Lecture Notes in Energy 91

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Ammonia Energy Technologies

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Preface

We are in a critical era where increased levels of carbon dioxide emissions, global warming issues and local and global climate change problems require urgent responses and hence immediate actions. The way that energy is produced, stored, converted and consumed directly affects these issues and problems. One thing is clear that energy consumption has been increasing exponentially in the world due to the increasing population and demand, technological advancements and increased life standards and comfort requirements. Almost everyday, new energy-intensive technologies, systems and applications for various sectors, including transportation sector, are entering into our daily routines, which drastically increase the fuel and power requirements for economic activities and societal developments. Such needs have greatly impacted the energy equation with various constraints related to the environment, health and sustainable development will continue to do so in the next decades. It is now terribly necessary to set up the energy equation without hydrocarbon fuels which is fully recognized by many researchers, scientists, organizations, companies, etc. A new era is now on where it is really time to move for renewables and carbon-free fuels (particularly with hydrogen and ammonia). Today, hydrogen energy technologies are offering a promising option to solve energy and environmental-related issues. Therefore, governments, agencies, companies and local authorities have been developing new strategies and policies particularly for hydrogen economy and implementing them accordingly. However, such a transition brings high costs for investment, research, development and innovation as well as technology developments. It is better to go one step ahead of hydrogen to consider ammonia as a unique option to better achieve the hydrogen economy, which will serve as a shortcut solution in this transition to hydrogen economy.

This book is an outcome of a comprehensive project on ammonia utilization and aims to cover all necessary information regarding ammonia from production to utilization, particularly including the entire life cycle. Firstly, some introductory information regarding hydrogen and ammonia and their productions along with numerous energetic, environmental and economic dimensions are provided and discussed thoroughly. Secondly, there is a strong focus on ammonia production methods along with ammonia storage techniques. Thirdly, there are case studies presented on the methods of ammonia utilization with various scenarios. The methods for analysis of ammonia energy systems will be introduced with the illustrative examples. Furthermore, the book covers detailed modeling and analysis studies, experimental investigations and life cycle assessment studies. Finally, the concluding remarks and future directions of ammonia energy technologies, in addition to the potential developments in the area, are discussed.

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Contents

Chapter 1
Ammonia

Nomenclature

CCUS	Carbon capture utilization and storage
CNG	Compressed natural gas
CO	Carbon monoxide
DME	Dimethyl ether
GJ	Gigajoule
ICE	Internal combustion engine
IEA	International Energy Agency
kJ	Kilojoule
LHV	Lower heating value
LNG	Liquified natural gas
LPG	Liquefied petroleum gas
MJ	Megajoule
NO_x	Nitrate oxides
PM	Particulate matter
SCR	Selective catalytic reduction
SO_2	Sulfur dioxide
VOC	Volatile organic compounds

1.1 Introduction

The need for fossil fuels has risen drastically with the increases of population and human activities as well as technological developments. Although there were some concerns as we will run out of these sources, (as they have been depleted so fast), increased levels of greenhouse gas emissions, particularly CO_2 emissions, have brought global warming and climate change issues forefront, due to the excessive

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consumption of fossil fuels. Although the unconventional fossil fuel sources are four times higher compared to conventional fossil fuels, those sources are located at extreme geographic formations and may require advanced technologies and their extraction costs are much higher [1].

Not only the depletion of fossil fuels, but also the environmental effects of using these fuels are one of the main reasons to turn onto alternatives due to the fact that the emissions resulting from the extensive consumption of fossil fuels have also causing harms on the environment. The CO, NO_x, VOC, SO_2 and PM emissions caused by the transportation sector in Canada were 53.9, 51.7, 15.9, 1.6, and 2% in 2017, respectively [2]. Depletion of ozone layer, photochemical smog formation, acid rains, and chronic respiratory diseases are caused by those gases.

The systems should be evaluated in detail from source to end use to reduce environmental problems caused by energy production and to develop a truly sustainable approach. For this reason, a 3S concept (Source-System-Service) which was wisely introduced by Prof. Ibrahim Dincer in various conferences and formally published in Dincer and Acar [3]. This 3S concept covers the energy spectrum from source to system and system to service. Here, it is important to emphasize for any energy application, a source is needed, and for the targeted application we need commodities which are treated under services. Once we identify the source(s) and services, we need to design the systems to cover the needs by using the sources. This is illustrated in Fig. 1.1, by adopting this methodology, there are now three steps that should be assessed accordingly:

- Source: Identifying a clean, abundant, economically feasible, and available energy source.
- System: Developing a right system based on what sources are available and what useful outputs are needed by the users and/or communities.
- Service: Determining the needs, in terms of power, heat, cooling, freshwater, fuel, etc., for the targeted application.

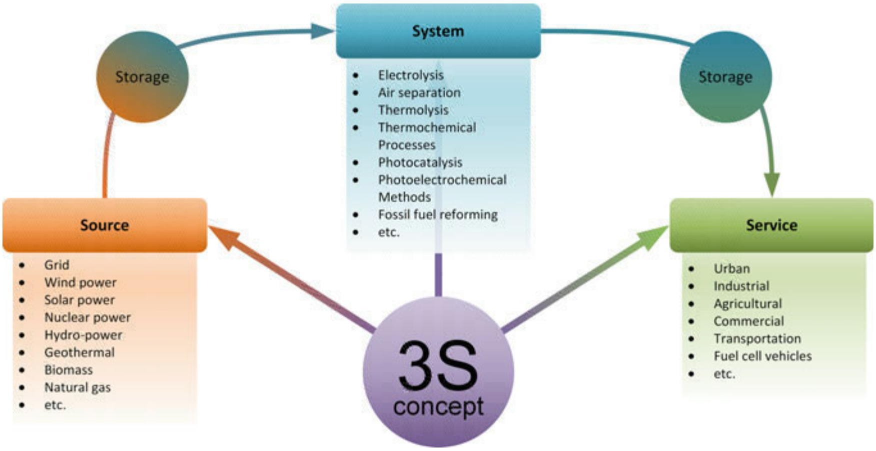

Fig. 1.1 3S concept for sustainable energy systems

For this reason, fuel alternatives such as natural gas, hydrogen, methanol, and ammonia has become one of the main topics of researchers. There are studies for various types of compounds that can be an alternative to fossil fuels or to reduce fossil fuel consumption. In addition to the use of fuels such as methanol, hydrogen, ammonia alone in the engines, there are studies in which these fuels are used by mixing with conventional fuels such as diesel and gasoline.

Ammonia is recognized as a colorless gaseous molecule under normal conditions and has a distinctive odour. Three hydrogen and one nitrogen atoms form a polar structure to create ammonia. Ammonia was discovered for the first time in history as ammonia salt near the temple of Jupiter Ammon in a region of Libya. The name ammonia derives from the name of the temple, Ammon [4]. Ammonium chloride salt, *sal ammoniac*, is a chemical known and used since ancient times. Salt derivatives of ammonia are found in nature, especially in regions with volcanic activities. These substances are formed with the decomposition of nitrogen-containing organic materials in volcanic regions. Also, ammonium salts can be found near coal deposits.

Ammonia and ammonium ions are generally released to nature because of biological activities in every water source where there is life, and they function as an important component of the nitrogen cycle. Figure 1.2 summarizes the nitrogen cycle in nature. The nitrogen cycle is essential for the continuation of life. Ammonia is formed by the decomposition of nitrogen-containing organic materials, and then converted to nitrate derivatives through bacterial activities to be used as nutrients by plants [5].

