store, working in the required temperature range, with cooling properties and also potential for hydrogen engine development. However, due to the lack of motivation and no clear understanding of the need for using ammonia and the need for gravimetric energy density based fuels, the programme stopped. During the period that the project ran, the X-15 aircraft was developed. The aircraft, a powerful device commissioned by NASA, set unofficial world records in speed and altitude [176].

Thomas [237] and Thomas et al. [238] discussed the use of methane-ammonia-oxygen blends in terms of their potential to allow deflagration to detonation transition in small piping lines, a technique that can be used for propulsion applications. Compositional ranges were obtained by varying the oxygen content whilst maintaining methane/ammonia ratios of 1.00:1.18. The results showed that flame speeds were modest for all mixtures where the oxygen percentage was 39% or less. Similarly, violent pressure transients were not observed for mixtures with less than 40% oxygen. Beyond these values, violent and sometimes detonating transitions were observed for the cases analysed, especially for initial pressures above ambient.

Micro-thrusters fuelled with ammonia, a revolutionary concept for propulsion of small space vehicles, has also received some interest especially in Russia, China and the USA. Blinov et al. [239,240] presented some work in terms of the design features and performance of ammonia electrothermal micro-thrusters, showing that they can become a competitive, cost effective option due to their specific impulse increase ~20%. Fatuev et al. [241] have also presented work on the development of ACETAM, a rocket fuel based on the fluidization of gaseous acetylene by a highly concentrated dilution in liquefied ammonia. The characteristics of the fuel show improvement and higher stability when compared to other blends at various operating pressures, nozzle expansion degrees and efficiency through various stages during space launching.

Chinese groups have also studied the thermodynamic properties and potential of propellants using acetylene and ammonia [242]. Various concentrations of acetylene-ammonia with LOX and other fuels such as rocket kerosene and methane were evaluated thermodynamically. The results indicated that a 25% acetylene content was the best in terms of specific impulse and security, with properties that were superior to LOX with rocket kerosene.

Some published work can also be found for the development ‘of ammonia micro-resisto-jets (MRJ) for micro-satellites by Busek Co. Inc. Robin et al. [243] evaluated the use of ammonia MRJs to cope with weight and complexity constraints whilst creating a high thrust/power system. Laboratory experiments showed exit temperatures of 573–1448 K, with trust levels of 5–12 mN with specific impulses as high as 210 s. These ammonia micro-resistojet provided up to 25 W nominal power level. Due to the small nature of the system and its innovative design using platinum tubes, the total device weight is about 15 gm. A successful 100 h Engineering Model (EM) was carried out, leading to further plans for development.

Although the technology is promising, literature on this topic is still scarce, opening the possibilities for further research for micro-satellites and other micro-propulsion systems using ammonia.

3.5. *Combustion fundamentals of ammonia flames*

As presented, ammonia is a potential fuel that could be used for cooling, transportation and storage of integrated systems based on combustion processes, thus delivering significant power for industrial applications.

3.5.1. *Ammonia characteristics*

As discussed, ammonia still faces a long way before being entirely recognised as a fuel for power applications. Although technical barriers are overcome by continuous, high quality research combined with advanced innovation, i.e. as the ones presented in previous sections, one of the main reasons of this trend is the fierce competition between ammonia and other fuels. As stated, ammonia should not be regarded as a competitor to the hydrogen economy, but as an enabler. Therefore, ammonia can find its niche of application amongst some other fuels that are currently under research. In order to recognise these applications, it is necessary to know some specific characteristics of ammonia to allow comparison with other hydrogen sources employed in power systems. Out of the vast range of alternatives, methanol and pure hydrogen were selected for this review, Table 6. Methane is also mentioned as baseline.

Table 6
Ammonia combustion characteristics and comparison with other fuels, 300 K at 100 kPa.

	Methane (CH_4)	Hydrogen (H_2)	Methanol (CH_3OH)	Ammonia (NH_3)
Density (kg/m^3)	0.66 [244]	0.08 [244]	786 [244]	0.73 [244]
Dynamic viscosity $\times 10^{-5}$ (P)	11.0 [245]	8.80 [245]	594 [245]	9.90 [245]
Low heating value (MJ/kg)	50.05 [246]	120.00 [246]	19.92 [246]	18.80 [25]
Laminar burning velocity (m/s) – close to stoich.	0.38 [247]	3.51 [203]	0.36 [247]	0.07 [248]
Minimum ignition energy (mJ)	0.280 [249]	0.011 [249]	0.140 [249]	8.000 [212]
Auto-ignition temperature (K)	859 [10]	773–850 [250]	712 [251]	930 [10]
Octane number	120 [252]	–	119 [253]	130 [10]
Adiabatic flame temperature (with air) (K)	2223	2483	1910	1850 [10]
Heat capacity ratio, γ	1.32 [244]	1.41 [244]	1.20 [244]	1.32 [244]
Gravimetric Hydrogen density (wt%)	25.0	100.0	12.5	17.8

It is clear that pure ammonia shows both low specific energy and laminar burning velocities combined with high auto-ignition temperatures and elevated ignition energies, making it more difficult to burn in its pure form. As a consequence, blends with hydrogen, i.e. which can be obtained relatively easy from cracking of the ammonia molecule, have been mostly attempted in more practical applications. Moreover, the use of ammonia with gases such as methane, i.e. that shares similar density, viscosity and heat capacity, makes relatively easy its implementation in co-firing applications. Thus, ammonia has considerable potential to compete with other hydrogen-carrier fuels. However, before ammonia can be implemented in power devices, further understanding of its combustion behaviour is required, mainly by further research that not only demonstrates the concept but also details the chemistry of burning ammonia for enhancement and control of such a process.

3.5.2. Reaction models for ammonia

To develop combustion-based technologies for ammonia utilisation, it is essential to have a deep understanding of the detailed chemical process through the ammonia combustion phenomena. Therefore, research has been dedicated to understand the fundamental characteristics of ammonia and the detailed reactions that occur throughout the combustion process.

As early as 1960s, studies [254,255] were performed to understand the chemical reactions of flames containing ammonia. A wide range of compositions and conditions were investigated to gain more insight into the kinetics of ammonia-fuelled flames [256–258]. The first complete description of a detailed chemical mechanism for ammonia oxidation was proposed by Miller and Bowman [259] based on the ammonia combustion experiments. Comparison between the theoretical kinetic model and experimental data showed good performance of the Miller mechanism for ammonia combustion over a range of temperatures, equivalence ratios and pressures, with especial emphasis on the performance of the NOx chemistry. Actually, mechanisms for NOx formation and removal processes are carefully considered in this study, of which important elementary reactions and their coefficients were provided. The results enabled analyses that demonstrated that NO/N_2 production is mainly dependant on the fate of NHx radicals, which are oxidised to form NO through the nitroxyl (HNO) molecule. Miller's mechanism has been correlated to a wide range of conditions in several ammonia combustion studies across the years [260–262].

Based on the Miller's [259] mechanism, Lindstedt et al. [263] developed a chemical kinetic mechanism model for ammonia oxidation in a wide range of flat laminar flames. Important elementary reactions were recognised for NO formation processes for pure ammonia and its blends doped with hydrogen. It was found that the Zeldovich mechanism is responsible for the NO formation and conversion under greater fuel concentrations of ammonia/hydrogen flames while the reaction $NH + OH$ plays a more significant role in NO formation when using pure ammonia.

