Future Trends

K.H.R. Rouwenhorst, O. Elishav, B. Mosevitzky Lis, G.S. Grader, Christine Mounaïm-Rousselle, A. Roldan, A. Valera-Medina

To cite this version:

K.H.R. Rouwenhorst, O. Elishav, B. Mosevitzky Lis, G.S. Grader, Christine Mounaïm-Rousselle, et al.. Future Trends. Techno-Economic Challenges of Green Ammonia as an Energy Vector, Elsevier, pp.303-319, 2021, 10.1016/B978-0-12-820560-0.00013-8 . hal-03135310

13. Future Trends

K.H.R. Rouwenhors[1], O. Elishav[2], B. Mosevitzky-Lis[3], G.S. Grader[3], C. Rousselle[4], A. Roldan[5], A. Valera-Medina[5]

[1] Department of Science & Technology, University of Twente, The Netherlands
[2] The Nancy and Stephen Grand Technion Energy Program, Technion – Israel Institute of Technology, Israel
[3] The Wolfson Department of Chemical Engineering, Technion – Israel Institute of Technology, Haifa 3200003, Israel.
[4] PRISMA, University of Orleans, France
[5] College of Physical Sciences and Engineering, Cardiff University, UK

Abstract

Considerable works have been conducted on the topic of ammonia and its production, storage, distribution, use and impacts (climate and public). It seems clear that the molecule will play a role in the near- and long-term future in supporting the decarbonisation of our energy-hungry society. However, several questions arise from both these works and current support given to the transition of a zero-carbon economy via ammonia. Technical barriers, economic challenges and missing feasibility studies along with skepticism pose a threat to the concept. Therefore, the path to progress needs to be clear in order to efficiently enable the use of ammonia as a large contributor to tomorrow's worldwide economy, utilizing novel ideas to challenge old concepts. These future trends, mostly based on current works aforementioned in this book, will establish the scientific, industrial and governmental agendas that will foresee the creation of systems and techniques capable of using ammonia as a unique energy vector. Therefore, this chapter approaches many of these trends, seeding the grounds for ideas that will break through old stigmas and position ammonia in a leading role for a clean future.

Keywords: Ammonia, P2A2P, future trends, techno-economics.

13.1. Introduction

The future use of ammonia as an energy vector has been the subject of much discussion over the past few decades. From the early works in the nineteenth century UK to the cold war era US army developments, the use of NH_3 as an energy carrier has always been challenged by the competition with higher energy density vectors. However, new developments and ideas have positioned it as a major role player in the future energy portfolio. Recognition from several organizations across the globe (i.e. International Energy Agency, European Commission, Japanese Government, US Scientific Councils, etc.) has resulted in renewed interest in the use of ammonia as a vector that not only enables the vital delivery of nitrogen needed for crops growth, but also serves as a chemical that is capable of producing cooling, heating, power and propulsion with minimum storage cost. As a major hydrogen carrier and the vast production chain of the latter, Fig. 13.1, ammonia presents a unique opportunity to employ well-developed technologies while keeping true to the idea a truly zero-carbon world.

Although emissions from ammonia are still an issue, and its toxicity and corrosiveness have been detrimental towards health, safety and public perception views, progress over the years and new trends have all been working towards lifting these barriers. Therefore, roadmaps and policies, new international trade routes, advanced-decentralized production, flexible distribution and unique power generation are all under development to provide a novel solution to one of the biggest threats to human civilization – climate change. Accordingly, this chapter approaches some of the most relevant ideas under this scope of research that can be combined to deliver a zero-carbon ammonia-based economy in the near and long future.

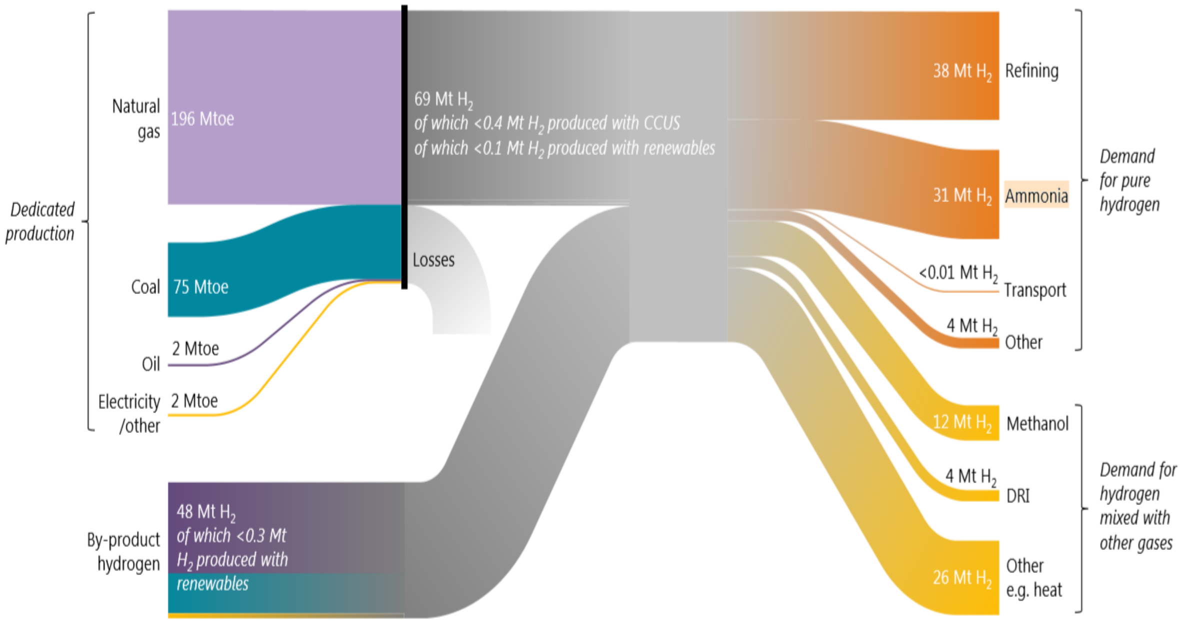

Fig. 13.1. Today's hydrogen chain [1].

13.2. Roadmaps, policies and economy

Renewable energies such as wind, solar, wave and hydroelectric power are sustainable sources with intermittent and seasonal generation profiles. Commonly, their distance from end-users lowers their attractiveness compared to traditional energy sources. To further complicate matters, sustainable energy generation must be capable of satisfying an ever-increasing demand. To achieve this, efficient production and distribution are crucial, requiring major modification of existing power grids. Further potential improvements lie in adjusting linear production and distribution, i.e. power plant-to-user, using a network of scaled-down power plants and locally interconnected networks with effective utilization.

Therefore, changing the current power distribution infrastructure to more local and resilient networks will highly benefit the use of ammonia as an energy vector. Ammonia, in its unaltered form, retains its properties indefinitely and can release the same amount of energy independently of how far it has travelled before utilization. Thus, ammonia produced by renewable sources can be distributed and stored in small-scale power plants. Ammonia can release the energy stored in its molecular bonds in-situ and on-demand, thereby compensating for any seasonal intermittence while eliminating the risks associated to hydrogen gas, i.e. highly flammable, large storage volumes and high pressure containers.

The production of this ammonia, via renewable sources, is highly achivable in countries with high renewable energy capacity. As an example, Australia can support the implementation of the concept in less resourceful economies such as Japan, permitting a larger scale mobilization of goods in a more integrated international distribution chain. Similarly, there are signs of interest from regions such as Morocco, Argentina, Chile, the Middle East and North Europe, all interested in joining the deployment of renewable energies via alternative fuels such as ammonia as described below. Thus, the implementation of these concepts can offer an economic solution to current constraints in those areas, whilst ensuring that developing economies become exporters of valuable chemicals such as NH_3.

In Europe, the production of cheap energy due to the proliferation of wind farms and cost reduction of large-scale projects has necessitated the development of technologies capable of storing some of the stranded energy produced during off-peak consumption periods. For example, the North Sea accounts for 70% of the offshore wind capacity of Europe [2]. It is expected that by 2040 the production of electricity from these facilities will reach between 70-150 GW. However, recent events have led to occasional negative prices of the electricity produced on these sites (i.e. -$88 per MWh) due to energy market fluctuations and excessive supply [3]. Therefore, the use of ammonia can enable the storage of this excess energy, thus creating a market opportunity for cost-effective energy storage. Companies such as Thyssenkrupp are assessing the potential for producing hydrogen in-situ at off-shore wind farms along with delivery as ammonia to mainland locations. Similarly, renewable ammonia can be produced on offshore facilities such as old platforms using energy from other renewables, thereby facilitating the distribution of ammonia, Fig. 13.2. The distributed ammonia can also be received in a similar approach, Fig. 13.3, thus facilitating the distribution of large quantities of the chemical at a global scale.

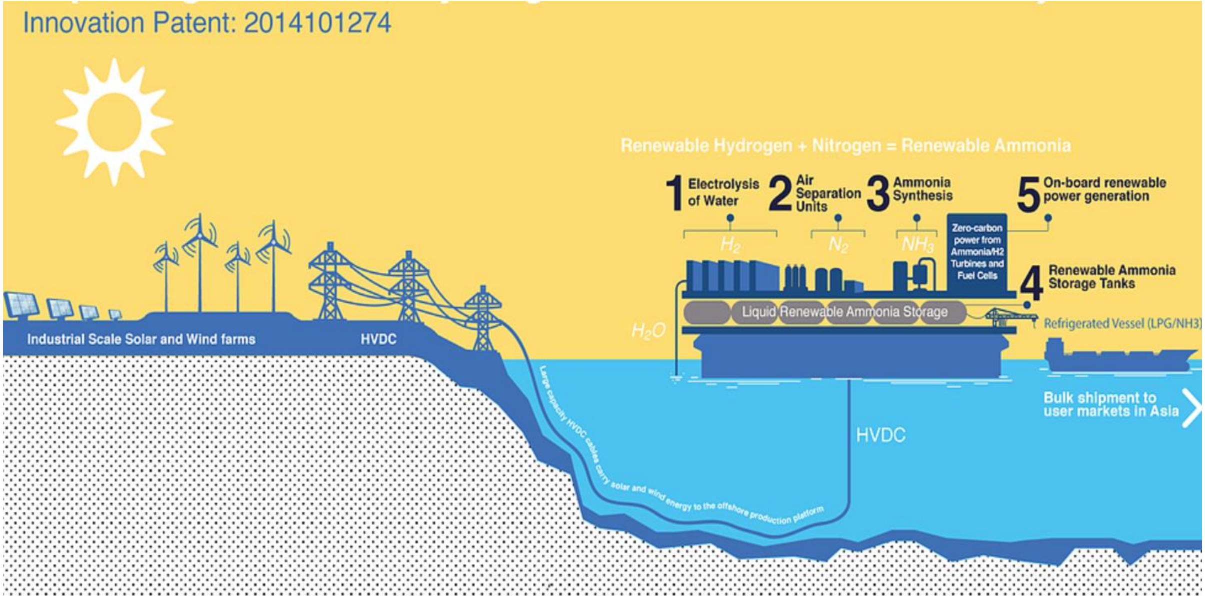

Fig. 13.2. Production and storage of ammonia from renewable sources [4].