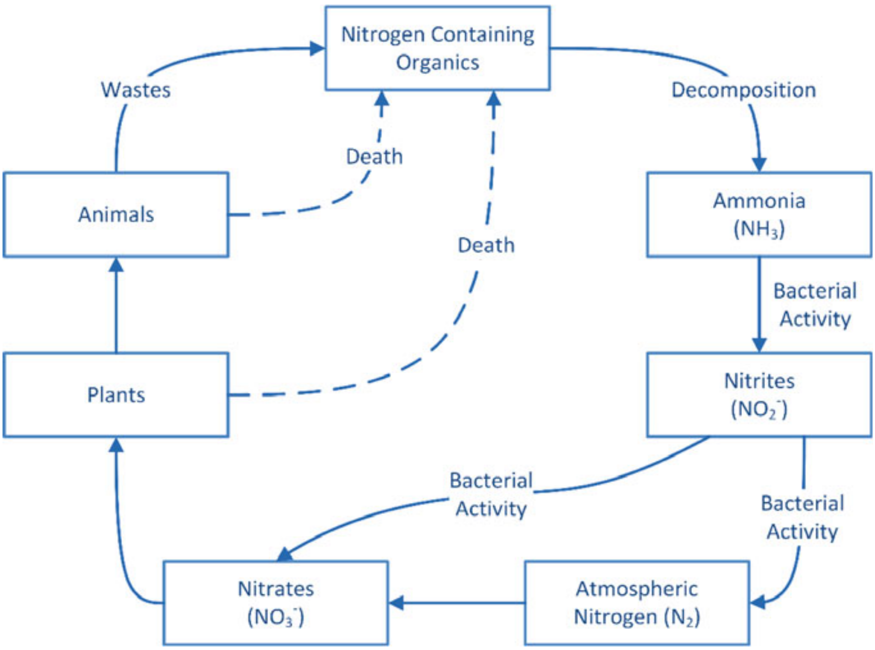

Fig. 1.2 The nitrogen cycle in the nature (modified from [5])

The industrial production of ammonia essentially began with the discovery of the Haber–Bosch reactor, which produces ammonia catalytically under high pressure and temperature, by the German chemists Fritz Haber and Carl Bosch. About 235 million metric tonnes of ammonia was manufactured by the industry in 2019 [6]. The energy spent for the production of ammonia in 2021 corresponds to 2% of the global energy consumption [7]. Ammonia is utilized as a feedstock in chemical and fertilizer production. Only a minor fraction is used in direct applications. A simplified life cycle of ammonia describing its production sources, methods and application areas is given in Fig. 1.3. Today, industrial production of ammonia is carried out with modified versions of Haber–Bosch process. Nitrogen is provided from the air using various technologies. Carbon-free nitrogen production can be achieved through renewable energy sources. However, carbon emissions from the Haber-Bosch process are mainly caused by hydrogen production. Industrial hydrogen production relies on fossil-fuel based technologies such as steam methane reforming and coal gasification. Although near-zero carbon emissions can be achieved with carbon capture utilization and storage (CCUS) technologies, electrolysis, and other clean hydrogen production technologies, those technologies increase the ammonia production costs.

Figure 1.4 shows the market share of exports for ammonia in 2019. China, Russia, Middle East and the US are the largest producers of ammonia [8]. However, most of the ammonia produced in those countries utilized by domestic sources. On the other hand, Saudi Arabia, Russia, and Trinidad and Tobago are the largest ammonia exporting countries. The export price of ammonia per ton varied between $230 and $470 in 2019, and the world average was $286 [9]. However, energy and ammonia production costs have increased drastically due to Russia's attack on Ukraine in 2022. It is known that a total of 96% of ammonia is globally produced by the Haber–Bosch processes, and CO_2 emissions are estimated to account for 1.2% of total anthropogenic emissions [10]. These emissions mainly originate from hydrogen production technologies that utilize fossil fuels and the heating requirements of the process.

In summary, ammonia is a chemical that can be used in many sectors and for many different purposes. Although the utilization of ammonia is vastly in agricultural sector, it is an important feedstock for many chemical products. And also, it could be the key to finalize the ever-increasing search for an alternative clean fuel, since it does not contain carbon.

1.2 Ammonia and Its Importance

Ammonia is a crucial part of the life cycle, due to its nitrogen content. Nitrogen is an essential component of biochemical processes. It is one of the basic building blocks to produce chlorophyll in plants and the production of amino acids and enzymes in living beings. For this reason, ammonia and fertilizer products produced from ammonia are needed for the growth of plants in the agriculture sector. Aside from

