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Recent advances in ammonia synthesis technologies: Toward future zero carbon emissions

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HIGHLIGHTS

- The ammonia synthesis processes were assessed including conventional Haber-Bosch technology.
- The catalytic materials of ammonia synthesis were reviewed.
- The novel analysis of ammonia production methods has been compared.
- Fundamental of ammonia combustion was reviewed.
- The future end-use vision of energy sources was proposed to achieve low carbon emissions.

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ABSTRACT

As a carbon-free molecule, ammonia has gained great global interest in being considered a significant future candidate for the transition toward renewable energy. Numerous applications of ammonia as a fuel have been developed for energy generation, heavy transportation, and clean, distributed energy storage. There is a clear global target to achieve a sustainable economy and carbon neutrality. Therefore, most of the research's efforts are concentrated on generating cost-effective renewable energy on a large scale rather than fossil fuels. However, storage and transportation are still roadblocks for these technologies, for example, hydrogen technologies. Ammonia could be replaced as a viable fuel for a clean and sustainable future of global energy. More efforts from governments and scientists can lead to making ammonia a clean energy vector in most energy applications. In this review, ammonia synthesis was assessed, including conventional Haber–Bosch technology. Current hydrogen technologies as the key parameters for ammonia generation are also evaluated. The role of ammonia as a hydrogen-based fuel and generation roadmap are discussed for future utilization of energy mix. Further, ammonia generation processes are addressed in depth, including blue and green ammonia generation. A survey of ammonia synthesis catalytic materials was conducted and the role of catalyst materials in ammonia generation was compared, which showed that the Ru-based catalyst generated the maximum ammonia after 20 h of starting experiment. An end-use plan for using ammonia as a clean energy fuel in vehicles, marines, gas turbines as well as fuel cells, is briefly discussed to recognize the potential applications of ammonia use. The practical and future end-use vision of energy sources is proposed to achieve great benefits at low carbon emissions and costs. This review can provide prospective knowledge of large-scale aspects and environmental considerations of ammonia. Herein, we conclude that ammonia will become the “clean energy carrier link” that will achieve the global energy and economy sustainability targets.

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Introduction

All emitted greenhouse gases (GHGs), especially carbon dioxide (CO_2) massively contribute to the climate change effect by creating greenhouse thermal radiation traps that lead to increased atmosphere or environment temperature. As a result, a sharp increase in global temperatures has been reported [1]. This increase in temperature will promote ice melting that will raise the ocean's water level and have many other impacts on the environment. The registered global temperature increase is approximately 1 °C. Because of the impact of GHGs on climate change, various technologies have been developed to reduce or avoid the CO_2 emission from current fossil fuels and their applications. The predicted, human-caused annual emission by from 2015 to 2100 has been investigated [2].

Thus, the transformation from conventional fuels to renewable energy is considered an urgent issue to reduce GHG emissions. Recently, renewable energy sources have received much more interest in creating new global energy shifts for low-carbon or carbon-free energy resources. Solar and wind energy are the solutions for most large-scale power generation. Battery storage can address some of the current energy challenges, but it cannot be applied to large-scale applications. Wind energy is the most commercial renewable energy source in the world. Wind turbines have been developed to become taller, bigger hubs with large-diameter rotors. The wind turbine farm capacity has reached 659 MW [3]. Power generation from wind turbines will increase in the next 20 years [2].

Solar energy, such as wind energy, has also gained great worldwide attention. It is considered as a paramount energy source for renewable energy production. Solar energy technology applications, such as photovoltaics (PVs), solar heating/cooling, and solar thermal electricity, are well established [2,4]. Nonetheless, solar and wind energy depend on environmental conditions, locations, and seasonal periods. The liquefied form is the preferred option for energy storage, which is generated from renewable energy sources in a low-cost and sustainable manner [5]. A development system has been proposed for the production of carbon-free hydrogen from the liquefied natural gas through a solar-driven catalytic thermal cracking process integrated into the ammonia synthesis unit [6]. Further, a new, integrated solar-based ammonia synthesis and fuel cell system has been presented [7]. The integrated solar system was simulated on the average day of each month, and the energy and exergy analysis were also demonstrated. The design and optimization of an ammonia synthesis system is also presented in this review for ammonia-based solar thermochemical energy storage consisting of a heat recovery reactor to heat supercritical steam and a preconditioning system to preheat the feed gas to a sufficiently high temperature [8,9].

Liquid organic hydrogen carrier (LOHC) systems have recently received great interest for hydrogen storage and transportation. State-of-the-art catalysts for hydrogen storage in LOHC have been developed [10]. There are different options for generating liquid energy carriers, such as liquefied hydrogen, LOHCs, ammonia, and products of CO_2 reduction. The processes of CO_2 reduction and liquefying hydrogen are the costliest, which should also be considered, apart from

factors like safety and utility. The effect of the degree of hydrogenation on the viscosity, surface tension, and density of the LOHC system based on diphenylmethane has been investigated [11]. The mechanisms of hydrogen transfer processes for different LOHCs have been reviewed. It has been found that the evaluation was significant for large-scale implementation of LOHCs in sustainable fuel production [12]. Ammonia has emerged as a great clean energy source for future global renewable energy fuel sources [13,14]. The process of electrochemical ammonia synthesis at ambient temperature and pressure can be used to generate green ammonia. The main challenges are the low ammonia production and the low long-term stability of the catalyst materials. Recently, green ammonia synthesis using $\text{CeO}_2/\text{RuO}_2$ nanolayers on vertical graphene catalyst via electrochemical route in alkaline electrolytes has been investigated to enhance ammonia yield and catalytic material lifetime [15]. The CeO_2 showed the highest performance of the ammonia synthesis yield. Furthermore, green ammonia synthesis using photo-assisted electrochemical-based demonstrators has been studied [16]. The ammonia synthesis without CO_2 emission and low energy consumption is considered significant. Hence, an energy-efficient process of small-scale ammonia synthesis with plasma-enabled nitrogen oxidation and catalytic reduction of adsorbed NO_x is presented [17]. The renewable electric sources, such as water electrolysis powered by solar or wind energy sources, should be used in the electrochemical ammonia synthesis process. A global transition to the massive production of carbon-free energy is needed. However, processes of storage, transportation, and utilization of renewable energy on a large scale have still not been fully developed. Energy decarbonization via green hydrogen or ammonia has been reviewed [18]. Green hydrogen and green ammonia as sustainable future energy vectors have been considered.

Ammonia can be easily liquefied at ambient temperature and a moderate pressure of 10 bar or at atmospheric pressure by cooling down to -33 °C. Furthermore, ammonia as a fuel exposed a narrow flammability range, high power to fuel efficiency which making it safe [19]. However, ammonia is a toxic compound, high emission of NO_x , NH_3 residuals, and the reactivity as a fuel is relatively low [20]. Various studies were conducted to enhance the ammonia combustion process and pollutant reduction. Ammonia is primarily generated by a well-established conventional process called "Haber-Bosch". Most of the ammonia thus generated is utilized in fertilizer production; the annual worldwide ammonia production is about 180 million tons, making it the second most global commercially manufactured chemical [21,22]. Haber-Bosch technology has been used for industrial ammonia production. Hydrogen is produced by the steam reforming process from fossil fuels (methane or coal), and then it combines with nitrogen generated from air by the cryogenic process to produce ammonia [23]. Ammonia can be transported using the current infrastructure of fossil fuels. Ammonia can be seen as a clean hydrogen energy carrier link, which can be used as a hydrogen supplier. An investigation of the supply chain context, including ammonia decomposition to hydrogen and nitrogen gas, has been conducted to distribute ammonia like hydrogen [24]. Ammonia decomposition has been investigated

using plasma and catalytic materials [25–27]. Also, energy and exergy of hydrogen production from ammonia decomposition systems have been analyzed for different systems [28]. In the last few years, ammonia usage in energy applications has increased; it has been directly used as a fuel in some applications, such as marine, heavy transport vehicles, and large-scale power generators [29]. A combined plant with SOFC has been developed for hydrogen and ammonia generation. Energy and exergy analyses of the modeled plant have been estimated [30]. A new, geothermal-based multigenerational plant with primary outputs of hydrogen and ammonia and performance of the plant, including energy and exergy, have been analyzed [31]. Various energy sources can be utilized for ammonia synthesis and hydrogen production processes. Solar energy as a renewable power source has been proposed for a solar power-based combined plant for power, hydrogen, methane, ammonia, and urea production [32]. According to the type of heat source, the produced ammonia is called as “green,” “blue,” or “gray.” The latest trends in the use of green ammonia as an energy carrier in the maritime industry have been described. The challenges involved with blue ammonia have been reported to have large energy penalty and associated operational costs [33]. The role of plasma has shown great results in the ammonia production process. The status and properties of ammonia production by nonthermal plasma have been demonstrated, and it has been outlined that plasma technology enables a sustainable and flexible ammonia industry [34]. Combining plasma and catalytic materials enhances the ammonia synthesis process. The role of heterogeneous catalysts in the plasma-catalytic ammonia synthesis process has been investigated [35]. It has been noted that the dielectric barrier discharge (DBD) plasma can enhance the ammonia synthesis process, and silica material supports the Ni-based catalyst that enhances ammonia synthesis by DBD plasma [36].

In this review article, current ammonia synthesis technologies are assessed as the key link of renewable energy sources. First, hydrogen production technologies are evaluated as the main ammonia synthesis component and a potential, unprecedented clean energy solution. Further, the fundamentals of ammonia synthesis technologies are discussed in depth, including blue and green ammonia generation processes. Furthermore, a survey of catalyst materials used in ammonia production technologies is addressed for different catalytic materials, such as Fe-, Ru-, Ni-, and Co-based materials. The highest ammonia synthesis rate from different catalytic-based materials was compared. The end-use plan of ammonia as a clean energy fuel in vehicles, marines, and gas turbines as well as fuel cells is briefly discussed to recognize potential ammonia applications. Moreover, the key findings of the ammonia combustion are summarized at the end of ammonia use as a fuel. Then, the future end use of energy sources is discussed and investigated to understand the energy transition toward renewable energy sources.

Ammonia characteristics

In this review, direct use of ammonia as a carbon-free fuel in combustion engines, such as vehicles, marines, etc., will be

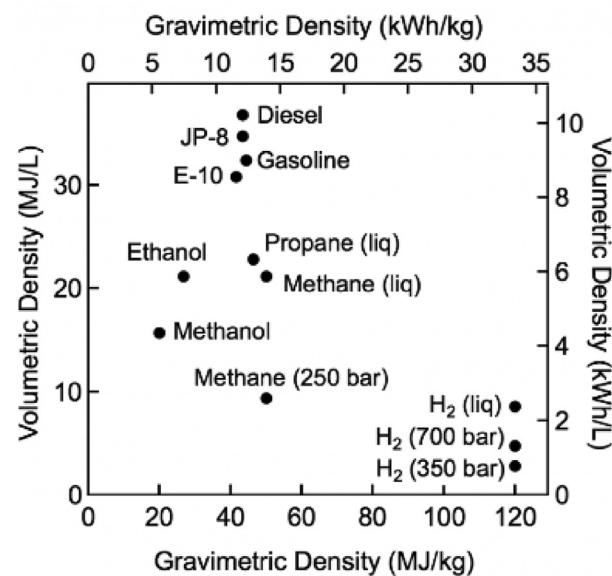


Fig. 1 – Comparison between ammonia, hydrogen, and other fuels [37].

discussed briefly in section 6. Ammonia can be relatively liquefied at (e.g., -33°C at 1 atm). Therefore, it can be efficiently stored more than hydrogen. Figure (1) demonstrates that ammonia has a great characteristic such as higher volumetric energy density (10.8 MJ/L at 300 K and 8.6 bar) than liquefied hydrogen [37]. The infrastructure of ammonia storage and transportation is well established; thus, ammonia is currently used to manufacture fertilizer. The heating value of ammonia is about (18.6 MJ/kg), which is larger than that of the coal gas (16.7 MJ/kg), but compared to ethanol and natural gas, ammonia is low [38].

A comparison of the thermal properties and combustion characteristics of ammonia and other common fuels is presented in Table 1. It is clear that the liquefaction of hydrogen gas needs a very low temperature of -252.9°C , which means that high-cost equipment for hydrogen storage is required. Also, very high pressure is needed to store hydrogen at ambient temperatures. Therefore, hydrogen storage and transportation require more sustainable energy and high technology costs. However, ammonia can be seen as a potential carrier of higher hydrogen energy [39]. The boiling temperature and condensation pressure of ammonia are the same as those of propane; this means that propane transportation ships can be easily used for ammonia storage and transportation. The drawback of ammonia combustion is that the flame temperature of NH_3/air mixture ignition is lower than that of hydrocarbon fuels. Moreover, high NO_x emission is generated from ammonia combustion when compared with conventional fuels. Nonetheless, the NO_x products are not the final combustion reaction products; overall reaction of ammonia production can be written as follows [40]:



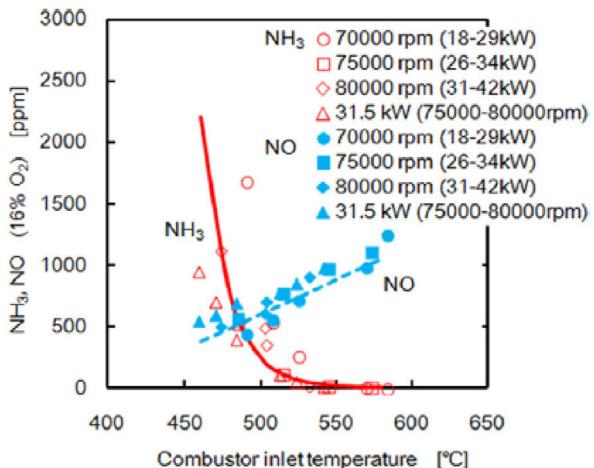
The variation of NO_x emission for pure ammonia combustion is shown in Fig. 2. The microgas turbine system was

Table 1 – Thermal properties and fundamental combustion characteristics of ammonia and other hydrocarbon fuels [39].

Fuel	NH ₃	H ₂	CH ₄	C ₃ H ₈
Boiling temperature at 1 atm (°C)	-33.4	-253	-161	-42.1
Condensation pressure at 25 °C (atm)	9.9	N/A	N/A	9.4
Low heating value, LHV (MJ/kg)	18.6	120	50	46.4
Flammability limit (equivalence ratio)	0.63–1.4	0.1–7.1	0.5–1.7	0.51–2.5
Adiabatic flame temperature (°C)	1800	2110	1950	2000
Maximum laminar burning velocity (m/s)	0.07	2.91	0.37	0.43
Minimum Autoignition temperature (°C)	650	520	630	450

Table 2 – Comparison between the physical properties of hydrogen and other fuels.

Property	Hydrogen	Gasoline	Methane
Chemical formula	H ₂	C ₈ H ₁₈	CH ₄
Flammability limits (Φ)	0.1–7.1	0.7–4	0.4–1.6
Minimum ignition energy (MJ)	0.02	0.25	0.28
Molecular weight (g/mol)	2.016	170	16.043
Flame velocity (m/s)	2.65–3.25	0.30–0.50	0.4–0.6
Auto ignition temperature (°C)	585	220	650
Density at 1 atm and 300 K (kg/m ³)	0.082	730	0.651
Stoichiometric composition in air (% by volume)	29.53	1.65	9.48
Stoichiometric fuel/air mass ratio	0.029	0.0664	0.058
Low heating value (MJ/kg)	119.93	42.5	50
High heating value (MJ/kg)	141.7	48.29	52.68
CO ₂ emissions (%)	0	13.4	9.5
Boiling point (K)	20.2	453–653	111.5

**Fig. 2 – NO_x emission variations in pure ammonia combustion [41].**

designed by the Fukushima Renewable Energy Institute of the National Institute of Advanced Industrial Science and Technology (FREA-AIST). Ammonia is fed to the combustor as pure gas, ammonia/kerosene, and ammonia/methane. The combustor prototype is designed to operate using kerosene as fuel and then modified to operate on ammonia by adding an injector for ammonia.

Hydrogen as a potential clean energy solution

Hydrogen as clean energy solution is currently receiving unprecedented business and political attention. Recently, various hydrogen production projects from different feedstocks have expanded around the world. The use of hydrogen will help tackle energy challenges and overcome all environmental issues. It will also participate in solving global CO₂-related problems. Hydrogen production technologies have been investigated to generate hydrogen in different ways [42–44]. A review of the challenges and opportunities of hydrogen production has been conducted [45]. The green,

blue, and purple hydrogen production types have also been reviewed. Furthermore, hydrogen in energy transition has been developed, and it was found that the hydrogen infrastructure increased, which expressed the progress of hydrogen usage [46]. Different feedstocks can be used to produce hydrogen, including natural gas, coal, liquefied oil, and renewables methods. Table 2 shows a comparison between hydrogen and other fuels in terms of physical properties. These data illustrate that hydrogen, as a clean alternative fuel, includes more energy than gaseous and liquefied fuels. However, hydrogen has the lowest energy density per unit volume, which means that if compared with other fuels, higher hydrogen volumes are needed to meet the typical energy demands. Hydrogen storage and transportation are still the most important issues to be considered in hydrogen production. Therefore, larger pipelines and containers can be used; H₂ can be liquefied, compressed, and transported as hydrogen-based fuels that have high energy density.

