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A Technological Roadmap to the Ammonia Energy Economy: Current State and Missing Technologies

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Abstract

Ammonia is considered a key energy carrier with potential applications for low carbon energy storage, transportation and power generation. This carbon-free molecule offers several advantages, including high energy density and a wide and well-established production and distribution infrastructure that have been optimized for over a century. In this perspective, we analyze the potential roles of ammonia as an energy carrier, and summarize research areas requiring further development for the implementation of ammonia as a building block in the global sustainable energy landscape. Ammonia technologies are reviewed with an emphasis on current limitations and recent advances. Focus is placed on available technologies for ammonia synthesis, decomposition into CO_x-free hydrogen and direct use of ammonia for power generation and transportation.

Keywords: ammonia as energy carrier, ammonia synthesis, CO_x-free hydrogen by ammonia decomposition, ammonia direct utilization.

1. Introduction

The future of a carbon-free society depends on the exploitation of renewables to address challenges associated with energy security while minimizing the environmental impact of energy generation processes.¹ In this new paradigm, the ability to effectively store and distribute large quantities of energy is essential to ensure security and flexibility.² Chemical storage in energy dense fuels (hydrogen, ammonia, methanol, cyclohexane) is preferable for storing large quantities of energy over long-time periods and enables widespread distribution, while electrical storage (batteries) offers short-term, localized storage. The commercial viability of ammonia as an energy carrier is supported by:²⁻⁵ 1) its high volumetric (108 kgH₂/m³ NH₃ at 20°C and 8.6 bar) and gravimetric (17.8 wt.%) energy density,² and the lower cost per unit

of energy stored (0.54 \$/kg-H₂, 182 days),⁵ compared to hydrogen (14.95 \$/kg-H₂), 2) the fact that ammonia can be either catalytically decomposed into CO_x-free hydrogen,⁶ or directly used in power generation devices (fuel cells, combustion engines, gas turbines) with zero carbon footprint;⁵ and 3) the availability of a well-established production and distribution infrastructure, with well-defined regulations and a positive safety history.⁷ Ammonia has been manufactured and transported throughout the world for more than a century, with an already existing high-capacity infrastructure for liquefied ammonia, including pipelines, bunker shipping, tank-trucks etc.⁸