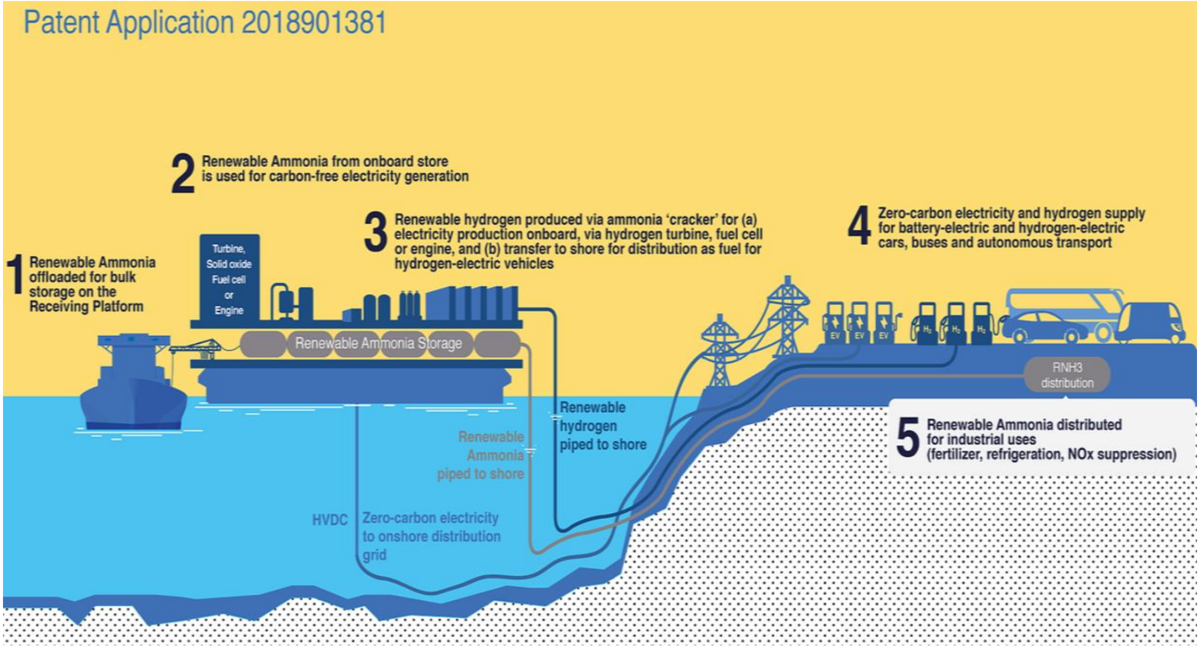

Fig. 13.3. Distribution of ammonia from offshore platforms [4].

Some economies are considering similar solutions but at a much larger scale. In Australia, different institutions across the country have recently published material presenting the vast opportunities of the continent in renewable energy production and storage. Some of the most prominent ideas deal with producing green hydrogen and ammonia by utilizing the strong solar irradiation in Australia's Northern Territory, and South and Western regions. Such a study was conducted by ENGIE and Yara, major energy and ammonia companies respectively, leading to the design of large-scale facilities to produce green hydrogen in Pilbara, Australia. Parallel works from organizations such as CSIRO dealing with the development of PEM technologies fueled by ammonia-derived hydrogen have reached the demonstration stage and are under commercial development. Combined, these works support the use of ammonia as a renewable hydrogen vector in Australia.

Current studies in Australia also support the large-scale exportation to economies such as Japan that have committed to decarbonizing their economy via hydrogenated vectors such as ammonia. In 2015, the Strategic Innovation Promotion (SIP) Program established a large consortium for innovation in the production and consumption chain of ammonia as energy vector (more info can be found in Chapter 6). Resulting technologies, through demonstration projects, will be used to generate zero-carbon energy during the Tokyo Olympics in 2020. Due to the success of the program, the Ministry of Energy, Trade and Industry added ammonia to its latest technology roadmap, suggesting the creation of "ammonia-based technologies" for large-scale production and use by 2030. This progress has been signed into law, calling for imports of green ammonia by the mid 2020s [5].

The United Kingdom has also played an important role in the progression towards the use of ammonia. The Decoupled Energy Supply project led by Siemens (Chapter 7) was the first major 21st century attempt at utilizing ammonia as a renewable fuel. Derived results spurred new initiatives to demonstrate the feasibility of large-scale storage of renewable energy in ammonia whilst further developments to create new strategies for the use of ammonia as heat, power and propulsion medium have been supported through national Research Councils. These works have led to the recognition of ammonia as a major role player in the deployment of hydrogen across the country, leading to the Department for Business, Energy and Industrial Strategy (BEIS) funding multi-million projects for demonstrating innovative large scale energy storage solutions, EPSRC fellowships for the design of new engines, and EPSRC grants for novel ammonia powered cycles.

The Netherlands has also engaged actively with these initiatives. Their efforts go from fundamental and numerical studies across many of its institutions, to the promotion of ammonia in large international delegations. The work carried out by companies such as Proton Ventures have opened windows of opportunity for the recognition of the molecule as an energy vector, opportunities that now receive the support of the Ministry of Economic Affairs and Climate Policy and European funds for development of improved ammonia production and storage methods.

In China, the wind and solar energy potentials in regions such as East China have been suggested as suitable locations for the production of hydrogen and ammonia as means of energy storage. These analyses have showed that a cost reduction of 10-20% can be achieved with the integration of appropriate technologies. These studies, if materialized, could enable the reduction of renewable ammonia costs to current market values, making the production of ammonia using green technologies competitive with only minor amounts of carbon dioxide being produced (i.e. carbon dioxide being the product of other components in the entire Life Cycle of the value chain).

Other developing economies such as Morocco, Chile, Argentina, etc., whose wind and solar resources are in proximity with large water reservoirs or seas, also present a vast potential for the production of green hydrogen and ammonia in the near future. For example, it has been predicted that Morocco will become a net exporter of renewable energy to Europe in the future [6,7]. This prediction demonstrates the potential to decentralize and democratize energy production through the development of smaller, more compact systems that work at both local and regional scales. Recent studies conducted by the Energy Defense Fund (EDF) discuss the use of ammonia to decarbonize the maritime sector, highlighting the contributions that Morocco could add in the production of the chemical and its distribution to large European economies. Offshore potentials of ~250 GW could satisfy a vast percentage of the continental consumption of electricity with enough surplus to supply almost 30% of the current shipping industry's total energy consumption [8].

Meanwhile, the International Maritime Organization (IMO), who committed to a vast reduction in CO_2 emissions in the coming decades (i.e. 70% by 2050 compared with 2008 emissions [9]), has defined new strategies for fueling applications using zero-carbon "electrofuels". The term, coined from the production of fuels coming from processes such as electrolysis, places hydrogen and ammonia as major contenders in this field. The goal, along with the reduction of other emissions such as SOx and NOx, is to minimize the industry's impact on climate change.

As previously presented (Chapter 7), the maritime industry has already recognized the potential of using ammonia for storage and reconversion via internal combustion engines and fuel cells. These developments have enabled companies such as MAN Energy solutions, which provides engines for over half the world's shipping industry, to set development programs for the creation of efficient engines capable of replacing LPG technologies in the near future. It is estimated that a current program, expected to deliver initial results by 2022, will enable the replacement of almost 3,000 LPG units by ammonia internal combustion systems in China [10]. Although relevant codes and guidelines are still under scrutiny, and a more international effort still needs to be enacted by the IMO for full deployment of the technology across all regions, it is clear that the first sector that will see a large use of ammonia for fueling will be the maritime industry.

Other initiatives such as the ABS Global Sustainable Center (which named ammonia as a "Hydrogen 2.0" vector), the Poseidon Principles (backed by 11 banks that account for more than $100 billion USD) and the UK's Clean Maritime Plan (to create demonstration programs for hydrogen and ammonia engines at an industrial scale) will all be crucial for the progression of the technology. Similarly, projects such as the "Viking Energy" ship reconversion will serve to demonstrate that large vessels (i.e. 2MW) can be modified for ammonia fuel cell use, thus supporting decarbonisation of companies such as Equinor [11]. On similar grounds, Statoil and Siemens projects, supported by NTNU and Sintef, will also progress the retrofitting of current technologies to enable the use of ammonia/hydrogen at different scales [12]. Combined, these programs unequivocally demonstrate that ammonia, a molecule isolated and discovered more than 150 years ago, is definitely here to stay.

13.3. Production

The Haber-Bosch process for synthetic ammonia production has been one of the most impactful inventions in human history since it made *bread from air*, thereby facilitating a dramatic increase in the world population [13]. The Haber-Bosch process has been optimized over the past century, starting with an energy consumption of about 100 GJ $t_{NH_3}^{-1}$ in the 1930s down to about 26 GJ $t_{NH_3}^{-1}$ today. A century later, the challenge is no longer to make bread from air, but rather to store *energy from sun and air* in a potential *hydrogen economy*, in which green ammonia can play a crucial role [14–17]. When ammonia is used as a hydrogen carrier, ammonia is converted into electricity in a gas turbine, an engine, or a fuel cell. Typical roundtrip efficiencies for power-to-ammonia-to-power are 33-43% [18–21].

Current trends for ammonia synthesis technologies are decarbonisation and electrification. Green ammonia synthesis has been technologically feasible at large scale for almost a century, as is evident from the hydro-powered electrolysis-based ammonia plants that operated in Norway from the 1920s until the 1970s. The transition to green ammonia is a matter of cost, electrolyser production capacity and coupling with intermittent renewables [22]. The main driver for green ammonia synthesis is low-cost electricity from renewable sources. Furthermore, electrolyzers with high electrical efficiency and with low investment cost will enable the transition to green ammonia synthesis [23–25]. However, it is not only about the cost. As recently presented by the International Energy Agency, the cost of producing ammonia via electricity is lower than that of other fuels, Figure 13.4. However, the implementation of ammonia for fuelling applications and the replacement of fossil fuels requires further research and development. Regarding other technologies, even though academic research is mainly focused on nonconventional ammonia synthesis processes, the design of ammonia synthesis loop concepts has been remarkably similar for decades. Little academic attention has been given to improving the industrially used iron-based catalysts in recent years [26,27]. However, minor improvements in the commercial catalyst can decrease the operating temperature and pressure, enabling scale-down and some minor efficiency gains.