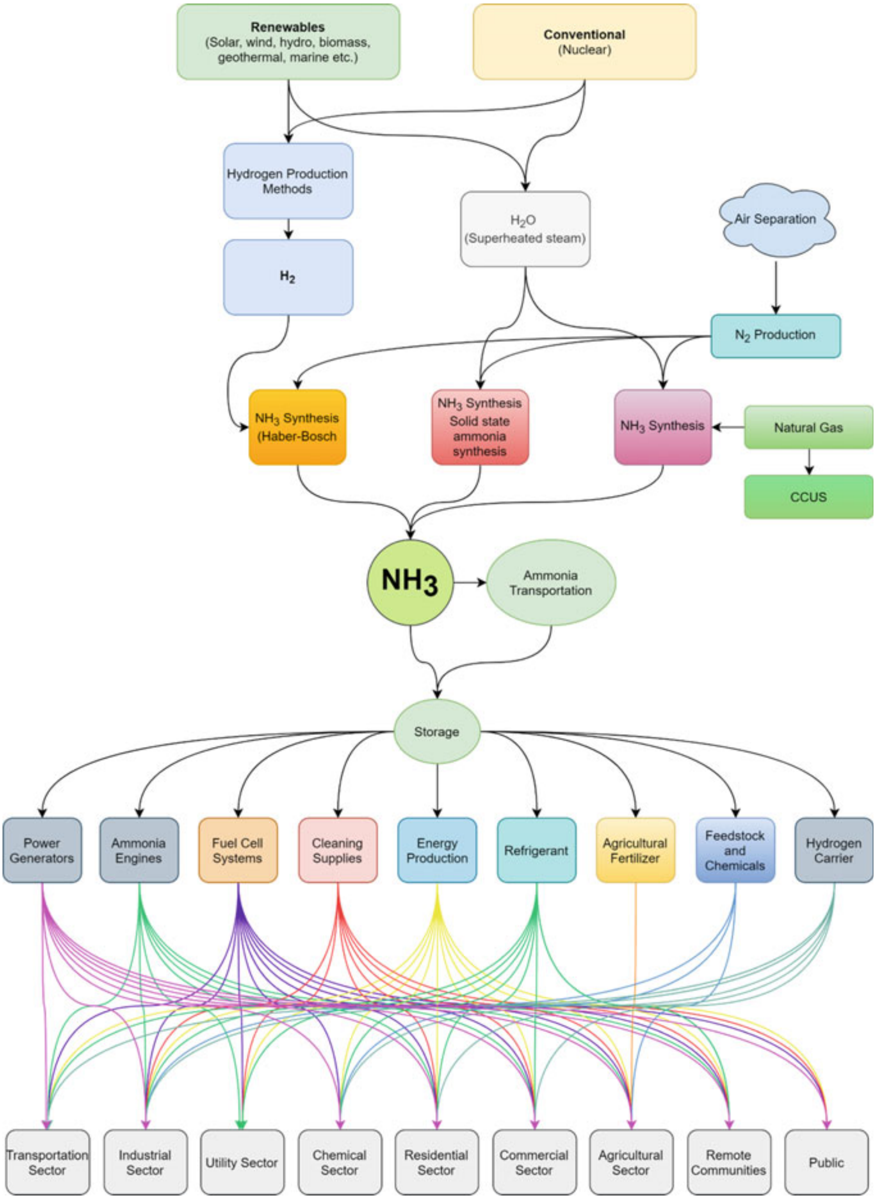

Fig. 1.3 Cradle-to-grave life cycle of ammonia

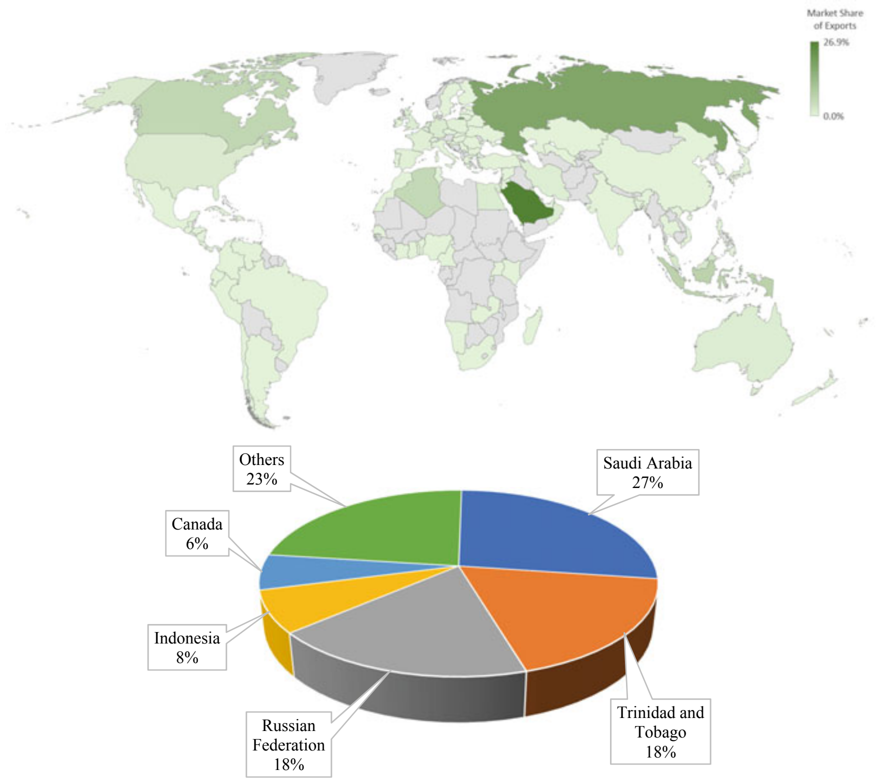

Fig. 1.4 Ammonia export market share by countries in 2019 (data from [8])

fertilizers, ammonia is used in the chemical industry to produce derivatives such as nitric acid, nitroglycerin for dynamite production, acrylonitrile and caprolactam for fiber production.

Ammonia is also considered as an excellent hydrogen carrier, with the recent shift to zero-emission vehicles in the fight against climate change. To transport the hydrogen properly, it must be stored under high pressure. Hydrogen is compressed under 200 bar to transport using the tube-trailers. For fuel cell devices, hydrogen refueling stations are expected to operate at high pressures such as 350–700 bar. Cryogenic liquefaction at −123.15 °C and below should be performed to store hydrogen at 700 bar [11]. Liquefaction process increases the operating and transportation costs of hydrogen production and storage systems. Therefore, ammonia emerges as a good alternative as a hydrogen carrier. Ammonia turns into liquid under atmospheric conditions at −33 °C. Also, its auto ignition temperature is higher than hydrogen, and it can be easily detected in the environment with its pungent, sharp odor.

In addition, ammonia has the potential to be a working fluid for thermodynamic cycles, including heat engines (such as Rankine cycles). Note that cooling/refrigeration, heating, electricity production, and combination of those cycles can easily be done in an integrated fashion by utilizing ammonia. Furthermore, it can be utilized as fuel in internal combustion engines, power generators, gas turbines, etc. Some key facts about ammonia can be listed as follows:

- Ammonia molecule has one nitrogen and three hydrogen atoms in its structure. Nitrogen can be obtained with air separation, and the hydrogen can be obtained either from conventional fossil fuel based production methods or from clean hydrogen production technologies with renewable resources.
- Ammonia is the second major chemical that is produced globally.
- The physical properties of ammonia (and three hydrogen atoms in its structure) make it an excellent hydrogen carrier. Also, it has no carbon atom in its structure thus makes it a zero-carbon and sustainable option.
- Making ammonia life cycle carbon free requires clean hydrogen production where renewable sources are deployed.
- Ammonia can be utilized in gas or liquid phases, also some of the derivatives of ammonia can be stored in solid phase.
- Ammonia can be stored utilizing relatively low pressures compared to hydrogen, thus making it easier to transport.
- Ammonia can be transported with existing stainless-steel pipelines with minimum maintenance requirements.
- Ammonia can be utilized in ammonia fuel cells directly, or in combustion engines with modifications.
- Ammonia can be used as a refrigerant in various applications.

Compared to hydrogen, the transportation costs of ammonia are lower. Special cooling systems and tank designs are required to transport liquid hydrogen due to safety concerns. While the density of liquefied hydrogen is 70.85 kg/m^3, this value for liquefied ammonia is 609 kg/m^3 at 20 °C under 10 bar. Figure 1.5 shows the seaborne transport costs for ammonia and hydrogen. While the transportation price for liquefied hydrogen is around 0.12 US$/t km, this value may become about 0.03 US$/t km for ammonia.

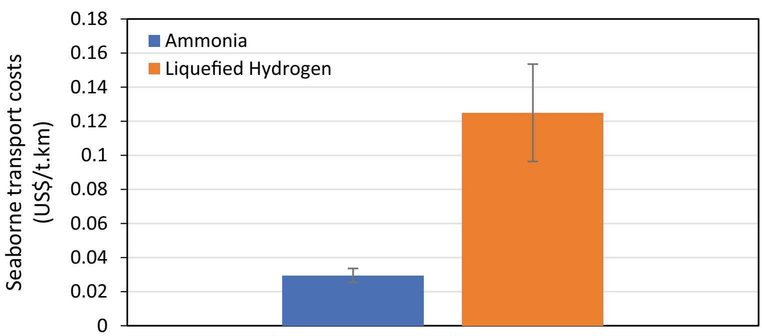

Fig. 1.5 Seaborn transport costs for ammonia and liquefied hydrogen (data from [12])

1.3 Ammonia and Its Properties

Ammonia consists of 17.6% hydrogen and 82.4% nitrogen. Approximately, one liter of ammonia contains 0.137 kg of hydrogen, which is higher than most of the chemicals. A detailed information on various chemicals and their hydrogen content was given in Table 1.1. The energy density of ammonia is 13.6 GJ/m^3 at 10 bar. Table 1.2 shows the comparison of various properties of ammonia with other types of fuels. Its energy density is very close to methanol; however, its specific energetic cost is low compared to methanol. At the same time, the hydrogen content makes the ammonia a suitable hydrogen carrier. Hydrogen is an excellent clean fuel, albeit utilizing hydrogen as an energy carrier has its difficulties. Liquefaction of hydrogen requires high energy. Also, providing adequate safety standards for transportation and storage of hydrogen is harder than ammonia. Hydrogen's liquefaction temperature is −253 °C. However, ammonia can be liquified at −33 °C and can be stored under room temperature without additional cooling unlike hydrogen. Although hydrogen has the highest higher heating value among other fuels, its energy density is very low. The autoignition temperature of ammonia is 651 °C. The flammability limit is in the range of 16–25% in air, making ammonia a safer hydrogen carrier [13].