Skreiberg et al. [264] established a detailed chemical kinetic model for ammonia oxidation in the presence of hydrogen, carbon monoxide, and methane. The H/N/O submechanism draws primarily on Miller's work on ammonia flames. In this mechanism, several reactions were characterized more accurately and the mechanism model satisfactorily predicts flow reactor measurements data. The results are summarised for low temperatures which will promote the reaction path $NH_3 \rightarrow NH_2 \rightarrow N_2$, whilst $NH_3 \rightarrow NH_2 \rightarrow NH \rightarrow N$ is important at higher temperatures. Lindstedt's model has also been employed in several ammonia combustion studies [261,265,266].

Among the detailed mechanisms proposed for ammonia combustion, Konnov's kinetics model [267] has been widely used and verified for ammonia combustion studies, proving a better performance on the prediction of NOx emission and propagation among many other mechanisms available [266,268–271]. This detailed chemical kinetics mechanism [272] was originally developed for the combustion of small hydrocarbon fuels considering the presence of ammonia. The mechanism model has been updated continuously and in the latest version the model was greatly improved compared to previous versions, with particular attention paid to the upgrading of the H/N/O sub-mechanism in the development of the model. Specifically, with the improved implementation of the NCN pathway, a more accurate calculation of NO formation and NCN radicals in the flame were obtained. It has been tested against experimental data available for oxidation, ignition, and flame structures in mixtures of nitrogen-containing species, hydrogen, carbon monoxide and hydrocarbons.

Duynslaegher et al. [268] found in her stabilised flame experiments of ammonia–oxygen–hydrogen mixtures that using the Konnov mechanism would overestimate the mole fraction profiles of radical NH_2 while underestimating the ones of N_2O. Therefore, Duynslaegher et al. [273] improved Konnov's ammonia combustion mechanism model by modifying the reactions containing nitrous oxide (N_2O) and amidogen radical (NH_2). In this work, rate constants were modified for four elementary reactions $NH + NO = N2O + H$, $N2O + H = N2 + OH$, $NH2 + H = NH + H2$, $NH2 + NH2 = N2H2 + H2$, on the basis of Konnov's mechanism. As NH_2 is the main intermediate in the oxidation of ammonia and therefore the precursor related to the formation of almost all the combustion products, the improvement of NH_2 radical profile predictions lead to a significant prediction improvement on radicals such as nitrous oxide, nitrogen monoxide and the amidogen radical. In this study a reduction version of the mechanism model was also provided for the use in internal combustion engine conditions.

The Tian mechanism [274] was then developed based on $NH_3/CH_4/O_2/Ar$ flame data under low pressure conditions. In Tian's research, profiles of combustion intermediates and products were determined in 11 premixed flames of different mole ratios of NH_3/CH_4. The updated chemical mechanism model by Tian et al. satisfactorily identified detailed flame structure features. The model and experiments showed that with more ammonia fraction in the fuel mixtures the products of H_2O, NO and N_2 increase whilst those of H_2, CO, CO_2 and NO_2 indicate reverse tendencies. Analyses performed with this mechanism have demonstrated key reactions such as $H + O_2 = O + OH$, $NH_2 + O = HNO + H$, $NH_2 + NO = N_2 + H_2O$, and $NH + NO = N_2O + H$, which have prominent effect for NO and N_2 conversion. Also key species such as CH_3, $1CH_2$, $3CH_2$, CH_2O, NH_2, NH and HNO were identified in the oxidation of CH_4/NH_3 mixtures. Tian's mechanism has been widely used recently over a wide range of conditions [269,275].

Mendiara and Glarborg [276] also conducted an experimental study in a laminar flow reactor and developed a chemical kinetics model for NH_3 oxidation in oxy-fuel combustion of CH_4/NH_3 with temperatures ranging from 973 to 1773 K. The reactor in the experiments was operated under atmospheric pressure conditions and stoichiometries between 0.13 and 0.55 equivalence ratios. The kinetic mechanism model is based on the Tian mechanism describing CH_4/NH_3 oxidation, especially extending hydrocarbon/amine interaction subsets. Through pathway analyses it was identified that the formation of NO is mostly related to HNO which is primarily sourced from $NH_2 + O$. This detailed chemical mechanism also successfully captured experimental trends for the effects of high CO_2 concentration.

Mathieu and Petersen [277] studied the oxidation of ammonia under high temperatures (1560–2455 K) and high pressures (around 0.14, 1.1, and 3.0 MPa) conditions. A detailed mechanism model was established for ammonia oxidation from shock tube experiments. The mechanism also provided a state-of-the-art NOx sub-mechanism which can be used for a wide range of conditions. The established chemical mechanism has proved accurate in predicting ignition delay times of ammonia oxidation under elevated conditions, which are more relevant to many industrial applications.

There are some other detailed chemical mechanisms, which are originally developed for hydrocarbon fuels, also potentially able to be used in ammonia combustion studies. For instance, the famous GRI Mech 3.0 mechanism [278] is extensively employed for combustion of natural gas, which includes the formation of NOx and reburn chemistry. GRI-Mech 3.0 mechanism is also used as reference for NH_3 oxidation in some literature [266,269,279], since ammonia-doped methane/air flames using this mechanism have also been studied in the past with satisfactory results [280]. Other mechanisms such as Åbo Akademi (ÅA) kinetic reaction scheme [281] were created for specific conditions. Particular for ÅA, the mechanism was developed for combustion of biomass-derived gases under moderate temperature, being validated in the flameless ammonia chemistry study of [282].

Nozari and Karabeyoglu [283] developed a reduced chemical mechanism for the combustion of ammonia/hydrogen based on the Konnov mechanism, which aims to expedite the design of future ammonia combustors. Li et al. [284] numerically analysed the enhancement of hydrogen addition in ammonia-fuelled blends, with emphasis on flame speed and ignition. Reactions of $O+H_2=OH+H$, $H+O_2=OH+O$ and $H_2+OH=H_2O+H$ were identified as playing the most important role in the increased reactivity of the blend. At high temperature, these findings suggest that blow-off limits, the concentration of radicals H, OH and O and the maximum flame temperature are enhanced with H_2 substitution in benchmark NH_3/air flames, demonstrating that hydrogen doping could potentially facilitate the use of ammonia as a reliable alternative fuel, with increased laminar flame speed, reduction of emissions and positive changes in Markstein length.

Xiao et al. [231] studied ammonia/hydrogen blends with various kinetic models, suggesting that all these mechanism present considerable variance between experimental results at various conditions, Fig. 28. This was expected as most of the models are developed for specific equivalence ratios, mixtures, pressures, etc. However, it is found with great interest that does not exist yet a reaction model capable of capturing accurately the great variety of conditions at which ammonia can be burned. There is still considerable progress to be made before a generalised model can be proposed and implemented, particularly at specific conditions where low NOx are measured. Currently, each condition will present different degrees of reaction, making critical the development of mechanisms for specific conditions and fuel blends.

