Chapter 7
Ammonia as a Potential Substance

7.1 Introduction

Ammonia is a substance formed from hydrogen, the most abundant chemical element of the universe, and nitrogen, the major component of the terrestrial atmosphere (79%). It is interesting to note that the second major component of the terrestrial atmosphere, oxygen (21%) in combination with hydrogen forms water. Similarly to water, ammonia plays a major role in the global ecosystem: it represents a nitrogen source for all living species. At the same time, ammonia can play a major role in the sustainable development of mankind since it is a hydrogen source that packs 1.5 mol of hydrogen per mol of NH_3 at a density as high as 106 kg H_2/m^3. Moreover, ammonia is produced industrially in large quantities as artificial fertilizer for agriculture. With respect to sustainable development, it is of major importance to find and promote cleaner and more efficient technologies of ammonia production, since NH_3 is produced currently from fossil fuels, and its synthesis process leads to major greenhouse gas emissions on a global scale and consumes a significant amount of the world's energy budget. Recently, ammonia has been proposed as a hydrogen source because hydrogen can be generated from ammonia at a relatively low energy expense. That is, ammonia is an attractive medium to store hydrogen through chemical bonding. Storing hydrogen in the form of ammonia (detailed in this chapter) is one of the most promising and least expensive long-term storage methods. Last but not least, ammonia is an excellent refrigerant, a working fluid in power cycles, and an NO_x reducing agent.

In brief, ammonia is a special substance that can potentially play a major role in sustainable development because of its unique qualities. We will analyze in this chapter various aspects regarding the use of ammonia in advanced/sustainable energy systems, and the possible paths for the clean and efficient synthesis of ammonia.

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7.2 Ammonia Synthesis

An ammonia molecule can be formed by reacting nitrogen with hydrogen according to the following exothermic reaction:

$$1.5\,\mathrm{H_2} + 0.5\,\mathrm{N_2} \rightarrow \mathrm{NH_3} - 45.2\,\mathrm{kJ/mol} \cdot \mathrm{NH_3}. \tag{7.1}$$

However, the activation energy of this reaction, which is equivalent to that needed for breaking the triple covalent bond of nitrogen molecule ($N \equiv N \rightarrow 2\,N^{3+} + 6e^{-}$), namely, 460 kJ/mol, appears to be insurmountable (note that this is higher than that of CO_2 and water formation, −393.5 kJ/mol and −241.82 kJ/mol, respectively).

The Haber–Bosch process was invented at the beginning of the twentieth century to combine hydrogen and nitrogen thermo-catalytically according to the reaction in Eq. (7.1). The principle of this process is based on increasing the temperature of the reactants such that the nitrogen molecule receives enough energy to be cracked. The catalyst breaks the nitrogen bonds at the surface. If the temperature is not high enough, nitrogen atoms remain strongly bound at the surface and inhibit the catalyst from performing a new catalytic cycle. However, because in the reaction in Eq. (7.1) 2 mol of reactants produces 1 mol of products, the forward reaction is facilitated by low temperatures and high pressures. Since the reaction temperature cannot be set low (because of catalyst poisoning), the operating pressure must be extremely high. Typically, the operating temperature and pressure are 600°C and 100 to 250 bar, respectively, for 25% to 35% conversion (see Appl 1999).

A commonly used conversion loop is shown in Fig. 7.1 and operates as follows. Make-up gas consisting of hydrogen and nitrogen is provided as input and compressed up to an intermediate pressure. The make-up gas is combined with unreacted gases returned from the loop and compressed further up to the conversion pressure. The feed is directed toward the catalytic converter, which contains mainly iron-based catalysts. The resultant gases containing converted ammonia product enter the ammonia separator that operates at the intermediate pressure. There, ammonia is separated by condensation and collected as liquid from the bottom of the separator. A refrigeration plant based on ammonia is used to cool, condensate, and separate the product. The remaining gases, containing mainly unreacted nitrogen and hydrogen, are partly recycled (recompressed together with the make-up gas) and partly used in a combustor to produce process heat. Additional fuel may also be fed into the combustor. The flue gases and the heat of the exothermic ammonia reaction are used to generate steam in a Rankine cycle that drives a turbine.

For better efficiency, the pump and the compressors are mounted on the same shaft with the turbine. Pressure is the parameter that controls the ammonia conversion. For a typical case at 200 bar, ammonia conversion is ~15% and increases up to 25% at 400 bar. Two types of catalytic ammonia converters are commonly used. The first is cooled internally with a coil running through the catalyst bed, and the

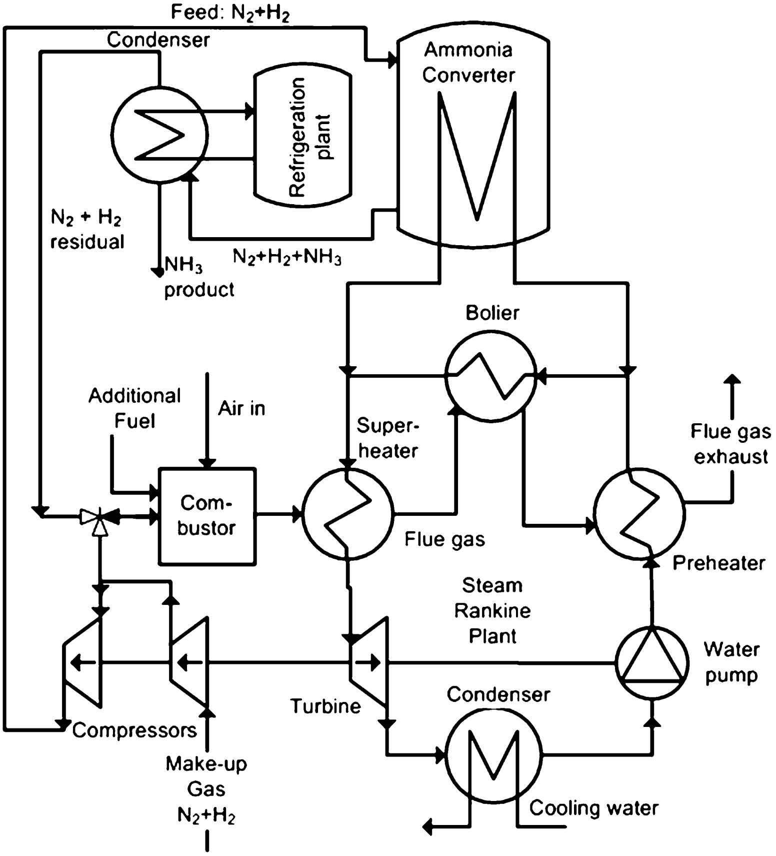


Fig. 7.1 Possible configuration of a Haber–Bosch ammonia plant with energy recovery [modified from Zamfirescu and Dincer (2009b)]

second divides the chemical reactor into modules, and after each module the products are cooled in separate heat exchangers.