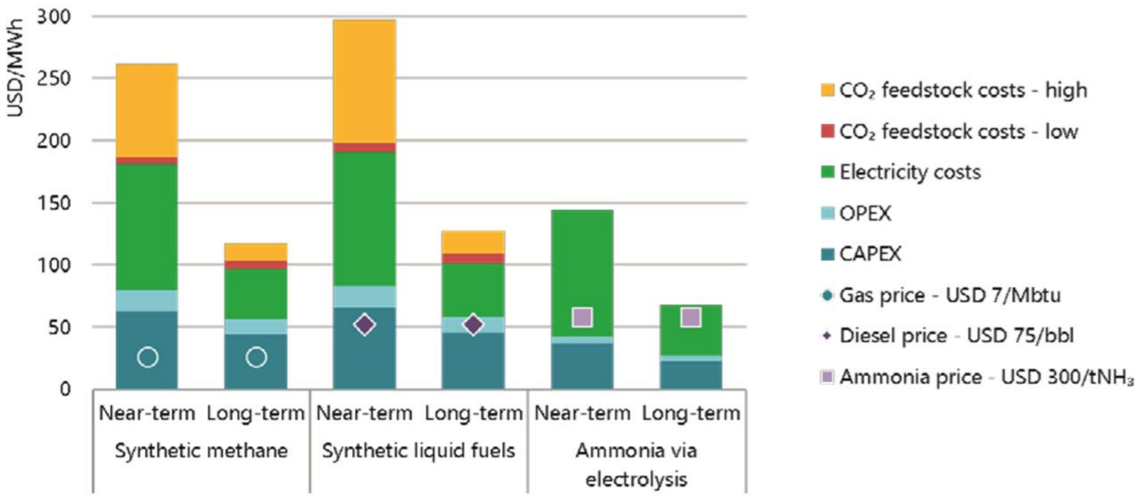

Fig. 13.4. Indicative production costs of electricity-based pathways in the near- and long-term future [1].

Materials discovery, driven by understanding their fundamental mechanisms, is transforming renewable energy's (i.e. solar radiation) harvesting efficiency. These materials are developed and tested mainly for artificial photosynthesis and hydrogen production from water. However, oxygen reduction and evolution into the gas phase are challenging steps which commonly saturate the catalyst's surface. Part of the challenge is the large reduction potential of oxygen ($E^{\Theta} = +1.23$ V), which for nitrogen is rather small in an acid environment ($1/2\ N_2 + 3[H^+ + e^-] \rightarrow NH_3$; $E^{\Theta} = +0.035$ V [28]). Further challenges may rise for the stability of designed catalysts under such conditions and the optimisation of the liquid-gas interface in the presence of the catalysts and light.

This transition is also concerned with ammonia synthesis at milder conditions, which remains a topic of active research [29,30]. It is already technologically possible to lower the operating pressure from 10.0-30.0 MPa to 1.0-3.0 MPa in an absorbent- or adsorbent-enhanced Haber-Bosch, albeit at a higher energy cost. Furthermore, the operating temperature may be lowered to 520-620 K by operating with nonconventional heterogeneous catalysts and plasma-catalytic reactors, thereby allowing for higher equilibrium conversions. The direct synthetic production of ammonia from air and water via electrochemical or photochemical synthesis routes remains an unsolved scientific challenge. Ammonia synthesized directly from air and water may find applications in decentralized, remote fertilizer production. All in all, it can be concluded that there has been an extensive research effort on ammonia synthesis with nonconventional technologies in recent years [31]. Possibly, some of these technologies find widespread application in the long term, or niche applications in the short term. However, the electrolysis-based Haber-Bosch process will remain the dominant alternative at large scale for the upcoming decade(s). In areas with insufficient solar, tidal and wind power, biomass-based ammonia synthesis can be considered as well. Apart from renewable sources for hydrogen production, converting nitrogen oxides from point sources to ammonia may become relevant as well.

Electrochemical synthesis seems to have been reborn in recent years, and legitimately so as this pathway still offers room for significant development. The accurate control of potentials with ion-selective membranes, made of either polymeric or solid-supported polymeric membranes materials, allows high efficiency and reversibility, i.e. formation and utilisation of ammonia to generate electric current. The utilisation of cold plasma (low-energy demands) may allow the activation of nitrogen bond leading to hydrogenated species of nitrogen such as hydrazine, that, once away from the plasma, decay to more stable species. That could be a very efficient way to produce large amounts of ammonia as it is thermodynamically favoured.

Anticipated near-term developments include the transition from brown ammonia to blue ammonia using less carbon-intensive hydrogen sources, as well as carbon capture technologies. Next to this, existing plants based on steam methane reforming technology can be revamped to provide a hybrid solution with both electrolysis-based hydrogen production and steam methane reforming-based hydrogen production [21,32–34]. After 2025-2030, fully electrolysis-based technologies are expected to be commercially viable at an industrial scale in some locations [21,33,34]. Currently, electrolysis-based green ammonia is already becoming cost competitive with imported brown ammonia in various regions in Argentina, Chile and China [35,36]. The choice among the electrolysis technologies depends on the scale of application and the synthesis loop pressure. At the scale of 3-150 t_{NH_3} d^{-1}, alkaline electrolysis or PEM electrolysis coupled with pressure swing adsorption for N_2 generation combined with a conventional Haber-Bosch process or adsorbent-enhanced Haber-Bosch process appears feasible, at an energy consumption of about 30-35 GJ $t_{NH_3}^{-1}$ [19,30]. At larger capacities (300-15,000 t_{NH_3} d^{-1}), alkaline electrolysis, PEM electrolysis, or solid oxide electrolysis technology combined with a conventional Haber-Bosch process is expected to be most feasible, at an energy consumption of about 26-33 GJ $t_{NH_3}^{-1}$ [33,37].

Several research groups are making innovative advances on the efficient and low temperature decomposition ammonia. Small quantities of catalysts will allow the formation of hydrogen on-demand and in-situ, avoiding the risks and costs associated to storing and distributing hydrogen. A crucial step in developing these catalytic materials is understanding their fundamental structure—activity relationships. Basic metal-oxide/carbon nanotube supported ruthenium catalysts offer the highest decomposition rates of all heterogenous catalysts tested so far [38]. However, the high cost of ruthenium makes the use of such catalysts economically burdensome in ammonia decomposition systems. By elucidating the active sites involved in the catalytic surface reactions and the effect of the support (electronic/textural), surface site optimization leading to increased ammonia decomposition performance could be unlocked. More importantly, this could potentially pave the way for replacing the precious ruthenium in non-noble metal element, reducing costs significantly. Another crucial step in the application of such catalysts is their stability. Commonly as nano-scale metals deposited over supports which may or may not be active, these catalysts need to remain resilient and functional in a wide range of conditions depending on the inlet blend and temperatures. Thus, thermal and chemical stability are crucial steps along the technology validation stage. For instance, catalysts close to a combustion chamber may suffer from large temperature changes promoting the sintering of supported catalysts and loss of activity. Similarly, the presence of common species such as CO and SO_2 may dramatically deactivate the catalysts by poisoning the active sites, i.e. adsorbing irreversible and therefore blocking ammonia to access them. Thus, the future will see improvements in these materials and methods for the generation decentralized ammonia.

13.4. Distribution and Storage

Vast ammonia distribution and storage infrastructure already exists today to satisfy agricultural and industrial demand. With increasing demand for ammonia in both traditional markets and ammonia energy applications, new routes and facilities will have to be developed. In the short-term, these facilities will be based on existing practices as detailed in Chapter 5. Current carbon steel ammonia storage vessels are low-cost compared to other construction material alternatives, and satisfactory corrosion resistant when conditioned and maintained correctly. Therefore, little to no change is expected in current ammonia storage materials, with carbon steel enduring in such services. Yet, the appearance of new materials for ammonia storage and distribution is predicted to evolve at a fast rate as well. Programs such as ARPA-REFUEL that have heavily invested in the development of new materials for the storage of ammonia, will receive additional momentum from other international programs. For example, novel metal halide amines (solid salts) have been recently developed to enable the attachment of ammonia to metal ions. Mixing these materials with ammonia causes it to be trapped, limiting its release at atmospheric conditions (consequence of the vapour pressure of ammonia under those conditions). Hexa-ammine-magnesium chloride is a material that although used for DeNOxing applications can also be employed as an indirect hydrogen carrier, with high gravimetric and volumetric hydrogen content. Prepared from magnesium chloride, a low cost, abundant and safe material, it binds ammonia reversibly [39,40]. The material can contain up to 615 kg of ammonia per cubic meter (almost the same as liquid ammonia). Thus, hexa-ammine-magnesium chloride ($Mg(NH_3)_6Cl_2$) and similar solid state materials present a unique opportunity for ammonia distribution [41,42].

Ammonia boranes, materials well known to store ammonia, have also received considerable attention over the years. Most of the related research has focused on the structure and identity of the metals and the resultant thermal stability [43]. Amine metal borohybrides (comprised of 3D framework structures capable of releasing either hydrogen or ammonia), sorbents and membranes (such as lithium exchange type X zeolites, layered palladium-vanadium membranes, etc.), halides, metal hydrides [44], computationally designed materials and many other solid-state media will demonstrate their versatility for ammonia storage in the near future, as some have done it over the years, Fig. 13.5. Further information can be found elsewhere [43,45,46].

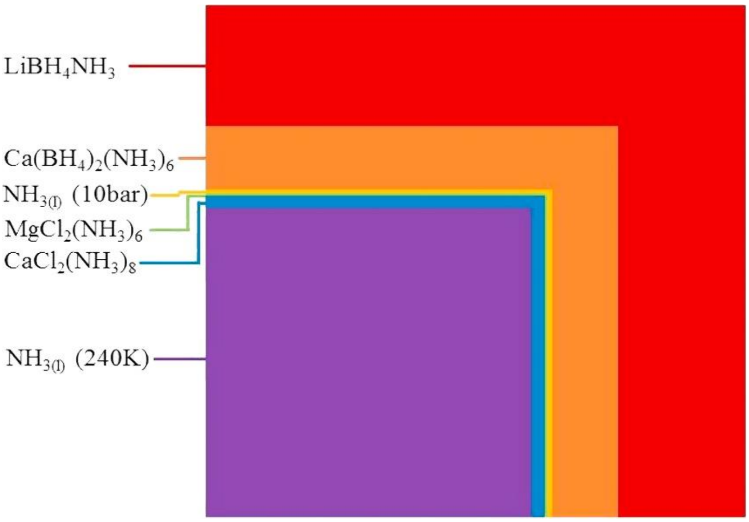

Fig. 13.5. Storage volume comparison between different ammonia storage methods [43].