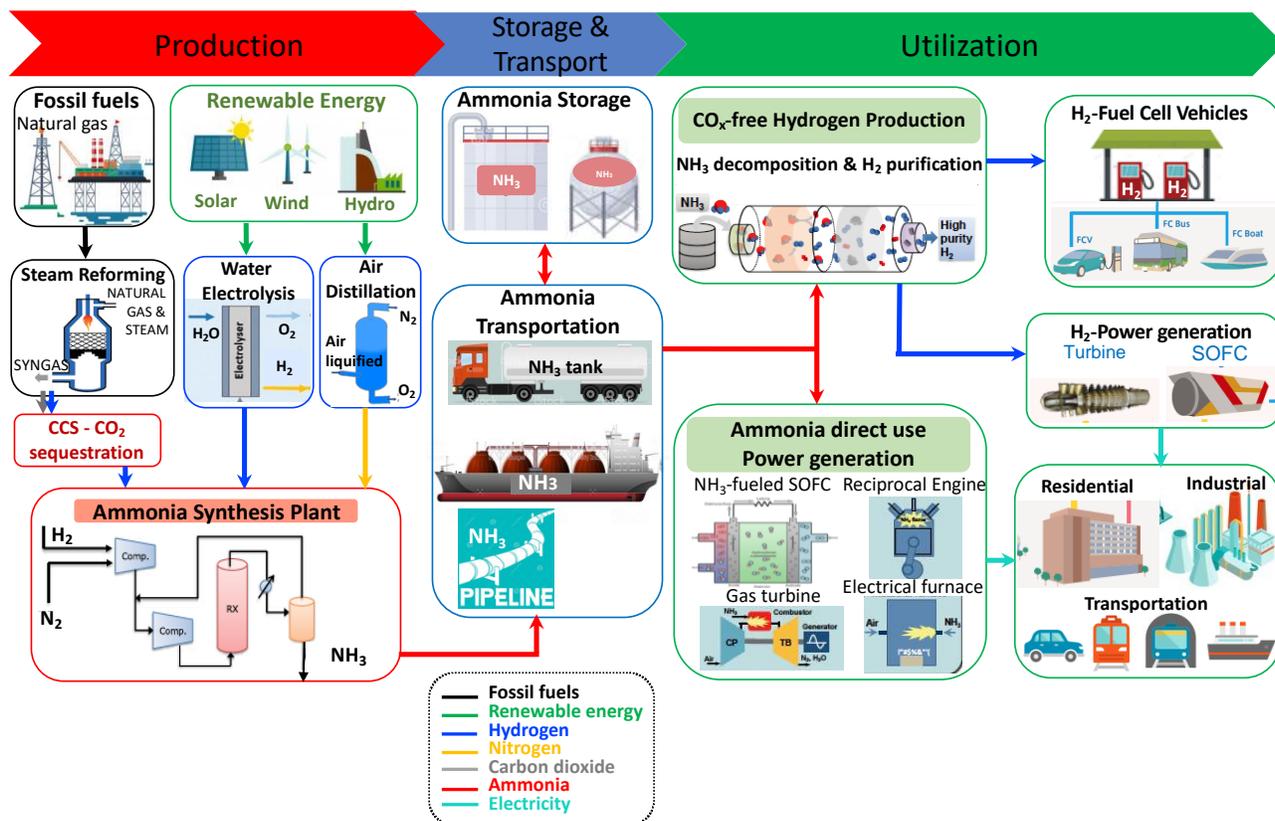
Consequently, ammonia is increasingly considered to be a key energy carrier in the development of the future energy system.³⁻⁵ As shown in Figure 1, ammonia, produced from fossil fuels with CO₂ sequestration (leading to blue hydrogen) or from renewable energy (green hydrogen), could provide a practical next generation system for energy storage, transportation, and power generation, rather directly or via decomposition to hydrogen.

The use of “energy carriers” could be the key to utilize renewables by balancing the intermittent production with the continuous and increasing energy demand, and to meet net zero emission targets by decarbonizing this crucial sector (including transport, industry, residential, shipping, heating and cooling).^{1, 9-10} The potential of ammonia as an energy carrier to transport renewable energy was evaluated comparing the round-trip efficiency (RTE, net useful energy for end application from energy input to produce ammonia) for residential (RTE 40-50%) or automotive applications (RTE 20-30%).¹¹ Despite the low maturity and efficiencies of current technologies, these values place ammonia among the most efficient carriers.

Many countries,^{5, 12} EU,¹³⁻¹⁴ USA,¹⁵ UK,¹⁶ Japan,¹⁷ Australia¹⁸ are funding research programs in this direction, including the development of scalable technologies for converting ammonia into hydrogen or electricity on demand. In the transition to a low carbon economy, new market opportunities might arise with the creation of an ammonia-based energy market similar to the current one based on fossil fuels.⁴ At

the time of this publication, commercial production and utilization of ammonia as an energy carrier has been attracting significant interest from various companies. Technology providers^{12, 19} such as JGC, Siemens, Haldor Topsoe, ThyssenKrupp and Yara,²⁰ are developing CO₂-free ammonia plants in Japan, UK, Netherlands, US and Australia. Announcements of the largest green ammonia plant²¹ and carbon-free ammonia production²² being planned in Saudi Arabia for export.

This work highlights the ongoing research related to the use of ammonia as an energy carrier, focusing on the available technologies for ammonia synthesis and hydrogen necessary for its production; ammonia decomposition into hydrogen and further purification; and direct use of ammonia for power generation. This perspective article further emphasizes the challenges related to these technologies and research areas that require further development before their implementation and commercial deployment can be achieved at larger scale.