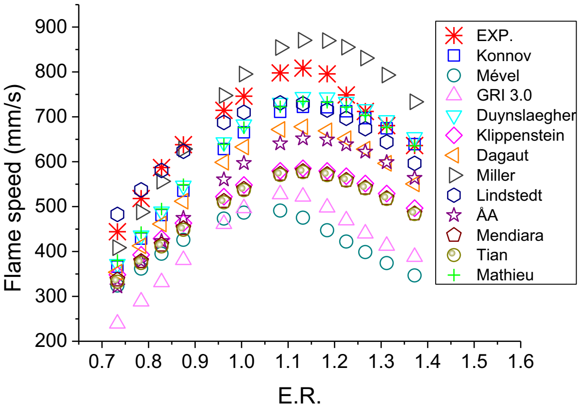


Fig. 28. Flame speed calculation of 40% NH3 flame at normal temperature and pressure. Experiments as in [215]. Reprinted from [231] with permission from ASME.

Therefore, there is still much debate on these phenomena and their impact on both the flame and the combustion process when using NH_3. For example, the work done by Okafor et al. [285] enabled the development of a more accurate reaction model for studies of ammonia-methane flames under atmospheric conditions using a combination of laminar burning studies and advanced ammonia kinetic models. The GRI-Mech 3.0 and Tian's models were utilised to develop a detailed reaction mechanism suitable for ammonia-methane combustion, finding that Tian's model underestimates the un-stretched laminar burning velocity owing to the dominance of $HCO(+H, OH, O_2) \rightarrow CO$ (H_2, H_2O, HO_2) over $HCO \rightarrow CO + H$. This is in accord to recent studies carried out by Xiao et al. [286], who through studies of ignition delay, flame speed and emissions suggests that Tian's model was better suited for analyses of ammonia-methane blends, although there is still a need for improvement.

Hence, there is still considerable debate on the parameters required for development of a most appropriate model for ammonia combustion analyses, problem that has been largely solved by selecting models based on their accuracy at the particular conditions at which they have shown superior performance compared to the rest. This problem has paved the path for current research on the topic, with groups across the globe trying to determine the best model that fits all the different flame and combustion variables.

3.5.3. Fundamental studies of flame characteristics

Many parameters influence the flame characteristics. For example, laminar burning velocity is an important combustion property defined based on an adiabatic planar un-stretched flame, and is required for characterisation of phenomena such as flame stability and validation of reaction models. Flame speed, a combination of the burning rate and density ratio, is also an important parameter in understanding the fundamentals of a particular flame. Similarly, the Markstein length, another important combustion parameter, expresses the sensitivity of the laminar burning velocity to flame stretch rate due to themo-diffusive effects [287]. Of course equivalence and compression ratios, ignition delay time, radical formation, etc. have an important impact on the adiabatic flame. These

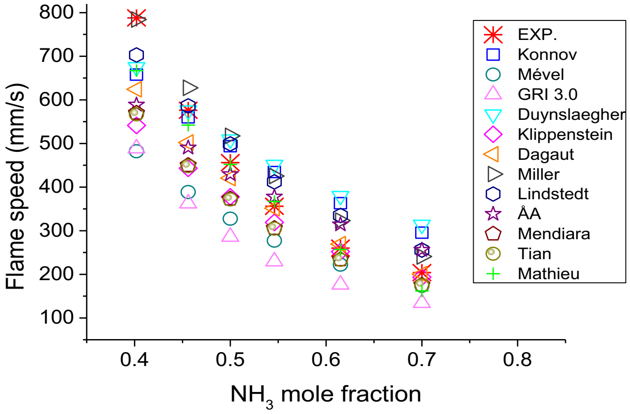


Fig. 29. Flame speed calculation of stoichiometric condition (ER = 1.00). Experiments as in [215]. Reprinted from [231] with permission from ASME.

and some other parameters are essential to understand the combustion process of a particular fuel.

There are already plenty of work performed on the propagation property of ammonia-based fuels. Takizawa et al. [288] measured the flame speed for NH_3/air mixtures of different stoichiometry by the spherical vessel method under atmospheric conditions, obtaining a maximum value of 0.072 m/s at equivalence ratio of 1.10. Lee et al. [261] tested laminar premixed hydrogen-added ammonia/air flames to determine flame speed and NOx and N_2O emissions. The results suggested hydrogen as a promising additive for improving the combustion performance with low NOx and N_2O emissions under fuel-rich conditions. Furthermore, other studies [289] were performed by the same group on the effect of ammonia substitution on ammonia/hydrogen/air flames both experimentally and computationally. The results showed that ammonia substitution will significantly reduce laminar flame speed and increase nitrogen oxide emissions in hydrogen/air flames. It was also found that nitrogen oxide emission of fuel rich conditions are much lower than fuel lean conditions.

Kumar and Meyer [269] performed a series of measurements of laminar flame speeds for ammonia/hydrogen/air jet flames. In this study, ammonia fraction within the fuel was varied in step increases of energy delivered up to a maximum of 80% for equivalence ratios between 0.5 and 1.1. Computational models were developed using the GRI-Mech 3.0, Tian, and Konnov reaction mechanisms. Numerical calculations on laminar flame speed considering heat loss showed that Konnov mechanism and Tian mechanism have good prediction accuracy against experimental data, highlighting production of the OH radical as the key performance variable in modelling laminar NH_3 decomposition. Simultaneously, work conducted by Xiao et al. [231] has demonstrated that the use of GRI-Mech 3.0 for prediction of ammonia based flames underpredicts several fundamental characteristics of such flames. Although Konnov's and Tian's provided good results, as shown by others [269], Mathieu's performed better when using fundamental parameters such as flame speed.

As shown in Fig. 29 [231], different mechanisms present different performance while predicting flame speed when compared with experimental data [215]. Results show that performance of these mechanisms for prediction of various ammonia fractions significantly varies, e.g. when ammonia fraction of ammonia is less than 50% the predictions are relatively poor as compared to those using greater mole fractions. This indicates that low ammonia fraction combustion chemistry for NH_3/H_2 blends still needs to be optimized. Furthermore, it was identified that hydrogen has an accelerant role in hydrogen/ammonia/air combustion, while ammonia has a major detrimental effect in laminar flame speed.

In the research of Ichikawa et al. [290], hydrogen/ammonia/air flames were experimentally and numerically investigated at elevated pressures up to 0.5 MPa. The laminar flame speed increased exponentially as the hydrogen fraction in the blend was increased, reaching a similar order of magnitude observed for conventional hydrocarbon flames when the hydrogen fraction in the fuel is 0.4. Decrease of laminar flame speed was identified with increasing initial pressure conditions in this study. Moreover, it was demonstrated that the Markstein length decreases when the ambient mixture pressure was increased from 0.1 to 0.3 MPa, with the Markstein lengths at 0.5 MPa very similar to those at 0.3 MPa.

To determine the impact of practical conditions such as elevated ambient temperatures and pressures on the combustion of ammonia, analysis using premixed ammonia–air mixtures with equivalence ratios around unity, at conditions which are encountered in Spark Ignition engines have also been performed. Duynslaegher et al. [265] numerically investigated laminar flame speed and NOx emission concentrations of premixed ammonia combustion using Konnov's mechanism at elevated pressure and temperature conditions (0.1–4.9 MPa, 298–732 K), relevant conditions for engine operation. In this study, corresponding to a 40% increase in compression ratio, the laminar flame speed increases up to 30% whilst a difference of 100 K is noted for the adiabatic flame temperature. It is suggested that both equivalence ratio and compression ratios have an important impact on the adiabatic flame temperature and laminar flame speed while equivalence ratio is the major factor influencing the NO formation. Then Hayakawa et al. [266] evaluated the flame speed for spherically propagating premixed flames of ammonia/air under elevated conditions. It was the first experimental work that clarified the decrease of flame speed under high pressure condition up to 0.5 Mpa. It demonstrated that Konnov's model, established for ammonia combustion analyses, over-predicts laminar burning velocity. At the same time, Li et al. [284] numerically investigated the ammonia combustion characteristics under oxygen enriched conditions and proposed it as a potential method to improve ammonia combustion performance and flame speed.