Due to important heat generated during ammonia synthesis (i.e., 2.7 GJ/ton of ammonia), great emphasis is put on heat recovery. High-pressure steam further expanded in turbines (as explained above) has been found to be the most beneficial solution for heat recovery. In principle, high pressure steam at ~125 bar can be generated. According to Appl (1999), an advanced ammonia plant produces ~1.5 ton of high pressure steam per ton of ammonia, representing 90% recovery of ammonia formation enthalpy. Other gas-handling operations (e.g., hydrogen separation from returning stream, purge gas management, nitrogen separation, and hydrogen production) consume some amount of primary energy and degrade the synthesis loop efficiency. According to Rafiqul et al. (2005), ammonia production efficiency from a primary thermal energy source, through the Haber–Bosch process, varies between 37% and 65%. If hydrogen is derived from a sustainable

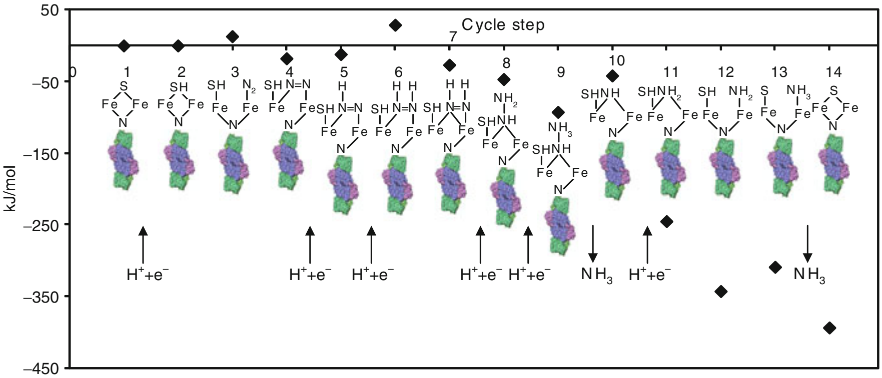


Fig. 7.2 The 14-step nitrogenase cycle for ammonia synthesis (*upward-pointed arrows* represent proton–electron inputs, *downward-pointed arrows* represent ammonia outputs, and diamonds represent the energy level) [modified from Zamfirescu and Dincer (2009b)]

source (meaning that no CO_2 emission could be associated with the hydrogen production), then the greenhouse gases (GHGs) equivalent to the energy needed to run the plants are of the order of 0.4 tCO_2/tNH_3, see Rafiqul et al. (2005). Typical CO_2 emissions are 2.2 tCO_2/tNH_3 if hydrogen is produced from natural gas, and 16.2 tCO_2/tNH_3 if coal is the primary source; the minimum possible value for GHG emission with today's technology is 1.6 tCO_2/tNH_3. In recent years, ammonia prices fluctuated between $150/t and $700/t.

In biological systems, nitrogenase enzyme is used to break the nitrogen molecule and to bond nitrogen to protons to form ammonia. Nitrogenase, which is one of the most complex enzymes, performs ammonia synthesis in a very "intelligent" way, by not breaking dinitrogen directly, but rather bond by bond. Nitrogenase consists of two protein clusters: (1) one that has an electron-acceptor active site based on iron (Fe) and molybdenum (Mo) having the stoichiometry $MoFe_7S_9N$ (in some alternative versions of nitrogenase, the active center is based on Fe and V), and (2) one that has an iron-sulfur center that hydrolyzes adenosine triphosphate (ATP) to obtain energy and provide electrons to the active site of the first cluster. During the ATP hydrolysis (ATP $\rightarrow$ ADP + Pi), adenosine diphosphate (ADP) and inorganic phosphate (Pi, standing for HPO_4^{2-}) are produced. The ATP comes from glucose oxidation and is the basic compound that biological systems use to store and release chemical energy. Nitrogenase uses gaseous nitrogen (N_2) directly, which is "captured" from the atmosphere by organisms by specific respiration mechanisms. Hydrogen is not used by nitrogenase in a molecular form; rather it is used in the form of protons produced by H_2 ionization at the electron-acceptor active site, and electrons provided by the electron-donor active site. Intensive efforts were dedicated in recent years to clarifying the ammonia production cycle by nitrogenase. The main findings are summarized in papers by Hinnemann and Nørskov (2006) and Kästner and Blöchl (2007). The synthesis process at the active site is presented in Fig. 7.2. Ammonia synthesis consists of 14 steps in which various intermediate compounds are formed at the active site. All intermediates are recycled, and globally, from one nitrogen molecule and six hydrogen molecules, two NH_3 molecules are produced per cycle. Figure 7.2 presents the reactions at the active site as derived from the work by Kästner and Blöchl (2007).

The required energy for producing 1 mol of ammonia is 395 kJ, and the higher heating value (HHV) of NH_3 is 382 kJ/mol; therefore, the efficiency of the reaction itself appears to be ~96%. There are, however, possible variations in the reaction steps and in their number as the nitrogenase adapts to the substrate (i.e., the organic matter encountered for processing). Therefore, the energy per production cycle may vary. One source of irreversibilities at ammonia synthesis by nitrogenase (see Fig. 7.2) is due to the competition of ammonia formation and hydrogen formation. In this process, some protons and electrons can be lost. In any situation, nitrogenase synthesizes small quantities of hydrogen during the ammonia production. Hydrogen is mainly used for energy recovery through oxidation (see Mousdale 2008).

Nitrogenase is produced by a number of microbes that live in symbiosis with root nodules of legumes and plants such alfalfa, clover, or peas. There are also free-living microbes that produce nitrogenase, most of them being anaerobic (e.g., clostridium, *Klebsiella pneumoniae*, *Bacillus polymyxa*, *Bacillus macerans*, *Escherichia intermedia*, *Rhodobacter sphaeroides*, *Rhodopseudomonas palustris*, *Rhodobacter capsulatus*) and others being aerobic (e.g., *Azotobacter vinelandii*, *Anabaena cylindrical*, and *Nostoc commune*).

7.3 Ammonia Storage

Because of the major interest in industrial ammonia as a fertilizer, large-capacity seasonal storage tanks were developed. Ammonia demand peaks during the summer when it must be spread on agricultural fields. Ammonia is produced throughout the year, and the winter's production is stored for the summer season. Tanks with a capacity of 15,000 to 60,000 m^3 were constructed before the 1970s (Walter and Lesicki 1998). Ammonia is stored in the refrigerated state at ambient pressure and at its normal boiling point, which is $-33°C$. The tanks are cylindrical with a 38- to 52-m inner diameter and 18 to 32 m of useful height. In order to compensate for the heat penetrations, the whole construction is well insulated (a double-wall technology is used) and compressors are employed to remove the heat by simulating a refrigeration plant for which the tank plays the role of an evaporator. Basically, ammonia vapors existent above the liquid are aspired by the compressors and delivered at high pressure where the vapors are condensed and the liquid is returned back to the tank. In this way, the temperature and the pressure in the tank are kept constant.