Ammonia can be produced using fossil fuels such as heavy fuel oil, coal, coke oven gas, refinery gas, and natural gas. Note that a total of 72% of ammonia is produced worldwide by steam reforming of natural gas, and 22% of ammonia is produced by coal gasification as shown in Fig. 1.6. The rest 6% of ammonia is produced using other feedstock such as fuel oil, naphtha etc. Among the several methods of ammonia production, steam methane reforming is currently the least energy intensive technique. Coal is widely employed in China and is often associated with high energy intensities. The cost of natural gas is 70–90% of the cost of producing ammonia. Because ammonia production is based on natural gas in the SMR process, as natural gas prices rise, so the do ammonia production costs [15].

Table 1.1 Hydrogen content of various fluids (Modified from [16])

Carrier	H_2 in one liter of liquid (kg)	Energy to release one kg of H_2 (kWh)
Ammonia	0.137	6.3
Dodecahydro-N-ethylcarbazole	0.055	7.6
Formic Acid	0.053	4.3
Methanol	0.149	6.7
Perhydro-benzyltoluene	0.055	9
Perhydro-dibenzyltoluene	0.057	12.7
Toluene	0.047	11.2
Water	0.112	50.4

Source Davies et al. [16]

Table 1.2 Comparison of ammonia with other fuel types

Properties	Gasoline	Diesel	LPG	CNG	Gaseous hydrogen	Liquid hydrogen	Ammonia
Formula	C_8H_{18}	$C_{12}H_{23}$	C_3H_8	CH_4	H_2	H_2	NH_3
Lower heating value (MJ/kg)	44.5	43.5	45.7	38.1	120.1	120.1	18.8
Flammability limits, gas in air (vol.%)	1.4–7.6	0.6–5.5	1.81–8.86	5.0–15.0	4–75	4–75	16–25
Flame speed (m/s)	0.58	0.87	0.83	8.45	3.51	3.51	0.15
Autoignition temperature (°C)	300	230	470	450	571	571	651
Minimum ignition energy (MJ)	0.14	N/A	N/A	N/A	0.018	N/A	8
Flash point (°C)	− 42.7	73.8	− 87.7	− 184.4	N/A	N/A	− 33.4
Octane	90–98	N/A	112	107	> 130	> 130	110
Fuel density (kg/m^3)	698.3	838.8	1898	187.2	17.5	71.1	602.8
Energy density (MJ/m^3)	31,074	36,403	86,487	7132	2101	8539	11,333
Latent heat of vaporization (kJ/kg)	71.78	47.86	44.4	104.8	0	N/A	1369
Storage method	Liquid	Liquid	Comp. liquid	Comp. gas	Comp. gas	Comp. liquid	Comp. liquid
Storage temperature (°C)	25	25	25	25	25	− 253	25
Storage pressure (kPa)	101.3	101.3	850	24,821	24,821	102	1030
Cost (US$/l)	1.19	1.49	0.79	0.57	1.16	1.18	0.85
Cost (US$/MJ)	0.038	0.041	0.009	0.080	0.552	0.138	0.075

Source Erdemir and Dincer [14]

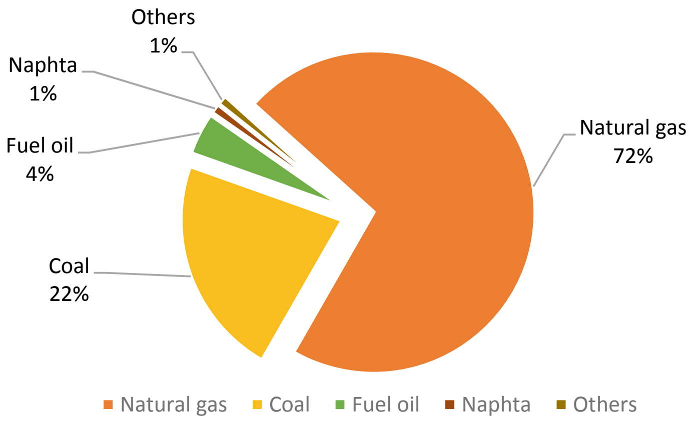

Fig. 1.6 Sources of global ammonia production based on feedstock use (data from [17])

1.4 Sectoral Ammonia Utilization

Ammonia has a wide range of possible applications in many sectors, including agriculture, transportation, power generation, refrigeration, food, chemical, petrochemical, etc. for various useful commodities. It is been using as a refrigerant, fertilizer, cleaning agent, hydrogen carrier, nitrogen source for fermentation and many more, as depicted in Fig. 1.7. In 2019, global ammonia production was around 235 M tonnes, thus making ammonia the second most-produced chemical after sulfuric acid [6]. Figure 1.8 shows the market share of ammonia. Today, almost a total of 80% of ammonia production is supplied to the agricultural sector by fertilizer use. Also, ammonia is used in many production pathways such as polyamide, nitric acid, nylon, explosives, pharmaceutical production. Ammonia can be used directly as fertilizer, or it can be used to produce ammonium nitrate, ammonium sulfate, ammonium hydrogen phosphate, and urea by using different processes. Although it has the highest nitrogen content as a percentage, ammonia is not preferred as fertilizer, except in the United States. The reason for this can be listed as the presence of ammonia as a gas under normal conditions, storage conditions, environmental and health risks. For this reason, ammonia derivatives containing ammonium are preferred in the rest of the world [18].

As noted earlier, ammonia is a zero-carbon fuel that can be used in transportation sector. It has no global warming potential throughout the usage phase. Besides to its desirable features as a fuel, ammonia is frequently employed as a reducing agent for nitrogen oxides in exhaust emmision gases. Renewable ammonia is a carbon-free fuel, refrigerant, and working fluid, as well as a hydrogen storage medium. After electric and hydrogen powered cars, ammonia as a clean and sustainable fuel for road vehicles has the lowest global warming potential. Consequently, the use of ammonia in the transportation industry will result in considerable financial and environmental advantages, as well as public satisfaction.