Sullivan et al. [282] performed both experimental and modelling studies of a laminar ammonia-seeded methane diffusion flames. Within the conditions of this investigation, it was identified that with higher ammonia concentration, more percentage of ammonia is converted to N_2 rather than to NO. In the work from Henshaw et al. [291] the flame speed and combustion products of premixed NH_3–CH_4-air flames at atmospheric ambient conditions were measured using an adiabatic flat flame burner, complemented by numerical simulation. This study was undertaken for equivalence ratios between 0.5–1.5 and for NH_3 fractions of 0% to 5% by volume in the fuel, as observed in some industrial processes. The measured flame speed agreed well with simulated results and the addition of 4% ammonia was seen to result in a 10%–20% decrease in flame speed. Both simulations and experiments showed that adding NH_3 to CH_4-air mixtures resulted in an increase in NOx concentration, especially at stoichiometric conditions, with a minimal effect on CO formation. Near the flammability limits, less than 0.1% of the incoming NH_3 penetrated the flame. Konnov et al. [292] conducted an experimental study of methane/oxygen/nitrogen flames doped with ammonia (0.5% of the fuel), in which flame speed with different equivalence ratios was measured. Li et al. [293] studied ammonia-doped methane/air flames on a perforated plate burner at atmospheric pressure using laser-saturated fluorescence (LSF) and probe sampling for NO concentrations measurement. It was suggested that the results of ammonia conversion disagree with some other earlier experiments due to their lack of proper coating in cylinders. Also, the exper-

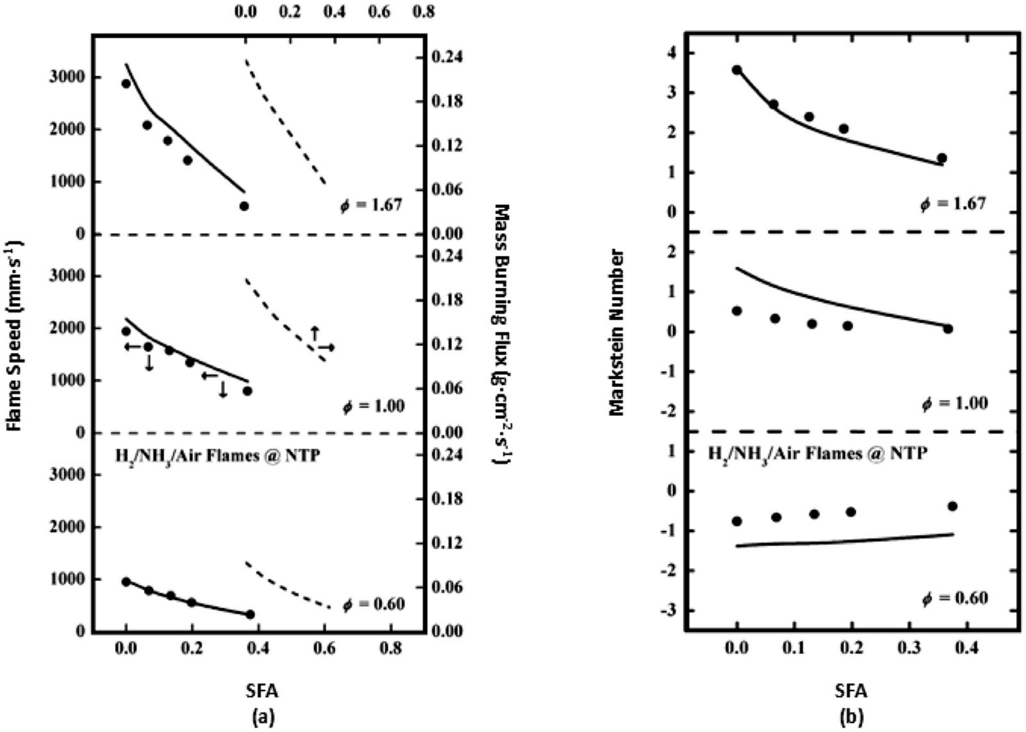


Fig. 30. Tests carried out at 3 different equivalence ratios (ie. 1.67, 1.00 and 0.60) a) Change in flame speed and mass burning flux for varying Hydrogen-Ammonia ratio, specified by the Stoichiometric Fraction of Ammonia (SFA). b) Change in Markstein Number for varying Hydrogen-Ammonia ratio. Symbols for measurements and lines (solid: unstretched laminar burning velocities; dashed: mass burning fluxes) for predictions. Reprinted from [262] with permission from Int J Hydrogen Energy, Elsevier.

imental results of NOx formation were accurately reproduced by the flame modelling with the Konnov mechanism, which verified the capability in predicting ammonia conversion both in lean and in rich flames.

At high temperature, findings suggest that blow-off limits, the concentration of radicals H, OH and O and the maximum flame temperature are enhanced with H_2 substitution in benchmark NH_3/air flames, demonstrating that hydrogen doping could potentially facilitate the use of ammonia as a reliable alternative fuel, with increased laminar burning velocity, reduction of emissions and positive changes in Markstein length [261,262,290,294–297]. Moreover, the peak laminar flame speed for NH_3-air combustion across equivalence ratio is ~0.08 m/s, compared to an equivalent value of ~2.80 m/s for H_2. This provides the opportunity for significant variation as the mixture ratio changes. Results presented by Lee et al. [262] analyse three different equivalence ratios (0.60, 1.00, 1.67), increasing the NH_3 mole fraction in hydrogen at five stages in the range of 0.0–0.3. The changes in flame speed and mass burning flux measured are shown in Fig. 30 results are presented against equivalent Stoichiometric Fraction of Ammonia (SFA), in the range 0.000 – 0.375.

Further progress in understanding the behaviour of these flames is reported in [290,298] using hydrogen flames doped with NO and ammonia. Results presented the analysis of using different molecules in lean and rich hydrogen blends with O_2, Ar and N_2. The findings showed that the doping with NH_3 did not affect concentration profiles of the stable species, H_2, O_2 and H_2O species. The zone of NH_3 consumption was reported to be about 0.6–0.8 mm in the lean and near-stoichiometric flames and approximately 1.7–1.9 mm for the fuel rich flames. The laminar burning velocity increased exponentially as the hydrogen fraction in the blend was increased, reaching a similar order of magnitude observed for conventional hydrocarbon flames when the hydrogen fraction in the fuel is 0.4. Moreover, it was demonstrated that the Markstein length decreases when the ambient mixture pressure was increased from 0.1 to 0.3 MPa, with the Markstein lengths at 0.5 MPa very similar to those at 0.3 MPa.