Figure 7.3 presents a typical seasonal ammonia storage system. Cold vapors in state 1 are aspired and compressed with a two-stage compression station up to state 2 that corresponds to a condensation temperature for winter season. The liquid condensate at ambient temperature in state 3 is throttled and returned as a cold

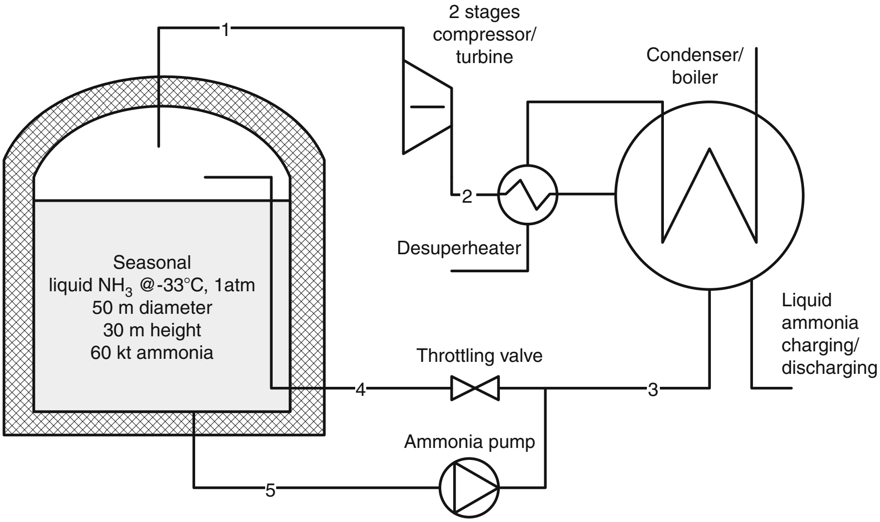


Fig. 7.3 Seasonal ammonia storage system [modified from Zamfirescu and Dincer (2009b)]

two-phase vapor–liquid mixture into the tank. The circulated ammonia flow rate must be such that it compensates for the effect of heat penetration from outside and the associated ammonia evaporation. In practice, according to Bartles (2008), 0.1% of ammonia from stored liquid evaporates per day. The latent heat of ammonia at 1 bar is 1370 kJ/kg; thus about 1.4 kJ of cooling must be provided per kg of liquid ammonia, each day. In the wintertime, ammonia refrigeration plants operating at −33°C evaporation and +15°C condensation temperature can achieve COP = 2.5; therefore, the corresponding compressor shaft energy is 0.6 kJ/kg every day, or 110 kJ/kg per 6 months of storage. The total energy required for running a 60-kt tank is, therefore, 6.6 GJ per storage season (the season is the 6-month winter-to-summer storage period).

Charging of ammonia into a tank is normally done by using liquid at high pressure, that is, at the condenser level. During charging, the liquid is expanded to 1 bar and, therefore, the cooling demand compensates only for the fraction of generated vapors that must be condensed. Vapor fraction in winter conditions during ammonia filling is ~15%; therefore, about 9 kt of vapors must be condensed for the 60-kt tank, or 4.9 GJ shaft energy must be provided for complete filling. In total, the shaft energy needed to drive refrigeration is ~11.5 GJ per season.

Note that cold-stored ammonia has a high exergy content, which, in principle, can be converted back into power. The specific exergy of refrigerated ammonia with reference to summer ambient temperature (e.g., 25°C) is given by

$$ex = (h - h_0) - T_0(s - s_0), \tag{7.2}$$

where h and s are specific enthalpy and entropy of liquid in the tank, respectively, and h_0 and s_0 represent the enthalpy of saturated liquid at ambient temperature.

The liquid in the tank is subcooled because it is subjected to a hydrostatic overpressure $\Delta P = \rho g \Delta z$, where Δz is the mean height of the liquid. The overpressure is estimated in these conditions to be about 1 bar, and the estimated specific exergy is 19 kJ/kg or 1.1 GJ/60 kt. In principle, 50% of this exergy can be recovered through a heat engine operating between the ambient and the low temperature of the cold storage; the recovered exergy represents ~5% of the energy spent to fill the tank and keep it refrigerated for the whole season.

Tank emptying with work recovery can be imagined as follows (see the diagram in Fig. 7.3): cold liquid is extracted at point 5 from the tank bottom, and pumped to high pressure at point 3; a part of the liquid is extracted from the tank at the discharge port from the bottom of the condenser/boiler heat exchanger; the other part of the subcooled liquid is heated, boiled, and superheated up to state 2. The superheated vapors are expanded over a turbine and expanded back into the tank. The process is repeated until all liquid is eliminated.

Ammonia is stored in smaller quantities in tanks made from regular carbon steel, designed for ~20 bar operating pressure where ammonia is kept in a liquid state at ambient temperature. A rule of thumb according to Appl (1999) is that at least 3 tons of ammonia can be stored per ton of steel. Therefore, the tank weight is about one fourth of the ammonia mass. Various sizes of cylinders are available in the industry. The size of ammonia pressurized tanks is limited for practical reasons to about 300 tons.

There is considerable experience with ammonia distribution using trucks, barges, ships, and rail. In road transport, the typical cisterns have 45-kl capacity, while rail cars have ~130-kl capacity. Ocean ships transport ammonia in low-temperature storage tanks of up to 50-kton capacity. Regarding pipeline transportation, following Bartles (2008), the distribution energy efficiency is 93% with respect to HHV at an energy density of 14 GJ/m^3.

Ammonia can be stored onboard a vehicle in pressurized cylinders in an anhydrous form or in some chemical form such as metal amines or ammonia boranes, which are produced using recently developed physical–chemical reversible methods; see Heldebrant et al. (2008) and Christensen et al. (2005). In this technology, ammonia is adsorbed on a porous metal–amine complex, for example, hexaamine-magnesium chloride, $Mg(NH_3)_6Cl_2$; to do this, NH_3 is passed over an anhydrous magnesium chloride ($MgCl_2$) powder at room temperature. The absorption and desorption of ammonia in and from $MgCl_2$ are completely reversible. The metal amine can be shaped in the desired form and can store 0.09 kgH$_2$/kg and 100 kgH$_2$/m^3.

7.4 Ammonia Use in Power Generation Systems

The use of ammonia in power generation and energy conversion applications presents unique opportunities. Ammonia can play multiple roles simultaneously: it can be used as a fuel, a hydrogen source, a working fluid, a refrigerant, and an

NO_x-reducing agent. In this and the next sections, we analyze all these roles and the relevant ammonia system for power generation and energy conversion based on the work of Zamfirescu and Dincer (2008a, b, c, 2009a, b).

Regarding the role of ammonia as an NO_x-reducing agent, the reaction of NO_x with ammonia over catalysts produces only steam and nitrogen. An average car needs only ~30 ml of NH_3 per 100 km to neutralize any NO_x emissions. Reduction of the NO_x formed during fuel combustion in many kinds of engines and furnaces is done according to the following reactions, conducted catalytically over zeolites:

$$\begin{cases} 4\,NO + 4\,NH_3 + O_2 \rightarrow 4\,N_2 + 6\,H_2O \\ 6\,NO_2 + 8\,NH_3 \rightarrow 7\,N_2 + 12\,H_2O. \end{cases} \tag{7.3}$$

When ammonia is used as a fuel in any combustion system or a fuel cell, the desired chemical reaction is the complete oxidation that produces only steam and nitrogen and some considerable amount of heat, according to the equation given below:

$$2NH_3(g) + 1.5O_2(g) \rightarrow N_2(g) + 3H_2O(g) - 634\,kJ. \tag{7.4}$$

However, in most of the practical situations, the reaction kinetics is favorable to nitric oxide formation. Thus, the partial oxidation of ammonia occurs normally as

$$2\,NH_3 + 2.5\,O_2 \rightarrow 2\,NO + 3\,H_2O - 454\,kJ. \tag{7.5}$$

The reaction heats in Eqs. (7.4) and (7.5) are indicated only for order of magnitude estimation in standard conditions (25°C, 1 atm). Considering the operating temperature range of high-temperature fuel cells and of internal combustion engines (ICEs), that is, 500°C to 1,000°C, the reaction heat for partial and complete oxidation cases is calculated using the equations, correlations, and data given in NIST (2010). The results obtained in terms of reaction heat versus process temperature are shown in Fig. 7.4. From Fig. 7.4, it can be inferred that the partial oxidation of ammonia reduces the useful reaction heat by 33%, and moreover, the reaction heat dependence on temperature is more profound than that in the case of complete oxidation. Therefore, it potentially causes problems with process control. One way to minimize partial ammonia oxidation is to crack (decompose) ammonia first, according to the endothermic reaction $2NH_3 \rightarrow N_2 + 3H_2 + 94$ kJ, thus producing hydrogen, which is used further as a fuel.