Scheme 1. Key role of ammonia as energy carrier in a future energy system.¹⁶⁻¹⁷

2. Ammonia synthesis

The large-scale production of ammonia (150-180 Mtons/year, increasing 2.3% per year) relies on the well-known Haber-Bosch process. The catalytic reaction ($\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$) is carried out at 400-550°C and 10-25MPa and makes use of circa 1% of the global energy consumption. In the absence of CO₂ capture, this process leads to 1.9 tons CO₂/ton ammonia (1.2% of global CO₂ emissions).^{7, 23-24} Reducing the CO₂ footprint of the ammonia production by using low-carbon hydrogen, is critical to achieve net-zero targets by 2050.

The multi-promoted iron catalyst developed 100 years ago is very similar to the one used today, and is extremely difficult to develop a more cost-effective ammonia synthesis catalyst.⁷ Improvements made over the last century have been related to the optimization of the overall energy efficiency from 36% to the current 62–65% (Figure 1A).⁴ Another challenge is to decrease ammonia production costs, controlled by the geographical market price of natural gas feedstock used for hydrogen production, accounting for 70-90% of the total cost (Figure 1B).^{16, 18}

Efforts have been made to decrease the operating pressure. However, at lower pressures, the equilibrium single pass conversion decreases (15% at 10MPa) and recycling of unreacted H₂ and N₂ after condensation of the ammonia product becomes more difficult and require a larger recycle compressor and heat exchanger.²³ This results in higher overall energy and capital costs than for conventional high-pressure processes. Alternative technologies under development focus on the development and integration of absorbers to replace condensation.¹⁶

To date, natural gas steam reforming (SMR) is the most economical route to produce the hydrogen required for large-scale ammonia production (brown ammonia).²⁵ Near CO₂-neutral processes (blue hydrogen) could be achieved by the implementation of carbon capture and sequestration strategies (CCS) that eliminate CO₂ emissions up to 90-95%.²⁶⁻²⁷ In the near future, the use of green hydrogen produced

from renewable energy by electrolysis of water may further decrease (and eventually eliminate) the CO₂ penalty. Other renewable technologies to produce hydrogen include²⁸ biomass gasification, biological fermentation, photoelectrochemical and thermochemical, which are all still in the early stages of development with low energy efficiencies.

Electrochemical ammonia synthesis,⁷ in spite of the current hype, is twice as costly as conventional Haber-Bosch processes with hydrogen produced *via* SMR and it still needs to be demonstrated that the observed ammonia is truly synthesized by N₂ reduction and not emerging from contamination sources.²⁹ Other technologies such as photocatalytic ammonia synthesis,³⁰ non-thermal plasma,³¹ nitrogenase enzyme in microbes,³² or biomass,³³ and membrane reactors³⁴⁻³⁵ show very low energy efficiencies and have only been demonstrated at lab-scale. The production of ammonia directly from air and sea water using solar energy is still far from being able to produce the large demand needed and requires intensive development.³⁶⁻³⁷

Figure 1A, shows energy efficiency improvements in ammonia synthesis during the last century. In Figure 1C a new dashed line shows the energy efficiency future trends by feedstock: natural gas>naphtha>heavy oil>coal. Other technologies that are more sustainable and carbon neutral (Figure 1C-1D), are less energy efficient than SMR with CCS.