As for the combustibility of ammonia and hydrogen doped ammonia/air flames, in the experiments of Shebeko et al. [299] flammability limits for ammonia and ammonia/hydrogen mixtures were studied at temperatures and pressures of up to 343 K and 1.0 MPa respectively. It was identified that the lower concentration limit of ammonia/oxygen flame decreases significantly at elevated temperature and pressure. Pfahl et al. [300] also studied the flammability limits, ignition energies, and flame speeds of different ammonia contained mixtures experimentally. The experiments were carried out in a closed combustion vessel at initial pressures of 0.1 MPa and temperatures of 295 K. The ignition energy experiment results of lean ammonia–nitrous oxide mixtures indicate that under high ignition energies (higher than 5000 J) the initiation of combustion occurs independent of fuel amount of ammonia, while there is an obvious minimum concentration of ammonia fuel for low ignition energies (up to 10 J). It is also shown that increasing the initial amount of nitrous oxide in ammonia–air–nitrous oxide gases increases the laminar flame speed. Ciccarelli et al. [301] explored the flammability map of ammonia and ammonia/hydrogen mixtures in air at the initial temperature up to 873 K and atmospheric pressure conditions. The flammability map showed to widen linearly with increased initial temperature. It was also shown that as the mixture fraction of the ammonia dissociation products increased in mixtures of ammonia and hydrogen and nitrogen - the ammonia dissociation products, the flammability limits tend to widen.

Lee and Kwon [302] numerically studied counterflow nonpremixed ammonia/hydrogen/air flames at normal temperature and pressure to improve the safety of hydrogen use. Effects of ammonia on reducing high-stretch extinction limits of hydrogen/air flames were identified. Um et al. [260] experimentally examined the combustion stability limits and nitrogen oxide emissions of non-premixed ammonia/hydrogen/air flames at normal tempera-

Table 7
Summary of flammability and stability limit studies in the recent literature for ammonia-based mixtures.

Reference	Methodology	Fuel mixture	Initial conditions
Shebeko et al. [299]	Experimental reaction vessel	NH_3/O_2, $NH_3/H_2/O_2$, $NH_3/O_2/N_2$, $NH_3/H_2/O_2/N_2$,	20–70 °C 0.1–1MPa
Pfahl et al. [300]	Experimental combustion vessel	$NH_3/N_2O/N_2$, $NH_3/N_2O/O_2/N_2$	100 kPa and 295 K
Ciccarelli et al. [301]	Experimental combustion vessel	$NH_3/H_2/O_2/N_2$	20–600 °C 1 atm
Lee and Kwon [302]	Numerical counterflow	$NH_3/H_2/O_2/N_2$	NTP
Um et al. [260]	Experimental and numerical nozzle	$NH_3/H_2/O_2/N_2$	NTP
Choi et al. [294]	Experimental and numerical counterflow	$NH_3/H_2/O_2/N_2$	348–495 K 1atm

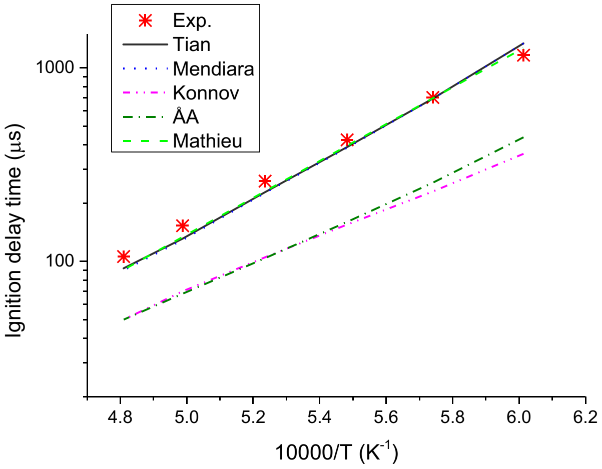


Fig. 31. Ignition delay times of NH3 mixtures (0.4%NH_3/0.6%O_2/99%Ar), 1.1 MPa. Experiments from [277]. Reprinted from [286] with permission from FUEL, Elsevier.

ture and pressure conditions. The study justified the potential of NH_3 substitution for improving the safety of H_2 combustion with significant reduction observed in stability limit. Choi et al. [294] explored the potential of using H_2 as an additive for improving the reactivity and ignition of nonpremixed NH_3/air flames. The extinction limits, flame temperature and morphology of the counterflow nonpremixed ammonia/hydrogen/air flames were experimentally determined at elevated temperatures and normal pressure. Results showed enhanced blow-off limits and the maximum flame temperature with hydrogen substitution in ammonia /air flames. A summary of the relevant studies on ammonia combustion stability is presented in Table 7.

Ignition delay, another important combustion parameter, can also provide insights of the accuracy of various chemical models. In the work of Mathieu et al. [277], ammonia oxidation and ignition delay time were measured in a shock tube for a wide range of conditions at pressures above 1.0 MPa. As can be seen from Fig. 31, data from Mathieu et al. [277] are compared to several updated literature models. As for Konnov and ÅA mechanism, it is clear that differences of more than an order of magnitude are recorded, while Tian, Mendiara and Mathieu's mechanisms show good prediction. Thus, chemistry prediction under various conditions is still a problem for modelling purposes, as the reaction of ammonia is highly dependent on the conditions used for development of each reaction mechanism [231]. For this particular case, high pressurised conditions seem to be better predicted using the latest mechanism.

Emissions related, Li et al. [215] have studied a range of hydrogen and ammonia blends in order to observe the emissions produced at different equivalence ratios, simultaneously showing that NH_3 burning velocity improved with increasing H_2 concentration in the flame. In addition, fuel-NOx has a dominant role and thermal-NOx has a negligible role in H_2–NH_3-air combustion. It was observed that thermal-NOx decreases in H_2–NH_3-air combustion compared to pure H_2-air combustion, while NOx concentration reached its maximum at the stoichiometric condition. Further works provide modelling analyses of hydrogen-doped ammonia blends with preheating of the reactants. Results showed that the formation reaction rates of thermal NO from $N + O_2 \rightarrow NO + O$, and $N + OH \rightarrow NO + H$ increased with increasing reactant preheating under fuel lean condition. Under fuel rich conditions, the reactions of $NH_2 + NO \rightarrow N_2 + H_2O$, $NH + NO \rightarrow NNH + OH$ were shown to have a great effect on the decomposition of NO at all preheating temperatures of the reactants, which results in an extremely low NO formation rate, indicating the potential to reduce NO formation in NH_3 combustion [303]. However, it must be emphasized that current technologies have been only capable of reducing NOx in the combustion zone by a trade-off between the latter and unburned ammonia. Hence, the results suggest that combustion of H_2 and NH_3 should be carefully considered for the practical utilization of this blend.

Characterisation of emission profiles of species such as NH_3, O_2, H_2O, NO and N_2O are crucial in gaining understanding and confidence in the behaviour of reaction mechanisms with ammonia fuels. In the work of Brackmann et al. [304] data were provided of OH, NH and NO profiles for premixed ammonia/air flames using contemporary laser-induced fluorescence at atmospheric pressure. The kinetics analysis combined with this experimental data showed that the Mendiara mechanism performed best prediction for temperature, radical profiles and flame front positions.