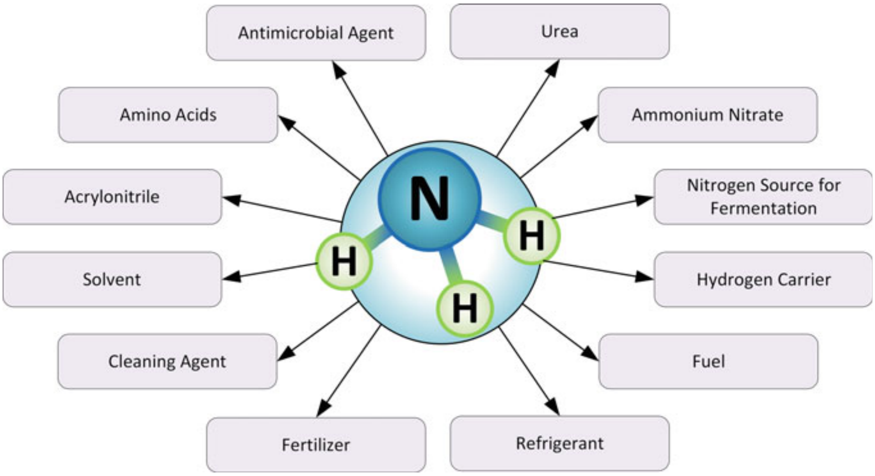

Fig. 1.7 Uses of ammonia in various sectors

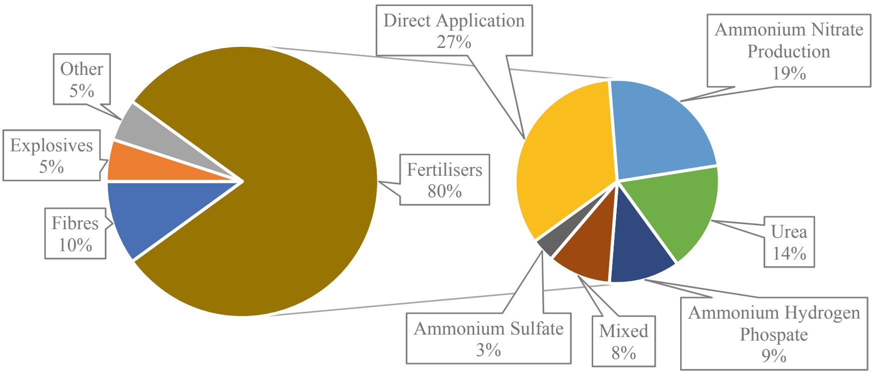

Fig. 1.8 Market share of ammonia related products (data from [8])

It is expected that the use of ammonia will increase since ammonia is used in many sectors for various purposes. Figure 1.9 depicts the ammonia production changes over the years. The data between 1940 and 2017 is recorded from the U.S. Geological Survey [14]. Global capacity of ammonia production was about 150 million metric tonnes in 2019 [6]. Less then 3% of ammonia is used in direct applications in agricultural sector. Those applications mostly limited to United States. Remaining portion of the production is utilized in chemical processing and fertilizer production [7]. Because of widespread application in agriculture, and being a good energy carrier, the production is expected to rise in the future. Utilization of ammonia as a carbon-free fuel is researched globally due to environmental concerns and endeavors to reduce CO_2 emissions. Countries have shifted some of their attention to ammonia-related projects for off-grid applications, internal combustion engines, and power

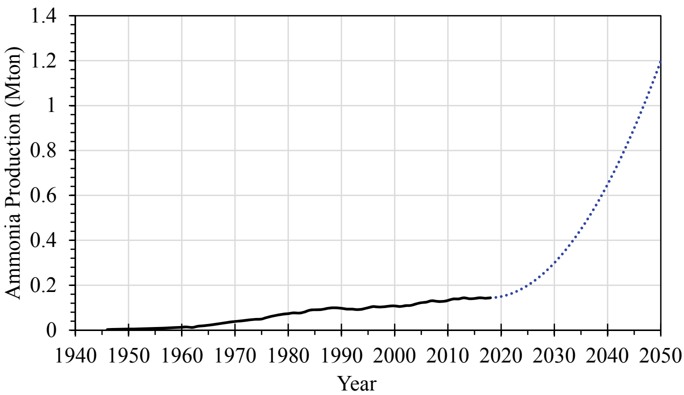

Fig. 1.9 The amount of ammonia produced around the world (modified from [14])

generation, etc. In addition, studies on the use of ammonia as a hydrogen carrier will increase in accordance with the research on clean hydrogen technologies. We foresee that the production and consumption of ammonia will be increasing exponentially. Our projection is illustrated in Fig. 1.9 with a blue-dotted line. In 2050, we expect that about 1.2 billion metric tonnes of ammonia will be produced globally. It is nearly 8.2 times higher than the amount of ammonia produced in 2019.

As comparatively illustrated in Fig. 1.10, an ammonia driven vehicle can travel 100 km with a fuel cost of US$6.30 as of June 2021. On the other hand, driving 100 km with same car but with gasoline fuel option costs US$8.11. It costs a driver US$18.1 more per 1000 km distance travelled. If we assume a driver who drives

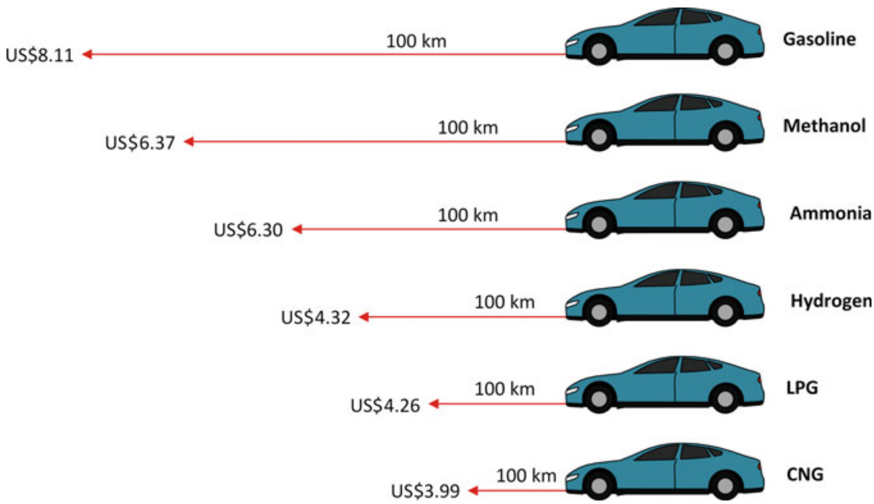

Fig. 1.10 Comparison of driving cost per 100 km for various fueled vehicles

40,000 km per year, then this driver must pay US$724 more per year. In terms of cost and on an energy content basis, ammonia has traditionally been priced competitively with gasoline and diesel. The ability of ammonia fuel to be utilized in diesel engines, gasoline engines, fuel cells, and gas turbines is a huge benefits. Ammonia is a promising transportation fuel. By-product refrigeration has the benefit of lowering costs and requiring less maintenance during vehicle service. Economic availability and feasibility, a worldwide distribution network, and ease of handling are all benefits of ammonia. In comparison with gasoline and methanol, ammonia is a cost-effective fuel per unit energy stored onboard.

Both hydrogen and ammonia are recognized as clean fuels, as they contain no carbon and result in no carbon footprint when used. Due to the increased levels of environmental concerns, there has been increasing attention to these two clean fuels. The researchers, scientists and technologists have been intensely working on systems using ammonia and hydrogen in order to increase sustainability indexes of systems. Many recent studies in the open literature have focused on either developing novel systems that using ammonia or hydrogen or converting present conventional systems into systems that using ammonia or hydrogen as a fuel [19–24].