Hydrogen has been used for over 200 years in internal combustion engines (ICEs). It was first generated by water electrolysis process. The H₂/O₂ precombustion mixture is reported to improve the combustion efficiency of ICEs. Moreover, the use of this state-of-the-art technology enhances the fuel economy [47]. A single-cylinder engine operating on the H₂/O₂/Ar mixture has been experimentally analyzed [48], and its combustion efficiency varied from 30% to 50% at low and high argon concentrations, respectively. In addition, the effect of adding hydrogen–oxygen mixture obtained from water electrolysis on exhaust emissions and the performance of a spark-ignition engine have been investigated at several engine loads [49]. Platinum electrodes were used to enhance catalytic combustion for environmental by-products. Furthermore, the use of hydrogen as an alternative fuel in ICEs has been found to be inefficient because of insufficient mixing of hydrogen with other gases [50]. The cylinder head design and the inlet valve controlled the swirling motion of the mixture inside the cylinder. Another invention has been introduced using hydrogen peroxide/water/alcohol solution for direct propulsion in engines [51]. The electronic and mechanical systems have been designed to use only gas pressure

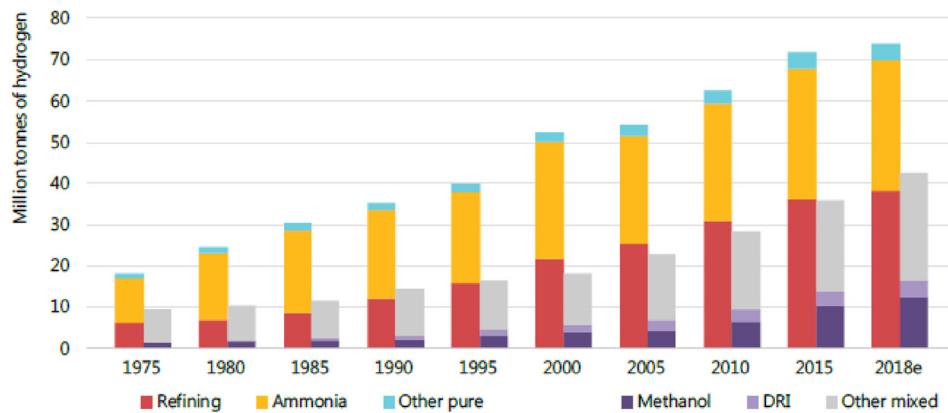


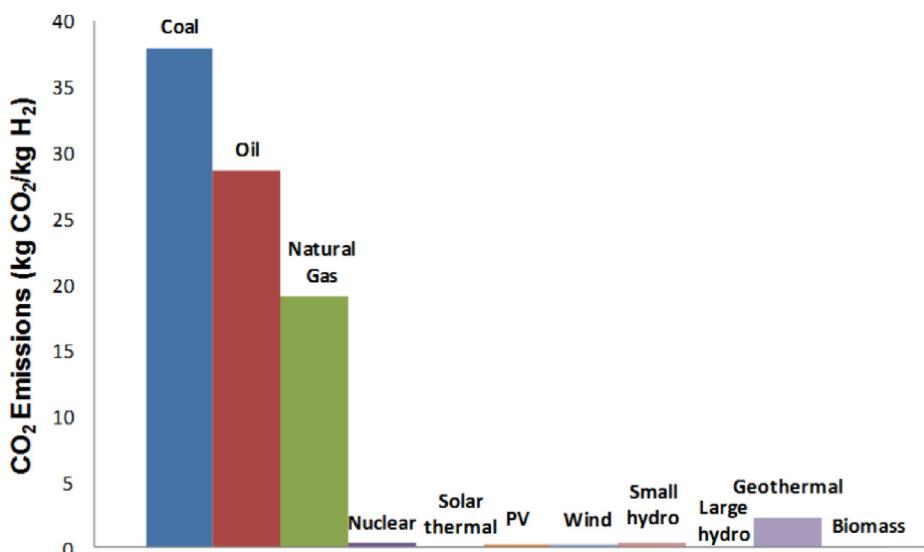
Fig. 3 – Global annual demand for hydrogen since 1975 [2].

as energy of the system, which may act as a fuel supplement in the existing combustion engine by using the existing oil-based fuel engine's sensor signals, to make the engine run much leaner conditions. The problems of hydrogen-fueled ICEs have been elaborated on [52]. The main problems of hydrogen-fueled engines can be concluded as follows: (i) preignition, (ii) backfiring, (iii) rapid rate of pressure rise, and (iv) knocking. These problems can be overcome through further development and optimization of the system design.

Now, the hydrogen demand has grown to include some industrial applications. Currently, there are some global hydrogen projects, including production and storage. The growth of hydrogen demand from 1975 to 2018 is depicted in Fig. 3. Most of pure hydrogen is produced using fossil fuels, and the hydrogen production rate is about 70 MtH₂/year. However, hydrogen production based on natural gas and coal is 6% and 2%, respectively. It is clear that the hydrogen demand has increased; the total worldwide annual hydrogen demand is about 330 Mt. Because of the global tendency to use energy with zero carbon emissions, hydrogen production at low carbon emissions is significant for achieving global energy transition goals. The CO₂ emissions from different hydrogen

production energy resources are shown in Fig. 4. The use of coal energy clearly produces the highest CO₂ emissions of 38 kgCO₂/kg H₂ compared to those obtained from oil and natural gas as fossil energy sources [53]. However, CO₂ emissions were negligible for hydrogen production when compared with renewable and nuclear energy sources.

Using hydrogen has following advantages: (i) it can be used without GHG emissions and (ii) it can be generated from a wide range of low-carbon energy sources. Hydrogen can be stored and transformed into hydrogen-based fuel, such as ammonia, methanol, etc. The layout of the hydrogen production routes is displayed in Fig. 5. The hydrogen production route presents two different feedstock pathways: renewables and fossil fuels. Green hydrogen is generated from renewable electricity, such as wind and solar energy, while gray hydrogen is generated from fossil fuels accompanied by CO₂ emissions. Hydrogen can also be produced through steam reforming process (SMR), using hydrocarbon fuels as feedstock with carbon capture and storage (CCS). Other colors of hydrogen have also been investigated, including brown hydrogen produced from coal gasification [54], turquoise hydrogen generated from methane pyrolysis, and pink

Fig. 4 – Comparison of CO₂ emissions from different hydrogen production energy resources [53].

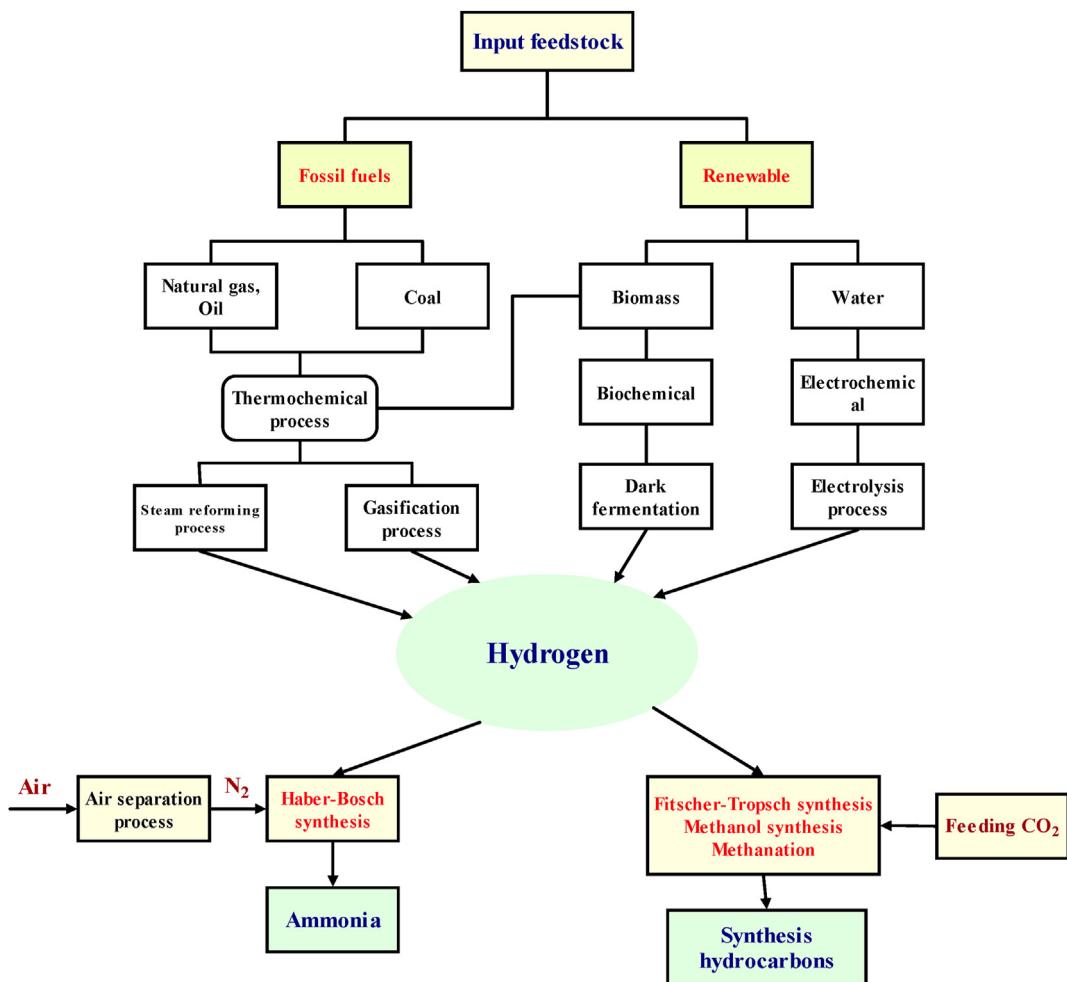


Fig. 5 – Hydrogen production pathway and routes.

hydrogen produced from water electrolysis using nuclear-powered electricity [55,56]. Ammonia production from nuclear power electricity has the lowest operating costs, 40–50% less than SMR.

However, nuclear-powered ammonia still has higher capital costs than SMR process (more than 400–430%) [57]. The most common sources of hydrogen production from biomass gasification are wood wastes, bio crops and agricultural waste, municipal solid waste, waste from food processing plants, animal wastes, aquatic plants, and algae [58]. The resulting hydrogen can be converted into larger energy density hydrogen-based fuels (ammonia or hydrocarbons). Ammonia is also named according to the hydrogen production methods discussed in Fig. 5. A small amount of heat is required for the reconversion process—the decomposition process of ammonia to generate hydrogen with temperature higher than 300 °C. Less than 25% of the generated hydrogen is reported to be used for heating process purposes, either by the hydrogen combustion in a heat exchange reactor or by converting it into electricity in the fuel cell and using it to raise the NH₃ decomposition reactor temperature [59]. Ammonia can be synthesized from the elements of hydrogen and nitrogen as an exothermic reaction, and consequently the decomposition process of ammonia is endothermic reaction ($\Delta H = 45.6 \text{ kJ/mol}$

NH₃). Ammonia can be used for storage and transportation of green hydrogen. Different ammonia synthesis and decomposition methods will be discussed in the next section.

Ammonia synthesis as a hydrogen-based fuel

Ammonia has recently received great interest from global energy organizations and researchers because it can be used as a zero-carbon medium for renewable energy sources. Ammonia as clean energy storage and carrier can be easily stored as a refrigerant or at pressure ranging from 0.8 MPa to 1 MPa [2]. Furthermore, ammonia has a high hydrogen volumetric density that makes it versatile to be commercially available in the global market. The hydrogen content of ammonia is 17.6 wt%, which is known as indirect hydrogen energy storage. The energy density of ammonia is 4.32 kWh/L, which is the same as methanol (CH₃OH) [34]. The liquefying process of hydrogen is too difficult when compared to ammonia, which can be liquefied at -33.4 °C and at atmospheric pressure. Further, hydrogen can typically be liquefied by chilling it at temperatures less than -253 °C [60]. The main challenge of utilizing hydrogen as an energy carrier is the difficulty of transporting and storing it without dissipation.

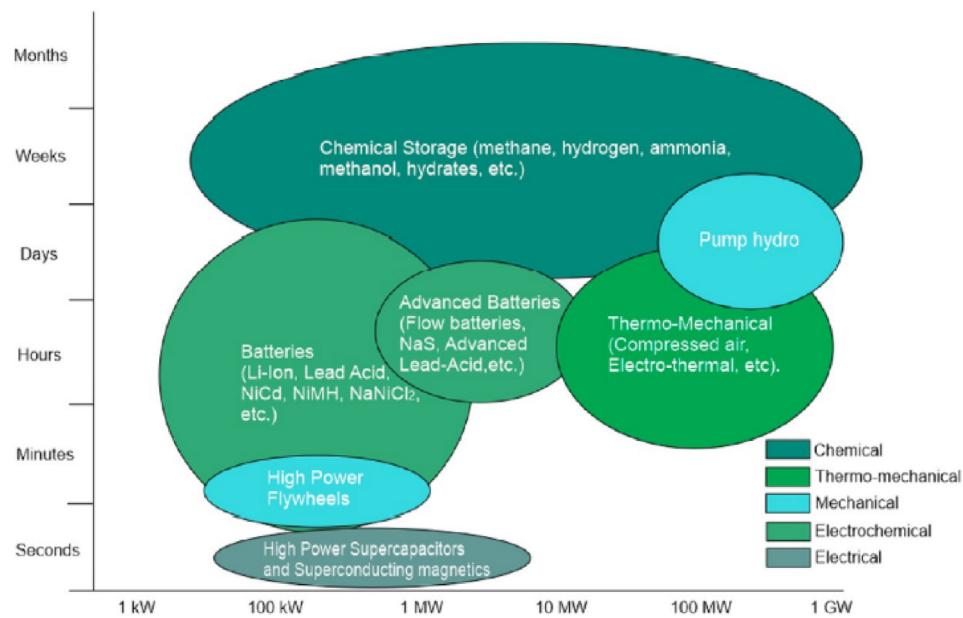


Fig. 6 – Energy storage technology comparison [62].

Therefore, ammonia is seen as a practical carbon-free energy carrier vector for hydrogen. It has been generated annually in the global market with a value of 180 million tons per year (Mt/year). Ammonia is considered as the second most global commercial chemical [61]. Ammonia production is expected to increase to ~270 MT/year by 2050, and most of the generated ammonia (~80%) will be utilized as fertilizer [60]. Therefore, ammonia infrastructures are available to support the economic energy transition to hydrogen. Among all hydrogen energy storages, ammonia is considered to have a higher hydrogen volumetric density content at zero carbon emission. Fig. 6 compares the energy storage technologies, including that of ammonia. Various methods can be utilized to store energy for long and limited periods [62]. Furthermore, mechanical devices and chemical storage are exposed to high flexibility. Hydrogen, ammonia, and hydrazine are the best solutions to be used as potential zero-carbon fuels [63]. Hydrazine has shown limited use in aerospace applications because of different issues related to its reactivity and toxicity, making it unsuitable for power generation [64]. Therefore, hydrogen production technologies are currently under evaluation as clean energy source pathway scenarios. Hydrogen production, consumption, and transportation represent great variation in terms of scalability, emissions, and cost parameters [65]. The hydrogen economy still requires more development to overcome the constraints faced by hydrogen production scenarios. Thus, several developments in infrastructure and equipment are needed to enhance the energy transition process. Being a clean energy carrier, ammonia can be used as a fuel in different applications. A roadmap of ammonia generation processes is shown in Fig. 7. First, ammonia is produced from methane (Gen 1), and CCS should be applied for the current technology because CO₂ molecule is generated. Therefore, the hydrogen generated from ammonia in Gen 1 is named “blue ammonia.” The second ammonia generation method, Gen 2, is carried out using renewable energy sources, such as solar and wind energy. The generated

ammonia is named “green ammonia,” subsequently green hydrogen. Also, green ammonia can be finally generated from renewable energy sources (Gen 3), avoiding generating hydrogen, and ammonia delivered with N₂ electroreduction helps avoiding generating ammonia by the commercial method named the Haber–Bosch method [63].