Solid oxide fuel cell (SOFC) or intermediate temperature fuel cells and ICEs present an advantage in this respect due to their high operating temperatures at which ammonia can be decomposed thermally over catalysts. Keeping this aspect in mind, let us consider some possible power systems with NH_3. As shown in Fig. 7.5, two main approaches are applicable to ammonia-fueled power generation in transportation vehicles: ICEs and fuel cell systems.

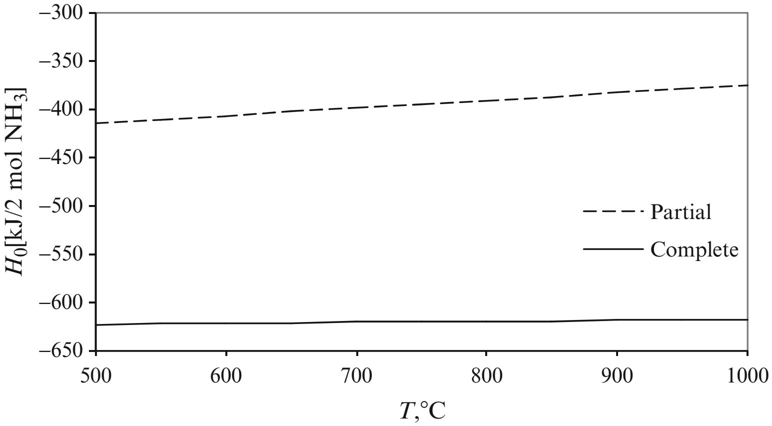


Fig. 7.4 Partial oxidation vs. complete oxidation during the anodic reaction [modified from Zamfirescu and Dincer (2008a)]

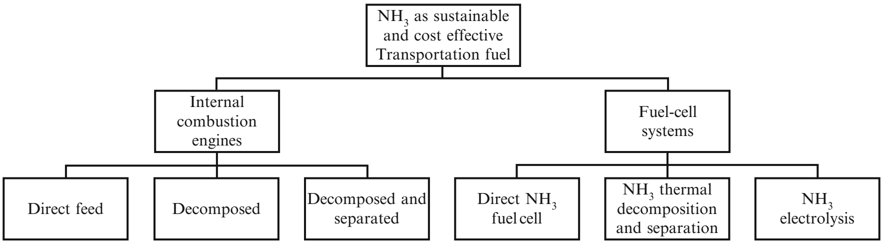


Fig. 7.5 Possible power systems fueled with ammonia

7.5 Hydrogen from Ammonia Route

The common approach to hydrogen economy is illustrated in Fig. 7.6 and consists of the following steps: production of hydrogen from primary energy sources at some locations, hydrogen distribution (infrastructure not yet developed), and hydrogen delivery on vehicles to plants where it is used for power generation/ propulsion. Our aim here is to assess the total cost of hydrogen per unit mass at the utilization point (i.e., in the vehicle) for two alternative layouts of the hydrogen transportation economy. The first layout was introduced above and is illustrated in Fig. 7.6. The second layout refers to the production of hydrogen from ammonia and will be described later. For a preliminary analysis, let us assume that hydrogen is produced from liquid water, either by electrolysis or by thermo-chemical splitting. The corresponding chemical reaction is given below with the heat generated:

$$H_2O(l) \rightarrow H_2 + \frac{1}{2}O_2 + 286\,\mathrm{MJ}. \tag{7.6}$$

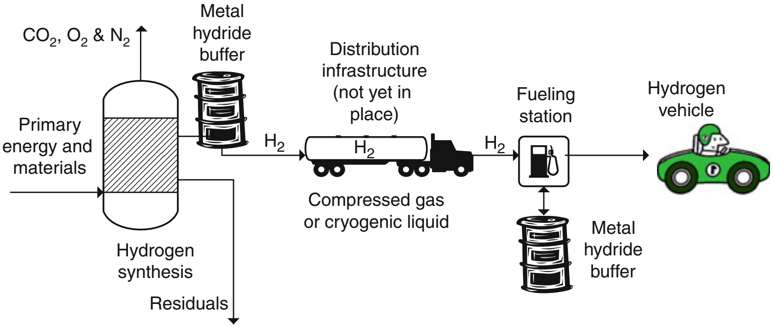


Fig. 7.6 The layout of hydrogen economy for transportation

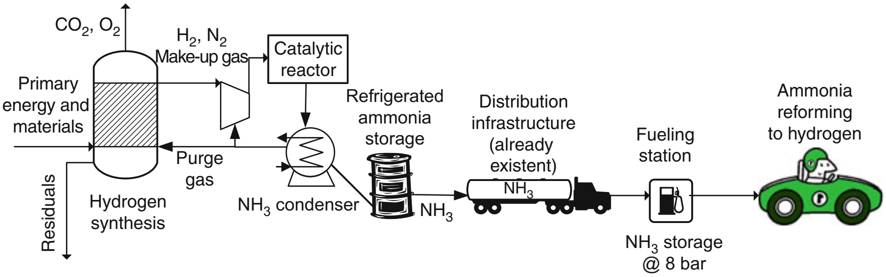


Fig. 7.7 The layout of hydrogen-from-ammonia economy for transportation

Here, in the ideal situation, for every kmol of hydrogen produced, one needs $\Delta H_{H_2O} = 286\,\text{MJ/kmol} \cdot H_2$ of energy to split the water molecule. Obviously, the practical energy needed to drive this process is larger than the theoretical one due to the imperfections. The produced hydrogen has to be stored in buffers at the production place, and then charged on vehicles specialized for pressurized or cryogenic hydrogen transport. It is then distributed to fueling stations and finally delivered to the consumers' vehicles. Along this complex chain, the cost of hydrogen will increase by amounts proportional to the energy utilization specific to each phase. We will later study the distribution costs and discuss the total cost of hydrogen delivery.

We will now study the second alternative where, instead of hydrogen, ammonia is produced at a synthesis plant, buffered locally, distributed to fueling stations, and then charged on vehicles where it is reformed to hydrogen by thermal cracking of the ammonia molecule. This scenario is illustrated in Fig. 7.7. Only ~12% from ammonia's HHV is needed for reforming. There is enough heat onboard a vehicle; the most advanced H_2ICEs have an efficiency of 50% to 60% and that of the most advanced fuel cell systems is 60% to 70%; the rest of the hydrogen energy is dissipated as heat. Thus, the onboard reforming process is "for free." An exception is the proton exchange membrane (PEM) fuel cell system in which heat is rejected at a low temperature, making it unsuitable for ammonia cracking. In this case, which is not analyzed in this chapter, a small part of the produced hydrogen can be combusted for generating the reformation heat.