Another method for ammonia storage is gelation. The concept was initially presented by the U.S. Army under their ammonia fueling program in the 1960s [47]. Although no further details are available to the general public, some research using silica gel was presented around that time. Bliznakov and Polikarova [48] showed that silica gel could store ammonia, although they observed that some ammonia was irreversibly bounded, the quantity decreased with the desorption temperature. Nevertheless, recent experiments have demonstrated that ammonia can be efficiently absorbed by incorporating metallic ionin liquids into silica gel. Zeng et al. employed $[Bmim]_2[CuCl_4]$, $[Bmim]_2[NiCl_4]$ and $[Bmim]_2[Co(NCS)_4]$ by impregnating them over porous silica gels with large surface areas and abundant hydroxyl groups. The final product, Metal Ionic Liquid Silica Gel composites (MIL@silica gel) showed adsorption capacities up to 99.8 mg of ammonia per gram of adsorbent material, with high reversibility and complete release of ammonia in 15 minutes over various cycles [49]. Therefore, the technique seems likely to continue evolving as a support for ammonia capture (i.e. in waste streams) and storage.

A different approach is to convert ammonia to other easier to handle molecules that can act as ammonia-derived energy carriers. Urea and other aqueous nitrogen-based fuels were previously investigated as such carriers [50–52]. Their utilization as carriers requires the development of innovative technologies for their conversion to power. Urea can be utilized directly in a fuel cell generating power and producing CO_2, N_2 and water [53]. Furthermore, urea can be recovered from animal waste streams [53]. Aqueous solutions of ammonia and ammonia derivatives can be combusted to produce high temperature and pressure gasses capable of turning a gas turbine, demonstrating their potential as energy carriers. However, the full utilization of these aqueous solutions is still out of reach. The ongoing research on ammonia derivatives may lead down the road to the identification of an effective carrier with similarly attractive energy density and overall conversion efficiency while providing a safer and more convenient energy storage media.

One of the considerations that the International Energy Agency (IEA) has recently included in their Hydrogen Report [1] highlights the differences between using trucks and pipelines for various distances, locations and hydrogen carriers. Compared with liquid hydrogen and liquid organic hydrogen carriers (LOHC), ammonia demonstrated lower costs for long distance pipelines and even for local networks, with an outstanding cost of only 0.4 USD/kg_{H_2} when transported by trucks over a distance of 500 km. It must be emphasized that this cost assumes that no further reconversion to hydrogen would be performed, thus requiring technologies that can use ammonia directly. Therefore, ammonia is clearly a favored medium for the hydrogen energy distribution. Further analyses by the IEA depict the potential reduction compared to other hydrogen carriers, recommending the implementation of new initiatives for the creation of marine routes and new pipelines that can efficiently deliver the chemical across the globe, Fig. 13.6. The possibility of reconditioning current gas line networks and commissioning to distribute ammonia, a topic that will surely receive further attention in the future, compliments the previously established benefits of ammonia-based hydrogen energy distribution. The types of steel utilized in such lines are relatively ammonia corrosion resistant, and can therefore be utilized in ammonia distribution services with relatively minor alterations.

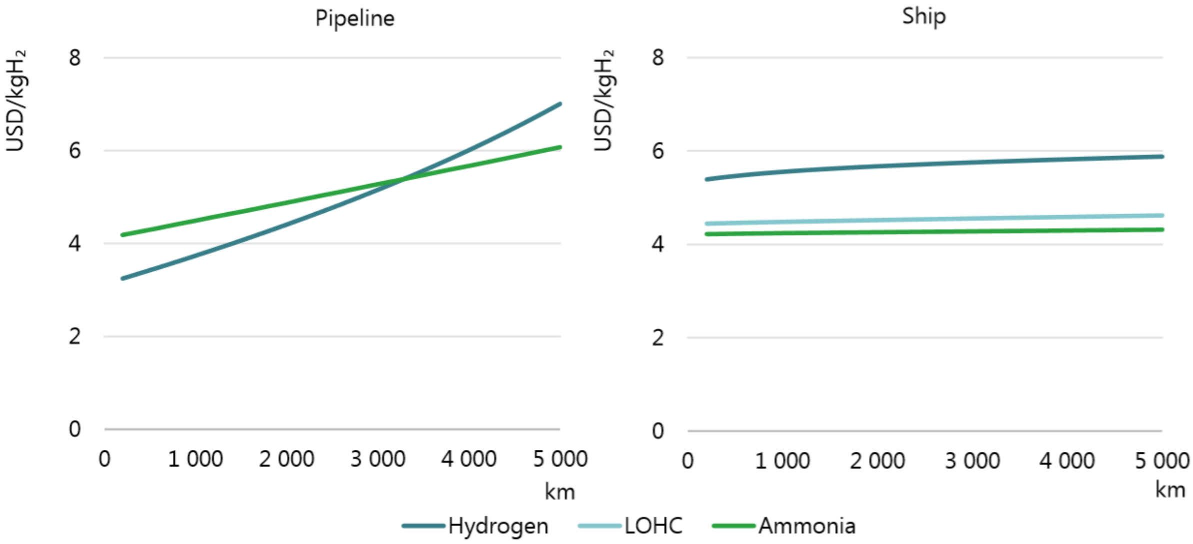

Fig. 13.6. Full cost of hydrogen delivery to the industrial market by pipeline or by ship in 2030 for different transmission distances [1].

Accordingly, the creation of new economic trade routes involving the production and transportation of ammonia as a hydrogen/direct renewable energy storage medium. For example, future projections forecast that the cheaper production and transportation costs of ammonia in North Africa compared to Europe will propagate new ammonia trade routes across the Mediterranean [1]. Therefore, transportation of such resources over long distances with minor to no reconversion appears to be viable and economic using ammonia

13.5. Utilization

In terms of utilization, the challenges with the use of ammonia present series of opportunities for researchers and industries to establish programs of research and development that can benefit not only existing processes, but also novel ventures. For example, the development of more accurate reaction models can lead to better catalytic systems that can be employed for better reduction of NOx emissions in automotive systems. Similarly, the improved understanding of reaction mechanisms can provide better insight into the recombination of species, thus enabling the use of molecules such as NO to change heat transfer properties that can benefit overall cycle efficiencies whilst ensuring their posterior recovery in combustion systems, thus avoiding environmental. Similarly, many other concepts can be assessed for further use of the molecule in a great variety of applications.

It is now clear that ammonia possesses a great potential as energy carrier. However, acknowledging ammonia as hydrogen carrier and its feasible storage are still not enough to consider it a comprehensive energy vector. The main question remaining is how to extract this energy content. Three solutions could be considered: to decompose ammonia by means of new optimized reactors in order to provide hydrogen, to use ammonia directly in fuel cells, or to employ the chemical in combustion systems such as turbines or internal combustion engines. An interesting comparative review between different potential hydrogen storage media, energy efficiencies and costs, concluded that NH_3 seems to be the cheapest alternative with the highest energy efficiency when directly used for energy generation (i.e.

without decomposition), especially when compared to liquid hydrogen [54]. Already in 2014, researchers from the UK announced that ammonia is a clean and secure hydrogen-containing energy source [55], proposing the idea to use it directly in engines. As it was underlined in another recent analysis based on the opportunity for NH_3 to be one of best environmentally benign energy carriers for China, other advantages of direct ammonia injection were highlighted, raising that '[ammonia is an] ideal fuel since it is not a greenhouse gas and its complete combustion forms only N_2 and H_2O' [56].

However, several parameters need to be solved to remove barriers for system development and further deployment of this technology. One parameter that has become critical and now is in trend relates to the full understanding of chemical reaction mechanism and their reduction for their assessment in complex computational modelling tools.. The reduction can enable the use of the latter in 0, 1, 2 and 3D numerical calculations, minimizing the computational cost whilst delivering a correct and detailed set of results for the interaction of species. Some of the most recent findings in this field have attempted to construct reduced reaction mechanisms capable of simulating the reactivity of hydrogen-ammonia mixtures. Li et al. have achieved this whilst using only 28 species and 218 reactions [57]. Works by Xiao et al. [58,59] have dealt with the reduction of various mechanisms for 2D model implementation, whilst a reduced version of the Okafor, Glarborg and Li mechanisms have been tested in advanced numerical model simulations [60]. Similar results have enabled the identification of parameters that impact the performance of energy systems fueled with ammonia blends. For example, analyses from Somarathne et al. [61], Honzawa et al. [62], Vigueras-Zuniga et al. [63], etc. have all employed improved, reduced mechanisms to numerically assess various combustion regimes, Fig. 13.7. Such results show how the appropriate use of more advanced and better reduced mechanisms under complex geometries enables the use of complex chemical modelling with highly demanding turbulence models such as URANS, LES and DNS. The near future will see the development of more accurate reduced models for the use of these modelling techniques, thus informing manufacturers and companies of the effects of geometry and operational conditions using ammonia.