Evaluation of ammonia production using Haber–Bosch technology

The development of catalyst materials has received more interest in enhancing ammonia synthesis from the Haber–Bosch process. In 1908, Carl Bosch addressed the following three significant challenges of the ammonia synthesis process: (i) developing equipment and materials for high-pressure ammonia production, (ii) designing a methodology for low hydrogen and nitrogen production costs, and (iii) investigating new efficient and high-stability catalytic materials for the ammonia synthesis process [66]. Fritz Haber and his team investigated two great-performance catalyst material types for ammonia synthesis: osmium and uranium carbide. The ammonia synthesis process was industrialized in 1911 by Carl Bosch [66]. Fritz Haber and Carl Bosch won the chemistry Nobel Prize for their contribution in enhancing iron catalysts for the ammonia synthesis process in 1918 and 1931, respectively [67]. Nowadays, ammonia's contribution as the second chemical material is almost generated by the Haber–Bosch process using conventional fossil fuels (oil, natural gas, and coal). The production process of ammonia using the Haber–Bosch plant acts as the largest NH₃ production route (with ~96% production) as well as being exposed to higher GHG emissions; it is responsible for 1.2% of the total global CO₂ emission [68]. Therefore, researchers have investigated alternative ammonia production methods to minimize CO₂ emissions from the Haber–Bosch method. Fossil fuels are used as feedstock in the Haber–Bosch method for ammonia production, with current values of 50% natural gas, 31% oil, or 19%

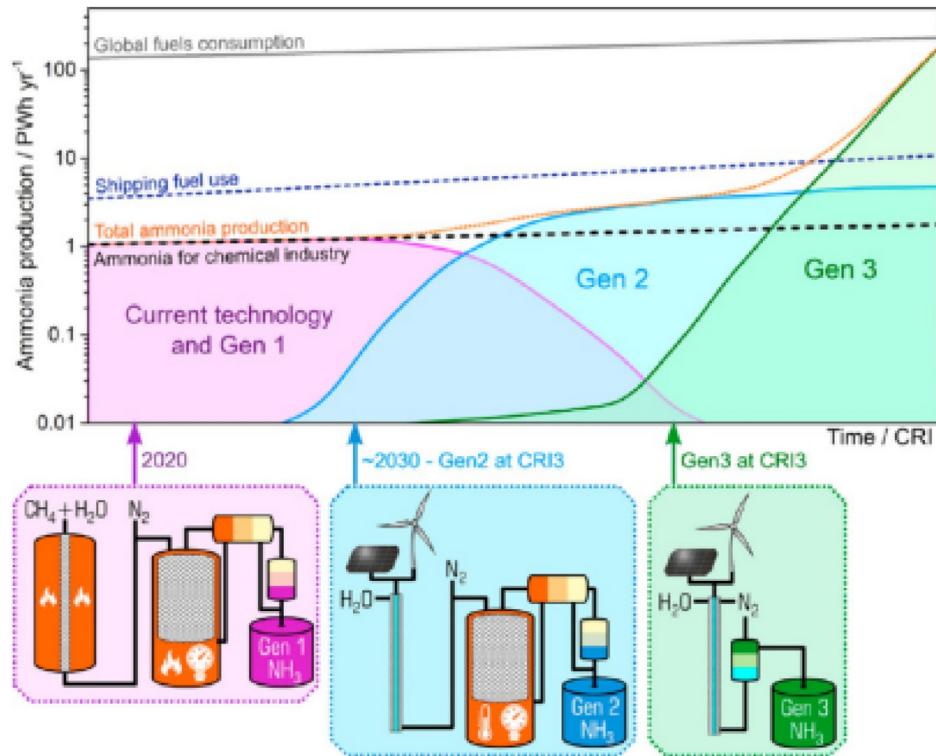
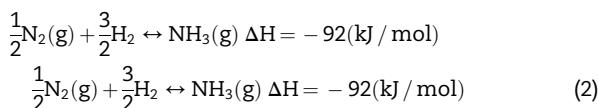


Fig. 7 – Roadmap of ammonia economy and the current projects' contributions. Gen 1, purple hydrogen; Gen 2, light blue; and Gen 3, green ammonia production technologies [63]. (For interpretation of the references to color/colour in this figure legend, the reader is referred to the Web version of this article.)

coal [69]. Lower carbon emissions and higher energy efficiency are obtained from the Haber–Bosch process using methane as a feedstock. Ammonia production by methane Haber–Bosch natural gas act by the Haber–Bosch method leads to CO₂ emission. Ammonia is generated from the hydrogen and nitrogen exothermic reaction as follows [70,71]:



Modern ammonia synthesis processes can be classified into two main steps: hydrogen production from methane and ammonia production by the Haber–Bosch process. Fig. 8 presents a schematic diagram of methane as a feeding gas for ammonia synthesis by the Haber–Bosch process. In this process, the steam methane reforming process is followed by a water gas shift (WGS) reactor, a carbon dioxide removal process, and methanation. The SMR process operates at 850–900 °C temperature and 25–35 bar pressure, while the required energy is produced from methane fuel combustion. Autothermal reaction is also carried out at 900–1000 °C temperature; compressed air is fed into the second SMR reactor to provide reaction heat [72]. The Haber–Bosch downstream process can use nitrogen generated from the air added in the second SMR reactor. The steam is generated from the SMR process and can be utilized for energy compression applications. The outlet species of SMR process hydrogen, carbon monoxide, unreacted steam, and unreacted

methane, which are fed into the WGS reactor to enhance hydrogen production.

In an exothermic WGS reaction, the CO concentration must be minimized by removing heat. Furthermore, carbon dioxide is removed by the Benfield or Selexol process. To decrease catalyst poisoning in the Haber–Bosch reactor, the methanation reactor is used to convert the remaining CO into methane. Also, argon gas and methane are accumulated as inert in the ammonia synthesis downstream loop. The SMR process is performed at a high temperature, whereas heat is removed in the WGS, which means too wastage of heat energy. High-pressure steam can be generated and used in steam turbines; it is mainly used for compression in the Haber–Bosch process. The main drawback of using methane as a Haber–Bosch process feedstock is the CO₂ emission.

Recently, the transition to a sustainable Haber–Bosch process using renewable energy has received a lot of interest [73]. Renewable energy can meet all the requirements for the ammonia synthesis process by replacing methane and other fossil fuels with renewable hydrogen production technologies. Different hydrogen production technologies have been investigated for generating renewable hydrogen [42,43,74]. The ammonia synthesis using hydrogen generated from the renewable energy process will treat the CO₂ emission to the environment. In Fig. 8B, hydrogen is generated through water electrolysis process and is then utilized in the Haber–Bosch reactor for ammonia production, as it is used in the conventional process described in Fig. 8A.

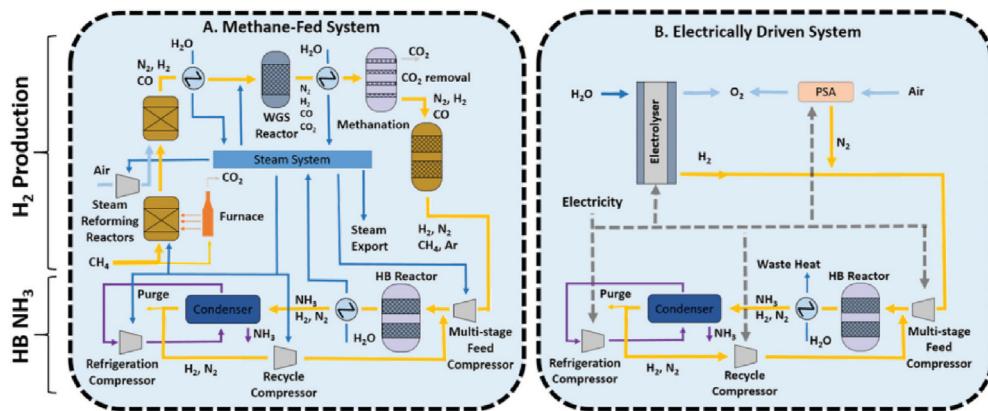


Fig. 8 – A. Conventional Haber–Bosch process using methane as a feedstock. B. An alternative electrical power ammonia synthesis process. Yellow lines are the process gas, dark blue lines are water/steam, light blue line is air, dash line is electricity, and purple line is ammonia [72]. (For interpretation of the references to color/color in this figure legend, the reader is referred to the Web version of this article.)

The nitrogen gas molecule is needed for the ammonia synthesis process; the pressure swing adsorption (PSA) process is used to deliver nitrogen for the downstream Haber–Bosch process. The PSA process is more suitable for small-scale applications, and it can be applied in the N_2 production process. Alternative pure N_2 production applications have been investigated for large-scale applications, such as the cryogenic distillation process [75,76]. Nitrogen production from air separation by cryogenic technology has been widely applied in many industrial processes. It can be utilized as an inert gas for purging equipment. Most commercial nitrogen gas is distributed in large pipelines or in small volumes as a liquefied or compressed gaseous form stored inside steel cylinders. The cryogenic process can generate pure nitrogen and pure oxygen. The conventional double column (low-pressure (LP) and high-pressure (HP)) has been investigated to describe in detail the nitrogen production process [77–79]. The major inefficiency challenge of the conventional double-column process is the nitrogen production process from the thermal link between the HP and LP columns. The exergy analysis of a more efficient cryogenic large nitrogen quantity production has been studied [75].

Various hydrogen production processes, such as electrochemical, thermochemical, and biochemical processes, are briefly described in Table 3. The ammonia synthesis by the Haber–Bosch process is a carbon-free and sustainable ammonia production method as it replaces methane or fossil fuel as feedstock with renewable hydrogen production technologies, such as the water electrolysis process. Main renewable energy inputs will be briefly compared; different technological parameters are influenced by the electric process, such as energy efficiency, and faster response. The use of water electrolysis has already begun to enable renewable hydrogen production with much higher heat integration than the SMR process. The hydrogen production by alkaline electrolyzers is commercially available with an energy efficiency range of 51–60% and approximately energy loss of approximately 14.2 GJ/t_{NH₃} [80].

Recently, different researches have been investigated to enhance the hydrogen production by electrolyzer methods, in

which the energy efficiency can reach 81% [80,83]. The most significant challenges of electrolyzers are the material cost and their durability. Although efficiencies are improving, the cost of these systems is still prohibitive when compared to hydrogen production from fossil fuels. Therefore, more development for electrolyzers is needed to minimize energy consumption and operations costs, as well as enhance durability. More analysis of hydrogen production technologies has been done to compare the efficiency of each of the processes [42,43,83]. Due to the importance of ammonia synthesis as a clean energy carrier and agricultural fertilizer source, different alternative NH₃ synthesis attempts are made to enhance energy efficiency and reduce production process costs.

Renewable ammonia synthesis technologies

Alternative ammonia synthesis technologies have been developed, such as electrochemical ammonia production, nonthermal plasma (NTP) technology, and nitrogenase-motivated peptide-functionalized for electrochemical NH₃ production. According to the operating temperature, the electrochemical ammonia production processes can be those that operate in lower temperature range of 100–400 °C and those that operate in higher temperature range of 400–750 °C [84,85]. The electrochemical ammonia synthesis technology has significant advantages compared with the conventional thermochemical Haber–Bosch process, which are as follows: (i) high efficiency, (ii) lower operating temperature and pressures, leading to minimizing the capital cost, (iii) high selectivity and less requirement of purification, and (iv) suitable for small-to medium-scale ammonia synthesis.

Lower temperature (<100 °C) electrochemical ammonia synthesis

In this electrochemical process, ammonia is generated at a temperature lower than 100 °C, potassium hydroxide (KOH) is utilized as an electrolyte, and the separation process is carried out by Nafion membrane type. The anode and cathode material types are platinum (Pt), and ruthenium (Ru)/C, respectively [86]. It has been reported that the highest ammonia

Table 3 – Renewable hydrogen production processes [81,82].

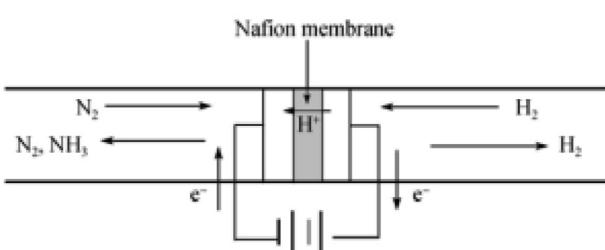
Main energy inputs	Technologies	Brief description	Scale
Electrical	Water electrolysis CH ₄ -assisted solid oxide fuel electrolysis cell (SOFEC)/natural-gas-assisted steam electrolysis (NGASE)	Direct current is applied to split water into hydrogen and oxygen. The entire process of a CH ₄ -assisted SOFEC is based on substituting high-value electricity with cheaper methane. In the CH ₄ -assisted-SOFC, methane is added to the anode side of the electrolyzer, and the decomposition potential (voltage) of water is decreased, resulting in a lower energy usage and higher conversion ratio of electricity for hydrogen production.	Large
	Plasma arc decomposition	Purified natural gas (without H ₂ S, CO ₂ , H ₂ O, etc.) is passed throughout the plasma arc to produce hydrogen and carbon soot.	Medium/small
Electrical and thermal	High-temperature electrolysis (HTE)	Both electrical and thermal energy are utilized to initiate water splitting for hydrogen production.	Large
	Hybrid thermochemical cycles	Both electrical and thermal energy are utilized in cyclical reactions.	Large
			Medium
Thermochemical	Coal gasification	Conversion of coal is done through thermochemical process into syngas.	Large
	Fossil fuel reforming	Fossil fuels are converted into hydrogen and carbon dioxide.	Large
	Thermolysis	Thermal decomposition of steam at temperatures higher than 2226.85 °C.	Large
Photonic	Thermochemical processes	- Cyclic reactions (net reaction: water splitting into hydrogen). - Thermocatalytic conversion—biomass conversion into hydrogen.	Large
	Photo-electrochemical cells (PEC)	A hybrid cell that simultaneously generates voltage and current through absorption of light.	Small
	Artificial photosynthesis	Mimicking photosynthesis process for hydrogen production.	Small
Photonic and biochemical	Photocatalysis	Direct water splitting via photo-catalyst.	Small
	Biophotolysis	Biological processes (microbes/bacteria, etc.) through which water dissociates into hydrogen and oxygen in the presence of light.	Small
Biochemical	Dark fermentation	Biological processes are utilized for hydrogen production in the absence of light.	Small
	Photofermentation	Fermentation process initiates through exposure to light.	Small

production rate is $2 \times 10^{-11} \text{ mol s}^{-1} \cdot \text{cm}^{-2}$ at the operating temperature of 90 °C, generating from steam and nitrogen at Faradaic efficiency (FE) of 0.2–1%. Faradaic efficiency can be defined as the proportion of protons that convert into NH₃ by migrating across the electrolyte. The polymeric membranes, such as sulfonated-poly-sulfone (SPSF) membranes and Nafion membranes, are used for low-temperature NH₃ synthesis at an operating temperature of 80 °C and applied voltage of 2 V [87,88]. Fig. 9 shows the ammonia synthesis apparatus layout using the Nafion membrane. The ammonia production rate was $1.13 \times 10^{-8} \text{ mol s}^{-1} \text{ cm}^{-2}$ using ceramic anode and cathode composition types of SDC (Ni-SDC) and SFCN (SmFe_{0.7}Cu_{0.3-x}Ni_xO₃), respectively [88]. The main challenge of this ammonia synthesis experiment is the low FE,

because the catalytic material type requires more effort for high nitrogen reduction. Pure nitrogen can be obtained from air. During the ammonia synthesis process, the resulting oxygen has been observed to have a poison effect on the catalyst material [89,90].

Higher-temperature (>400 °C) electrochemical ammonia synthesis

The higher ammonia synthesis production rate can be obtained from the higher-temperature electrochemical process at 400–700 °C. An oxide ion conductor or proton ion conductor is used as an electrolyte for the higher electrochemical synthesis process. Steam and nitrogen are utilized at 450–700 °C operating temperature or generate ammonia by proton and oxide ion conductors, with the ruthenium catalyst materials supporting the palladium (Pd) or silver (Ag) as a cathode [91,92]. Fig. 10 illustrates a schematic diagram of the double-chamber reactor cell for the ammonia synthesis process [91]. The proton conductor type of SrCe_{0.95}Yb_{0.05}O_{3-δ} and oxide ion conductor of ZrY_{0.92}Y_{0.08}O_{2-δ} are utilized as electrolytes. Furthermore, carbonate oxide is utilized as electrolyte at 400–450 °C with larger ammonia production rate of $5.39 \times 10^{-9} \text{ mol s}^{-1} \cdot \text{cm}^{-2}$ [84]. Using hydrogen and nitrogen, the maximum FE from higher-temperature electrochemical ammonia synthesis was 90%. The maximum ammonia production rate at 400–600 °C operating temperature, using

**Fig. 9 – Outlines of NH₃ synthesis apparatus [88].**

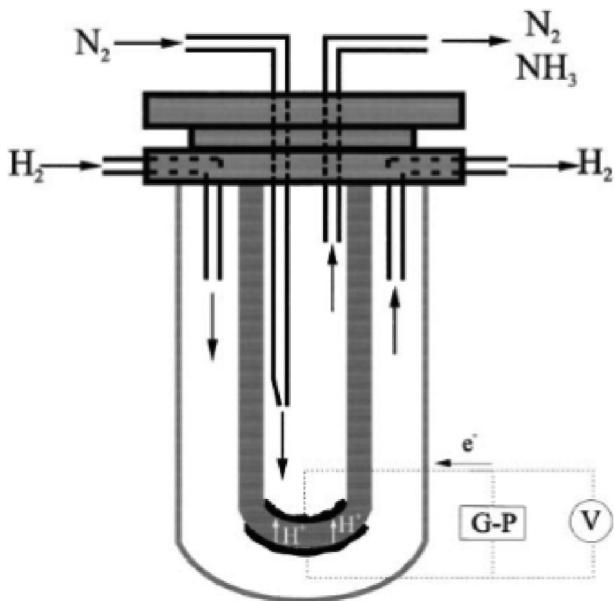


Fig. 10 – Ammonia synthesis diagram of a double-chamber reactor cell [91].

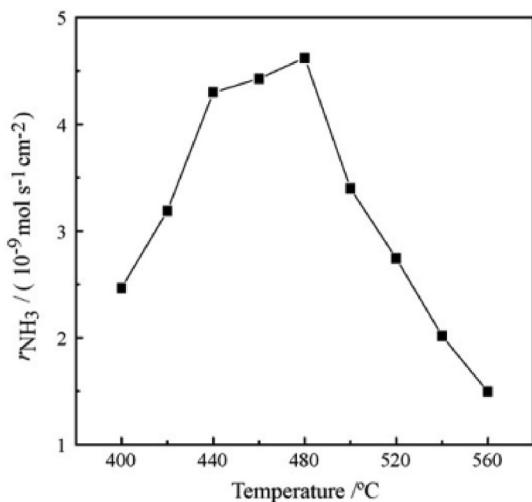


Fig. 11 – Ammonia formation rate as a function of operating temperature [94].

electrode type of (Ag–Pd) has been reported as $1\text{--}5 \times 10^{-9} \text{ mol s}^{-1} \cdot \text{cm}^{-2}$ at 40–50% FE [93].

Because proton conductivity depends on the electrolyte temperature, Fig. 11 illustrates the ammonia production rate as a function of the electrolytic temperature [94]. Ammonia formation rate has been reported to have increased from the 400°C of electrolytic temperature to 480°C due to the higher protonic conductivity. However, at higher operating temperatures, the ammonia production rate decreased. One of the significant challenges of the current technology is that generated ammonia can be thermally decomposed into H_2 and N_2 at high operating temperatures after the synthesis process [95].