The potential use of ammonia as energy carrier could increase the ammonia demand, rising up to >>100 Mton/year more, considering the displacement of conventional fuels and power generation applications.^{3, 20, 38} Assuming 3 MWh per metric ton of ammonia, to meet the energy demand would require to increase around five times the existing installed ammonia capacity;³⁹ currently dedicated to fertilizers industry and suggesting the competition between the energy and fertilizers markets. Whatever the fraction of this energy market captured by an ammonia-based system, would be a significant business opportunity for the ammonia synthesis technology providers, estimated as multi-billion USD market.⁴⁰

Conventional ammonia production, to cover this huge demand, is constrained by the large carbon footprint.⁴¹ On the other hand, the carbon-free process for green ammonia using renewable energy, is about 3 times more costly than the current process, and would require an intense decrease in the operation costs together with affordable renewable electricity.²⁰ While green ammonia will gradually replace the conventional ammonia, over the next two decades, green ammonia production is expected to reach 10-20 Mton/year, and therefore it is unlikely to cover the demand and penetrate in the energy markets.^{20, 38} In the near term, greening the natural gas-based process via CCS would be the feasible solution, while in the long-term taxes might favor the green approach. Small and distributed plants would be required to match the new and unconventional needs.

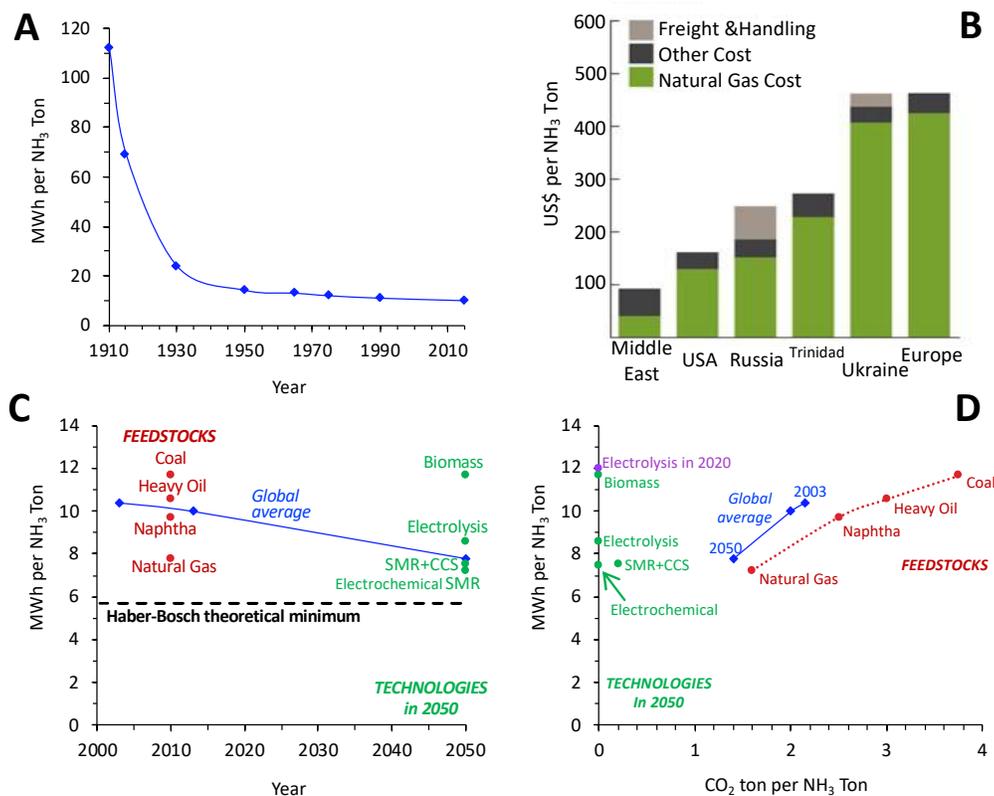


Figure 1. Ammonia synthesis: A) energy efficiency improvements in the last century; B) ammonia production costs; C) efficiency perspective to 2050, feedstocks and technologies; D) CO₂ emissions. Several sources^{14, 16, 42}