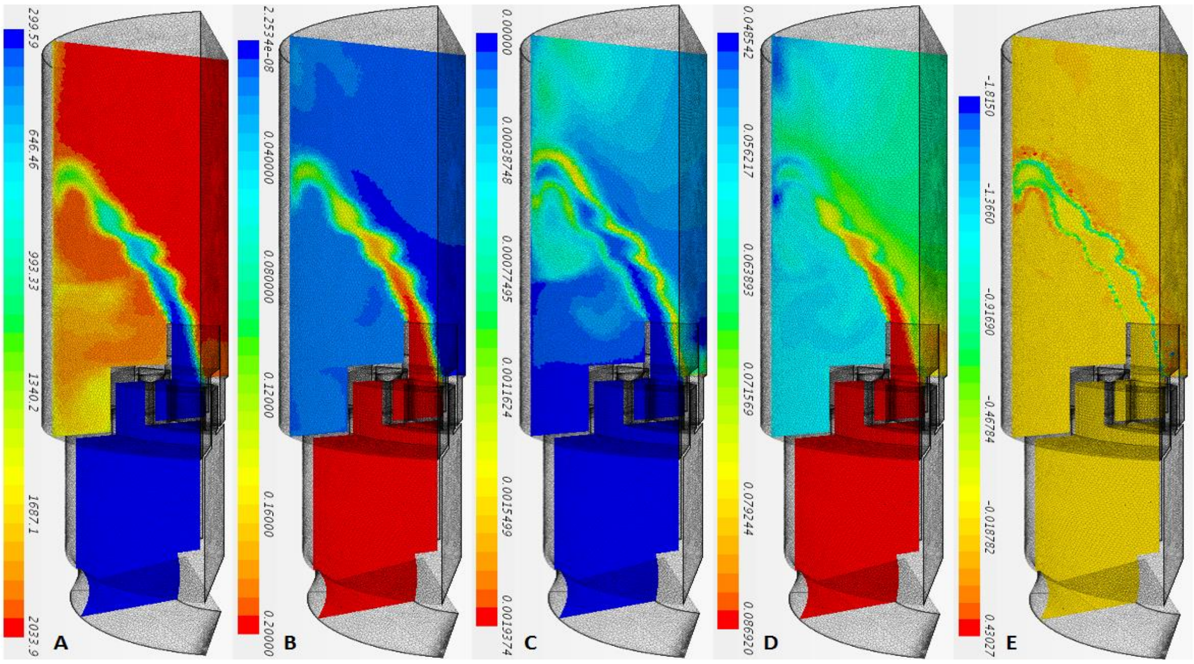

Fig. 13.7. Combustion of ammonia/hydrogen using Okafor's reduced mechanism. A) Temperature [K]; B) Ammonia concentration [mol%]; C) NO concentration [mol%]; D) Hydrogen concentration [mol%]; E) Hydrogen rate of production [kg/m3-s]. Operating conditions: 101 kPa, 304 K. Permission from MPDI [63].

Another technique on the horizon that might employ the use of advanced modelling to determine geometries and operation conditions is plasmas. Plasmas, different to gases, are formed by atoms in which electrons have been stripped away leaving positively charged nuclei. These plasmas have been assessed for their ammonia production capabilities [64] through the formation of excited nitrogen molecules. Similarly, the concept is now under evaluation for the improvement of ammonia combustion systems. Plasma alters the kinetics of combustion by producing photon, electron and ions, chemically active species, and heat. This in turn increases the reactivity of the mixture and the flame speed. The increase in flame speed can improve the combustion stability. On the other hand, plasma alters the local flame temperature and the chemical composition, hence, the thermophysical physical properties of the mixture are modified, e.g., the thermal diffusivity and viscosity of the mixture increase by temperature The full impact of plasma utilization in the case of ammonia combustion systems is still unknown.

The use of plasmas could present a new solution to the high level of emissions inherent to more stable ammonia flames. Since plasmas are ionized gases that contain chemically active species and radicals that can promote the combustion behavior of low-calorific value gases, they can play an active role in the ignition of difficult to ignite combustible mixtures such as ammonia. Other enhancement effects already reported in the literature are flame stabilization and pollutant emissions reduction (NOx, soot, etc.). Academic studies [65] on the plasma-chemical process for ammonia dissociation have reported the formation of amine radicals (NH_2) which have been identified as a NOx reducing agent in the post-flame zone of ammonia blends [66,67]. However, the extent of combustion enhancement strongly depends on the types of plasma sources selected. Another path for the use of plasmas in ammonia blends is the direct decomposition of the chemical into hydrogen for fuel cells or combustion systems. According to Yi et al. [68] the use of plasmas can assist in the decomposition of the molecule over monometallic and bimetallic compounds (i.e. Fe, Co, Ni, Mo and their combinations) increasing the activity of the latter by the activation of ammonia into excited-state species such as NH_2 and NH. The results produced hydrogen quantities of 0.96 mol g^{-1} h^{-1}, demonstrating the feasibility of the concept.

Similarly, non-equilibrium microwave plasmas can also be employed as they have higher electron temperatures and are kinetically more active due to the rapid production of active radicals and excited species. Furthermore, they have high plasma densities and high uniformity due to formation by 2.45 GHz electromagnetic waves [69]. A dramatic promotion of ignition and combustion is expected when the microwave-induced non-equilibrium plasma overlaps with the flame zone. Ammonia-derived radicals and active species that are expected to act as deNOx agents have a short lifetime and their propagation in the flame region will improve NOx reduction. The concept, still under assessment, will likely be evaluated for combustion enhancement in the near future. The process, already assessed numerically via perfectly stirred reactors and laminar flames, has demonstrated that increasing the electrical field augments the decomposition of ammonia, thus raising the burning velocity as a consequence of the increasing H atoms [70]. Similarly, the possibility of using lasers to produce plasmas [71] can also improve the ignition of ammonia blends, and enhanced when combined with more reactive blends such as highly oxygenated ones (i.e. high O_2 or even ozone).

As previously presented, fuel cells are major players in the use of ammonia technologies. From automotive applications that are under evaluation to applied concepts such as ALKAMMONIA, the implementation of these devices in commercial hubs will be faster than anticipated. Some of the expected results from projects around the globe, especially in Japan, the USA and Europe, will see the implementation of more robust fuel cells capable of withstanding longer operation whilst working at lower temperatures. One instance is the technology developed by Chemtronergy (via the ARPA-E's REFUEL program), which will integrate Solid Oxide Fuel Cells (SOFC) units running at lower temperatures than those currently required for SOFC technology. Simultaneously, the company expects that a combination of better materials and advanced design techniques (better reaction modelling, 3D printing, etc.) will ensure a reduction in costs, thus enabling a competitive technology [72]. Similarly, the use of Direct Ammonia Fuel Cells (DAFC) will also see an accelerated development that will support similar initiatives. For example, the work from Zhao et al. [73] recently achieved the production of peak power densities of 135 mW $cm\text{-}^{2}$ under optimized operating conditions and high ammonia concentrations. Similarly, Nikkei Sangyo reported on the work at IHI for the creation of commercial direct ammonia solid oxide fuel cells capable of operating above 1 kW power with efficiencies above 40% with potential implementation in residential applications [74]. Additional projects on the area are ongoing, promising the development of reliable technology for transportation, processes and domestic consumption [75–79].

On that line of work, several companies and institutions are actively conducting research. A novel concept, Solid Acid Fuel Cells (SAFCs) developed by SAFCell, is based on the use of a new electrolyte called solid acid. Operating at temperatures as low as 523 K (250 °C), these fuel cells can tolerate high concentration of impurities whilst using inexpensive materials. The technology promises a reduction in costs, whilst also presenting an option to produce ammonia from energy, thus making these devices reversible [72,80]. Therefore, the onset of new cost-effective ammonia fuel cell technologies capable of working over long periods of time at lower temperatures is likely in the near future.

Ammonia can also be considered as a good candidate to secure the decarbonization of both energy production and the transportation sector. In terms of internal combustion engines, recent projects will enable the construction of more stable and efficient, and less dangerous units for implementation in trucks and marine applications. These may require the use of new construction metals due to the increased risk of nitridation and hydrogen embrittlement along with ammonia-derived stress corrosion cracking, conditions relatively unknown in traditional fossil-fueled internal combustion engines.

For example, AreNH3a (Advanced materials and Reactors for ENergy storage tHrough Ammonia), a H2020 project leaded by Technalia and ENGIE, has established as main goal the development, integration and demonstration of key material solutions enabling the flexible, secure and profitable storage and utilization of energy under the form of green ammonia.. Even though the first implementation of such technology will be in trucks and marine applications, other transportation systems such as trucks, delivery cargos or 'floating' vehicles have been also considered. Therefore, amongst the potential technologies, heavy duty transport and marine systems for long distances seem the best candidates for the technology. As previously presented, ammonia will not be a "silver bullet" that will solve all energy problems, but a chemical that will support certain niche applications such as those already mentioned. Therefore, works are ongoing to demonstrate and improve engines capable of moving farming trucks [81], on-road and off-road heavy duty trucks [82], some car applications [83,84] and marine vessels [85]. Injection systems combined with ammonia control monitoring will ensure that ammonia temperatures, flowrates and quantity are all monitored. Some applications have also the feasibility to go back 100% to the use of diesel when ammonia has been fully consumed [82].

It must be remembered that ammonia in internal combustion engines has already been tried in the past (Chapter 6). However, it must be considered that classical engine architectures were employed at the time. Due to ammonia's particular characteristics, i.e. a high auto-ignition temperature and narrow flammability limits, the chemical presents difficulties when used as fuel in such systems. These facts combined with low flame speeds cause incomplete combustion in engines that require novel designs and ingenious injection philosophies. New technologies should consider the high-octane number of ammonia which presents an advantage to avoid knocking phenomena at high pressures and elevated temperature environments such as those found in high Compression Ratio and/or turbocharged conditions. Moreover, the high latent heat of vaporization of ammonia has also to be included in those calculations, as this parameter causes very large gas temperature drops at the time of injection in the case of liquid injection (as is usually done in compression ignition engines). In the case of Spark Ignition (SI) engines, the fuel injection needs also to be properly assessed. There are two methods that can be applied for the injection of fuel in SI engines namely port-injection or direct-injection. Particularly, port-fuel injection displaces the air supplied to the combustion chamber and reduces thereby the volumetric efficiency of the engine. However, injecting liquid ammonia gives better volumetric efficiency since it does not displace the air and cools the intake mixture.

Different practical methods for improving engine performance while burning ammonia include increasing spark energy, increasing compression ratio, use engine supercharging configurations or adding hydrogen to the blends. All these potential avenues have been evaluated in the past without real universal conclusions. Recent works [86–88] have concluded that modern engines normally designed for gasoline could be satisfactorily operated on gaseous ammonia, but at slightly reduced output and only at stabilized working temperatures. This means that for cold starts, some solutions have still to be improved and evaluated (i.e. fuel blending, high power igniters, on board partial ammonia decomposition reactors, plasma, variable compression ratio, etc.).

As mentioned, utilization of ammonia in marine systems is under development. Out of all possible applications, marine systems will be the first seeing international deployment. Three separate projects were announced recently for the design of ammonia-fueled engines capable of supporting the shipping industry. ABS has announced a project to design an ammonia-fueled Chittagongmax container carrier of 2,700 Twenty-foot Equivalent Unit (TEU) capacity. Meanwhile, Lloyd's Register commenced on designs for an ammonia-fueled 23,000 TEU Ultra-Large Container Ship (ULCS) concept design while reaching an agreement in principle for the design of a 180,000 ton bulk carrier. All these projects, led by Chinese shipbuilders, will employ MAN two stroke engines [85]. Moreover, the units, currently under development, will ensure that LPG storage systems can be replaced by ammonia, thus enabling the replacement of more than 3,000 systems already working with liquified petroleum gas. The B&W engine (1050 HP) ammonia engine might be operational by 2022, and will be expanded to power outputs between 5 to 85 MW [10,89]. Part of the concept consists on add-ons to the ME-LGIP engine that functions with LPG fuel. The cylinder cover with LPG injection valves and valve control blocks will be the same as used in the ammonia engine, Fig. 13.8. This will also complement an ammonia low-flashpoint fuel supply system. Further information can be found elsewhere [90]. The technology could be employed in the development of engines for larger systems such as trains. The concept, still under assessment, could replace currently available hydrogen systems [91] due to ammonia's better distribution network and safer record compared with hydrogen.