Novel ammonia production methods

In this section, we describe the novel ammonia synthesis methods. Various studies have suggested reducing

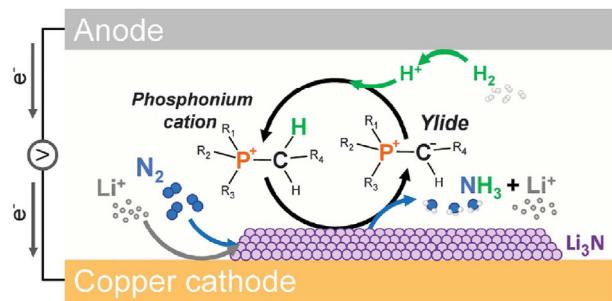


Fig. 12 – Sustainable electrosynthesis process ammonia from hydrogen and nitrogen [96].

electrocatalytic nitrogen to generate sustainable ammonia pathways. This way, ammonia can be produced with higher energy efficiency. Hence, the electrochemical ammonia synthesis method is considered a promising technology, but the production efficiency is lower than 1%. Therefore, catalyst materials can play an important role in enhancing the ammonia synthesis process. The most significant parameter for ammonia production by electrochemical is the nitrogen reduction reaction (NRR). It can be generated by electrocatalysts powered by renewable energy sources. Nitrogen reduction reaction (NRR) into ammonia has received great interest and is a sustainable ammonia production pathway. Nitrogen reduction to ammonia at high efficiency and rates based on a phosphonium proton shuttle has been studied [96]. Fig. 12 illustrates the sustainable electrosynthesis process of ammonia obtained from hydrogen and nitrogen. In this ammonia synthesis process, a reaction was electrochemically generated. The reaction between lithium nitride and the phosphonium cation produces ammonia and an ammonium ylide.

Furthermore, a catalytic reduction of dinitrogen and hydrazine using iron–dinitrogen complexes bearing anionic benzene-based PCP-type pincer ligands have been investigated for ammonia production [97]. The reactions were carried out at atmospheric pressure. The ammonia production by the NRR methods still has low faradaic efficiencies and ammonia production rates compared with Haber–Bosch technology. Ammonia can be generated from hydrogen sulfide (H_2S) through the membrane technology. In this process, consumption of less water quantity was reported in water electrolyzer [98]. Different ammonia production methods are compared in Fig. 13 in terms of CO_2 emission and water and energy consumption. It has been reported that ammonia production from hydrogen sulfide has lower water consumption but high energy consumption compared to steam methane reforming technology. Various studies have been conducted on sustainable ammonia synthesis processes focusing on hydrogen production from water electrolysis powered by electricity generated from renewable energy sources (wind and solar energy) [85,99–101]. Moreover, hydrogen production from water electrolyzers requires high-purity water; it has been reported that producing 1 ton of hydrogen requires 9 tons of treated water [102].

Hydrogen and nitrogen are important in the ammonia synthesis process. However, the enhancement of design of an efficient and eco-friendly ammonia production pathway

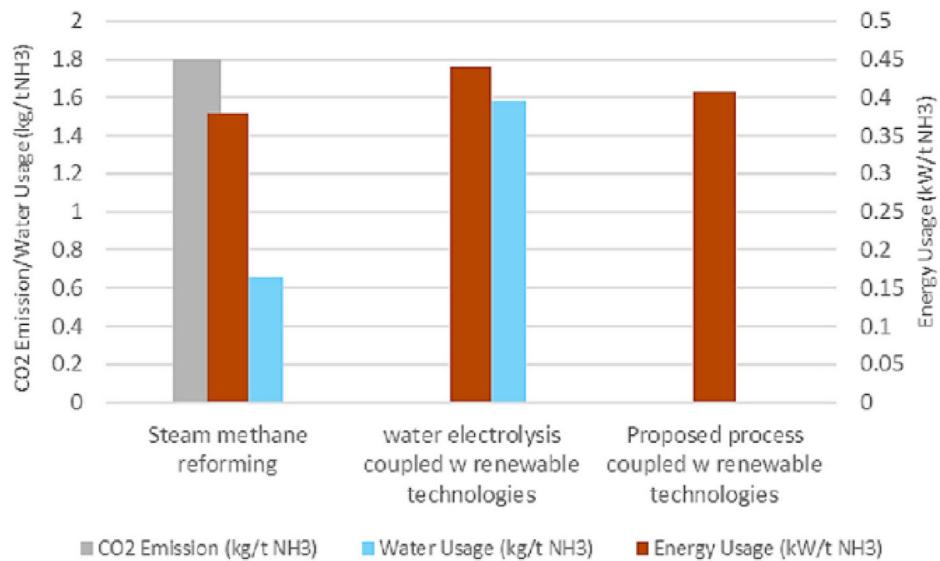


Fig. 13 – Comparisons of CO₂ emissions, water, and energy consumption among different ammonia synthesis technologies [98].

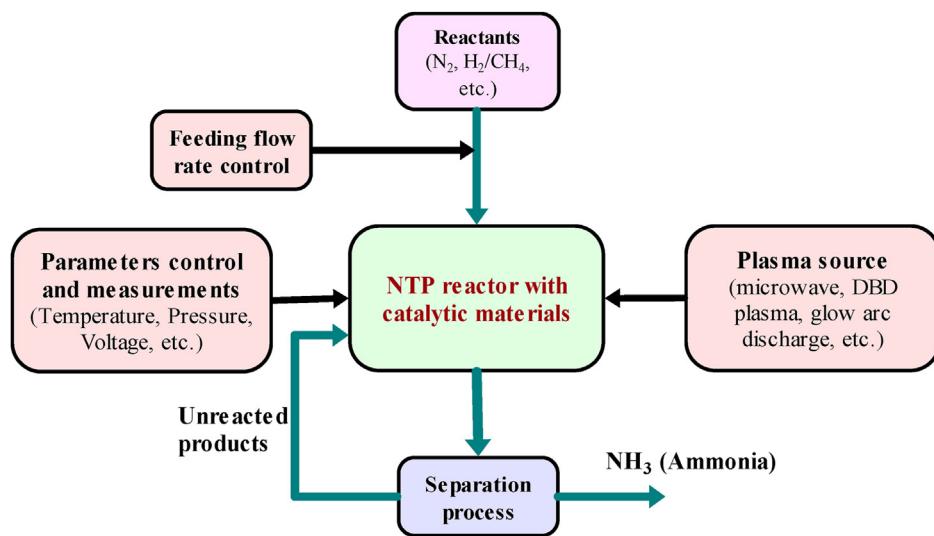


Fig. 14 – Ammonia synthesis by a nonthermal plasma process [105].

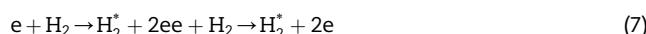
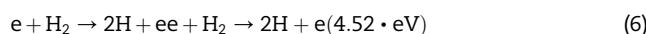
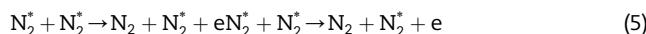
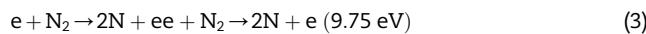
requires more efforts. A novel conceptual design of ammonia synthesis routes has been simulated for high performance with exergy recovery and heat integration [103]. Furthermore, a novel powering system using ammonia to generate power and hydrogen for vehicles has been investigated [104]. The waste heat from the solid-oxide fuel cell (SOFC) was utilized to dissociate ammonia into hydrogen and nitrogen.

Nonthermal plasma (NTP) for ammonia synthesis

The conventional Haber–Bosch process depends mainly on fossil fuels as feedstock, making it an energy-intensive process. In addition, it needs great operational costs due to the requirement of higher operating pressure (150–300 bar) and temperature (400–500 °C) [105]. The ammonia synthesis by NTP has received more attention because the ammonia synthesis by NTP operates at atmospheric pressure and 50 °C

temperature [105]. The current ammonia synthesis technology can overcome the Haber–Bosch-associated problems, such as depending on fossil fuels, high capital cost, etc. However, the main significant challenges are reported to be: (i) ammonia recombination reaction and (ii) fixation of the nitrogen gas [105]. The ammonia synthesis process flow diagram by NTP technology is shown in Fig. 14. Different nonthermal plasma types can be applied to the ammonia synthesis process. Moreover, the conversion rate and energy efficiency still need to be enhanced, and the NTP technology is still to be investigated on a small scale. Ammonia production by NTP technology can be used in local farms, because ammonia is generated at atmospheric pressure. NTP plasma technology has been developed for converting water, renewable electricity, and atmospheric air into ammonia gas [106].

NTP ammonia synthesis reaction mechanism. Ammonia can be generated by nonthermal plasma with the activation of reactants N₂ and H₂/H₂O. Nonthermal plasma converts the feeding reactants into reactive species of H, N, and OH radicals. NH radicals are generated from the reactive species and then recombine to produce NH₃. Nitrogen gas and H₂O are the main raw material sources of the ammonia synthesis process. The activation process of N₂ species can include atomic nitrogen, nitrogen molecular ions (N₂*), and excited nitrogen molecules (N₂*). The hydrogen molecule is dissociated into hydrogen atoms under the NTP phase condition and through the H₂ collisional dissociation. The catalytic materials combined with the plasma enhance the hydrogen dissociation process. In the ammonia synthesis process, H₂O is utilized to produce hydrogen atoms under NTP conditions. The reactive radicals recombine to generate NH radicals. The NH species is the key to ammonia synthesis process. It has been reported that the higher the NH radical concentration, the higher is the ammonia production yield [107–109]. The combination of N and H radicals will form NH and NH₂ radicals, the NH radicals can also form as a result of ammonia decomposition process. The ammonia synthesis reaction mechanism by NTP can be seen as follows [34]:



The development of ammonia synthesis by NTP. One of the most significant advantages of ammonia synthesis by NTP is that it can operate at a lower pressure and temperature. The first trial of ammonia synthesis by NTP was conducted in 1929 using glow and arc plasma discharges [110–112]. In 1971, ammonia synthesis by DBD plasma was first investigated using palladium as a catalytic material [113]. The surface reaction has been reported to play an important role in the ammonia synthesis process. Ammonia synthesis production yield has been enhanced by high plasma frequency using MgO catalyst material [114]. Radio frequency (RF) and microwave (MW) plasmas have been used in ammonia synthesis [107,108,115]. Moreover, most researchers have worked on optimizing energy efficiency by developing new catalytic materials and plasma devices that were carried out for ammonia synthesis by the DBD plasma type. Ammonia synthesis energy efficiency is found to be 35.7 g-NH₃/kWh using

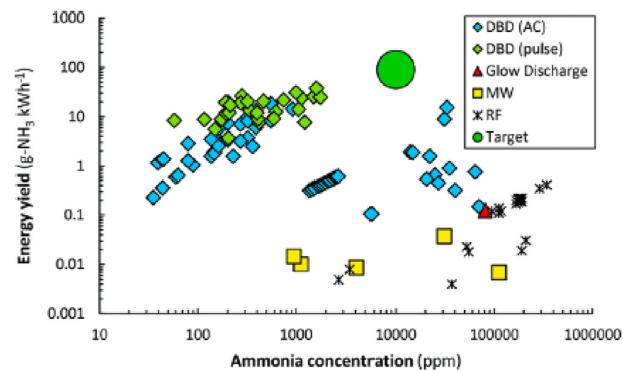


Fig. 15 – Literature on energy efficiency versus ammonia production yield [118].

pulsed plasma combined with Ru–Mg/Al₂O₃ as a catalytic material [116]. The conversion rate of ammonia synthesis by NTP is five times that of the Haber–Bosch process, and it operates at lower pressure and temperature. Plasma is able to activate hydrogen and nitrogen, which leads to the generation of new radicals and ions; it reacts with the catalyst materials and then ammonia production. The performance of plasma-driven ammonia synthesis using different catalytic materials in various reactors has been reviewed [117–119]. The energy efficiency of the plasma-driven ammonia synthesis systems versus the ammonia concentration is demonstrated in Fig. 15. Higher conversion and ammonia production rates were obtained from the RF and MW plasmas with energy efficiency as low as 0.01–0.3 g-NH₃/kWh [120–123]. Most of the ammonia synthesis using DBD plasma operates at atmospheric pressure. Higher ammonia synthesis energy efficiency and ammonia production rates can be achieved under DBD plasma. Furthermore, the DBD plasma type driven by pulse power has higher energy efficiency than those operated by the AC power supply because of the larger electron temperature and low power consumption [124–126]. Therefore, the best plasma-driven ammonia synthesis was obtained from the DBD plasma reactor operated by pulsed voltage.

Various catalyst materials have been used to enhance the ammonia synthesis process using DBD plasma. Table 4 illustrates the energy efficiency of ammonia synthesis by DBD plasma with different catalyst materials [127]. Catalyst materials have been developed to achieve higher interactions between plasma and catalyst materials, subsequently improving the energy efficiency of the system. The catalyst material should be accurately selected to suit the excited species, radicals, and ions generated from plasma. The energy costs are also presented in Table 4. The selection of a low-price catalyst will help in reducing energy costs. Nitrogen is usually obtained from air separation via the cryogenic process. Nonthermal plasma has been used for nitrogen oxidation into ammonia; catalytic ammonia synthesis with nitrogen oxidation, water, air, and renewable energy reduced the energy cost of 4.61 MJ mol⁻¹ NH₃ [128,129]. The most common sources of hydrogen raw materials are natural gas and water [130].

The NTP has been reported to be much better for applying renewable energy sources. Ammonia production technologies using renewable energy sources are described in Table 5.

Table 4 – Ammonia synthesis by DBD reactor literature survey [127].

Year	Catalyst	Feed flow rate (mL/min.)	H ₂ /N ₂ ratio	Voltage (kV)	Power (W)	Ammonia yield (%)	Energy yield (g-NH ₃ /kWh)	Energy cost (MJ/mol-NH ₃)	Reference
1969	Pd wound on electrode	Batch	3	—	12.5	3.13	—	—	[113]
2000	MgO smeared on electrode	2266.7	0.8	0.58	—	0.33	—	—	[127]
2003	No catalyst	730	3.56	1.8	57.2	1.36	1.83	33.4	[126]
2004	Ru/alumina membrane	40	3	4.5	127	4.36	0.37	163.9	[131]
2007	Ru/alumina membrane	30	3	4.5	127	4.62	0.40	154.7	[132]
2008	No catalyst (methane as H ₂ source)	500	6	—	240	0.74	0.69	88.7	[133]
2015	Lead zirconium titanate	11.5	1	5	—	5.9	0.7	87.4	[134]
2016	Alumina and DLC coated alumina	60	3	15	90.5	0.67	0.18	340	[135]
2016	Cs–Ru/MgO	4000	3	6	—	2.41	2.3	26.6	[116]
2016	Lead zirconium titanate	11.5	3	5.5	—	0.5	0.75	81.6	[136]
2016	Ru–Mg/alumina	2000	4	5.4	—	2.55	35.7	1.7	[106]
2016	Cu wool	100	1	5	—	3.5	3.3	18.5	[137]
2016	Ru/alumina	—	1.5	—	—	—	0.64	95.6	[138]
2016	Ni/silica with barium titanate as dielectric	25	3	20	107	12	0.75	81	[139]
2017	Ru/alumina	1000	3	7.5	—	0.05	1.9	32.2	[140]
2017	Ru/Si-MCM-41 with Cs, K, Ba as promoters	—	1	5	—	—	1.7	3.6	[141]
2018	Ni nanoparticles/alumina	100	2	—	10	2	0.89	68.9	[142]
2019	MgCl ₂	4000	1	6.4	—	—	20.5	2.9	[125]
2020	Ru/ α -Al ₂ O ₃	120	0.5	8	38.4	1.49	1.89	32.39	[143]
2020	Zeolite 5A	25	1	7.5	13.3	—	15.5	3.95	[144]
2020	Alkaline γ -Al ₂ O ₃	100	3	—	24.25	—	6.58	9.30	[145]
2021	Rh/ γ -Al ₂ O ₃	100	0.5	8	24	1.43	0.94	65	[47]
2021	Ru/activated carbon	100	3	—	13.3	—	0.72	85	[146]

Table 5 – Renewable ammonia synthesis technologies [14].

Ammonia production technologies	Technology readiness level (TRL) ^a	Reference
Electric HB with alkaline electrolysis	8–9	[152]
Electric HB with high-pressure PEM electrolysis	6–7	[153–155] ^b
Electric HB with SO electrolysis	3–5	[156]
Electrochemical	1–3	[147,157,158]
Electric low-pressure HB with absorption	4–5	[159–163]
Electric low-pressure HB with in situ absorption	1–3	[164,165]
Nonthermal plasma	1–3	[105,116]
Photocatalytic	1–3	[166–168]
Metallocomplexes	1–3	[70]
Biological	1–3	[70]

^a TRLs estimated from a limited number of specific cases of technological implementation and current status of the research on the development level.

^b Low-pressure PEM, not high-pressure PEM.

Alternative ammonia production techniques can achieve sustainable future ammonia production, where ammonia can be directly generated by the electrochemical process by combining N₂ and water [147]. It is considered an attractive ammonia synthesis technology because ammonia is generated at lower pressure and temperature, but it still needs more

development [148]. However, the most important challenges of this technology are electrode selectivity and the electrochemical energy cost still being higher than the conventional ammonia synthesis by the Haber–Bosch (methane) process [149–151]. The most significant opportunity for ammonia synthesis by NTP technology is fossil fuel elimination that is used in the conventional NH₃ production process because of its carbon-free nature. Hydrogen can be generated from renewable energy sources, such as wind. High catalytic material activity is important for enhancing the conventional and renewable ammonia synthesis process to enable more energy-efficient technology. In the next section, we will discuss the different catalytic materials used in ammonia synthesis technology.

Catalyst materials for ammonia synthesis technologies

High catalytic material activity is important for the ammonia synthesis process, because newly developed catalytic materials ease the synthesis process and decrease the system operating temperature and pressure to achieve more efficient ammonia synthesis. The ammonia synthesis process depends mainly on the catalyst type and the surface reactions of hydrogen and nitrogen [66]. Ammonia synthesis over ruthe-nium catalyst materials from nitrogen and hydrogen has been investigated [169]. Different catalytic materials, such as iron, nickel, cobalt, and nitride for the blue ammonia or methane Haber–Bosch process and green ammonia synthesis, have

been investigated [170]. The proposed reaction model mechanism of catalytic ammonia synthesis has been investigated by Stolze and Norskove as follows [171,172]:



The main goal of using catalytic materials for ammonia synthesis is to achieve a maximum production rate at low operating temperatures.