Ammonia is industrially produced from hydrogen and nitrogen via the well-established Haber–Bosch process. Hydrogen can be obtained from water (by thermochemical water splitting or electrolysis) according to the reaction in Eq. (7.6), while the nitrogen comes from atmospheric air. In order to obtain an ammonia quantity corresponding to 1 mol of hydrogen, the following reactions have to be considered (ideal case):

$$\begin{cases} H_2O \rightarrow H_2 + \frac{1}{2}O_2 + 286\,\text{MJ} \\ H_2 + \frac{1}{3}N_2 \rightarrow \frac{2}{3}NH_3 - 30.7\,\text{MJ}. \end{cases} \tag{7.7}$$

Thus the energy needed to produce 1 mol of hydrogen embedded in ammonia is 286 − 30.7 MJ, which is $\Delta H_{NH_3} = 255.3\,\text{MJ/kmol} \cdot H_2$. Therefore, on a mass basis, the cost of NH_3 over the cost of H_2 can be estimated to be proportional to the energy required for their synthesis as

$$\frac{c_{NH_3}}{c_{H_2}} = \frac{3}{\mu_{NH_3}} \frac{\Delta H_{NH_3}}{\Delta H_{H_2O}} = 0.157. \tag{7.8}$$

According to Eq. (7.8), the ideal cost of ammonia is less than 16% the cost of hydrogen per unit mass. From the stoichiometry, it can be determined that 1 kg of ammonia contains 3/17 = 0.176 kg of hydrogen. As mentioned above, this quantity of hydrogen can be released by NH_3 cracking at no cost onboard vehicles, using the heat generated locally. Therefore, producing hydrogen from ammonia becomes attractive if

$$\frac{c_{NH_3}}{c_{H_2}} < 0.176. \tag{7.9}$$

Note that from Eqs. (7.8) and (7.9), it appears that, on an ideal basis, producing hydrogen locally from ammonia is more efficient than producing pure hydrogen and then using it onboard vehicles. Up to this moment, the irreversibilities of the chemical reactions and the fuel production and distribution costs were not considered in the analysis. For a detailed analysis, the price of hydrogen, and ammonia production and distribution, respectively, must be accounted for.

Hydrogen, as stated above, is the most difficult to store in a compact form. Therefore, the distribution- and storage-related costs will impact mostly on the total costs. Depending on the production method, hydrogen cost varies from ~\$1/kg at coal gasification to ~\$9.50/kg using solar energy for electricity generation, which in turn is used for water electrolysis. After production, hydrogen is stored at the manufacturer's location for a certain period prior to delivery. Hydrogen storage is costly, because the hydrogen molecule is small and leakage cannot be avoided.

The best option to store hydrogen at the production facility location (and at the distribution pump) is in metal hydrides. Metal hydride tanks may operate at pressures of 15 to 20 bar and store up to 25 to 30 kg H_2/m^3. In order to release hydrogen from the tank completely, some amount of heat is needed. It must be noted that metal hydrides do not appear as a feasible solution for transportation of hydrogen. For 1 kg of hydrogen, a metal hydride tank weighing about 160 kg is required.

For transportation, hydrogen must be either compressed to extremely high pressures (~300–800 bar) or cooled for liquefaction at cryogenic temperatures. Liquefaction adds at least 30% to the hydrogen price per kilogram, and in addition to this, one must add the cost of the energy consumed to keep the storage tank at cryogenic temperatures during the storage time. If the transportation takes 1 to 3 days, the minimum cost penalty for hydrogen storage on a transport vehicle is CN \$0.3/kg for compressed H_2 and CN \$0.7/kg for liquefied H_2.

If one assumes, for example, that the hydrogen transport is made in pressurized containers at 345 bar, the transported energy content is 8 GJ/m^3, that is, four times smaller than that for the transport of gasoline (32 GJ/m^3). If a pipeline is to be developed to distribute hydrogen at such high pressure, the tube's thickness must be more than 50% thicker than that of natural gas pipes.

At distribution points (fuel stations), hydrogen may be stored in metal hydrides also. Additional costs are associated with leakages during hydrogen delivery to consumers. The high explosion risk of hydrogen will raise the price even more because of the safety measures employed. Due to these factors, the estimated minimum cost of hydrogen distribution is more than \$1/kg H_2. Furthermore, one must realize that storage of hydrogen on vehicles (either as compressed gas or as cryogenic liquid) implies additional costs due to leakages, or continuous running of the cryogenic plant to maintain the hydrogen in liquid phase.

Thus, if one considers the production, storage, and distribution costs, the minimum expected hydrogen price at delivery point should be more than CN \$2.5/kg if produced from coal, and, respectively, ~CN \$11/kg if produced from electrolysis driven by solar energy. The U.S. Department of Energy goal for 2015 is to achieve the delivery for \$2 to \$3/kg H_2, untaxed and regardless of the production method. As a matter of fact, the North American selling price of hydrogen in 2002 varied from \$7.4 to \$11.3/kg.

Ammonia is easy to store and has a distribution network on roads, rail, ships, and pipeline already in place. The production of ammonia from fossil fuels has a common route with hydrogen production, because it involves gasification to produce syngas, gas cleaning, and CO_2 removal. In addition, the following steps are necessary for ammonia synthesis: compression of the reactants, catalytic conversion, and ammonia separation through condensation.

A highly energy-consuming component of the ammonia production process is represented by the make-up gas compression that is needed to facilitate the synthesis. This apparent drawback is compensated by a very efficient synthesis process that is possible at high pressure. Moreover, ammonia synthesis is an exothermic process, and modern technologies use work and heat recovery to reduce the production costs.

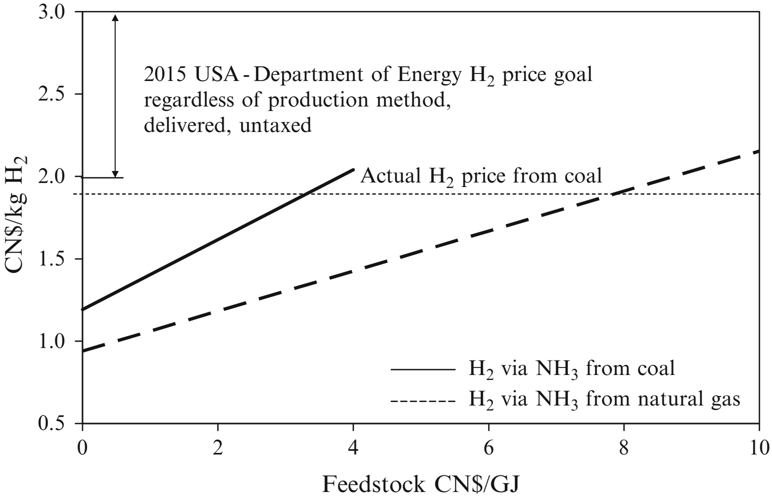


Fig. 7.8 Cost correlation for hydrogen obtained from ammonia at distribution points [modified from Zamfirescu and Dincer (2008b)]

The minimum cost for ammonia production per unit of energy is obtained with natural gas as the feedstock; the technical limit is 28 GJ natural gas for the production of 22.5 GJ of ammonia. The maximum energy cost is obtained with coal as the feedstock: ~65 GJ coal per 22.5 GJ of ammonia product. For other methods of production except those using solar energy, the cost falls in between the two extremes. The actual cost of North American coal is on average ~CN $1.5/GJ and that of natural gas is ~CN $10/GJ. These figures give an estimate of the ammonia price range at the production place, which is CN $5.25 to $20.0/GJ, or about CN $0.10 to $0.38/$NH_3$ kg.