It is anticipated that the usage of ammonia and hydrogen will expand significantly in the near future due to energy supply/demand challenges and environmental concerns. The MAN Energy Solutions, for instance, intends to provide a retrofit kit for their ammonia engine by 2025 [25]. In recent times, the Japanese shipping company NYK line has launched a number of prominent technology development agreements targeted at the building of ammonia-fueled ships and the delivery of fuel. Among its partners in these enterprises are the classification society Class NK, the engine producer IHI Power Systems, and the shipbuilding Japan Marine United Corporation. Three kinds of ships, including an ammonia-powered ammonia gas carrier, an offshore ammonia barge, and an ammonia-powered tugboat, have been disclosed so far in the open literature. These partnerships seek to commercialize and bring these vessels into practical use, moving beyond the initial research process [26]. Japan is anticipated to be a major ammonia and/or hydrogen importer within the next decade, having already shown a keen interest in Australia's shipping of environmentally friendly products. JERA, the biggest power company in Japan, said recently that it wants to shut down all of its old coal-fired power plants by 2030 and replace them with green fuels like ammonia and hydrogen [27].

As indicated in Fig. 1.11, it is predicted that the total worldwide ammonia production will increase from around 235 million metric tonnes in 2019 to roughly 290 million metric tonnes by 2030. This expected increase in capacity is the result of roughly 107 planned and announced ammonia facilities, most of which are situated in Asia and the Middle East. In 2019, Canada generated over 5 million metric tonnes of ammonia [29]. Approximately 80% of the ammonia produced by industry is used as a fertilizer. Ammonia is being used in the manufacture of textiles, explosives, insecticides, as well as other chemicals. It is utilised in several home and commercial cleaning products. By combining ammonia gas with water, 5–10% ammonia cleaning

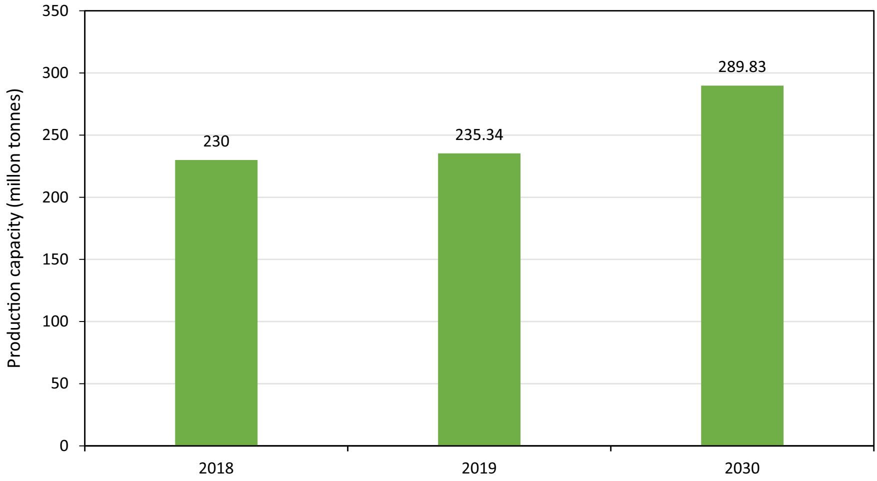

Fig. 1.11 Global production capacity of ammonia from 2018 to 2030 (data from [27])

solutions for the home may be produced. Ammonia solutions for industrial usage may have concentrations of at least 25% and are highly corrosive [30].

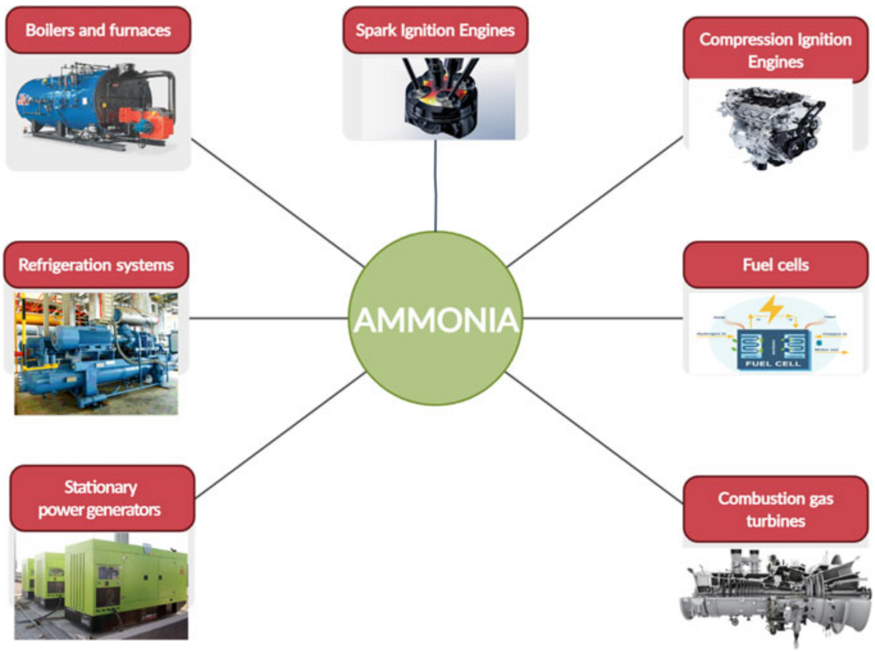

Fig. 1.12 Ammonia utilization in various applications

Ammonia can be used in many applications as illustrated in Fig. 1.12. On the present market, ammonia is mostly used as a fertiliser and a refrigerant. In addition, there are prototypes of cars powered by ammonia that use either engines or fuel cells. As an alternative fuel, ammonia may be used in all kinds of internal combustion engines, gas turbines, and burners, as well as directly in fuel cells, with only modest changes. This is a significant advantage compared to other fuel types. In an ammonia-based economy, fuel cells, stationary power generators, furnaces/boilers, and even automobiles will provide decentralised power production and smart grid applications. Due to very low energy needs, ammonia may be converted into hydrogen for almost any use [31].

Figure 1.13 depicts an illustrative cost comparison of various vehicle fuels in terms of energy cost per gigajoule. In terms of current energy market prices, ammonia is the cheapest fuel, and it costs US$10.27 per gigajoule of energy while gasoline costs US$22.48 per gigajoule, methanol costs US$47.05 per gigajoule, compressed natural gas (CNG) costs US$29.59, hydrogen costs US$27.19 per gigajoule, and liquefied petroleum gas (LPG) cost US$22.02 per gigajoule of energy. This demonstrates that ammonia is a cost-effective transportation fuel. By-product refrigeration has the advantage of lowering costs and requiring less maintenance during vehicle operation. Commercial availability and viability, a global distribution network, and ease of handling are all advantages of ammonia. As illustrated in Fig. 1.13, ammonia is a more cost-effective fuel per unit energy stored onboard than methanol, CNG, hydrogen, gasoline, and LPG.