Iron- and ruthenium-based catalysts for NH_3 synthesis

Catalytic ammonia synthesis can be classified into two main categories: fused-iron and supported metallic catalysts; fused-iron catalysts are mostly used in the ammonia synthesis process [173–188]. The fused-iron catalyst types are composed of three different iron oxides, Fe_2O_3 , Fe_3O_4 , and Fe_{1-x}O [66,189]. Catalyst promoters such as K_2O_3 and Al_2O_3 have been used with iron catalysts for the catalytic ammonia synthesis process [190]. The catalytic material's stability is the most important parameter for achieving a long lifetime. Furthermore, the poison effect of oxygen, which has been discussed in different studies, should be investigated [191,192]. The Fe-based catalytic materials' performance is related to the structure of iron crystals. Fig. 16 shows Fe-based catalyst crystal structures [193]. The magnetite Fe-based catalyst can provide the highest ammonia synthesis activity.

Ruthenium-based catalysts are the second most widely used catalysts for ammonia synthesis process. Ruthenium supported by a carbon graphite catalyst was developed for the ammonia synthesis process in 1980 by Kellogg [66]. Numerous studies on ruthenium catalyst materials have been developed for large ammonia synthesis processes using different support materials and promoters [194–196]. The ruthenium

catalyst activity was discussed in detail by Saadatjou et al. [169]. The Ru-based catalysts are influenced by the presence of oxygen in the same way as in the Fe-based catalysts. It has been reported that the ammonia production rate from 99.999% hydrogen and nitrogen as input gas over the Ru/ $\text{La}_{0.5}\text{Ce}_{0.5}\text{O}_{1.75}$ catalyst, decreased by 50% after 20 h at an operating pressure of 3 MPa and a temperature of 350 °C [167]. The surface of a wide range of support materials has been used for ruthenium materials installation. Table 6 shows the Fe-based and Ru-based catalysts' chemical composition and activity for the ammonia synthesis process. The maximum ammonia production rate was 310,000 $\mu\text{mol g}^{-1} \cdot \text{H}^{-1}$, which was obtained at operating conditions of 100 bar and 400 °C; the Ru-based catalyst promoted with Ba and supported on AC-G was utilized [197].

The presence of oxygen in the ammonia synthesis process over catalytic materials in the Haber–Bosch process is typically inevitable and included in the feeding gas. The purification process is significant in preventing the poisoning of Fe-based and Ru-based catalysts. Therefore, the development of catalytic materials is an important issue for enhancing the performance of the ammonia synthesis process with high energy efficiency and low cost. The Haber–Bosch process is mostly used for large-scale ammonia production plants.

Ruthenium-based catalysts can provide high ammonia synthesis at lower operating pressure and temperature [257]. However, the Ru material cost is too high, and the total global production rate was 35.5 tons/year, which means that ammonia synthesis plants cannot depend mainly on Ru-based catalysts. Therefore, various catalytic materials have been investigated for the high-activity ammonia synthesis process.

Cobalt- and nickel-based catalysts for ammonia synthesis

Cobalt-based or (Co-based) catalysts have received more attention due to their high ammonia synthesis activity. The supporting materials can similarly be used to Ru-based catalysts; they can be added (supported materials/promoters) with a high weight percentage [66]. Barium has been used as a promoter for cobalt catalysts supported by carbon for ammonia production [258]. The ammonia synthesis showed much more activity when using Co-based catalysts with Ba as a promoter supporting carbon or CeO_2 . The cobalt-based catalysts have been prepared supporting ceria for ammonia formation by Lin et al. [259]. The ammonia production rate at

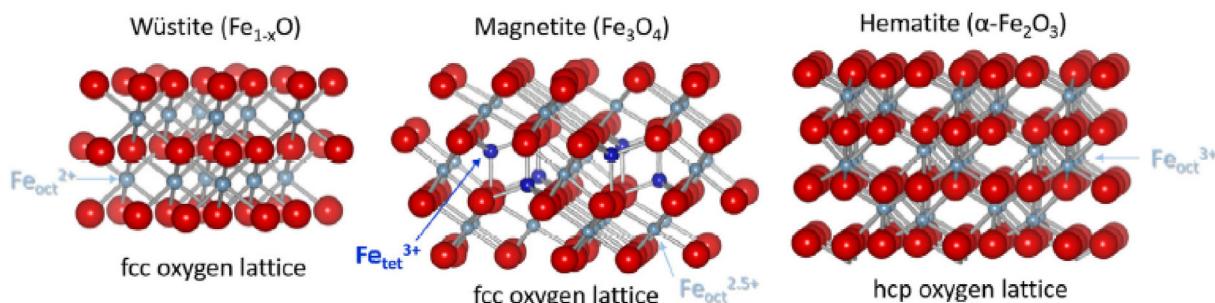


Fig. 16 – Fe-based catalyst material crystal structures [193].

Table 6 – Fe- and Ru-based catalyst materials for ammonia synthesis.

Catalyst composition (wt%)	Promoter (wt%)	Temperature (°C)	Pressure (MPa)	Weight hourly space velocity (WHSV) (mL·g⁻¹·h⁻¹)	NH₃ production rate (μmol·G⁻¹·h⁻¹)	Reference
Fe-based catalysts						
7% Fe/CeO₂ (applied electric field 6 mA)	—	100	0.1	144,000	155	[198]
20% Fe–BaH₂ (chemical looping synthesis)	—	300	0.1	60,000	1703	[199]
2.8% Fe/γ-Al₂O₃	—	320	0.1	—	0.12	[200]
20% Fe–BaH₂	—	350	0.1	60,000	384	[199]
Fe(95%)Co(5%)	—	400	0.1	—	820.07	[201]
Fe(85%)Ni(15%)	—	400	0.1	—	334.354	[201]
1.2% Fe/BaCeO _{3-x} H _y N _z	—	400	0.9	36,000	6800	[202]
Fe ₉₁ Zr ₉	—	417	0.9	—	72	[203]
Fe–5LiH	—	300	1	60,000	4840	[204]
Fe/LiH	40%LiH	350	1	60,000	11,428	[205]
10% Fe/C	3.5%Ba	400	1	53,400	14,400	[206]
80% Fe/Ce _{0.8} Sm _{0.2} O _{2-δ}	—	450	1	16,000	8700	[207]
FePc	10% Cs	400	3	12,000	14,000	[208]
Fe-metal organic framework derived catalyst (MDC)	1% K	400	3	13,500	30,400	[209]
Fe _{1-x} O	(Al ₂ O ₃ + CaCO ₃ + K ₂ CO ₃) < 10 wt%	430	3	7200	11,900	[210]
Fe ₃ O ₄	(Al ₂ O ₃ + CaCO ₃ + K ₂ CO ₃) < 10 wt%	430	3	7200	9200	[210]
1% Fe/BaTiO _{3-x} H _x	—	400	5	66,000	14,000	[211]
FeOOH/Al ₂ O ₃	K (5 wt%)	500	9	26,400	32,850	[212]
Ru-based catalysts						
Ru12%/CaFH	—	50	0.1	36,000	50	[213]
Ru10%/MgO (microwave-assisted 2.45 GHz)	—	320	0.1	3000	613	[214]
Ru2%/HT-C12A7:e ⁻	—	340	0.1	18,000	2290	[196]
Ru10%/BaO–CaH ₂	—	340	0.1	36,000	10,500	[215]
Ru10%/CaH ₂	—	340	0.1	36,000	7400	[215]
K/Ru10%/graphite	K (2 wt%)	400	0.1	—	490	[216]
Ru2%/HT–C12A7	—	400	0.1	36,000	3050	[217]
Ru0.27%/SAs/S-1	Ba (9 wt%)	400	0.1	18,000	1389.5	[218]
YRu ₂	—	400	0.1	18,000–36000	3318	[219]
Ru2%/BaZrO ₃	—	400	0.1	36,000	3630	[220]
Ru2%/BaZr _{0.9} Y _{0.1} O ₃	—	400	0.1	36,000	4000	[220]
Ru1.4%/graphene	Ba/Ru = 1	400	0.1	36,000	336	[221]
Ru2%/2.0SrNb	Cs/Ru = 8	450	0.1	36,000	5035	[222]
Ru4%/Sibunit	Ba (10.8 wt%)	350	0.7	—	1540	[223]
Catalyst composition (wt%)	Promoter (wt%)	Temperature (°C)	Pressure (MPa)	Weight hourly space velocity (WHSV) (mL·g⁻¹·h⁻¹)	NH₃ production rate (μmol·G⁻¹·h⁻¹)	Reference
Ru10%/Ca(NH ₂) ₂	—	300	0.8	36,000	15,800	[224]
Ru10%/Ba–Ca(NH ₂) ₂	Ba (3 wt%)	360	0.9	36,000	60,400	[225]
Ru4·5%/BaCeO _{3-x} H _y N _z (after 20 h)	—	400	0.9	36,000	28,570	[202]
Ru13.8%/mesoporous carbon(MPC)-18	Cs/Ru = 1.1	360	0.99	—	10,200	[226]
Ru10%/MPC	Cs (33 wt%)	370	0.99	—	8100	[227]

Ru10%/MPC	Ba/Ru = 0.5	380	0.99	—	10,400	[226]
Ru5%/Ce _{0.5} La _{0.5} O _{1.75}	—	350	1	72,000	31,300	[228]
Ru5%/Pr ₂ O ₃	—	400	1	18,000	19,000	[229]
Ru3%/Ti–Ce–S	—	400	1	—	14,580	[230]
Ru(0.4–1%)/Yittria Stabilized Zirconia (YSZ)	Ba/Ru = 1	400	1	72,000	5640–14,100	[231]
Ru5%/gC–Al ₂ O ₃	Ba (6 wt%)	400	1	60,000	5611	[232]
Ru5%/Al ₂ O ₃ -980	Ba (6 wt%)	400	1	60,000	7217	[233]
Ru5%/La _{0.5} Pr _{0.5} O _{1.75}	—	400	1	72,000	60,200	[234]
Ru3·1%/MgO–MIL	Cs/Ru = 1	400	1	24,000	22,290	[235]
Ru4%/CeO ₂ -r	—	400	1	18,000	3830	[236]
Ru4%/CeO ₂ -c	—	400	1	18,000	1289	[236]
Ru2.48%@CeO ₂ -9	—	425	1	60,000	8500	[237]
LaCo _{0.98} Ru _{0.02} O ₃	—	450	1	—	10,500	[238]
Ru2%/MgO	Cs (6.4 wt%)	400	2.6	—	4200	[239]
Ba/Ru4%/Graphitic Nanofilaments (GNFS)	Ba (1 wt%)	400	3	—	18,570	[240]
Ru3%/BaCeO ₃	—	400	3	—	6450	[241]
Ru/ZrO ₂ –KOH	—	400	3	—	11,100	[195]
Ru5%/Pr ₂ O ₃	—	400	3	72,000	64,000	[242]
Ru3·85%Y–layered double oxide (LDO)	—	425	3	—	16,120	[243]
Ru3·86%MgAl–LDO	—	425	3	—	14,760	[243]
Ru1·25%/BaCeO ₂ -a	Cs (4 wt%)	450	3	24,000	28,000	[244]
Ru2·5%/CeO ₂ –C ₁₂ H ₂₉ NO (TPAOH)	Cs (4 wt%)	450	3	24,000	32,000	[245]
Ru2·5%/CeO ₂ –CS	—	450	3	70,000	27,000	[246]
Ru4·8%/Li/AC	Li (7.6 wt%)	460	3	62,400	106,120	[247]
Ru2·5%/CeO ₂ –MS	Ba (5.25 wt%)	450	3.8	24,000	24,000	[248]
Ru4%/Al ₂ O ₃	Ba (6%)	400	5	—	390	[194]
Ru4%/MgO	—	400	5	—	7390	[194]
Ru4%/BaTiO ₃	—	400	5	—	15,670	[194]
Ru0·9%/TiH ₂	—	400	5	66,000	2800	[249]
Ru0·9%/BaTiO ₂ · ₅ H _{0.5}	—	400	5	66,000	1400	[249]
Ru1%/BaTiO ₂ · ₅ H _{0.5}	—	400	5	36,000	28,200	[211]
BaCs–RuC (N ₂)	Ru:Ba:Cs 1:0.05:0.2	400	9.5	—	287,647	[250]
Catalyst composition (wt %)	Promoter (wt%)	Temperature (°C)	Pressure (MPa)	Weight hourly space velocity (WHSV) (mL. g ⁻¹ .h ⁻¹)	NH ₃ production rate (μmol. G ⁻¹ .h ⁻¹)	Reference
Ru10%/CeO ₂ -r	—	400	10	70,000	115,000	[251]
Ba/Ru4·5%/BN	Ba (5.6 wt%)	400	10	—	186,600	[252]
Ru3.75%–N–mesoporous carbon (MC)	Ba (4 wt%)	400	10	—	79,000	[253]
Ru2.3%/MC	Ba (4 wt%) K (14%)	400	10	—	133,000	[254]
Ru10%/AC-G	Ba (9 wt%)	400	10	70,000	312,500	[197]
Ru4%/La2Ce ₂ O ₇	—	425	10	—	52,700	[255]
Ru3.4%/carbon nanotubes (CNT)-D	Ba (3.4 wt%)	450	10	—	110,000	[256]

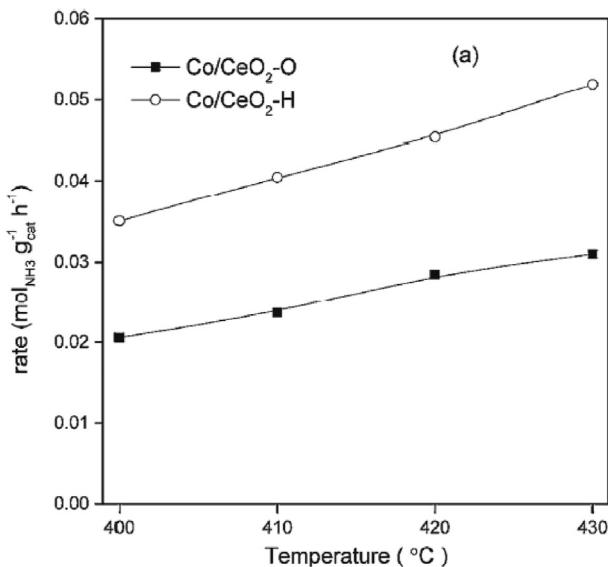


Fig. 17 – Ammonia production rate over Co/CeO₂ at a pressure of 10 MPa [259].

different operating temperatures and pressures of 10 MPa is depicted in Fig. 17. The results show that the catalyst activity is revealed after high-temperature catalyst reduction in hydrogen [259]. Compared with Ru-based catalysts, Co-based catalysts are available and their cost is low; they can be used as an alternative catalyst for a high ammonia formation rate. The cobalt catalyst type of Co₃Mo₃N is noted to be the highest ammonia synthesis catalyst; it is currently being used in industry [260–264].

Ni-based catalyst materials are also used in the ammonia synthesis process. However, Ni-based catalysts have low activity and high cost in the ammonia synthesis process. Higher catalytic activity at low pressure and temperature can be obtained from Ni-based catalysts supported by LaN [265]. It has been reported that the high Ni-based catalyst activity depends on the breakage of nitrogen triple bond due to the low Ni-binding energy. The main challenge of the ammonia synthesis process is using a catalyst and generating ammonia at a low temperature. Ru-based catalysts need the lowest temperature in ammonia synthesis process as compared with Fe-based catalysts; however, ruthenium catalysts are expensive.

It can be noted that high ammonia synthesis was obtained from the Ni-based catalysts at a lower temperature (300 °C) and cost. Table 7 illustrates ammonia synthesis rate using Ni-based catalysts of different chemical compositions. It was noted that the Ni-based catalyst is much more cost-effective than Ru-based catalysts and enables the production of ammonia at lower temperatures and pressure. The synthesis process of ammonia with Ni as a catalyst material shows less activation process as compared to Fe-based catalysts. The combination of Ba with the Ni catalyst (20%Ni–BaH₂) has shown larger ammonia activation than the 20%Fe–BaH₂ catalyst and 40 times greater activation than the Ni-based catalyst used in the conventional ammonia synthesis process [266]. The use of CeO₂ as a supported material for Fe catalytic material exhibited excellent ammonia synthesis activation at a lower temperature of 100 °C [198]. Furthermore, the pathway of ammonia synthesis over BaCeO₃ showed higher activation rate in the ammonia synthesis process [267]. The ammonia synthesis rate results of Ru, Co, Fe, and Ni-based catalysts at the same operating conditions of 400 °C, 0.9 MPa, and weight hourly space velocity (WHSV) of 36,000 mL g⁻¹.h⁻¹ is compared in Fig. 18. It was noted that the highest NH₃ activation and synthesis rate was obtained at the Ru- and Co-based catalysts supported on the Ce and using Ba as the promoter. Moreover, the Ni-based catalyst type of Ni50%–BaH₂ (chemical looping) can deliver higher activation for the ammonia synthesis process at lower temperature and pressure compared with other catalytic materials under the same operating conditions.