Regarding other radicals and their impact on emissions, HNO is an important radical for the production of NO which is mainly produced from the interaction of NH_x radicals with OH, H_2, O, O_2 and H_2O [305]. Thus, enhancement of these radicals can increase the production of NOx emissions. This has been recently demonstrated by Valera-Medina et al. [36] who showed the increase of NO emissions by a couple of orders of magnitude in transitioning from lean to rich conditions during experiments within an industrially-relevant generic swirl combustor. The increase of OH radicals in the lean region directly impacts on the production of HNO, thus increasing nitrogen oxides considerably. The trend was clearly identified not only by the experimental diagnostics, but also by reaction models. Recommendations are based on avoiding these regimes under fully premixed conditions, suggesting the use of stratified injection to eliminate lean combustion spots prone to the interaction of NH_x radicals and OH that will benefit production of HNO. A further study [306] utilising 1D and 2D numerical simulations using GRI-3.0 Mech predicts the production of NOx at different oxygen/hydrogen/ammonia concentrations. The results show the complex interaction between the different formation mechanisms of nitrogen oxides, with a competition between thermal and fuel based nitrogen reactions that reaches a peak followed by a reversal phenomenon. This reversal seems to be caused by a reduction in reaction rates combined with the impact of ammonia as NO production accelerator in the internal layers and as inhibitor of nitrogen oxides in the external layers. However, as previously stated, this chemical reaction model has shown a lower performance when analysing ammonia based fuels.

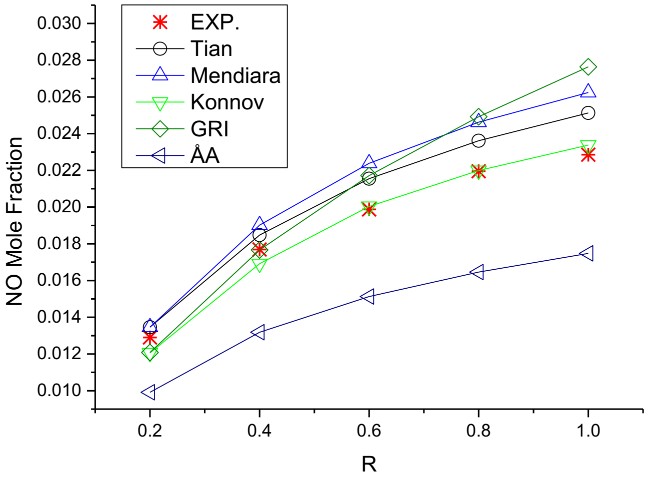


Fig. 32. Exhaust NO emission as a function of NH3/CH4 mole ratio. Some data from [286].

Methane, as previously stated, has also been proposed for blending with ammonia in power generation devices. Oxidation of NH_3 during oxy-methane combustion, i.e., at high CO_2 concentrations, has also been studied as another option to improve the combustion process [276]. High levels of CO_2 were shown to enhance the formation of NO under reducing conditions, whilst inhibiting NO formation under stoichiometric and lean conditions. The enhanced CO concentrations and variation of the quantity and relative proportion of O/H radicals, rather than direct reactions between N-radicals and CO_2, are responsible for the effect of a high CO_2 concentration on ammonia conversion. When CO_2 is present as a bulk gas, formation of NO is facilitated by an increased OH/H ratio, obtained from $CO_2 + H \rightleftharpoons CO + OH$. In addition, high CO levels also enhance HNCO formation. However, the reaction of $NH_2 + O$ to form HNO and $NH_2 + H$ to form NH are inhibited due to the reduced concentration of O and H radicals. Instead, reactions of NH_2 with species from the hydrocarbon/methylamine pool preserve reactive nitrogen as a reduced species. These reactions reduce the NH_2 availability to form NO by other pathways, for example via HNO or NH, and increase the probability of N_2 over NO formation.

In the work of Tian et al. [274], flames with different mole ratios (R) of NH_3 /CH_4 were experimentally studied. Mole fraction of flame species such as reactants, intermediates and products were specifically determined, providing a deep insight into the characteristics of ammonia/methane flame chemistry. As shown in Fig. 32, an increase in R increases the NO quantities at the exhaust. Comparison of experimental data against predictions of several widely tested kinetic models shows that Konnov mechanism gives the best performance, which is also widely verified in other ammonia combustion studies. The pathway of ammonia oxidation is also figure out in this study, Fig. 33. Thus, the study concludes that the main formation source of NO is from the reactions $HNO + H \rightarrow NO + H_2$, $HNO + OH \rightarrow NO + H_2O$ (SR306) and $NH + O \rightarrow NO + H$ (SR376).

In the work from Henshaw et al. [291] the burning velocity and combustion products of premixed NH_3–CH_4-air flames at atmospheric ambient conditions were measured using an adiabatic flat flame burner, complemented by CHEMKIN-PRO simulation. This study was undertaken for equivalence ratios between 0.5–1.5 and for NH_3 fractions of 0% to 5% by volume in the fuel, as observed in some industrial processes. The measured burning velocities agreed well with simulated results and the addition of 4% ammonia was seen to result in a 10% - 20% decrease in burning velocity. Both simulations and experiments showed that adding NH_3 to CH_4-air mixtures resulted in an increase in NOx concentration, especially at stoichiometric conditions, with a minimal effect on CO formation. Near the flammability limits, less than 0.1% of the incoming NH_3 penetrated the flame. Further numerical studies for premixed flames using methane/ammonia/air have been undertaken to characterise the use of these blends in industrial processes [230,291], Figs. 34 and 35. Results indicate the potential application of blends for backup power generation, especially at rich equivalence ratios due to the lower NO emissions. However, it is clear the complex path during production of emissions, as previously stated, thus requiring further research for their mitigation.

Other studies have considered the reaction of ammonia with species such as CH_4, CO and NOx [264] for practical scenarios. Numerical and experimental results showed that NH_3 may be converted mainly to NO or to N_2, depending on reaction conditions [264]. The aim of these primary measures is to promote the for-

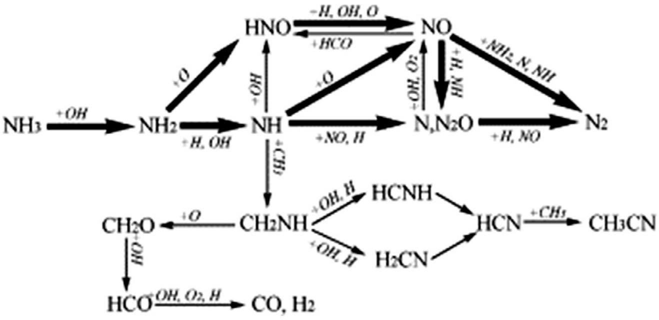


Fig. 33. Flow rate analysis of the consumption of NH3/CH4 in the flame R of 1.0. Reprinted from [274] with permission from Combustion and Flame, Elsevier.

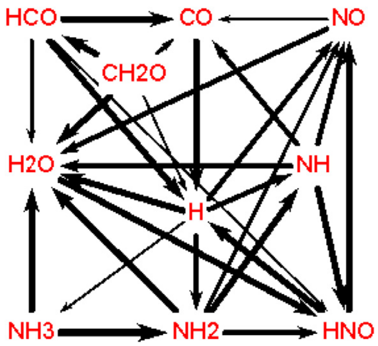


Fig. 34. Reaction path of NO formation. Reprinted from [230] with permission from Energy and Fuels, ACS.