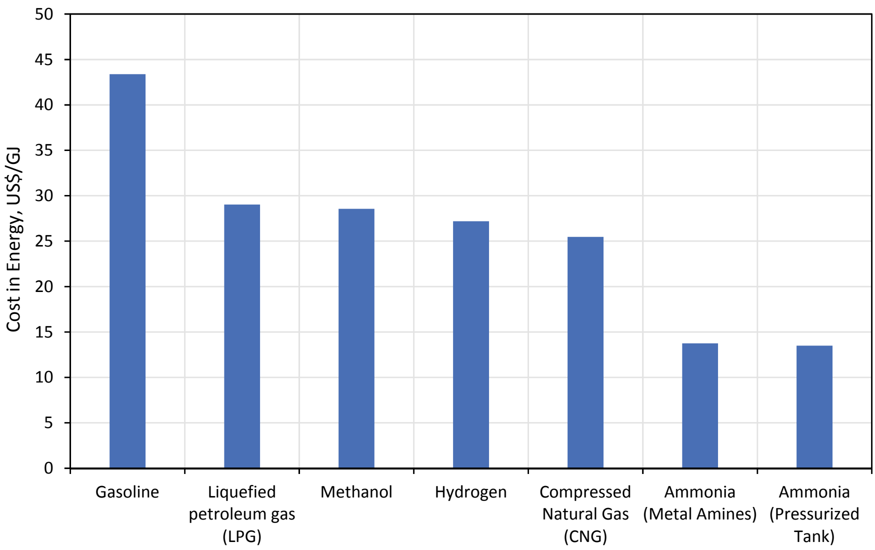

Fig. 1.13 Comparison of the cost per gigajoule of energy for different vehicle fuels (Modified from [33– 35])

In typical internal combustion engines (ICE), ammonia and a combustion promoter will be injected in tandem. Combustion of ammonia is characterised by low flame temperature, poor laminar burning velocity, high ignition energy, and low flammability limitations, which would substantially degrade engine performance. Combustion and emission characteristics of a compression-ignition engine that consumes ammonia and dimethyl ether (DME) mixtures were studied in a research [32]. The research advocated employing direct liquid injection to restrict combustion within the cylinder bowl so as to limit ammonia emissions. DME, which has a high cetane value, is combined with ammonia. Due to its great resistance to autoignition, ammonia cannot spontaneously ignite. DME, like ammonia, has a high vapour pressure and must be compressed to stay a liquid. DME and ammonia are mixable, and their polarity allows the combination to stay stable, making it more convenient. DME is an effective diesel engine fuel that contains little fossil fuels. The availability of certain ammonia/DME combinations as refrigerants increases its viability as an alternative fuel.

When ammonia is utilised, the operational capability of the engine is lowered. Possible causes include the following: ammonia has a high latent heat of 18.6 MJ/kg, but a low heating value of 42 MJ/kg compared to diesel fuel. To accomplish the same engine load with the same amount of fuel energy, roughly 2.26 times as much ammonia as diesel fuel is required. Assuming an equivalency ratio of 0.5 in a diesel engine running, this quantity of ammonia and its greater latent heat may lower the in-cylinder air temperature by about 100 °C. This chilling will slow down chemical reactions [32].

In cars, ammonia may be used as a mixed fuel. Ammonia is less expensive per kilogramme than traditional fuels. The energy costs of ammonia and diesel fuels, including blends, are shown in Table 1.3. As indicated, diesel fuel costs US$3.21 per gallon, ammonia costs US$680 per tonne, and DME costs US$555 per tonne. In dual fuelling of ammonia and diesel, the initial step is to provide gaseous ammonia to the intake manifold by producing a premixed combination of ammonia and air in the cylinder. Diesel or biodiesel is then injected to commence combustion. Thus, no alterations are made to the current diesel injection system. The efficiency of ammonia combustion may approach to 95% [36].

There are two methods to store ammonia: under pressure or at a low temperature [40, 41]. Pressurized storage retains ammonia in liquid state at a pressure greater

Table 1.3 Fuel prices comparison delivered to compression ignition engine

	40% ammonia/60% diesel	40% ammonia/ 60% dimethyl ether	Ammonia	Diesel fuel
LHV (MJ/kg)	32.6	24.5	18.6	42
Fuel rate (kg/kWh)	0.316	0.42	0.554	0.245
Fuel price (US$/kg)	0.78	0.61	0.68	0.85
Fuel energy cost (US$/kWh)	0.25	0.26	0.38	0.21

Source [37–39]

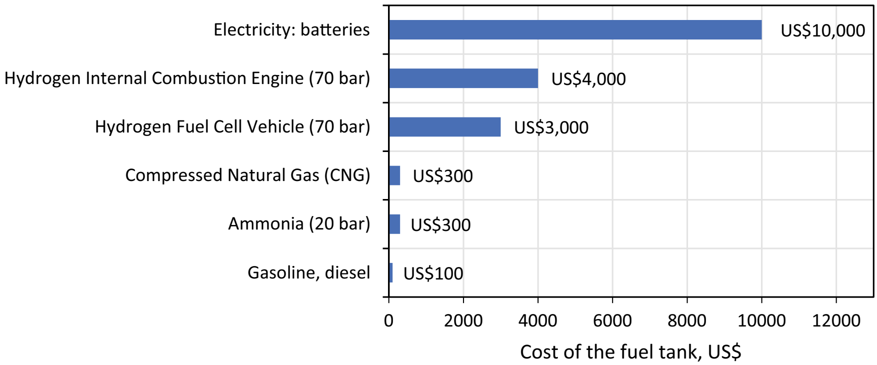

Fig. 1.14 Costs of on-board storage tanks for different types of fuelled vehicles

than 8.6 bar at ambient temperature (20 °C). However, ammonia is often kept above 17 bar to maintain liquid phase if ambient temperature rises. The energy density of pressurised liquid ammonia storage is 13.77 MJ/L. As a general rule, 2.8 tonnes of ammonia may be kept every tonne of steel. This storing requires no energy to maintain its compressed condition. Typically, storage at low temperatures is employed for large-scale storage.

This form of storage needs energy to maintain a low temperature and prevent boil-off caused by ambient temperature. For extended storage, low temperature is favoured due to its lower initial cost. The energy density of ammonia stored in this manner is 15.37 MJ/L, as opposed to 13.77 MJ/L for pressured storage. If 183 days of storage are considered, reflecting the interval between winter and summer, the ammonia storage cost will be US$4.03 per gigajoule. This price is much less than the cost of hydrogen storage, which is US$98.74/GJ.

As demonstrated in Fig. 1.14, the projected cost of a fuel tank for a personal car with a 300-mile range is smallest for ammonia after standard and traditional gasoline/diesel tanks. Figure 1.14 demonstrates that on-board ammonia storage is priced similarly to compressed natural gas and gasoline cars. As expected, since hydrogen storage requires more complicated systems, the cost of the storage tank is higher then gasoline, diesel, CNG and ammonia. The highest cost is seen in batteries.

Figure 1.15 depicts the driving costs of various fuels. At the current market prices, gasoline is most costly fuel per 1 km distance travelled and compressed natural gas (CNG) is the most low-cost option due low demand in the world for natural gas. However, when pre-pandemic price of fuels taken into consideration ammonia was most cost-effective fuel in various fuels. During COVID-19 pandemic, higher demands and lower supplies have caused ammonia prices to soar. The prices of ammonia shot up nearly 60% since fall 2020 and are now at US$680 per tonne as of June 2021 [42]. As a result, worldwide values have skyrocketed, as companies empty the storage, demand spikes. It is expected that ammonia prices will drop nearly pre-pandemic levels when ammonia production increase with shutdowns lifted [39]. On