As discussed previously, nonthermal plasma can enhance the ammonia synthesis process. Ammonia is generated from N₂ and H₂ mixture without catalytic materials [271]. Furthermore, the addition of catalyst materials to the ammonia synthesis process by nonthermal plasma has been investigated [124,131,132,272,273]. A wide range of metal catalytic materials have been studied for ammonia synthesis by NTP [272,274]. However, the ammonia synthesis reaction mechanism by NTP still requires more investigation to understand the ammonia production process, as well as the NTP interaction of N₂–H₂ with the catalyst materials. The Ru-, Ni-, and Co-based catalysts can also be used in the ammonia formation process by NTP. Fig. 19 compares the ammonia production rate as a function of the residence time over Ru, Ni, and Co catalysts [275,276]. These catalytic material types have the highest

Table 7 – Ammonia synthesis results for selected Ni-based catalysts.

Catalyst composition (wt%)	Temperature (°C)	Pressure (MPa)	Weight hourly space velocity (WHSV) (mL. g ⁻¹ .h ⁻¹)	NH ₃ production rate (μmol. G ⁻¹ .h ⁻¹)	Reference
Ni20%–BaH ₂	300	0.1	60,000	48	[199]
Ni50%–BaH ₂ (chemical looping)	300	0.1	60,000	3125	[199]
Ni59.5%–LiH	300	0.1	60,000	40	[205]
Ni50%–LiH (chemical looping)	300	0.1	60,000	1533	[199]
Ni12·5%/LaN NPs	340	0.1	36,000	2665	[265]
Ni5%/LaN bulk	340	0.1	36,000	820	[265]
Ni34.8%–Mo–N	400	0.1	9000	275	[268]
28%Ni ₂ Mo ₃ N	400	0.1	9000	395	[269]
Ni54%–BaZr _{0.1} Ce _{0.7} Y _{0.2} O _{3–δ}	620	0.1	30,000	250	[266]
Ni11·7%/CeN NPs	400	0.9	36,000	6500	[270]

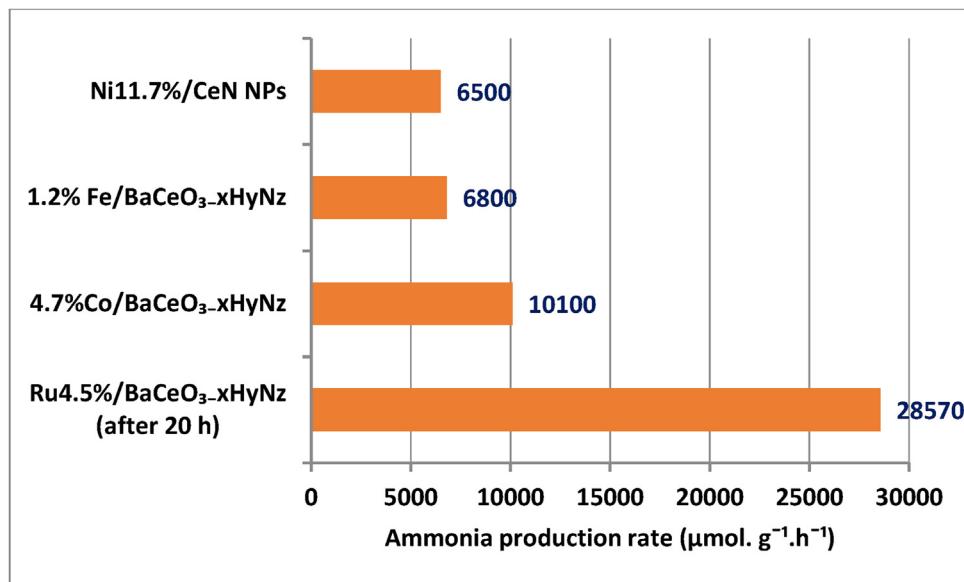


Fig. 18 – Comparison between the maximum ammonia synthesis rate over Ru, Co, Fe, and Ni-based catalysts at 400 °C, 0.9 MPa, and WHSV 36000 mL. g⁻¹. h⁻¹.

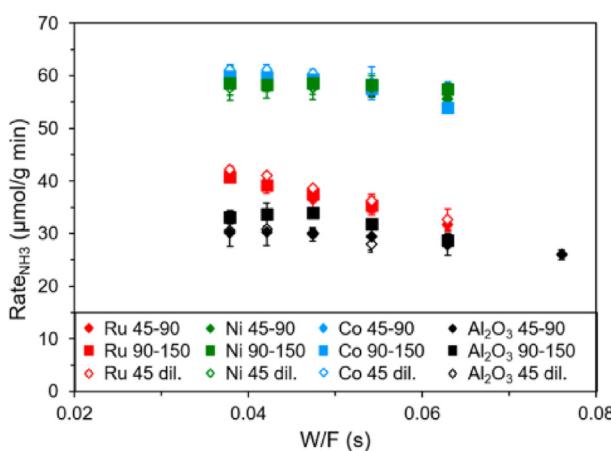


Fig. 19 – Comparison of the catalytic ammonia synthesis rate by NTP for different catalyst material types as a function of residence time in the catalyst bed reactor [275,276].

catalytic NH₃ activation and production rates [274]. However, the challenges for NH₃ synthesis by NTP are as follows: (i) gas purification, NO_x contaminants, and x-NH₃ should be removed; NO, NO₂, and N₂O gases are detected by gas chromatography measurements that have a negative environmental impact [132], (ii) control open-circuit measurements, (iii) N-containing active site materials, and (iv) Ar control the electrochemical measurements that is an important parameter for long-term tests. The NRR is typically important for understanding the importance of the catalyst design mechanism. Nitrogen reduction is known as an associative and dissociative mechanism, as shown in Fig. 20. The key role is that of the stage when the triple bond in the nitrogen molecule is broken during the reduction reaction steps. It can be seen in the dissociative mechanism that N≡N linkage is broken before the protonation steps initiate, while the N–N linkage in the

associative mechanism is still intact across most of the reduction steps [277]. The nitrogen reduction associative mechanism is categorized based on the sequence of the two N atoms in the N₂ molecule. The high-activation catalyst is significant for the ammonia synthesis process for nitrogen reduction and is broken in both conventional synthesis processes by Haber–Bosch using methane or Haber–Bosch using renewable energy sources and NTP methods. Therefore, more development of catalyst materials is required to provide much higher activated catalysts for N₂ energy transition and bonds for ammonia synthesis at low prices.

Ammonia in end use and future roadmap plans

In the last few years, ammonia has been included as a direct clean energy fuel for energy applications. Ammonia synthesis processes are currently being developed to integrate with renewable energy sources. The social acceptance of ammonia usage as a clean energy source is considered a significant issue, which should include development procedures, ongoing investigation, and governmental support to raise awareness of safety and economy in relation to the use of ammonia [63]. Ammonia has been utilized in some modified vehicles for a long time (in Belgium, 1940s). The replacement of fossil fuels with clean energy has received more attention, focusing on using ammonia in combustion engines or indirectly by fuel cells. Further ammonia usage in different energy applications has been investigated as a new vision of a sustainable supply chain cycle of the ammonia economy [278]. Fig. 21 demonstrates the sustainable cycle of energy applications, all based on ammonia. Renewable energy sources are combined to generate clean hydrogen and then used to produce ammonia as a clean energy carrier and fuel. As discussed previously, the main industrial method for ammonia synthesis is the Haber–Bosch process coupled with hydrocarbons, which has been optimized for a long time.

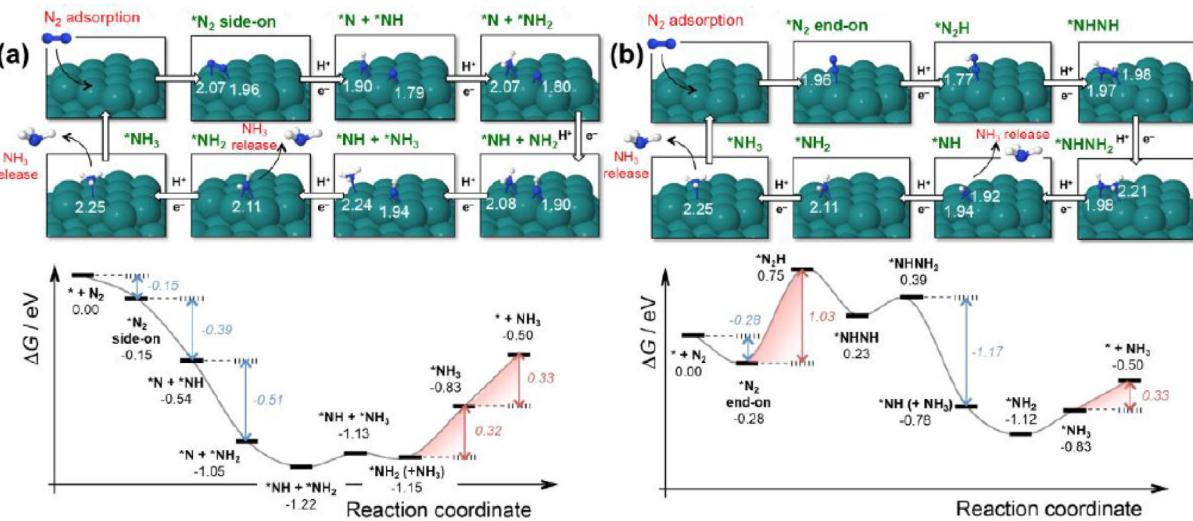


Fig. 20 – Comparison of DFT calculations of N_2 reduction mechanisms on Ru (100) [277]. (A) Associative mechanisms. (B) Dissociative mechanisms.

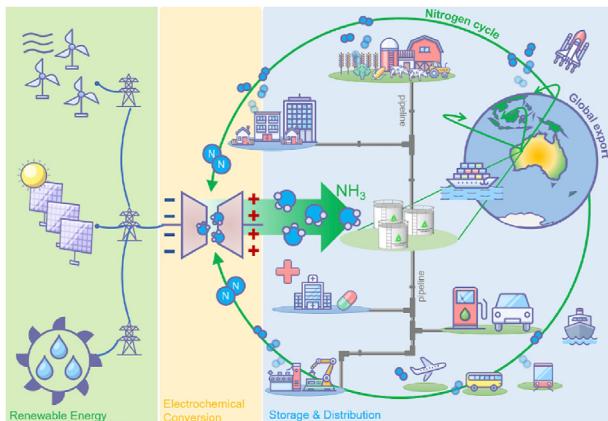


Fig. 21 – “Ammonia economy vision” in which all are based on ammonia [63].

Ammonia can be directly used as a fuel in heat engines, such as vehicles, marines, gas turbines, and power generators. Furthermore, the ammonia cracking technology used in fuel cells has also been investigated. The Australian Commonwealth Scientific and Industrial Research Organization (CSIRO) has developed H₂ production by thermal water splitting using solar energy, which can be converted into NH₃ or methanol-applicable fuels. Ammonia is not considered as the missing link to hydrogen; it can be considered the key link to global energy transformation and hydrogen carrier transportation. Thus, ammonia possesses most of the global interest. It could be generated in huge amounts to be used in energy applications and agricultural needs.

Vehicle engine, marine, and gas turbine applications

Several studies have investigated the use of ammonia as fuel since the 1960s [279–281]. Ammonia as fuel in an ICE is still not ready to be used in market applications because of concerns like safety, physical characteristics, and supply

compared with conventional fuels. Using ammonia as a fuel in compression ignition (CI) or spark-ignition (SI) engines, high ignition temperature, narrower flammability, and low combustion speed can be achieved. Therefore, the ignition conditions of ammonia should be improved by some adaptations, such as cofiring of ammonia with hydrogen or gasoline. South Korean researchers have tested fueling passenger cars with 70% ammonia and 30% gasoline [282]. Various studies have been developed for ammonia-based fuel usage in ICE [283,284]. The schematic diagram of different suitable and possible paths of the use of ammonia-based fuel in ICE is shown in Fig. 22. In this diagram, the possible pathways of using ammonia as a fuel “mixed or not mixed” with H₂ molecules are considered. The results indicate that the efficiency decreases with increase in hydrogen; the maximum efficiency can be obtained from the stoichiometric mixing ratio near the rich mixture. Different studies have been conducted to inject ammonia through an intake port (port fuel injection (PFI)), because ammonia remains in the gaseous phase at ambient temperature and pressure lower than 10 bar [285]. Higher efficiency can typically be obtained from the direct injection strategy. NO_x emissions from ammonia combustion are still the most important issue in vehicle ICE. Catalytic converters are considered the best-developed solution to control NO_x emission from the NH₃ fuel engines [286,287].

Various studies have investigated the use of ammonia as a potential carbon-free fuel on a laboratory and utility experiments scale. Ammonia-fueled heat engines have been numerically simulated, including gas turbines, ICE, and aerospace devices. The main challenge of using ammonia in practical combustion engines is large NO_x emissions [40]. Pure ammonia, ammonia ammonia-kerosene, or ammonia-methane have been successfully tested as fuels in practical industrial furnaces and gas turbines. However, the installation of the selective catalytic reduction (SCR) system downstream of the gas turbine achieved NO_x emissions lower than 10 ppm [288]. Different studies have studied the chemistry of NO_x emissions resulting from ammonia combustion. Flame

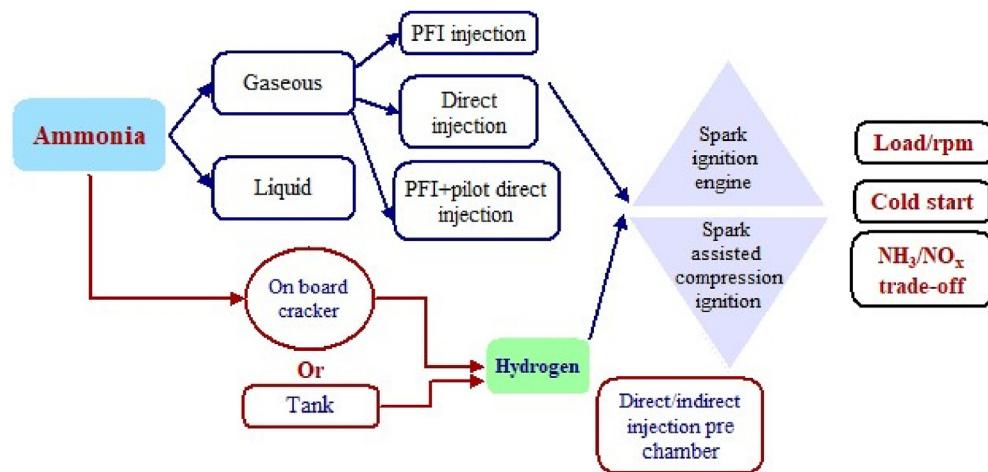
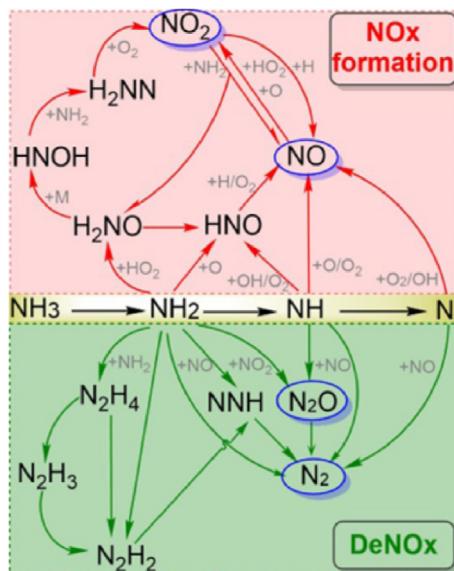


Fig. 22 – Pathways of different possible uses of ammonia as a fuel in ICE.

Fig. 23 – NO_x and de-NO_x formation pathways in a jet stirred reactor [291].

stability is a significant obstacle for the efficient utilization of ammonia because of its low reactivity [289]. Moreover, ammonia is not applicable to the current gas turbines, which are designed for hydrocarbon fuels. Ammonia–air flames have been reported to have multiple thousands of NO_x emissions for lean premixed NH₃–air flame [40]. Two-stage combustion has been reported with a low NO_x emission of 42 ppm for pure ammonia combustion at a pressure of 3 bar [290]. It has also been highlighted that high pressure leads to minimizing NO_x emissions and unburned ammonia. The NO_x and de-NO_x formation pathways are demonstrated in Fig. 23 in a jet stirred reactor [291]. The ammonia combustion in fuel–lean equivalence ratios is described by high O and OH radicals that are converted into NO. The main NO_x formation reaction pathway occurs through the reaction of these radicals NH₂, NH, and N with O₂, O, OH, and HO₂ to generate NO or form HNO and H₂NO species and then NO, as shown in Fig. 22. The HNO formation reaction can be expressed as follows:



This reaction can be written as: NH₂ + O = NH + H₂O, but the possibility of this reaction is low at high operating temperatures. It has been reported that reaction (19) is responsible for the NO formation in both NH₃/air/syngas and NH₃/CH₄/air combustion. Fig. 24 presents the sensitivity of the NO concentration of NH₃/air/syngas and NH₃/CH₄/air combustion reaction rate constants [292].

Moreover, it was found that the flame speed prediction of NH₃/H₂ combustion is highly sensitive to reaction (19) as well as increase in x_{NH₃} [293,294]. Although reaction (19) depends on the temperature, experimentally it only appeared at low temperature. Further investigations are needed for high-temperature flame rate constants. The reaction pathways of NH radicals with O₂, O, and OH to produce NO as follows:



The previous NH reactions (20–23) showed a high sensitivity to produce HNO and NO directly, which was confirmed in both Figures (24A) and (24B). The HNO can be directly converted into NO radicals [295]: HNO = NO + H, or transformed to a bimolecular reaction and three-body collision reactions suggested by Glarborg-Mech and Shrestha-Mech: HNO + H = NO + H₂ and HNO + OH = NO + H₂O.