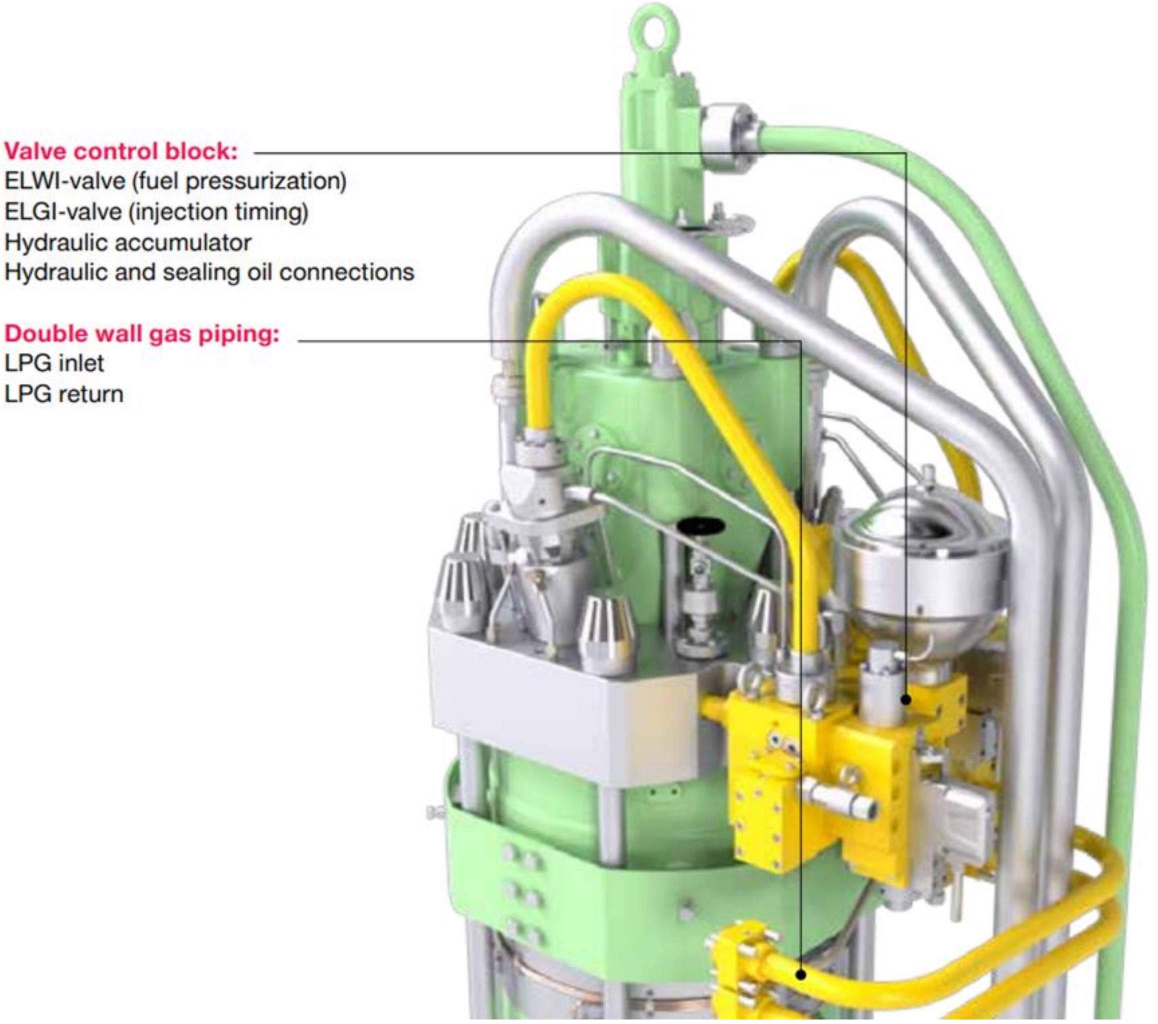

Fig. 13.8. The ammonia concept is based on the LGIP engine [90].

Another interesting concept is the use of linear engine generators. The concept, based on three subsystems (combustion chamber, linear generator and return unit), lacks the use of crankshafts, thus offering smaller and lighter units with variable compression/expansion ratios that enable the use of different fuels, along with high fuel to power conversion efficiencies [92]. The use of ammonia/hydrogen is still being investigated in such units. Future research will ensure that through novel configurations of the linear alternator and linear engine the efficiencies of conversion will reach values above 40%, similar to PEMFCs. The concept will ensure that systems with reduced transmission losses, and improved thermodynamics and friction reduction can achieve pressure ratios of 30:1, boosting the overall cycle efficiency for shipping applications. Further details can be found elsewhere [93].

Small, medium and large power generation using gas turbines will also see an incremental growth in terms of research and development for the efficient use of ammonia as energy vector. As previously presented, the SIP program seeks to establish the technology necessary to run ammonia gas turbines of >100 MW by 2030. This may require the use of novel steel alloys to withstand the severe corrosive environment inherent to ammonia combustion. In order to do so, the AIST center and its associated members are currently working towards the introduction of liquid-based gas turbines. As presented in Chapter 7, current field research outcomes have indicated the need for liquid injection, thus minimizing the impacts from both weather and Joules-Thomson effects. These effects combined with the reduction in distribution line size have already established a new trend. Therefore, liquid injection systems will be studied in the near future as a means to apply ammonia in power-generation turbine systems.

For similar reasons, several European research projects intent on finding the best configuration for the use of ammonia/hydrogen units have been established. Cardiff University has been recently awarded a project for the creation of new combustors that can be fueled using humidified ammonia/hydrogen blends [94]. The technology, capable of delivering efficiencies above 55%, will not only ensure the efficient use of these blends but also the recovery of waste streams (i.e. water and nitrogen) that can be recirculated to raise the final power outputs of the system even further. Moreover, integration of the water and nitrogen produced from the combustion process in both farming and heating applications will raise the applicability of such devices even further. The use of multi-stage combustion systems to realize these technologies is probable considering current ammonia gas turbine demonstration system configurations. Ammonia-derived hydrogen will be employed in either post-combustion zones or regeneration burners under lean conditions, mitigating NOx emissions whilst increasing combustion efficiency. These combustion features, combined with novel manufacturing techniques such as additive layer fabrication and novel materials, will bring down costs whilst maximizing the energy from such blends. In combination with cooling effects obtained from the expansion of ammonia, these new cycles might become competitive to current fossil-based systems.

Projects such as Flex&Confu, led by RINA and the University of Geneve, are expected to establish the first large scale demonstrations for the full deployment of Power-to-Ammonia-to-Power systems, employing off-peak power for the production of the chemical, thus ensuring that during peak periods of time ammonia can be used to produce zero-carbon power. The project, already approved by the European Commission (H2020), will strengthen the position of ammonia as a vital part of the mix of fuels that will decarbonize the power industry in the coming years [95].

In terms of propulsion systems, fuel cells combined with gas turbines may well determine the feasibility of using ammonia as a fuel. Advanced, high efficiency fuel cells are likely to be studied for short-range flights, whilst the implementation of ammonia blends with novel materials for safe and efficient storage will see the arrival of new set of devices that will ensure that the chemical is used for long-range distances. It is anticipated that blending will occur initially with kerosene, whilst future systems will employ ammonia (or ammonia derived hydrogen) to transition into zero-carbon emissions. It should be noted that since the production of ammonia/hydrogen systems is known to produce water and nitrogen, an increase in both molecules at stratospheric level will also produce impacts that are still unknown. However, the idea implies a “zero” nitrogen conditions, since all nitrogen will be derived from the atmosphere and released back to it. Only the addition of water is of interest, and even then, we should note that fossil fuels produce both carbon dioxide and water anyhow, so this will still be a conceptual improvement. However, this is a concept that will become important as the technologies described herein are fully implemented globally.

In terms of health, safety and public perception, further studies will follow, thus providing a better understanding of the use of ammonia and its acceptance as a global energy vector. Early works on the use of ammonia and its dispersion characteristics in heavy jets [96] will find more applications as the technologies evolve. Combined with a better understanding of the implications of enabling the use of ammonia by various groups (Chapter 12) and the recognition of strategies to ameliorate its negative reputation [97], will all ensure that ammonia is a key role player in future energy mix scenarios.

13.6. Summary

It is clear that ammonia as an energy vector will have a major role to play in the following years. New initiatives, novel discoveries and ingenious technological advancements will all support the use of ammonia in a productive, safe manner. Therefore, all those working on this book are convinced that ammonia will be a crucial part of our future, and we expect that the proliferation of technologies around the use of this chemical will evolve to reach every corner of the globe, democratizing energy production whilst leading to a "zero-carbon" economy.

Acknowledgment

Dr. A. Valera-Medina wants to thank the support from the Engineering and Physical Sciences Research Council (EPSRC) who has partially funded his time for the preparation of this chapter through the project EP/T009314/1.

References

[1] International Energy Agency. Future of Hydrogen 2019. https://www.iea.org/hydrogen2019/ (accessed June 19, 2019).

[2] Wind Europe. Offshore Wind in Europe. 2018.

[3] Current. Negative pricing, flexibility and the power sector's evolution. Current 2019. https://www.current-news.co.uk/blogs/negative-pricing-flexibility-and-the-power-sectors-evolution (accessed January 30, 2020).

[4] Renewable H2. Infrastructure for renewable hydrogen-ammonia production and export. Hydrog Carbon-Free Energy Secur 2019. https://www.renewablehydrogen.com.au/copy-of-our-ip-h2-supply-chain-infr (accessed January 30, 2020).

[5] Ministerial Council on Renewable Energy Hydrogen and Related Issues. Basic Hydrogen Strategy 2017. https://www.meti.go.jp/english/press/2017/pdf/1226_003b.pdf (accessed July 1, 2019).

[6] Geropoulos K. Morocco's renewable resources connect Europe and Africa. NewEurope 2018. https://www.neweurope.eu/article/moroccos-renewable-resources-connect-europe-and-africa/ (accessed June 18, 2019).