3. Ammonia decomposition

Ammonia decomposition ($2\text{NH}_3 \rightleftharpoons \text{N}_2 + 3\text{H}_2$) into CO_x -free hydrogen has been widely explored in the last decade.^{6, 43-45} The equilibrium conversion (99 to 99.7% at 400°C and 500°C, respectively at 1 atm) leads to small traces of unconverted ammonia that represent an issue for several applications, therefore requiring a hydrogen purification system.⁴⁶

The immaturity of this technology is currently one of the most important limitations in the use of ammonia as an energy carrier. This is especially true when compared to the maturity of the well-established process for ammonia production, handling and supply, which has been optimized for over a century. The key challenge to the development of CO_x -free hydrogen technology is the integration of ammonia decomposition with hydrogen purification, in an energy efficient, reliable and scalable manner.⁴⁶ Potential areas for research include catalysis development, H_2 purification methods and reactor design.

3.1. Catalyst

The recovery of hydrogen from ammonia requires the development of efficient catalysts based on cheap non-noble metals (mainly Ni, Fe, Co) as alternatives to the state of the art Ru-catalysts.⁴⁷⁻⁴⁸ However, transition metals show good catalytic activity at high temperatures (>600°C), not reaching the 99% conversion at 450°C (U.S. DOE specifications for hydrogen storage).⁸ Theoretical models predict bimetallic transition metal nanoparticles are adequate, cost-effective candidates to substitute the expensive Ru catalyst, based on the N-binding energy on the metal surface as descriptor for decomposition rates.^{44, 49-}

50

Recently developed catalysts based on bimetallic nanoparticles⁵¹ or alloys,⁵² showed promising catalytic performance, being excellent alternatives to Ru. Highly efficient catalysts synthesized from high-entropy alloys (HEA CoMoFeNiCu nanoparticles) demonstrate enhanced catalytic activity and stability; >20 improvement factor versus Ru catalysts (Figure 2A).

For bimetallic and alloy catalysts, the main concern is about structural stability under reaction conditions, regarding metal segregation. Since the improved interaction between the metals seems to lead to the higher activity, the choice of alloy preparation and the use of metal salts containing desired metals could be interesting. Other parameters affecting the catalytic performance are physical-chemical properties of the support (surface area, basicity, electron conductivity)^{43-45, 53} promoters (alkali, alkaline earth),⁴⁵ and preparation and pre-treatment conditions.⁶