The North African price is currently the lowest at $0.15/kg; other costs are $0.2/kg in Trinidad Tobago (based on $9/GJ natural gas feedstock), $0.25/kg in the Ukraine, and $0.3/kg in the United States. The cost of ammonia at Terra Industries in 2007 was $0.35/kg. The ammonia price in the U.S. in 2007 varied between $0.2 and $0.4/kg.

A correlation of the ammonia production price with the feedstock price in $/GJ from Zamfirescu and Dincer (2008b) is reproduced in Fig. 7.8. The cost of ammonia has been upgraded with the transportation costs. Since infrastructure development is not needed for ammonia distribution (e.g., a large pipeline network exists in the U.S. to transport ammonia at a cost of $0.1 hydrogen equivalent per 1,000 km), the ammonia transportation costs were combined with the costs of gasoline. Finally, the cost of ammonia, including that for transportation, has been multiplied by $17/3 = 5.67$ to obtain the cost per kilogram of hydrogen stored in ammonia, as shown in Fig. 7.8. Figure 7.8 shows that if ammonia is produced from coal (currently at about ~$1/GJ), hydrogen from ammonia is cost competitive with hydrogen transported in the pure state. Furthermore, if ammonia is produced from natural gas, the hydrogen obtained from ammonia remains economically viable up to natural gas prices of $8/GJ. It should be kept in mind that as the feedstock cost increases, the hydrogen production costs also increase.

Since ammonia is produced from hydrogen, it is interesting to estimate and compare the amount of CO_2 emission at NH_3 and H_2 production, respectively. We assume natural gas as the feedstock here. Modern ammonia synthesis systems that use extensive heat recovery need ~30 GJ equivalent natural gas to produce 1 ton of NH_3. Through stoichiometry, one may deduce that ~1.32 kg of CO_2 is generated in order to produce 1 kg of NH_3; this is equivalent to ~8 kg of CO_2 generated for 1 kg of H_2 in the form of NH_3, which is similar to the amount of CO_2 released during H_2 production from natural gas. This figure demonstrates the technical, economical, and ecological value of NH_3 as a hydrogen source.

Moreover, ammonia can be synthesized at any location of the oil or natural gas extraction wells, and the resulting CO_2 re-injected back into the ground for sequestration. Ammonia can then be easily transported via pipelines, auto-cisterns, railway cars, and ships, and delivered to consumption points where it can be used as a hydrogen source, chemical, fertilizer, refrigerant, and so on.

7.6 Thermo-Catalytic NH_3 Decomposition and Hydrogen Separation

Ammonia can be cracked thermo-catalytically to obtain hydrogen according to the following endothermic reaction:

$$\frac{2}{3}\mathrm{NH_3} + 30.1\ \mathrm{kJ/mol}\cdot \mathrm{H_2} \rightarrow \mathrm{H_2} + \frac{1}{3}\mathrm{N_2}. \tag{7.10}$$

Here, the required enthalpy represents 10.6% of HHV or 12.5% of the lower heating value (LHV) of the produced hydrogen. The ammonia cracking reaction does not need catalysis to be performed at high temperatures (e.g., over 1,000 K); however, at lower temperatures, the reaction rate is too low for practical applications such as hydrogen generation for energy conversion. Nevertheless, at 400°C, the equilibrium conversion of NH_3 is very high at 99.1% (Yin et al. 2004) and at about 430°C, almost all ammonia is converted to hydrogen at equilibrium, under atmospheric pressure conditions (Hacker and Kordesch 2003).

There is a large panoply of catalysts applicable to ammonia decomposition (e.g., Fe, Ni, Pt, Ir, Pd, and Rh), but ruthenium (Ru) appears to be the best one when supported on carbon nanotubes, generating hydrogen at more than 60 kW equivalent power per kilogram of catalyst (Yin et al. 2004). Over ruthenium catalysts, at temperatures lower than ~300°C, recombination of nitrogen atoms is rate limiting, while at temperatures higher than 550°C, the cleavage of ammonia's N–H bond is rate limiting. However, the activation energy is higher at lower temperatures (180 kJ/mol) and lower at higher temperatures (21 kJ/mol). The best temperature

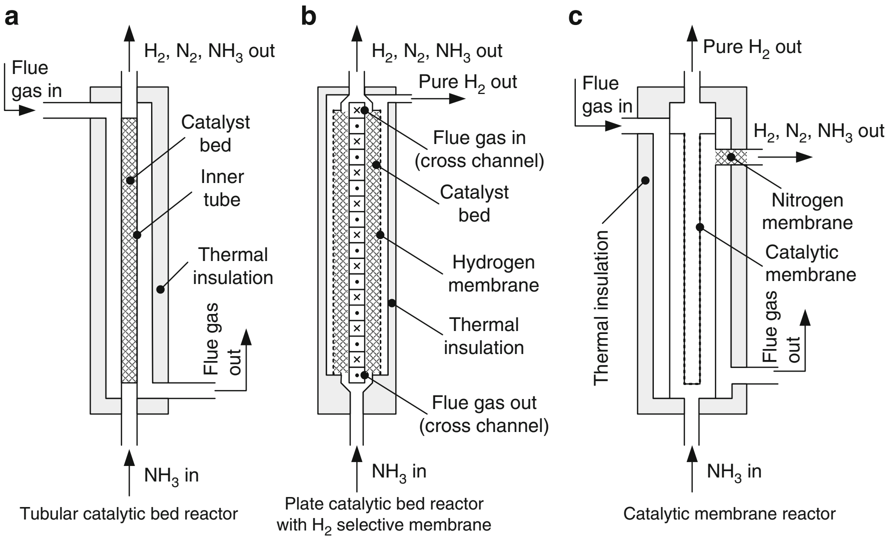


Fig. 7.9 Possible options for thermo-catalytic ammonia decomposition reactors

range for ammonia decomposition over ruthenium catalysts may be 350°C to 525°C, which suggests that flue gases from hydrogen ICEs, other hot exhausts from combustion processes, or electrochemical power conversion in high-temperature fuel cells can be used to drive ammonia decomposition.