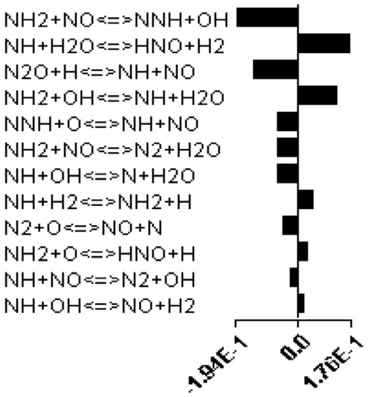


Fig. 35. Normalized sensitivity of NO using Konnov's. Reprinted from [230] with permission from Energy and Fuels, ACS.

mation of N_2 by limiting the availability of oxygen while oxidising other molecules. The reactions of NH_3 with the O/H radical pool is fairly well established over a wide temperature range, all showing significant non-Arrhenius behaviour. The chemistry of the smaller amines, NH_2 and NH, is more uncertain; in particular the rate constants for the radical–radical reactions. At moderate temperatures below 1400 K, the fate of NH_2 largely determines the oxidation pathway of the ammonia as well as the reaction selectivity toward NO and N_2. The key step in the production of NO is the fast $NH_x + HNO$ reaction. The reactions with these molecules have been barely studied experimentally in the intermediate temperature range, and so their rate constants present significant uncertainties. The comparatively low temperatures utilised in studies to date, as well as the presence of NO, promote the reaction path $NH_3 \rightarrow NH_2 \rightarrow N_2$ (directly or via NNH), rather than $NH_3 \rightarrow NH_2 \rightarrow NH \rightarrow N$, which is important at higher temperatures. The major reduction of fuel-N species to N_2 occurs by reaction of amine radicals with NO.

Although the results are relevant for the study of NH_3 and the role of radicals across the different boundaries of the flame towards production of nitrogen oxides, it is evident that considerable work is still required to determine the role of ammonia and other radicals in the formation and consumption of NOx through flames to determine a most general and accurate reaction model, as currently there are various available in the literature.

Therefore, knowing these parameters can provide support for development of new designs, equipment and control of emissions when employing ammonia combustion. Hence, research groups have been studying these fundamental parameters for the use of ammonia with various blends under different operational conditions. The ignition characteristics of ammonia, flame speed, Markstein length, combustibility, characterisation of emission profiles of species such as NH_3, O_2, H_2O, N_2O and NO [304], radical formation, etc. are all crucial in gaining understanding and confidence in the behaviour of reaction mechanisms with new fuels such as ammonia. Combination of all these parameters can provide more accurate data for development of new models capable of predicting the combustion regimes that are imposed in more complex systems.

3.5.4. *Practical conditions*

More complex scenarios such as combustion of turbulent flames under atmospheric conditions at high inlet temperatures have followed the work of ammonia combustion [307,308]. The studies elucidate the reduction of NO under fuel rich conditions, with a specific equivalence ratio where both unburned ammonia and nitrogen oxides reach their minimum level. Rich equivalence ratios of 1.15 and 1.20 have provided the best results with the lowest emissions in terms of NO and unburned NH_3 over these simulations and other data generated by Valera-Medina et al. [228], points that require further studies. Similarly, other experiments [309] have shown that this value changes to 1.05 under atmospheric conditions and isothermal chamber walls. Although fuel-rich conditions appear to be the most promising for low NOx ammonia combustion, it should be remembered that unburned ammonia is still produced, and its management needs to be considered for further applications.

Zieba et al. [280] have studied the interaction of ammonia at different concentrations (0 to 900 ppmV) with natural gas (mainly methane) and two syngases (i.e. one with methane, the other without it) for flameless applications (so-called ‘FLOX’ systems) at 20 kW power. The results showed that ammonia reacts relatively late compared to methane at fuel lean conditions, leading to high NOx emissions. In the pre-ignition zone, the ammonia chemistry is inhibited due to the absence of free radicals, which are consumed by the methane–methyl radical (CH_3) conversion. In the case of ammonia/methane-free syngas (i.e. 25%H_2, 18%CO, 15%CO_2, 42%N_2 vol%), ammonia was observed to react very rapidly, and complete decomposition was reached in the fuel-rich region of the flame. The hydrogen contained in the fuel ignites directly after the nozzle and releases enough radicals to start the ammonia decomposition. The released radicals are not completely consumed by other combustibles and easily react with NH_3 [280].

As a final remark of this subsection, it is clear from all the current research that there is still a knowledge gap related to the interaction of species and radicals at different conditions and fuel blends, thus prompting the research in these areas to create models that accurately predict the behaviour of ammonia doped flames under conditions relevant to practical industrial environments.

3.5.5. *Combustion catalysis*

Finally, an interesting topic that has contributed to the progression of combustion/power applications at small and medium scales is the use of combustion through catalytic materials. Recent research has shown that using porous blocks is an advantageous and practical way to stabilize premixed flames [310,311]. In summary, porous media improves the fluid properties to enhance burning velocity, thus increasing flame stabilisation. These characteristics can have considerable advantages for the consumption of ammonia for combustion purposes. In addition, the high thermal conductivity of some materials such as SiC increase the heat conduction from the flame to the surrounding zones, thus decreasing undesirable emissions [312].

Researchers in Turkey and Japan have started working on the concept of catalytic combustion of ammonia. Although the literature that exists on the topic is extremely limited, Hinokuma et al. [313] have recently published the use of copper oxides and silver catalysts supported on aluminium oxides for the combustion of NH_3. The concept allows low temperature combustion that minimizes NOx production, as thermal NOx are minimized. Although thermal NOx is a minor contributor to all nitrogen oxides produced in ammonia flames, nevertheless, their reduction contributes to emissions control. The use of novel thermal pretreatments have ensured that these materials can withstand the elevated temperatures of operation ($\sim$1173 K). Similarly, research conducted by Nozari et al. [314,315] showed the high efficiency of burning ammonia via SiC porous media with a large operational range. Simulations and experiments provided validated results that demonstrate the potential of burning ammonia at low power rates using these configurations, Fig. 36.

In Japan, ammonia is building momentum as an important element in a hydrogen-oriented energy economy [13]. Thus, the research complies with a new wave of studies that aim to demonstrate ammonia as a hydrogen carrier capable of providing flexibility whilst ensuring a cost-effective transition to a hydrogen economy. It is likely that these porous materials will support the use of small to medium size boilers, supporting the implementation of a “Hydrogen through Ammonia” economy.

4. Conclusions

Ammonia is one of the most widely transported bulk-manufactured chemicals, having been mass produced throughout the world for more than a century, and its manufacture thought to account for approximately 2% of global energy production. While ammonia is a toxic and corrosive gas, the wide-ranging experience and expertise in synthesis, transportation and utilisation of ammonia significantly reduces concerns about its further exploitation. Indeed, well tested and successful health and safety protocols and regulations already exist for every aspect of its industrial application, from synthesis through to combustion.