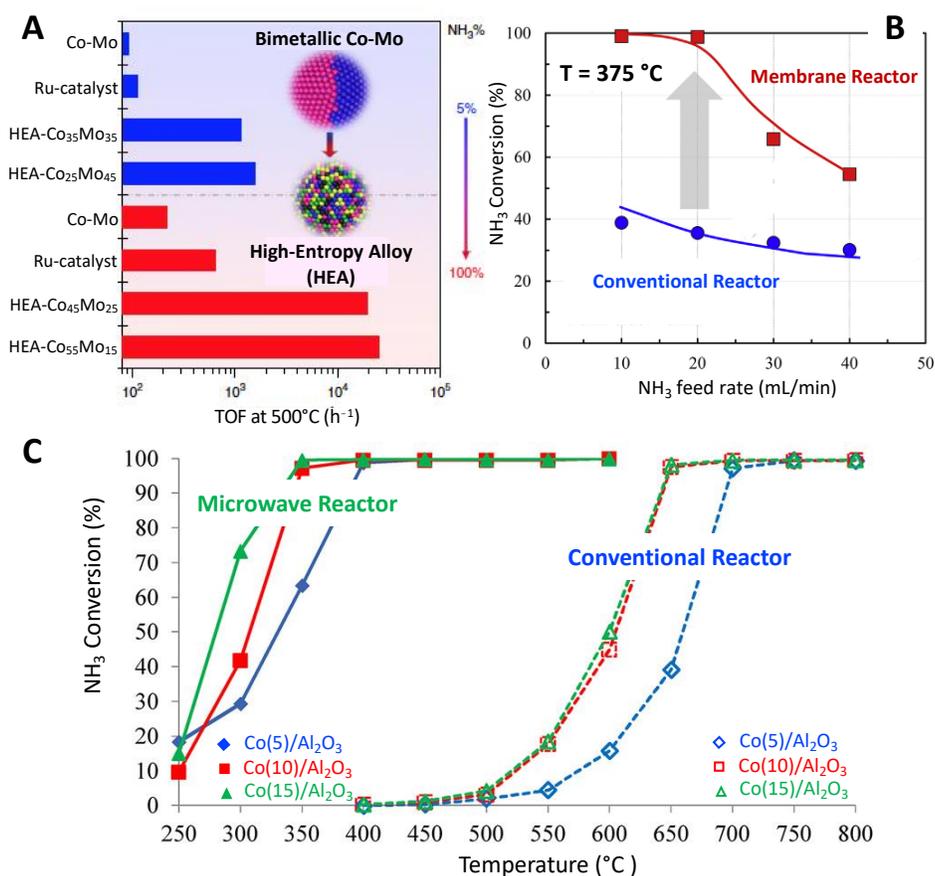


Figure 2. Ammonia decomposition advances: A) catalyst development;⁵² B) H₂-selective membrane with Ru/Al₂O₃ tube-wall catalyst (reaction pressure: 100 kPa, permeate pressure: 6 kPa);⁵⁴ C) microwave reactor.⁵⁵

3.2. Hydrogen purification

For some applications (low temperature fuel cells) hydrogen produced by ammonia decomposition must be purified to 99.97% (< 100 ppb NH₃, 100 ppm N₂)⁵⁶. The best strategy is the use of multifunctional H₂-

permeable membrane reactors, which integrate reaction, separation and purification in a single unit, offering several advantages.^{46, 57} 1) provides pure hydrogen, reaching full conversion at lower temperatures by shifting the thermodynamic equilibrium via the continuous removal of hydrogen, improving the efficiency of the system; and 2) avoids downstream separation units, lowering the installation and operational costs.⁵⁸⁻⁵⁹

The best option to achieve the purity requirements is the use of palladium membranes, and these have been widely explored and reviewed for many applications, including ammonia decomposition.^{28, 60} Pd membranes are stable in ammonia,⁶¹ however, development and scale-up of H₂-membrane technologies is one of the challenges that needs future work. The main drawbacks limiting the widespread use of Pd-based membranes are related to the cost of Pd coupled with the fragility and membrane durability. Furthermore, the membranes must be free of defects and have excellent high-temperature seals to achieve the required H₂ purity.⁶⁰ Future research for H₂ separation and purification systems using H₂-permeable membranes, are related to the lifetime limitations and the poor tolerance to thermal cycling. Significant improvements need to be demonstrated to make membrane-based technology competitive for this reaction before its implementation at larger scales.

Alternatives to expensive Pd-based membranes have been investigated to reduce the system cost, including silica-based and ceramics,⁶² Ni alloys, amorphous Ni-Nb-Zr, and Pd-coated V, Nb, and Ta.^{46, 63} However, limitations in stability, selectivity and permeability, requires intense research to improve their H₂ productivity and purity.

Recent advances on this topic include development of Vanadium⁶⁴ or Pd-based double-skinned membranes,⁶⁵ PdAg supported membranes, with a porous layer to protect the membrane surface from the particles in the catalytic-membrane reactor, showed outstanding H₂-permeance ($5 \cdot 10^{-6} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$), H₂/N₂ selectivity (>25,000), and stability (750-2000 hours). Pd-coated V

membranes have shown excellent selectivity, mechanical strength and stability. Strong robustness under fast heating /cooling cycles was achieved by a facile and effective approach using high performance stainless-steel supported Pd composite membranes with a finger-like gap structure (small gap of 1 μm between membrane and porous support).⁶⁶ The structure avoids direct contact between the Pd and porous support inhibiting the shear stresses, while ensuring H_2 -permeance. Stability was demonstrated under 20–50 fast heating/cooling cycles (10°C /min).