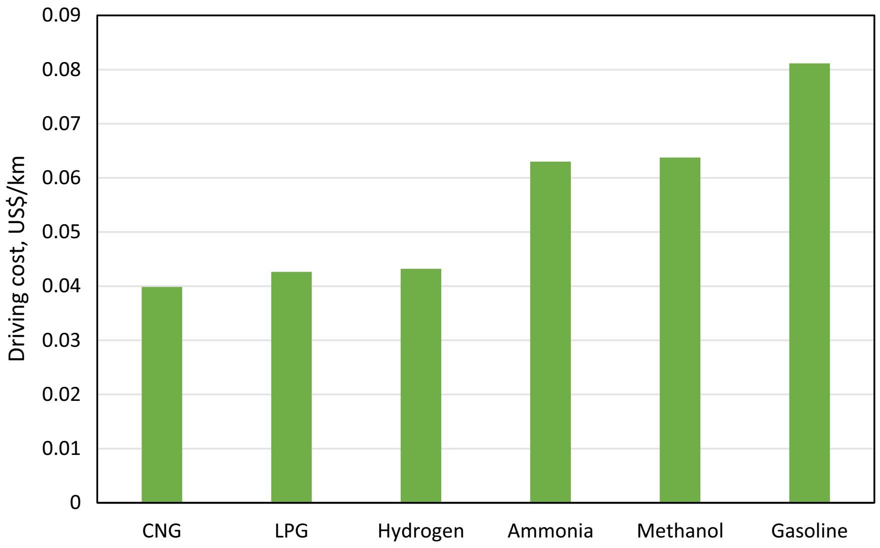

Fig. 1.15 Driving cost of various fuels

the other hand, the analysts expect coronavirus-related shutdowns to ease throughout the 2021, when the COVID-19 vaccine begins to reach the world.

According to the studies carried out by the analysts [43], the global oil demand will rise 6.6 million barrels per day in 2021, reversing nearly two-thirds of the nearly 10 million barrels per day decline seen in 2020. China's oil demand has already risen this quarter, surpassing levels observed in the same quarter of 2019. The reversal in China's oil consumption is the first indicator of what will soon become a reality: rapid global demand rise year over year in 2021. By the second half of 2021, this tendency will have tightened the supply–demand balance, supporting oil prices. Figures 1.16 and 1.17 illustrate comparative the energy and exergy efficiencies for several ammonia manufacturing strategies. The highest energy and exergy efficiencies are achieved when using hydropower as energy source. Also, solar PV has the lowest values. Although fossil fuel pathways, such as gasification, have high energy and exergy efficiencies, renewable energy pathways using tidal and wave and hydropower also yield high results in terms of energy and exergy efficiency. It is therefore possible to produce ammonia with high efficiency using renewable technologies. Fossil fuel-based pathways have mediocre efficiency ratings. However, they are more favored by industry due to lower costs, matured installed infrastructure and easy access to fossil fuels.

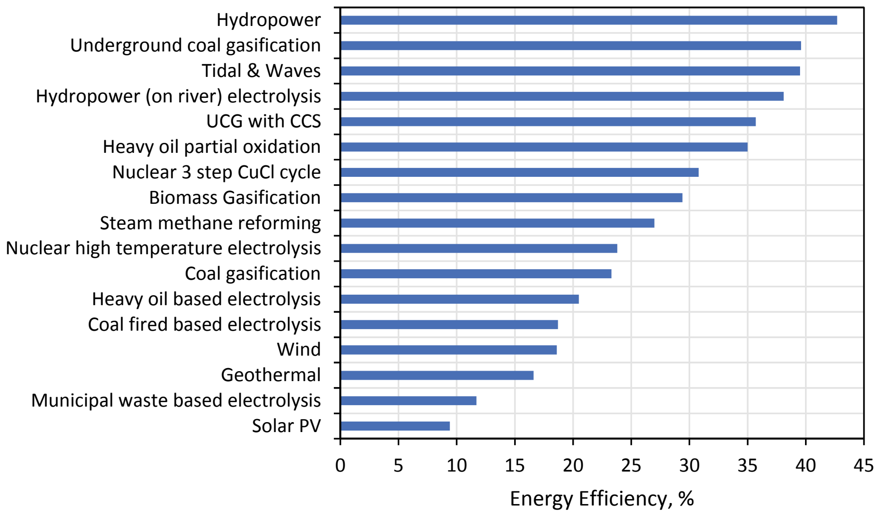

Fig. 1.16 Comparison of the energy efficiencies of diverse ammonia production techniques

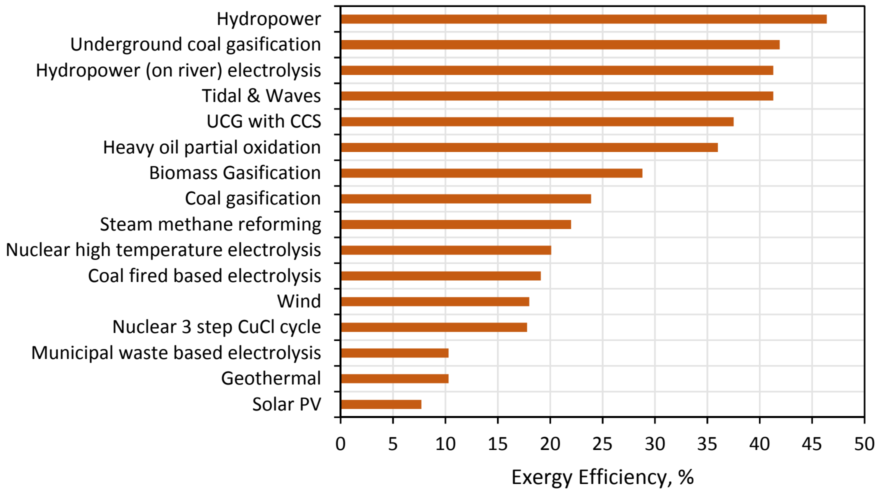

Fig. 1.17 Comparison of the exergy efficiencies of diverse ammonia production techniques

1.5 Closing Remarks

Ammonia is formed as a result of biological activities in nature and is an important part of the nitrogen cycle. The nitrogen cycle is an endless loop and is vital for the continuity of life. In nature, ammonia occurs as a result of decaying dead bodies of living beings and converted to nutrients by microorganisms to be used again by the living beings. Therefore, a large extent of industrial ammonia production supplies the agriculture sector. Nitrogen, which is necessary for the development of plants and animals, is provided by ammonia, which has made ammonia the second most produced chemical globally. In addition to the agriculture sector, ammonia is a chemical needed by many sectors.

Although a total of about 80% of the ammonia produced is used by the agricultural sector, it has an enormous potential due to its physical and chemical properties. Ammonia is a feedstock for nitric acid, plastics, fibres, explosives, and cleaning products in chemical production sector. It can be utilized as a fuel both in internal combustion engines and ammonia fuel cells. Also, it is an excellent energy carrier, due to the three hydrogen atoms in its structure. Ammonia serves as a viable, safe, cost-effective, and hassle-free alternative for the transportation of hydrogen.

The importance of ammonia emerges with the scope of climate change measures. Ammonia stands out as a carbon-free chemical, fuel, and energy carrier from production to consumption with the utilization of clean hydrogen technologies. Reducing carbon emissions depends on minimizing fossil fuel consumption. Therefore, ammonia utilization is important for a sustainable future to find carbon-free alternatives to fossil fuels in both production technologies and human activities. The key properties of ammonia can be summarized as follows:

- Ammonia has the second largest production infrastructure worldwide. Therefore, the infrastructure for ammonia production and transportation is a mature technology providing an excellent alternative for fossil-fuels.
- Although the main infrastructure depends on fossil-fuels today, it can be easily adapted to clean technologies to reduce CO_2 emissions. Zero-carbon or low-carbon technologies for ammonia production studied and researched extensively all around the world.
- Ammonia can be stored in gas or liquid phase with less energy compared to hydrogen.
- Existing stainless steel pipelines can potentially be utilized for ammonia transportation with little or no modification.

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