Figure 7.9 presents three possible reactor configurations for ammonia decomposition. The direct products of decomposition consist of hydrogen and nitrogen and traces of unreacted ammonia. For pure hydrogen generation, membrane technology can be applied either in the same reactor or separately. The reactor shown in Fig. 7.9a is the simplest one and does not separate the products in the output stream. It consists of a simple tube (which can be coiled) filled with the catalytic bed and heated from the outside with flue gases. The reaction occurs at the surface and cannot go beyond the chemical equilibrium conversion at the temperature of operation. Some old trials reported by Grimes (1966) to produce this kind of reactor were based on iron catalysis and achieved, for operation at 900°C, a production of 1.3 kW power equivalent of hydrogen (with respect to HHV) for 1 l of reactor plus auxiliary heat exchangers. More recent work by Hacker and Kordesch (2003) describes a tubular reactor based on a Ni–Ru catalyst, which produced a hydrogen equivalent (HHV) with 60 kW at 600°C and 240 kW at 800°C/l of reactor.

Figure 7.9b represents the construction of a plate-type catalytic reactor with integrated hydrogen-selective membrane. The reactor is heated with flue gases circulated in cross-flow with the reactants–products streams. Ammonia is fed at the bottom and passes over the catalytic bed where the disassociation reaction occurs. The catalytic bed is surrounded by a hydrogen-selective membrane that allows only pure hydrogen to pass through. Palladium-based membranes are the most efficient known for hydrogen separation. The reactor produces a pure stream of hydrogen and a stream of residuals, containing mainly nitrogen and traces of hydrogen and ammonia. Reactors of this kind were described by several researchers and tested with the present data in the laboratory. Garcia-Garcia et al. (2008) used Ru-based catalysis and a Pd membrane, and obtained ~20% conversion enhancement with respect to conventional (tubular) catalytic reactor; the conversion obtained at 350°C was 95%. Ganley et al. (2004) showed that hydrogen production up to 170 kW H_2 HHV equivalent is possible with 1 l of reactor.

The third decomposition reactor, shown in Fig. 7.9c, comprises a catalytic membrane and has been proposed by Skodras et al. (2006). The catalysts used were based on Ni on an alumina support. In this approach, the hydrogen-selective membrane is doped with ammonia cracking catalysts to form a catalytic membrane. The testing conditions were 500°C to 800°C, 2 to 10 bar, and 0.5 to 1 second of residence time, which are consistent with the situations specific to vehicle propulsion. At 550°C, the conversion was 85% at 2 bar pressure and 30% at 10 bar. In Fig. 7.9c, it is suggested that better product separation could be achieved if a nitrogen-selective membrane is placed at the outlet port of unreacted gases. Separating the nitrogen and hydrogen products simultaneously represents a way to shift the reaction equilibrium toward the right. By extracting nitrogen from the reactor, the recombinative nitrogen effect can be avoided and higher reaction rates could be achieved.

7.7 Simultaneous Ammonia Use as Fuel and Working Fluid

Once ammonia is decomposed (partially or totally) to produce hydrogen, the resulting gas—either pure hydrogen or a mixture of ammonia, nitrogen, and hydrogen—is used for power generation in fuel cells or ICEs. Alkaline fuel cells are tolerable to ammonia (Hacker and Kordesch 2003); therefore, there is no need to produce pure hydrogen from ammonia. A plug-flow catalytic bed reactor similar to alkaline fuel cells illustrated in Fig. 7.9a can be used. PEM fuel cells do not tolerate ammonia; in this case, membrane separation reactors such as those shown in Fig. 7.9b,c can be used. In addition, because the temperature in PEM fuel cell systems is not sufficient, some of the produced ammonia and the uncombusted fuel are burned to provide the necessary heat for ammonia decomposition. One such system is proposed by Sørensen et al. (2005) and comprises an ammonia fuel tank, a PEM fuel cell, an ammonia decomposition unit heated by a catalytic burner, and an ammonia absorber.

A possible power generation technique is presented in Fig. 7.10. The ammonia tank is thermally insulated in order to recover the cooling effect that manifests when liquid is drawn out, together with its associated enthalpy. This cooling may be used by the system (e.g., to cool gaseous streams prior to compression) or may serve some specific need (e.g., air cooling). Ammonia drawn out of the tank is pumped at high pressure and then expanded in two stages with intermediate reheating. The heat of exhaust gases is recovered by this method; if this is not possible (e.g., as in the case of a PEM fuel cell system that operates at low temperature), then a small part of the generated hydrogen must be combusted to deliver the heat necessary for ammonia

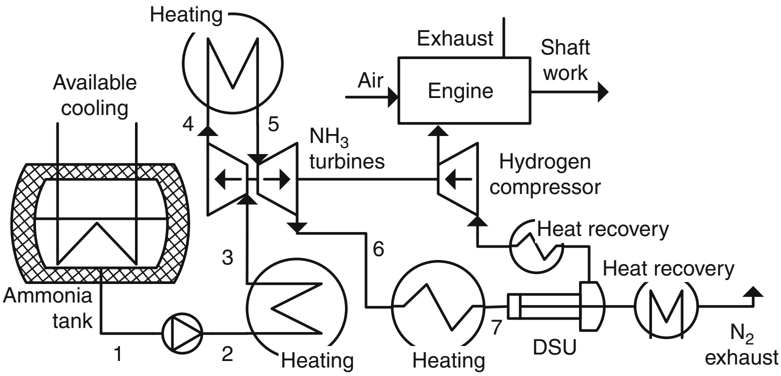


Fig. 7.10 Power generation system using hydrogen from ammonia [modified from Zamfirescu and Dincer (2009b)]

decomposition. After heating to elevated temperatures, ammonia is decomposed in the decomposition and separation unit (DSU) shown on the figure. Pure hydrogen is generated and compressed using the work recovered from the turbines. Prior to compression, the hydrogen stream is cooled with heat recovery. The resultant nitrogen stream is cooled with heat recovery and exhausted into the atmosphere.

Regarding power generation with ammonia as the hydrogen source, we are interested here in determining a practical upper bound for it. In order to do this, consider the energy conversion model introduced above in association with Fig. 7.10. We assume that the engine is either an ICE or a fuel cell operating at intermediate temperature such that the necessary quantity of thermal energy and the temperature level are satisfactory for at least 99% ammonia decomposition and generation of pure hydrogen. The aim is to maximize the power generation efficiency by generating some additional power from ammonia used as a working fluid prior to its decomposition.

The temperature per second (T-s) diagram of ammonia representing the heating process prior to decomposition is presented in Fig. 7.11. Heating of the ammonia fuel is done in three steps with two interlaced expansion processes, namely, 3–4 and 5–6. The work generated by these expansions is sufficient to drive the pump and the compressor for hydrogen. A simple calculation has been performed for the process 1–2–3–4–5–6–7 using the FluidProp software developed by Colonna and Van der Stelt (2004).