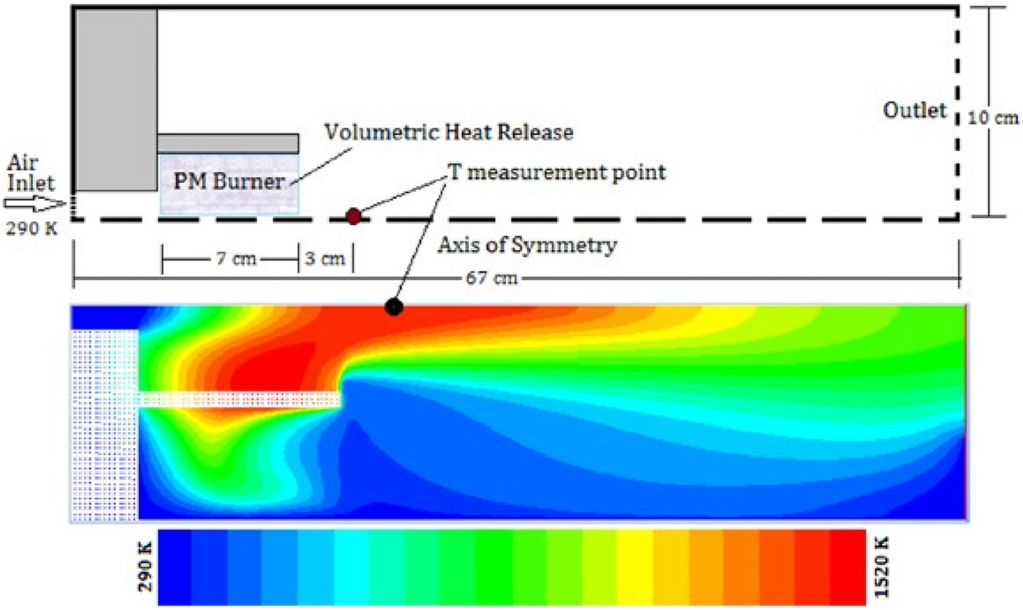


Fig. 36. Numerical simulation performed on a SiC porous material to burn ammonia efficiently. Reprinted from [315] with permission from Int J of Hydrogen Energy, Elsevier.

The original applications of ammonia were in the chemical and agriculture industries and it still finds its greatest application as a fertilizer for intensive crop farming. Nevertheless, in addition to its traditional applications, ammonia is an energetic chemical energy store with favourable physical properties, especially when compared to other chemical energy storage media. Notably, it forms a liquid at relatively low pressures (~0.8 MPa) and is readily and reversible stored within solids at high gravimetric densities, unlike hydrogen gas, and may be combusted without producing CO_2, unlike hydrocarbon fuels. Consequently, its energy content has been explored as a chemical for power generation globally in recent years. Although considerable research into its use as a working fluid in cycles, fuel for combustion engines, electrochemical devices and turbines presents many challenges, these technologies can become widely adopted and commercially viable with the appropriate research and investment. While significant empirical and theoretical progress has been made on optimising fuel/co-fuel/oxidant ratios and the nature and process of the combustion processes, more work is still required to develop optimised systems for specific applications, starting with the development of models that are accurate at specific, practical operational conditions. Moreover, the excessive NOx production using this molecule requires that models focus on developing chemical kinetic models that can be integrated within a more general model for use in the design and control of ammonia-based fuel systems for power generation.

Despite the long period since its inception, most notably in Belgium in 1942, it is only now that ammonia is being seriously considered as fuel both for mobile and large renewable energy storage applications, thus supporting reduction of CO_2 with high flexibility of supply. While ammonia is currently most cheaply synthesised from reforming of natural gas, producing H_2 and CO_2, it may also be synthesised using sustainable sources including solar, wind or tidal, air (for N_2 via liquefaction) and water (for H_2 via electrolysis), with minimal environmental pollutants.

Thus, ammonia can be produced using renewable sources which not only contributes to greenhouse emissions reduction, but also:

- Offers flexibility in terms of its utilisation, as it can be employed as working fluid in power cycles, energy storage from waste streams, cooling medium, or as chemical for CO_2 capture; however, there is still a need for research that will provide the foundations for the coupling of ammonia with the variety of available options for its use in power cycles, i.e. as a working fluid from waste streams that thermodynamically enhances cooling with combined CO_2 capture. Although such concept seems as a technological advantage, progression on the topic is in its infancy and needs further evaluation in terms of the impacts of the molecule at high temperatures and flowrates, consequence of the corrosive nature of ammonia;
- Allows fuel cells to be run effectively using smaller, safer and economically viable configurations that will enable efficient recovery and utilisation of hydrogen for lower environmental impact. However, fuel cells still generally produce per unit low power and many configurations require clean fuel sources – i.e. no carbon or ammonia from cracking- to avoid poisoning, a characteristic that increases equipment complexity and still needs further technological advances for deployment at scale and lower cost; other devices, such as high temperature solid oxide fuel cells and alkaline fuel cells, are appropriate for combined heat and power, and represent a real opportunity for commercial purposes to exploit ammonia as a fuel source;
- Enables combustion systems to be employed using a chemical that, once better understood and characterised, has the potential of operating at high power whilst producing tolerable levels of emissions. It must be emphasized that researchers around the world are now trying to characterise the complex nature of the interaction of the species and radicals that are formed during the combustion process of ammonia and the different combustion characteristics of the flames, thus focusing research on creating more accurate and simpler models that can be used for practical applications;
- In practical power generators such as engines and gas turbines, the recovery of hydrogen from a chemical capable of distributing it easily and economically provides great advantages, with longer operability ranges and feasibility to produce medium to large power outputs. However, the main issue with these technologies still relies on the NOx emissions produced through the combustion process along with unburned ammonia that usually appears in the flue gas streams. Promising results appear in the

range of rich fuel combustion ($\varphi > 1.10$), where the recombination of species seems to have positive effects on NOx reduction through the production of OH radicals, a concept that requires furthers investigation;

- Enables advanced propulsion systems to be developed with smaller tanks, and the capacity to use a chemical with wider accessibility. Previous developments produced highly advanced systems that compete with currently available technologies. Thus, the future for ammonia in propulsion systems could return to its development for commercial use in large propulsion devices. However, nowadays the use of ammonia appears to be focussed on smaller propulsion thrusters for satellites and rockets, which requires energy for splitting the ammonia molecule into its hydrogen components;
- Facilitates the development of burners based on catalytic materials which can be conceptualised for small-scale applications. These use ammonia and its inherent hydrogen in the production of heat, hence reducing the generation of heat from fossil fuel sources. However, these catalytic materials are still under development, currently providing miniscule heat rates under current operation conditions.

Thus, the ease of storage, transportation and use of ammonia makes it an attractive candidate to act as the energy vector between sustainable energy harvesting and mobile and static energy demands. Consequently, one could imagine its use across all application scales from micro-thrusters, small refrigerators and personal transportation through to large (> 1MW) energy buffering. However, as emphasised through this review, there are still many fields that require further development and understanding, some fundamental in nature while others practical in essence.

Thus, as industry, governments and society turn to more sustainable technologies for power generation, and the use of fossil fuels becomes ever more constrained “Hydrogen through Ammonia” economy via Ammonia for Power – with supporting research - provides an attractive, practical proposition which seems to have increasing industrial support.

Acknowledgements

Cardiff University gratefully acknowledges the support from the Welsh European Funding Office (WEFO) through its program “Flexible Integrated Energy Systems (FLEXIS)”, project no. 80835. The authors would like to thank the anonymous reviewers for their valuable comments and suggestion to improve the quality of this paper.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.pecs.2018.07.001.

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