3.3. Reactor Technology

Along with the efficient catalysts for ammonia decomposition, development of the reactor technology is equally essential.⁴⁴ Conventional packed bed reactors showed mechanical and thermal limitations. Microstructured reactors, with high surface area/volume ratios, offer high heat and mass transfer rates, easy separation, robustness, and minimize the H_2 inhibition of decomposition rates, enhancing the conversion efficiency.^{44, 67} Microreactors tested for NH_3 decomposition (made of graphite-coated silica, silicon carbide or alumina) showed higher activity per reactor volume than conventional reactors. Although, catalyst regeneration and recovery were drawbacks. Other structured catalysts in reactors (microfibers, monoliths, foams) showed better performance due to more uniform flow distribution. Microfibrous entrapped Ni/CeO₂-Al₂O₃ composite or monolithic catalysts, showed 9-fold reduction of catalyst dosage, and 100°C temperature reduction, compared to a packed bed. Microchannel reactors have even smaller volume/weight than monoliths, and easier scale-up.⁶⁸ Microstructured, monolithic and microchannel reactors are at a more advanced development phase than membrane reactors, displaying high conversion efficiency at moderate temperatures and offering great potential to develop the NH_3 decomposition technology.⁴⁶ Although further investigations are needed into durability and robustness under dynamic conditions, such as frequent start-up and shutdown cycles, which are prevalent under realistic operations.

Ammonia electrolysis (decomposition by an electric current), as an alternative to the thermal decomposition of ammonia, might be useful for distributed hydrogen production in the future.⁴⁶ However, current NH₃ electrolyzers cannot operate at the required current densities (>2200 mA/cm²) without deactivation. Research is required to improve the H₂ generation rate to compete with thermocatalytic NH₃ decomposition, and to reduce energy consumption to produce cost-effective H₂.

Exceptionally high ammonia conversion at very low temperature was recently achieved with a microwave-assisted process compared to the conventionally heated reactor (Figure 2C).⁵⁵ The higher activity observed was associated to the transfer of microwave energy directly to the catalysts; ammonia decomposition by microwave discharge was previously observed. However, several impediments need to be considered for implementation, including scale-up and commercial utilization of microwaves combined with catalytic reactors, which would require significant investment.⁶⁹

4. Ammonia direct utilization

Apart from energy transportation and storage, ammonia can be used for power generation directly in efficient high temperature solid oxide fuel cells (SOFC), internal combustion engines or gas turbines.⁵ These technologies are appropriate for combined heat and power, and represent an excellent opportunity to exploit ammonia as a carbon-free fuel, with zero-carbon footprint at its point of use. The main advantage of direct ammonia utilization is increased efficiency, as it does not require decomposition into hydrogen and subsequent purification.

Ammonia can be directly fed into high temperature (above 200°C) solid oxide fuel cells,⁷⁰ for stationary power generation, with similar or better performance to hydrogen fuel cells.⁷¹ The endothermic ammonia decomposition reaction helps cool the SOFC, thereby increasing high temperature fuel cell performance when directly using ammonia. Developments in ammonia decomposition catalysts are important for

direct ammonia fuel cells, since compatible catalytic-membranes combinations could considerably improve the performance of these systems.