[7] Fraunhofer IGB News. Morocco – Synthesis of green hydrogen and green ammonia 2019. https://www.igb.fraunhofer.de/en/press-media/press-releases/2019/morocco-green-ammonia-synthesis.html (accessed January 10, 2020).

[8] Environmental Defense Fund. Sailing on Solar. 2019.

[9] International Transport Forum. Decarbonising Maritime Transport: Pathways to Zero-Carbon Shipping by 2035 2018. https://www.itf-oecd.org/sites/default/files/docs/decarbonising-maritime-transport.pdf (accessed January 30, 2020).

[10] Brown T. MAN Energy Solutions: an ammonia engine for the maritime sector. Ammon Energy 2019. https://www.ammoniaenergy.org/articles/man-energy-solutions-an-ammonia-engine-for-the-maritime-sector/ (accessed January 14, 2020).

[11] Brown T. Viking Energy to be retrofit for ammonia fuel in 2024. Ammon Energy 2020. https://www.ammoniaenergy.org/articles/viking-energy-to-be-retrofit-for-ammonia-fuel-in-2024/?mc_cid=29b636f33c&mc_eid=81cd7b883e (accessed January 30, 2020).

[12] Midling AS. Ammonia may hold key to greener combustion. Sciencenorway 2019. https://partner.sciencenorway.no/aircraft-climate-hydrogen/ammonia-may-hold-key-to-greener-combustion/1574266 (accessed January 30, 2020).

[13] Smil V. Enriching the Earth: Fritz Haber, Carl Bosch, and the Transformation of World Food Production. Cambridge (MA): 2004.

[14] Nayak-Luke R, Bañares-Alcántara R, Wilkinson I. "Green" Ammonia: Impact of Renewable Energy Intermittency on Plant Sizing and Levelized Cost of Ammonia. Ind Eng Chem Res 2018:acs.iecr.8b02447. https://doi.org/10.1021/acs.iecr.8b02447.

[15] Nayak-Luke R, Bañares-Alcántara R. Long-Term Energy Storage: What is the Need and is Ammonia a Solution? Comput Aided Chem Eng 2018;44:1843–8. https://doi.org/10.1016/B978-0-444-64241-7.50302-5.

[16] Ye L, Nayak-Luke R, Bañares-Alcántara R, Tsang E. Reaction: "Green" Ammonia Production. Chem 2017. https://doi.org/10.1016/j.chempr.2017.10.016.

[17] Nayak-Luke R, Bañares-Alcántara R. Long-term chemical energy storage: electrofuels for

weekly/monthly storage. Perspect. Energy Storage Syst., Copenhagen (Denmark): 2018.

[18] Siddiqui O, Dincer I. Design and analysis of a novel solar-wind based integrated energy system utilizing ammonia for energy storage. Energy Convers Manag 2019;195:866–84. https://doi.org/10.1016/j.enconman.2019.05.001.

[19] Rouwenhorst KHR, Van Der Ham AGJ, Mul G, Kersten SRA. Islanded ammonia power systems: Technology review & conceptual process design. Renew Sustain Energy Rev 2019;114. https://doi.org/10.1016/j.rser.2019.109339.

[20] Grinberg Dana A, Elishav O, Bardow A, Shter GE, Grader GS. Nitrogen-Based Fuels: A Power-to-Fuel-to-Power Analysis. Angew Chemie Int Ed 2016. https://doi.org/10.1002/anie.201510618.

[21] Hansen JB, Han P. The SOC4NH3 Project in Denmark. NH3 Event, Rotterdam (the Netherlands): 2019.

[22] Ernst FA. Industrial Chemical Monographs: Fixation of Atmospheric Nitrogen. London (UK): Chapman & Hall, Ltd.; 1928.

[23] International Energy Agency. The Future of Hydrogen: Seizing today's opportunities. 2019.

[24] Landman A, Halabi R, Dias P, Dotan H, Mehlmann A, Shter GE, et al. Decoupled Photoelectrochemical Water Splitting System for Centralized Hydrogen Production. Joule 2020. https://doi.org/10.1016/J.JOULE.2019.12.006.

[25] Dotan H, Landman A, Sheehan SW, Malviya KD, Shter GE, Grave DA, et al. Decoupled hydrogen and oxygen evolution by a two-step electrochemical–chemical cycle for efficient overall water splitting. Nat Energy 2019;4:786–95. https://doi.org/10.1038/s41560-019-0462-7.

[26] Czekajło Ł, Lendzion-Bieluń Z. Wustite based iron-cobalt catalyst for ammonia synthesis. Catal Today 2017;286:114–7. https://doi.org/10.1016/j.cattod.2016.11.013.

[27] Liu H, Han W. Wüstite-based catalyst for ammonia synthesis : Structure , property and performance. Catal Today 2017;297:276–91. https://doi.org/10.1016/j.cattod.2017.04.062.

[28] Lindley BM, Appel AM, Krogh-Jespersen K, Mayer JM, Miller AJM. Evaluating the Thermodynamics of Electrocatalytic N2 Reduction in Acetonitrile. ACS Energy Lett 2016. https://doi.org/10.1021/acsenergylett.6b00319.

[29] U.S. Department of Energy. Sustainable Ammonia Synthesis. Dulles (VA): 2016.

[30] Smith C, Hill AK, Torrente-Murciano L. Current and future role of Haber–Bosch ammonia in a carbon-free energy landscape. Energy Environ Sci 2020. https://doi.org/10.1039/C9EE02873K.

[31] Schlögl R. Catalytic synthesis of ammonia - A "never-ending story"? Angew Chemie - Int Ed 2003;42:2004–8. https://doi.org/10.1002/anie.200301553.

[32] Rijksen C. Green Hydrogen in Ammonia Production, 2018.

[33] Küngas R, Blennow P, Nørby TH, Hansen JB, Moses PG. Progress in SOEC development activities at Haldor Topsøe. In: Eguchi K, Singhal SC, editors. ECS Trans., vol. 91, Kyoto (Japan): Electrochemical Society Inc.; 2019, p. 215–23. https://doi.org/10.1149/09101.0215ecst.

[34] Hansen JB, Han PA. Roadmap to All Electric Ammonia Plants. NH3 Fuel Conf., Pittsburgh (PA): 2018.

[35] Armijo J, Philibert C. Flexible production of green hydrogen and ammonia from variable solar and wind energy. Case study of Chile and Argentina 2019.

[36] Crolius S. IEA Analysis: Green Chinese P2A Could Compete with Brown NH3 2019.

[37] Rouwenhorst KHR, Krzywda P, Faria JA, Benes NE, Mul G, Lefferts L. Ammonia, 4. Green Ammonia Production. Ullmann's Encycl Ind Chem n.d. https://doi.org/In preparation.

[38] Bell TE, Torrente-Murciano L. H2 Production via Ammonia Decomposition Using Non-Noble Metal Catalysts: A Review. Top Catal 2016;59:1438–57. https://doi.org/10.1007/s11244-016-0653-4.

[39] Christensen CH, Johannessen T, Sørensen RZ, Nørskov JK. Towards an ammonia-mediated hydrogen economy? Catal Today 2006;111:140–4.

[40] Chakraborty D, Petersen HN, Johannessen T. Apparatus for generating hydrogen from ammonia stored in solid materials and integration thereof into low temperature fuel cells. WO2011107279A1, 2011.

[41] Jacobsen HS, Hansen HA, Andreasen JW, Shi Q, Andreasen A, Feidenhans'l R, et al. Nanoscale structural characterization of Mg(NH3)6Cl2 during NH3 desorption: An in situ small angle X-ray scattering study. Chem Phys Lett 2007. https://doi.org/10.1016/j.cplett.2007.05.001.

[42] Hummelshøj JS, Sørensen RZ, Kustova MY, Johannessen T, Nørskov JK, Christensen CH. Generation of nanopores during desorption of NH3 from Mg(NH 3)6Cl2. J Am Chem Soc 2006. https://doi.org/10.1021/ja0556070.

[43] Makepeace JW, He T, Weidenthaler C, Jensen TR, Chang F, Vegge T, et al. Reversible ammonia-based and liquid organic hydrogen carriers for high-density hydrogen storage: Recent progress. Int J Hydrogen Energy 2019. https://doi.org/10.1016/j.ijhydene.2019.01.144.

[44] Zhang T, Miyaoka H, Miyaoka H, Ichikawa T, Kojima Y. Review on Ammonia Absorption Materials: Metal Hydrides, Halides, and Borohydrides. ACS Appl Energy Mater 2018. https://doi.org/10.1021/acsaem.7b00111.

[45] Jensen PB. Computational Design of New Materials for Ammonia Storage. Technical University of

Denmark, 2014.

[46] Sørensen RZ, Hummelshøj JS, Klerke A, Reves JB, Vegge T, Nørskov JK, et al. Indirect, reversible high-density hydrogen storage in compact metal ammine salts. J Am Chem Soc 2008. https://doi.org/10.1021/ja076762c.

[47] Kailos NC. Utilization of Ammonia as an Alternative Fuel in Army Aircraft Engines: USAAVLABS Technical Report 66-52. 1966.

[48] Bliznakov G, Polikarova R. On the desorption of ammonia from silica gel. J Catal 1966. https://doi.org/10.1016/S0021-9517(66)80120-3.

[49] Zeng S, Wang J, Li P, Dong H, Wang H, Zhang X, et al. Efficient adsorption of ammonia by incorporation of metal ionic liquids into silica gels as mesoporous composites. Chem Eng J 2019. https://doi.org/10.1016/j.cej.2019.03.180.

[50] Dana AG, Shter GE, Grader GS. Nitrogen-based alternative fuel: An environmentally friendly combustion approach. RSC Adv 2014. https://doi.org/10.1039/c3ra47890d.

[51] Mosevitzky B, Shter GE, Grader GS. Effect of equivalence ratio on the thermal autoignition of aqueous ammonia ammonium nitrate monofuel. Combust Flame 2018;188. https://doi.org/10.1016/j.combustflame.2017.09.028.

[52] Elishav O, Lewin DR, Shter GE, Grader GS. The nitrogen economy: Economic feasibility analysis of nitrogen-based fuels as energy carriers. Appl Energy 2017. https://doi.org/10.1016/j.apenergy.2016.10.088.

[53] Sayed ET, Eisa T, Mohamed HO, Abdelkareem MA, Allagui A, Alawadhi H, et al. Direct urea fuel cells: Challenges and opportunities. J Power Sources 2019. https://doi.org/10.1016/j.jpowsour.2018.12.024.