However, the de-NO_x reaction pathway has been found to occur in 900–1100 °C in the presence of O₂ and NO_x reduction in the combustion flames called thermal de-NO_x. The de-NO_x pathway of ammonia oxidation occurs at a high equivalence ratio through the reaction of NH₂ and NH₃ with NO and NO₂ to generate NNH and N₂O, and then forming N₂ as follows:



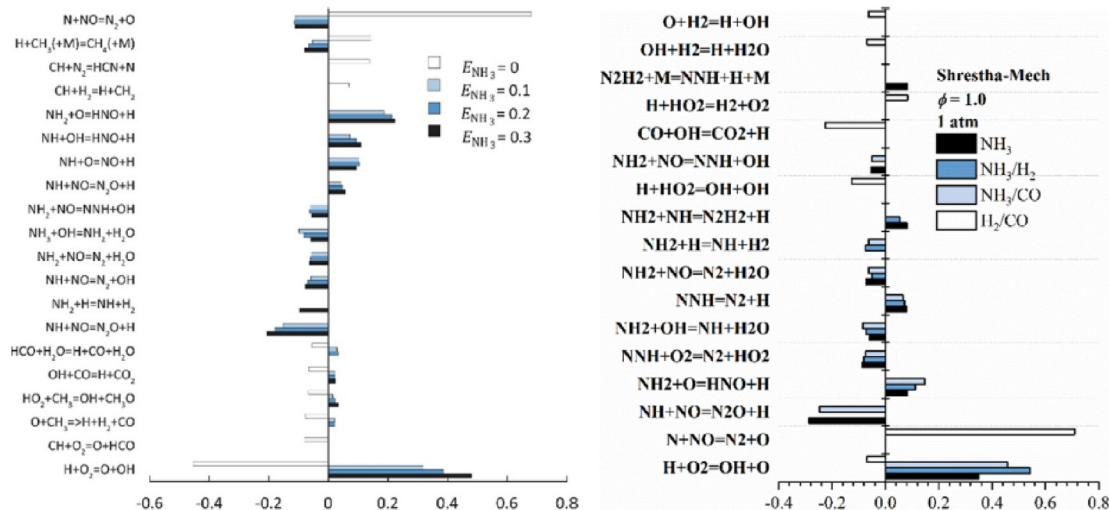


Fig. 24 – (A) The first-order sensitivity of NO concentration to the rate constants of elementary reactions of the maximum NO concentration for the NH₃/CH₄/air [292]. **(B)** NO concentration of NH₃/air, NH₃/H₂/air, NH₃/CO/air, and H₂/CO/air combustion flames for x_{NH₃} = 0.6 [293,294].



The most sensitive reactions for predicting flame speed and NO_x formation are reactions (24) and (25). It can be concluded that high NO_x emissions are the main drawback at the exhaust of several ammonia simulations and experimental analyses to use ammonia as a potential fuel. The formation of NO_x species is due to the N content in the ammonia. Moreover, the addition of hydrogen increases the NO radicals. The most important issue of NO_x emissions from ammonia combustion is to find an appropriate solution to eliminate the pollutants at the engine exhaust, which vary based on engine operating conditions. Redox catalyst materials have been used to avoid NO_x emissions [296]. Further experiments are required for heavy-duty engines. Because there are no experimental data; it is only simulation studies [297,298].

Marine engines, the use of ammonia as a fuel in marine engines has received great interest because it leads to minimizing the sulfur content produced from conventional fuels [299]. Ammonia is considered as an innovative solution for decarbonizing the shipment industry by 2050. Different reports, such as Volkswagen Group and the European-based Transport and Environment Group, showed a comparative analysis between conventional fuels and ammonia as a fuel that resulted in lowering ocean acidification and environmental impact [300–302]. Ammonia in marine applications can be used in the ICE without SO_x and with limited NO_x emissions compared to heavy oils. Several developments have been initiated by maritime companies to avoid NO_x emissions

from ammonia fuel combustion. Similarly, for vehicle applications, SI or dual-fuel engines will be the optional solutions. The advantages of dual-fuel engines are their fuel availability, low cost, and ability to adjust with CO₂ easily. However, some technical considerations regarding ammonia utilization still require further development. In addition to, the NO_x emissions problem needs to be resolved to cope with the energy transition and zero emission energy. Homogeneous combustion compression ignition (HCCI) is an alternative combustion method. It is employed based on injecting well-mixed fuel and oxidizer streams, which are compressed until they reach the auto ignition point [303–305]. Various configurations should be investigated to enhance ammonia combustion efficiency with high loads and low emissions.

Gas turbines, they can generate energy from different fossil fuels for a long time; they are composed of compressors, combustors, and turbines. Various studies have been recently investigated by different research centers to tackle the challenges of using ammonia for power generation, such as Cardiff University's Gas Turbine Research Center (GTRC) utility-scale gas turbine with its high-pressure optical chamber (HPOC), King Abdullah University of Science and Technology (KAUST) in Saudi Arabia using HP facilities and high precision measuring techniques, collaboration of Tohoku University with the National Institute of Advanced Industrial Science and Technology (AIST) that included a micro gas turbine (MGT). One of the main goals of these laboratory research was to define the images of ammonia combustion flames at different operating conditions. Ammonia flames distribution in swirl burners with cylindrical liners is shown in Fig. 25. The most stable flame was obtained at a heating value of 13.2 kW that for experimental investigation of swirl number range of 0.736–1.27 [306]. Comparisons of several NH₃ flame images at different operating conditions, as well as the resulting methane flame generated from the same burner, are typically investigated. The effects of the inlet velocity and equivalence number on ammonia image flames are also indicated. The ammonia-rich mixture showed a brighter and orange color.

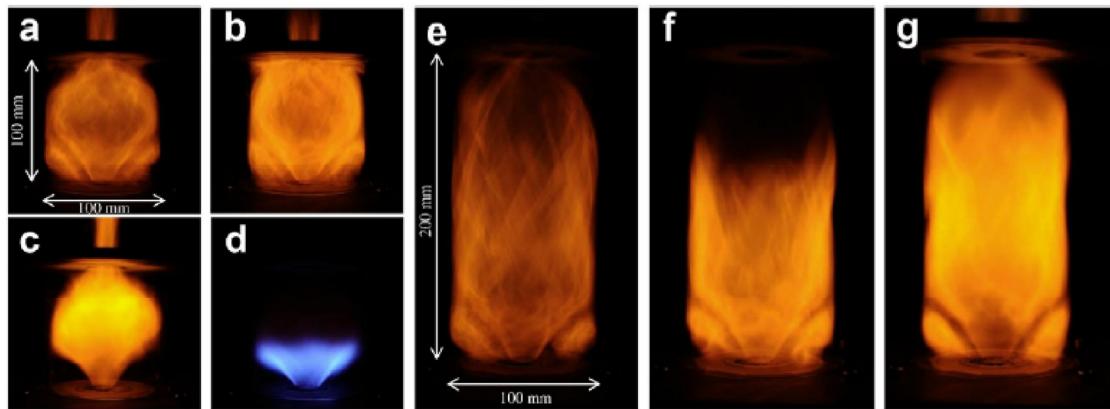


Fig. 25 – Swirl burner with cylindrical liners flame images. (A) NH_3/air flame, $\varphi = 1$, $h = 100 \text{ mm}$, and $U_{\text{in}} = 3.14 \text{ m/s}$ (B) NH_3/air flame, $\varphi = 1.2$, $h = 100 \text{ mm}$, and $U_{\text{in}} = 3.14 \text{ m/s}$ (C) NH_3/air flame, $\varphi = 1.2$, $h = 100 \text{ mm}$, and $U_{\text{in}} = 3.35 \text{ m/s}$ (D) methane/air flame, $\varphi = 1$, $h = 100 \text{ mm}$, and $U_{\text{in}} = 3.14 \text{ m/s}$ (E) NH_3/air flame, $\varphi = 0.8$, $h = 200 \text{ mm}$, and $U_{\text{in}} = 3.14 \text{ m/s}$ (F) NH_3/air flame, $\varphi = 1.2$, $h = 200 \text{ mm}$, and $U_{\text{in}} = 3.14 \text{ m/s}$ (G) NH_3/air flame, $\varphi = 1.2$, $h = 200 \text{ mm}$, and $U_{\text{in}} = 3.14 \text{ m/s}$ [306].

The flame images in the figure indicates aerodynamic features. Comparing equivalence ratios (φ) of 0.8, 1, and 1.2 of images e, f, and g, respectively, demonstrates the shortest flame length compared to rich and lean NH_3 combustion flames. The performance of nonpremixed combustion of ammonia-air and methane-air burned at high pressure has been compared in rich-lean, non-premixed environments in operating gas turbine combustors [307].

One of the important end uses of ammonia is gas turbines; it can be classified according to utilization as jet engines and stationary gas turbines. Poor results have been observed from

the injection of liquid ammonia instead of kerosene in jet engines. The vaporization of ammonia while maintaining the combustor wall at high temperature has enabled the maintenance of 93.5–94.5% efficiency [308]. Numerical simulation analysis of ammonia–air mixture combustion at different equivalence ratios is shown in Fig. 26. It has been reported that liquid ammonia is not efficient because of the major drop in total power output and combustion efficiency [309]. However, combustion efficiency is enhanced by using catalytic and vaporization ammonia combustion [309]. Experimental and numerical analysis methods have recently been addressed in

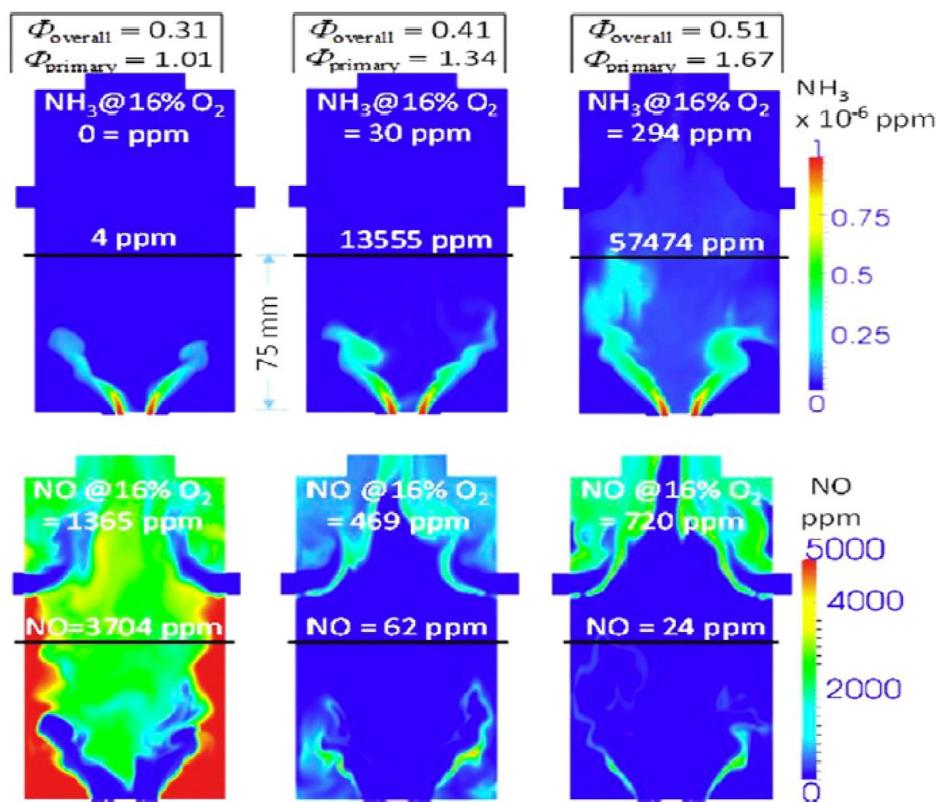


Fig. 26 – Ammonia and NO_x distribution of nonpremixed NH_3/air flame in terms of equivalence ratio [300].

a review paper [310]. Several research laboratories have been reported to contribute 44 articles in the field of ammonia as a potential fuel in gas turbines. Two suggested combustion stages, rich-lean combustion, have been demonstrated to minimize NO_x emission and unburned fuel. Further investigations are required to enhance the combustion of liquid ammonia to lower the start-up time and cost.

Furnaces and boilers, the industrial applications and residential sectors' energy consumption act greater than 50% of the total global energy consumption [311]. The industrial sector depends mainly on fossil fuels, including coal and natural gas; a small amount comes from renewable energy sources. Due to the world's energy transition into zero-carbon fuels or carbon neutrality, ammonia is considered the best alternative fuel candidate as a carbon-free energy carrier. Several studies have investigated ammonia utilization in furnace and boiler applications. Various difficulties are faced with ammonia utilization in furnaces and boilers, such as the characteristics of ammonia, flame stability, pollutant emissions, etc. The cofiring of ammonia in coal-fired plants has been studied in different experimental and numerical configurations [312–314]. It has been reported that the use of ammonia with coal reduce the CO_2 emissions, coal/ NH_3 co-combustion has been characterized in a 1.2 MW_{th} furnace [312]. The most significant factor controlling combustion behavior is furnace configuration. The coal combustion process was carried out in different steps from heating to devolatilization. Fig. 27 depicts the characteristics of coal combustion and the possibility of ammonia interaction. It was observed that the ammonia injection decreased the combustion flame temperature and had a positive effect on NO formation. However, ammonia injection in coal combustion leads to an increase in NO_x emissions, but the higher equivalence ratio and higher air staging strategy can achieve lower NO_x emissions. Ammonia usage as a potential fuel in the plant is attractive, but it is important to use a selective noncatalytic reduction to avoid NO_x production.

As discussed previously, the ammonia characteristic does not fit the standard configurations of combustors. Due to efficiency and pollutant targets, an innovative technology called fuel-flexible combustion technologies or MILD combustion has been developed. It has been characterized by different

stabilization mechanisms. The MILD combustion process was carried out by preheating reactants at temperatures higher than the autoignition temperature, which is called ignidiffusive or diffusion flame structures [316]. Ammonia MILD lean combustion conditions were reported to have stabilized at temperatures greater than 1300 K [317,318]. However, this technology is still on a laboratory scale and more investigations are required for more efficient cyclonic configurations.

The main experimental and numerical simulation results of ammonia combustion in SI and CI are summarized in Table (8). A very high ammonia mixing ratio has been used and tested by Yapıcıoglu and Dincer and Korean institute of Energy Research (KIER) [319,320]. The performance and key findings of ammonia blends of SI and CI engines have been presented at different operating conditions. Ammonia is added to hydrocarbon fuels as well as the combustion of ammonia in the presence of hydrogen are also presented.

Fuel cell applications

Hydrogen fuel cells have great potential to generate electricity from easy and cheaper applications; they can be combined with heat and power to raise electrical efficiency by 60% [334,335]. One of the most attractive end uses of ammonia applications is fuel cells. CSIRO has proposed an ammonia cracking pilot-scale unit using a hydrogen-permeable metal-based membrane for generating high-purity hydrogen from ammonia gas [22]. Fuel cells can be mainly classified according to electrolyte types, such as polymer electrolyte membrane fuel cells (PEMFC), molten electrolyte fuel cells (MCFC), SOFCs, alkaline fuel cells (AFC), etc. The fuel cell types of SOFCs, phosphoric acid (PAFC), and AFCs can be utilized with ammonia for power generation. Carbon-based fuels, such as methanol and ethanol, can generate a high amount of hydrogen [336,337] because carbon dioxide is generated from the synthesis process; therefore, these fuel types are not effective for fuel cells. Fuel cell applications depend on the fuel cell type and the fuel used. Fuel cells can generate a wide power range of 1–10 MW; therefore, the technical characteristics and energy efficiencies of various fuel cell technologies should be declared. Table 9 illustrates the comparisons between different parameters of fuel cell technologies. The advantages, applications, and system output power of fuel cell types were investigated. The operating temperature of the fuel cells versus the output power is shown in Fig. 28. The maximum output power was obtained at higher operating temperatures [338]. The SOFC fuel cell showed the highest output power at a larger operating temperature. The PEMFC fuel cell type can be used in stationary and portable applications.

The advantages of using ammonia in fuel cell applications include no environmental impact with a carbon-free system, the cost of ammonia as fuel is relatively low compared with other fuels, and ammonia leakage can be detected easily from its odors, making ammonia safer than hydrogen [339–342]. The SOFC fuel cells can direct decomposed ammonia into hydrogen and nitrogen at a high operating temperature of 600–800 °C; it can generate electricity at high efficiency [289]. The fuel cell cost and efficiency are significant factors in the selection of fuel cells. The costs of commercial fuel cell systems in cogeneration heat power plants (CHP) are presented in

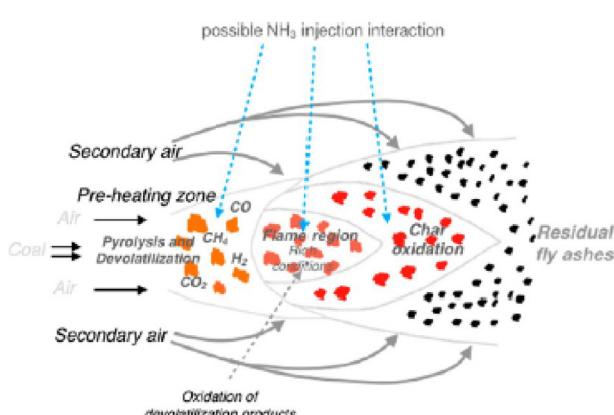


Fig. 27 – Coal combustion characteristics interacting with ammonia [315].