Ammonia can also be used as fuel directly in internal combustion engines⁷²⁻⁷³ and gas turbines,⁷⁴ replacing the need for carbon-based fuels (natural gas, gasoline, diesel) with several advantages compared to hydrogen (longer operability ranges, large power outputs).⁵ However, engine modifications may be required due to ammonia's poor ignition quality, lower energy density compared to hydrocarbon fuels, low burning velocity and narrow flammability limits (15–25% air). Therefore, ammonia combustion can be improved by blending with a more reactive fuel (e.g., hydrogen, methanol, etc.) to improve ignition quality and flame stability. A potential drawback of ammonia combustion is high NO_x emissions, but this can be mitigated by operating at slightly oxygen lean conditions.⁷⁵ The presence of unburnt ammonia in the exhaust gases is a hazard, but this can be prevented by using a reburn zone or using selective catalytic reduction to combine NH₃ and NO_x, forming N₂ and H₂O. Currently, most research is focused on using ammonia in large internal combustion engines for marine transport and gas turbines for stationary power generation.

Ammonia combustion efficiencies could be largely enhanced by incorporating integrated catalytic bed sections (with ammonia decomposition catalysts) before the combustion, for decomposing of part of the ammonia inlet fuel into H₂ and N₂. This would solve improve combustion performance and prevent the need for a separate fuel tank to deliver a high reactivity fuel.

5. Ammonia safety

Ammonia is not very flammable in air while hydrogen, natural gas, methanol or gasoline vapors are highly flammable. Regarding the explosion limits, ammonia requires significantly higher concentrations than gasoline vapor, hydrogen or natural gas. However, the toxicity of ammonia is clearly an important safety issue, since liquid ammonia is three orders of magnitude more toxic than gasoline or methanol.²

Despite its toxicity, the wide handling experience acquired over a century in the synthesis, transportation and utilization of ammonia, significantly decrease the concerns about its exploitation. For instance, successful health and safety protocols and regulations already exist for every feature of the ammonia industrial application, from its synthesis to its combustion.⁵

Definitively, following the safety regulations for adequate storage, transportation and utilization, the use of ammonia as an energy carrier should not represent more risks than the currently used fuels. Public acceptance through community engagement plans will be necessary for the implementation and widespread use of ammonia in our society.

6. Outlook and perspective

Ammonia can play an important role in the future by securing energy while decarbonizing various end-use sectors (transportation, industrial, residential). This carbon-free molecule with a high energy density, an established production/distribution infrastructure, and ease of conversion to CO_x-free hydrogen, is increasingly considered a key carrier for energy storage and transportation, and as a future sustainable fuel.

Despite significant advances in the last decade, technology developments are still required to lower the cost and improve efficiencies of ammonia related technologies. Limitations inhibiting the development of a viable energy system based on ammonia as an energy carrier at large scale are:

1. Carbon-free or low-carbon ammonia production. CO₂-sequestration is required to develop a sustainable technology to produce ammonia from SMR. Alternative renewable routes for hydrogen production are less developed and require intense efficiency improvement. Other routes to produce ammonia are less efficient and more energetically costly.
2. Development of efficient and scalable processes for hydrogen recovery from ammonia by integrating the ammonia decomposition reactor with H₂ purification system. Further efforts are

required to develop H₂-selective membranes to meet the hydrogen requirements, mechanical strength, durability, thermal and chemical stability with low production cost and reproducible fabrication methods.

3. Efficient and reliable power generation systems using ammonia directly as fuel. Issues with the direct use of ammonia that need to be resolved include control strategies to stabilize combustion across a wide range of operating conditions and aftertreatment systems to mitigate harmful exhaust emissions.
4. Technoeconomic and life cycle analysis studies are necessary to have a more realistic view and select the most efficient approach. However, there are currently many unknowns for accurate cost estimation to evaluate the potential for ammonia-to-power at this stage.
5. Public acceptance through safe regulations and community engagement. The toxicity of ammonia needs to be clearly addressed.

With the adequate development of these technologies, the future use of ammonia as an energy carrier will enable viable and economical storage and the transportation of carbon-free energy in the form of liquefied ammonia, with the additional possibility of exploiting renewable energy by enabling its storage and distribution. The use of ammonia for power generation on demand will allow the decarbonization of the energy system and secure energy supply to the full range of stationary and mobile applications. This will lead to new market opportunities for energy importers/exporters.

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