[54] Koike M, Miyagawa H, Suzuoki T, Ogasawara K. Ammonia as a hydrogen energy carrier and its application to internal combustion engines. Inst. Mech. Eng. - Sustain. Veh. Technol. Driv. Green Agenda, 2012. https://doi.org/10.1533/9780857094575.2.61.

[55] News: Research: UK researchers change game for hydrogen from ammonia for cars. Fuel Cells Bull 2014. https://doi.org/10.1016/S1464-2859(14)70208-1.

[56] Zhou M, Wang Y, Chu Y, Tang Y, Tian K, Zheng S, et al. Ammonia as an environmentally benign energy carrier for the fast growth of China. Energy Procedia, 2019. https://doi.org/10.1016/j.egypro.2019.01.668.

[57] Li R, Konnov AA, He G, Qin F, Zhang D. Chemical mechanism development and reduction for combustion of NH3/H2/CH4 mixtures. Fuel 2019. https://doi.org/10.1016/j.fuel.2019.116059.

[58] Xiao H, Valera-Medina A, Bowen PJ. Modeling Combustion of Ammonia/Hydrogen Fuel Blends under Gas Turbine Conditions. Energy & Fuels 2017;31:8631–42. https://doi.org/10.1021/acs.energyfuels.7b00709.

[59] Xiao H, Wang Z, Valera-Medina A, Bowen PJ. Study on Characteristics of Co-firing Ammonia/Methane Fuels under Oxygen Enriched Combustion Conditions. J Therm Sci 2018;27. https://doi.org/10.1007/s11630-018-1008-1.

[60] Valera-Medina A, Konnov A. Comparison between reduced reaction mechanisms for H2/NH3 flames in gas turbines. Fuel 2020.

[61] Somarathne KDKA, Hatakeyama S, Hayakawa A, Kobayashi H. Numerical study of a low emission gas turbine like combustor for turbulent ammonia/air premixed swirl flames with a secondary air injection at high pressure. Int J Hydrogen Energy 2017. https://doi.org/10.1016/j.ijhydene.2017.09.089.

[62] Honzawa T, Kai R, Okada A, Valera-Medina A, Bowen PJ, Kurose R. Predictions of NO and CO emissions in ammonia/methane/air combustion by LES using a non-adiabatic flamelet generated manifold. Energy 2019. https://doi.org/10.1016/j.energy.2019.07.101.

[63] Vigueras-Zuniga M, Tejeda-del-Cueto M, Vasquez-Santacruz J, Herrera-May A, Valera-Medina A. Numerical Predictions of a Swirl Combustor Using Complex Chemistry Fueled with Ammonia/Hydrogen Blends. Energies 2020;13:288. https://doi.org/doi.org/10.3390/en13020288.

[64] Kameoka S, Kuroda M, Aoyagi K, Ito S, Kunimori K. Formation of novel Al 2 O 3 surface (Al-O(black star)) by plasma-excited nitrogen and its catalytic application - Production of ammonia and oxygen from nitrogen and water. Appl Surf Sci 1997. https://doi.org/10.1016/S0169-4332(97)00329-2.

[65] Barker R. Decomposition of ammonia in a microwave discharge. J Chem Soc Faraday Trans 1 Phys Chem Condens Phases 1972. https://doi.org/10.1039/F19726800315.

[66] Pugh DG, Bowen PJ, Marsh R, Crayford AP, Runyon J, Morris S, et al. Dissociative influence of H2O vapour/spray on lean blowoff and NOx reduction for heavily carbonaceous syngas swirling flames. Combust Flame 2017;177. https://doi.org/10.1016/j.combustflame.2016.11.010.

[67] Kobayashi H, Hayakawa A, Somarathne KDKA, Okafor EC. Science and technology of ammonia combustion. Proc Combust Inst 2019;37:109–33. https://doi.org/10.1016/j.proci.2018.09.029.

[68] Yi Y, Wang L, Guo Y, Sun S, Guo H. Plasma-assisted ammonia decomposition over Fe–Ni alloy

catalysts for COx-Free hydrogen. AIChE J 2019. https://doi.org/10.1002/aic.16479.

[69] Ju Y, Sun W. Plasma assisted combustion: Dynamics and chemistry. Prog Energy Combust Sci 2015. https://doi.org/10.1016/j.proci.2014.05.021.

[70] Shioyoke A, Hayashi J, Murai R, Nakatsuka N, Akamatsu F. Numerical Investigation on Effects of Nonequilibrium Plasma on Laminar Burning Velocity of Ammonia Flame. Energy and Fuels 2018. https://doi.org/10.1021/acs.energyfuels.7b02733.

[71] Starikovskiy A, Aleksandrov N. Plasma-assisted ignition and combustion. Prog Energy Combust Sci 2013. https://doi.org/10.1016/j.pecs.2012.05.003.

[72] Brown T. Ammonia for Fuel Cells: AFC, SOFC, and PEM. Ammon Energy 2018. https://www.ammoniaenergy.org/articles/ammonia-for-fuel-cells-afc-sofc-and-pem/ (accessed January 14, 2020).

[73] Zhao Y, Setzler BP, Wang J, Nash J, Wang T, Xu B, et al. An Efficient Direct Ammonia Fuel Cell for Affordable Carbon-Neutral Transportation. Joule 2019. https://doi.org/10.1016/j.joule.2019.07.005.

[74] Eguchi K. Successful generation of 1 kilowatt by a fuel cell using ammonia directly as fuel. SIP Progr 2017. https://www.jst.go.jp/pr/announce/20170703-2/index.html (accessed December 1, 2019).

[75] Siddiqui O, Dincer I. Experimental investigation and assessment of direct ammonia fuel cells utilizing alkaline molten and solid electrolytes. Energy 2019. https://doi.org/10.1016/j.energy.2018.12.096.

[76] Siddiqui O, Dincer I. A review and comparative assessment of direct ammonia fuel cells. Therm Sci Eng Prog 2018. https://doi.org/10.1016/j.tsep.2018.02.011.

[77] Siddiqui O, Dincer I. Investigation of a New Anion Exchange Membrane-based Direct Ammonia Fuel Cell System. Fuel Cells 2018. https://doi.org/10.1002/fuce.201800052.

[78] Siddiqui O, Dincer I. Development and performance evaluation of a direct ammonia fuel cell stack. Chem Eng Sci 2019. https://doi.org/10.1016/j.ces.2019.01.059.

[79] Okanishi T, Okura K, Srifa A, Muroyama H, Matsui T, Kishimoto M, et al. Comparative Study of Ammonia-fueled Solid Oxide Fuel Cell Systems. Fuel Cells 2017. https://doi.org/10.1002/fuce.201600165.

[80] SAFCell Inc. SAFCell 2019. http://www.safcell.com/what-is-a-safc (accessed December 1, 2019).

[81] Brown T. University of Minnesota demonstrates efficient ammonia dual-fuel engine system. Ammon Energy 2019. https://www.ammoniaenergy.org/articles/university-of-minnesota-demonstrates-efficient-ammonia-dual-fuel-engine-system/ (accessed November 12, 2019).

[82] HYDROFUEL. Diesel-NH3 Injection 2020. https://nh3fuel.com/index.php/technology/18-engine-conversions/27-diesel-nh3-injection (accessed January 14, 2020).

[83] Woo Y. Recent progress on the Ammonia-Gasoline and the Ammonia-Diesel Dual Fueled Internal Combustion Engines in Korea. Hydrog. Energy Syst. Using Ammon., CMC Publishing Co.; 2015.

[84] Hikazudani S, Inazumi C, Nakanishi H, Nakamura N, Arikawa H. Ammonia Engine System. EP2348209A1, 2011.

[85] Brown T. Ammonia-fueled ships: entering the design phase. Ammon Energy 2019. https://www.ammoniaenergy.org/articles/ammonia-fueled-ships-entering-the-design-phase/?mc_cid=9926ad8cd1&mc_eid=81cd7b883e (accessed January 14, 2020).

[86] Lhuillier C, Brequigny P, Contino F, Rousselle C. Performance and Emissions of an Ammonia-Fueled SI Engine with Hydrogen Enrichment. SAE Tech. Pap., 2019. https://doi.org/10.4271/2019-24-0137.

[87] Lhuillier C, Brequigny P, Contino F, Rousselle C. Combustion Characteristics of Ammonia in a Modern Spark-Ignition Engine. SAE Tech. Pap., 2019. https://doi.org/10.4271/2019-24-0237.

[88] Lhuillier C, Brequigny P, Lamoureux N, Contino F, Mounaïm-Rousselle C. Experimental investigation on laminar burning velocities of ammonia/hydrogen/air mixtures at elevated temperatures. Fuel 2020. https://doi.org/10.1016/j.fuel.2019.116653.

[89] Laursen RS. Ship Operation Using LPG and Ammonia As Fuel on MAN B&W. NH3 Fuel Conf. 2018, Pittsburgh: 2018.

[90] MAN Energy Solutions. Engineering the future two-stroke green-ammonia engine. 2020.

[91] The Guardian. Germany launches world's first hydrogen-powered train. Hydrog Power 2018. https://www.theguardian.com/environment/2018/sep/17/germany-launches-worlds-first-hydrogen-powered-train (accessed January 14, 2020).

[92] Hung NB, Lim O. A review of free-piston linear engines. Appl Energy 2016. https://doi.org/10.1016/j.apenergy.2016.06.038.

[93] Wu D. Powering Carbon-free Autonomous Shipping: Ammonia/Hydrogen dual-fuelled Linear Engine-Generator. EPSRC 2019. https://gow.epsrc.ukri.org/NGBOViewGrant.aspx?GrantRef=EP/S00193X/1 (accessed November 11, 2019).

[94] Valera-Medina A. Storaged Ammonia For Energy (SAFE) - AGT Pilot. EPSRC 2019. https://gow.epsrc.ukri.org/NGBOViewGrant.aspx?GrantRef=EP/T009314/1 (accessed December 12, 2019).

[95] H2020. Integrated solutions for flexible operation of fossil fuel power plants through power-to-X-to-power and/or energy storage 2017. https://ec.europa.eu/info/funding-tenders/opportunities/portal/screen/opportunities/topic-details/lc-sc3-nze-4-2019 (accessed December 1, 2019).

[96] Nielsen M, Ott S, Jørgensen HE, Bengtsson R, Nyrén K, Winter S, et al. Field experiments with dispersion of pressure liquefied ammonia. J Hazard Mater 1997. https://doi.org/10.1016/S0304-3894(97)00029-0.

[97] Cojocaru D, Oroviceanu L. Answers to Technical Queries. Bracknell: n.d.