Table 8 – The performance and key findings of recent NH₃ blend in SI and CI engines.

a Performances of various NH ₃ blends in the SI engine.				
Tested fuels	Baseline	Operating Conditions	Key findings	Ref.
Gasoline/ammonia	Gasoline	1600 RPM CR = 8 IMEP ~550 kPa	Gasoline power% > 40%, combustion duration ↓ 10°. Gasoline power% < 30%, COV IMEP >5%, η ↓ 5%. Gasoline power % < 30%, COV IMEP >5%, η ~30%.	[321]
Methanol/gasoline/NH ₃ 20 vol %)	Methanol/gasoline (Methanol	NH ₃ vol% ~23% >35m00 RPM	Brake torque ↑. Brake effective mean pressure ↑.	[322]
Ethanol/gasoline/NH ₃	Ethanol/gasoline (Ethanol 10 vol %)	NH ₃ vol% ~6% >3500 RPM	Brake torque ↑. Brake effective mean pressure ↑.	[322]
NH ₃ /40–60% H ₂	NH ₃	CR = 10	Combustion efficiency constant at H ₂ mole fraction (α)>60%	[323]
NH ₃ /0–60% H ₂	NH ₃	1500 RPM	Maximum efficiency at low and moderate H ₂ addition	[324]
40%NH ₃ /60%H ₂		CR = 13.8	retarded spark timing and a high hydrogen ratio	[325]
Performances of various NH ₃ blends in CI engine.				
Biodiesel/ammonia	Diesel	1600 RPM Full load	Smoke ↓ ~25%. NOx ↓ ~100 ppm. CO ↓ ~40%.	[326]
DME/ammonia	DME	1000–2000 RPM Inlet air temperature = 25 °C Brake torque = 98 Nm DME vol% = 60% 2500 RPM Brake effective mean pressure = 0.32 MPa SOI = 160° bTDC DME vol% = 60% 2200 RPM Brake torque = 6.47 Nm SOI = 30°bTDC H ₂ vol % ~11%. 1500 RPM Indicated mean effective pressure = 4 bar.	BSFC ↑ ~0.03 kg/kW-hr. CO ↑ ~50 ppm (2000 RPM). NO ↑ ~60 ppm (2000 RPM). HRR ↑ ~5 J/°CA. NO ↑ 3 g/kW-hr. CO ↑ 10 g/kW-hr. HRR ↓~3 J/°CA. $\dot{m}_{\text{pilot}} \approx \dot{m}_{\text{main}}$, HRR ↑ ~20 J/° CA (DME 80 vol%).	[327] [328] [329]
H ₂ /ammonia	Diesel		η H ₂ /NH ₃ ≈ η diesel. HC and CO ↓~7.5%. NO _x was marginally higher than ULSD engine.	[330]
Diesel/ammonia	Diesel	Diesel power% = 60%. 1000 RPM 40 kW output power	NH ₃ wt. % ↑, ignition delay ↑, combustion duration ↑. BSFC ↑ 380 g/kW-hr. Brake power ↑ 15 kW. CO ↑ 60 g/kW-hr. NO ≈ NO diesel	[331]
NH ₃ (via fumigation)/100% diesel; NH ₃ (via fumigation)/50% diesel + 50% kerosene	Diesel	3600 RPM Rate power 75 kW	Nitrogen oxide emissions depend on combustion temperature, ammonia quantity and kinetics	[332]
NH ₃ /DEE	95–80% NH ₃ /5–20% DEE	CR up to 16.8	As little as 10% DEE in the NH ₃ /DEE blend produced an enhancement of pure ammonia laminar burning velocity by ~ 120%	[333]

^a CR: is the compression ratio, IMEP: indicated mean effective pressure, η: combustion efficiency, DME: Dimethyl Ether, BSFC: Brake Specific Fuel Consumption, HRR: heat release rate, SOI: start of ignition, and DEE: Diethyl Ether.

Table 9 – Comparison of fuel cell technologies.

Fuel cell type	Operating temperature (°C)	Fuel	Cell voltage	System output (kW)	Electrical efficiency (%)	Combi ned heat and power (CHP) efficiency	Applications	Advantages
Alkaline (AFC)	90–100	Pure H ₂	1	10–100	60	>80	Military; space	Faster cathode reaction in alkaline electrolyte leads to higher performance; can use a variety of catalysts
Phosphoric acid (PAFC)	150–200	Pure H ₂	1.1	50–1000	>40	>85	Distributed generation	Higher overall efficiency with CHP; increased tolerance to impurities in hydrogen
Solid oxide (SOFC)	600–1000	H ₂ , CO, CH ₄ , other	0.8–1	<1–3000	35–43	<90	Auxiliary power; electric utility; large distributed generation	High efficiency; fuel flexibility; can use a variety of catalysts; solid electrolyte reduces electrolyte; management problems; suitable for CHP, Hybrid/GT cycle
Molten carbonate (MCFC)	600–700	H ₂ , CO, CH ₄ , other	0.7–1	<1–1000	45–47	>80	Electric utility; large distributed generation	High efficiency; fuel flexibility; can use a variety of catalysts suitable for CHP
Polymer electrolyte membrane (PEMFC)	50–100	Pure H ₂	1.1	<1–250	53–58	70–90	Backup power; Portable power; small distributed generation; specialty vehicle; transportation	Solid electrolyte reduces corrosion and electrolyte management problems; low temperature; quick start-up
Direct methanol fuel cell (DMFC)	60–200	CH ₃ OH	0.2–0.4	0.001–100	40	80	Replace batteries in mobiles; computers and portable devices	Reduced cost due to absence of fuel reformer

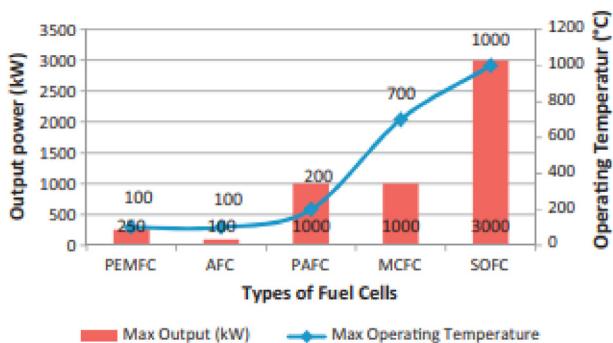


Fig. 28 – Fuel cell types' maximum operating temperature and output power [338].

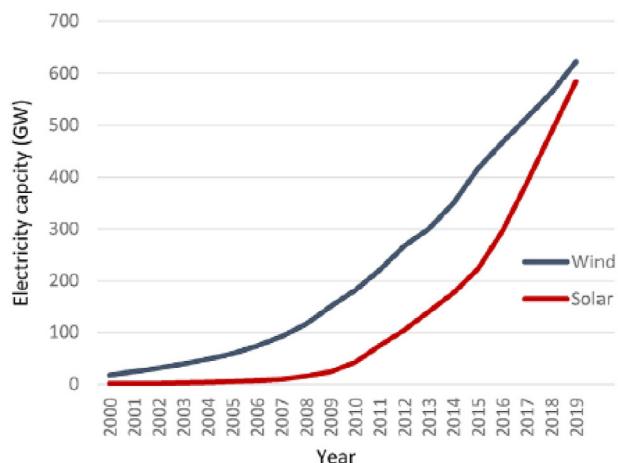


Fig. 29 – The wind and solar power capacities in the world [349].

Table 10 – Commercial fuel cell costs in CHP plants [343].

Items	PEMFC (BPS) ^a	PAFC (ONSI) ^b	MCFC (MTU) ^c	SOFC (SWPC) ^d
Electrical power (kWe)	250	200	280	100
Efficiency (%)	34	38	48	47
Specific cost (€/kWe)	~10,000	~5000	~8000	~20,000

^a BPS: Ballard Power System, e.g., BEWAG Berlin 250 kWe PEMFC, natural gas, cogeneration.
^b ONSI: 200 kWe PAFC, natural gas, cogeneration.
^c MTU: Hot module, e.g., Stardwerke Bielefeld, RWE, 250 kWe MCFC, natural gas, cogeneration.
^d SWPC: Siemens Westinghouse Power Corporation, 100 kWe SOFC, cogeneration.

Table 10. The electrical power of fuel cells has typically been reported in the range of 100–300 kW [343–347].

Another alternative ammonia fuel cell method is using direct ammonia fuel cells (DAFCs) as a power generation source. Ammonia is oxidized into N₂ with better performance and without NO_x emission. It can be used in mobile applications with moderate temperatures [348]. More investigations are needed for controlling NO_x emission from SOFCs and DAFCs fuel cell applications. Finally, the cost of ammonia as a fuel and its properties are compared with other traditional fuels in Table 11.

Perspectives on future end-use energy and conclusions

Shifting to renewable energy sources should be substantially increased to decrease the environmental impact of fossil fuel applications. Fig. 29 presents the capacities of solar and

renewable energy sources around the world. The output electricity capacity and production have been raised from solar and wind energy [349]. Both solar and wind energy are influenced by environmental nature; the resulting power cannot be accurately predicted, causing a variation between production and peak demand [350]. The energy production cost from solar and wind energy is still high, and so are predicted difficulties. It is important to raise awareness of GHG emissions' impact on humankind and the increase of environmental crisis that will lead to more investment in renewable energy sources.

Fig. 30 shows the overview of the future of global energy transmission from production to end use. The energy flow diagram illustrates that renewable electricity will be used by humans. It will also be used as a renewable energy source to generate hydrogen from water electrolysis technologies and other technologies. Moreover, the charging of electric vehicle batteries (BEVs) will be implemented using renewable electricity. The transition process to zero-carbon energy systems is too difficult; global energy transitions will gradually decay from carbon fuels to zero-carbon fuels. This transition of energy will mainly depend on how rapidly low-cost technology meets carbon neutrality. Hydrogen can be directly used in transportation applications (FCEVs) as a carbon-free energy carrier. Hydrogen energy is considered the best solution for energy transmission, but transportation and storage costs are exorbitant. The global availability of electricity has risen to 85% of the world's total population, which means that about 1.1 billion people around the world are still without electricity. Also, about 3 billion people use fuels that pollute the environment [351]. Different scenarios of the primary world energy demand have been investigated [351].

Table 11 – Ammonia cost and properties compared with fossil fuels [63].

Fuel	Pressure (bar)	Density (kg/m ³) at 15 °C	LHV (kWh/kg) at 25 °C	Cost (USD/kg)	Cost (USD/kWh)
Ammonia	10	603	5.18	0.3	0.058
Diesel	1	846	12.1	1 (USA)	0.083
LPG	14	388	12.6	1 (Germany)	0.079
Gasoline	1	736	12.1	1.81 (Japan)	0.15
Bunker fuel	1	980	10.8	0.59 (Global average)	0.055

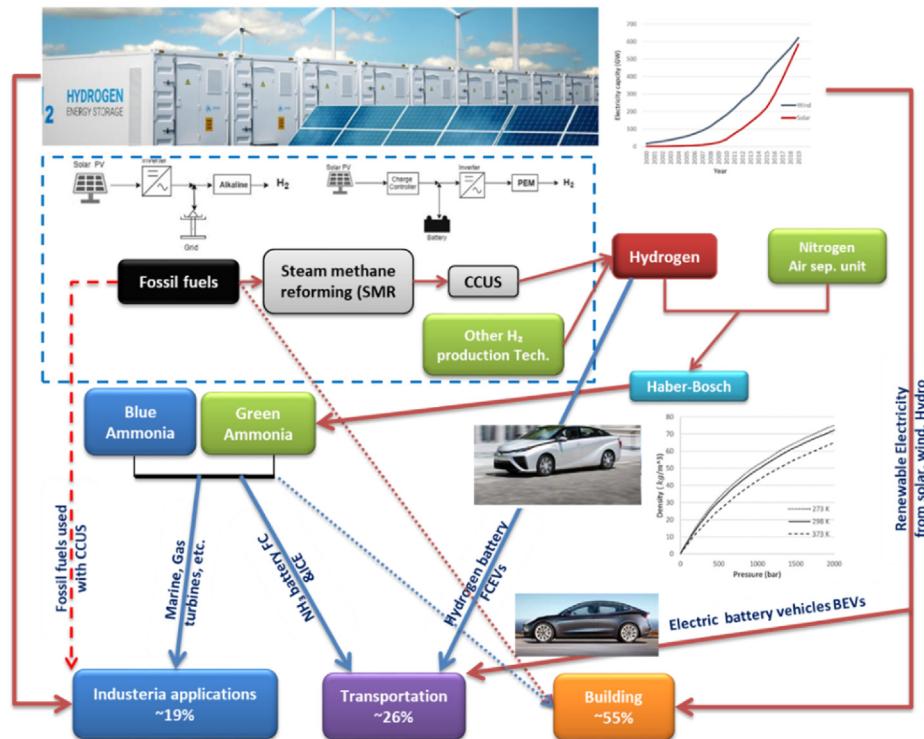


Fig. 30 – Overview of the future of the global energy transition from production to end use.

Fig. 31 demonstrates the world energy demand by fuel and CO₂ emissions scenario. These scenarios consider all aspects of global energy systems. It was clear all fuels' contributions with expectations of decreasing the coal, oil, NG, and nuclear power demand and increase depending on the renewable energy systems to meet the goals of sustainable development for CO₂ emissions [351]. Therefore, carbon fuels can still be seen to participate in global energy despite the sustainable development plans for global energy transitions. We think that the energy transition policies will be made by all countries, but a great plan to share knowledge and technology is required. More efforts should be made to create a real carbon-free world.

The hydrogen density versus pressure was measured at three different temperatures, as shown in Fig. 32. One of the critical challenges of hydrogen usage is that it needs to be stored in a HP tank (~700 bar) to be enabled using in FCEV applications. Moreover, the characteristics of the required energy for the world are that they should carbon-free, safe, and cost-effective large-scale alternative fuels. The most important parameters of energy problems are the lack of linkage between climate change or GHG emissions and energy access; in addition, millions of people around the world do not have sufficient energy to access.

Ammonia can enable transmission from conventional energy to renewable energy or carbon-free sources in the future.

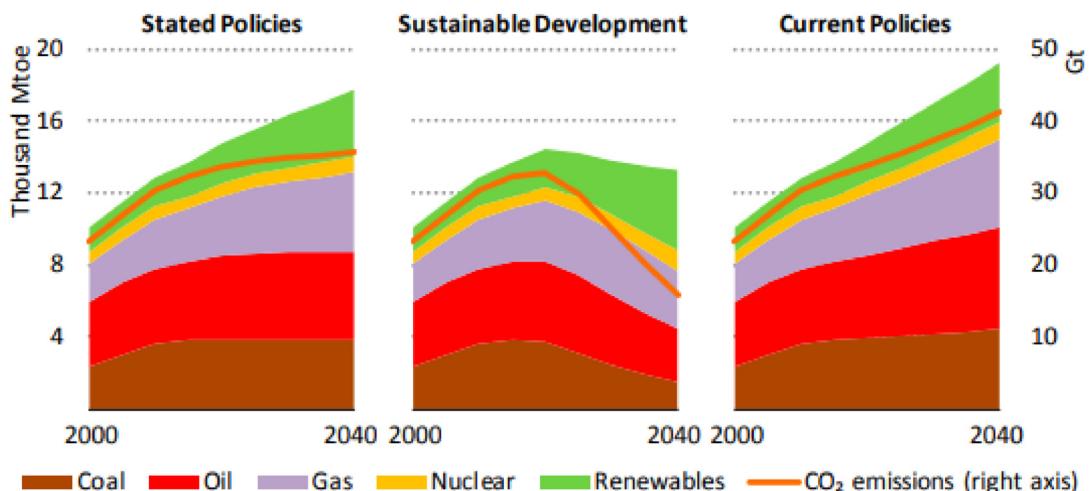


Fig. 31 – World's primary energy demand by fuel and CO₂ emissions scenario [351].

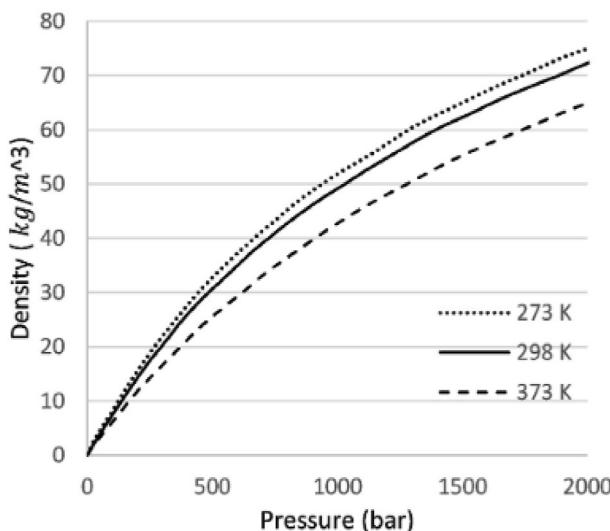


Fig. 32 – The volumetric density changes of $n\text{-H}_2$ (normal hydrogen) with respect to pressure change at different temperatures [352].

Ammonia can be the link to the climate change energy transition challenge in the form of chemical energy storage as the key to renewable carbon-free technology. Further, the main challenges of global warming and climate change are concluded in the energy transition, real evaluation of current energy status, and introduction of new and innovative energy technologies. Ammonia, as discussed previously, can become the key to the transition to renewable energy. More international collaboration is needed to develop ammonia usage as a clean energy carrier; it can currently be used as fuel in marine, gas turbines, etc., as well as in battery storage. Ammonia can be easily transported and stored as a liquid at low pressure (10 bar) and ambient temperature compared to hydrogen storage, which means that ammonia is low energy-intensive and cost-effective. Therefore, a vast amount of global research and development should be implemented to enhance ammonia utilization as an alternative clean energy carrier. The third RD20 conference elaborated a leader statement for carbon neutrality by 2050, and it was supported by R&D sectors [353].

The requirements to have a clean environment and clean energy carrier can be achieved by sharing knowledge, objectives, global collaboration, sharing technology, more commitment and cooperation to invest and help increase energy access for million people around the world, transition to carbon-free technologies, a new shared strategic plan for renewable energy applications, and accelerating the application of successful renewable energy technologies. The suggested future global energy transition in the current study has emerged with a conclusion that ammonia can be safely applied in all applications of human use with some considerations and more investment from governments. Sustainable energy can be achieved by using ammonia as clean energy alongside hydrogen and fossil fuels, with carbon dioxide recovery and decomposition.

Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ijhydene.2022.09.061>.

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