In this process, state 6 in a vacuum at 0.5 bar is chosen in order to facilitate the decomposition and separation process. Pure hydrogen produced by the DSU (Fig. 7.10) is then compressed up to 8 bar, a pressure sufficient for direct injection into the engine cylinder (if the engine is a fuel cell, the hydrogen pressure may be set at 2–3 bar). Prior to compression, the hydrogen stream is cooled with heat recovery down to 25°C for reducing the compression work. Nitrogen and the remaining unreacted gases are compressed separately after cooling with heat recovery down to 25°C; the chosen compression pressure is 1.2 bar, which is sufficient for expelling

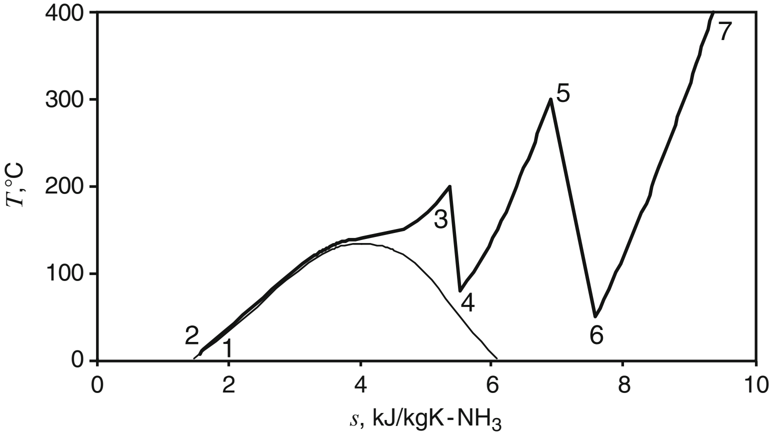


Fig. 7.11 Heating process and work recovery from the ammonia fuel stream (the state points are correlated with the system diagram in Fig. 7.10) [data from Zamfirescu and Dincer (2009b)]

the gas stream into the atmosphere after a second cooling to 25°C. Exhaust gas heat drives the process including ammonia heating and provides thermal energy for decomposition. We assumed that the decomposition unit efficiency is 80%, defined in terms of ideal decomposition heat over the actual one.

The cooling effect obtained from the ammonia tank represents, with the assumptions made, 6% from ammonia's HHV or 1% from that of hydrogen. The shaft work produced by the expander, which upgrades the engine power, was found to be 2% from the hydrogen's HHV, while the heat recovered from the exhaust gases was also 2% from the HHV. Note that this heat is mainly used for decomposition; for heating the ammonia stream prior to decomposition, most of the heat is retrieved from cooling the produced hydrogen and nitrogen streams prior to and after compression.

Figure 7.12 compares the energy balance of a hydrogen-fueled engine with that of the same engine modified according to the diagram in Fig. 7.10 and that is to be fueled with hydrogen generated by ammonia decomposition and separation. Because of internal heat recovery and heat-to-work conversion, the "hydrogen-from-ammonia" engine is 2% more efficient. This fact is felt to be of great importance in the fuel economy and greenhouse gases (GHG) mitigation.

7.8 Simultaneous Use of Ammonia as Fuel and Refrigerant

The cooling effect of ammonia is equivalent to the heat needed to raise its temperature and, if it applies, the heat needed to decompose it (partially or totally) prior to using it as fuel. Expressed in terms of enthalpy, this heat is

$$\Delta h_{\mathrm{c,NH_3}}(T) = h(T) - h'(T_0) + x_{\mathrm{d}}\eta_{\mathrm{d}}\Delta h_{\mathrm{d}}(T), \tag{7.11}$$

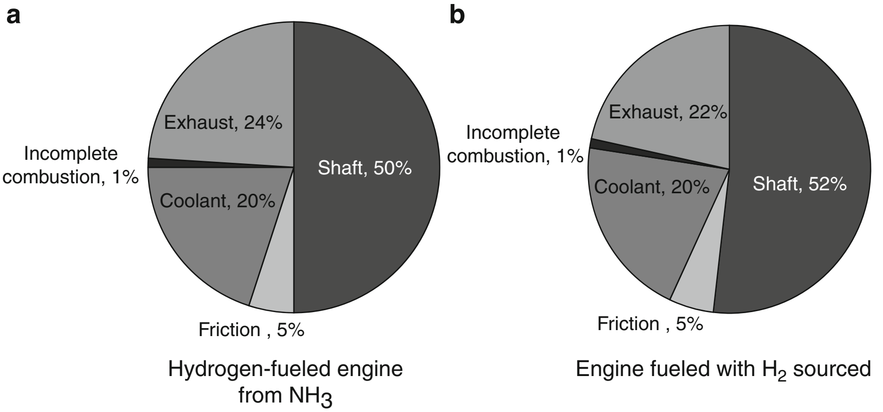


Fig. 7.12 Energy balance on two types of hydrogen-fueled engines [data from Zamfirescu and Dincer (2009b)]

where T represents the temperature at which NH_3 is used as fuel (either in an ICE or a fuel cell); x_d represents the fraction in which the ammonia stream is dissociated into H_2 and N_2 (if this applies); η_d is the efficiency of the decomposition unit, which is assumed here to be 0.9; and Δh_d represents the dissociation heat at T. In order to quantify the cooling effect of ammonia in relative terms, we use cooling effectiveness, defined through the dissociation heat given by Eq. (7.11) and the LHV of ammonia as

$$\varepsilon_{c,NH_3}(T) = \Delta h_{c,NH_3}(T)/\mathrm{LHV}. \quad (7.12)$$

The results of applying Eq. (7.12) for a range of ammonia reforming temperatures and various decomposition fractions are presented in Fig. 7.13. The thermodynamic data for plotting Fig. 7.13 are calculated using the FluidProp software developed by Colonna and Van der Stelt (2004). The case $x_d = 0\%$ represents the hypothetical situation when ammonia is only preheated prior to oxidation, and one assumes that no decomposition occurs. This case is illustrated for reference, because in reality, at temperatures over 300°C, some ammonia decomposes spontaneously, even without the presence of catalysts. The case for which $x_d = 5\%$ is applicable in ICEs, where, as discussed above, a small fraction of ammonia is usually decomposed to produce hydrogen that boosts the combustion process. The extreme situation when $x_d = 100\%$ is applicable to some fuel cell systems that are supplied with hydrogen produced from ammonia.

The results show that the maximum achievable engine cooling with ammonia represents slightly over 20% from the LHV. Thus, in ammonia-fueled ICEs, the usual water cooling system may be downsized by up to 20%. Optionally, a part of this cooling may satisfy some air-conditioning needs of the vehicle. A second observation is that the ε_r profile for complete decomposition is flat (i.e., it is not influenced by the temperature). If the decomposition is incomplete, the temperature

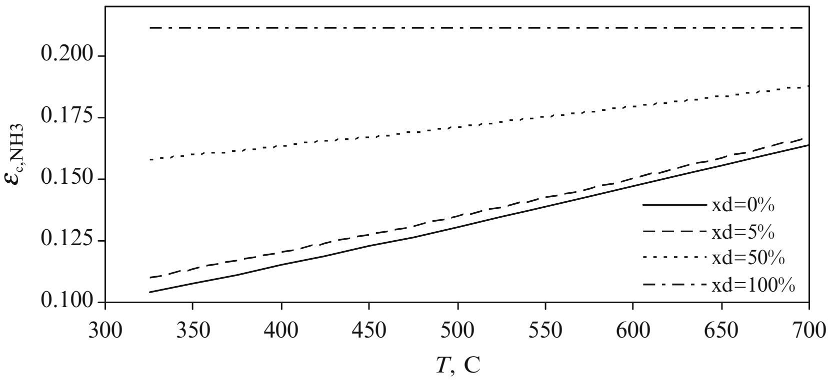


Fig. 7.13 The cooling effect of ammonia when it is consumed as fuel as a function of the decomposition temperature and for several decomposition fractions [modified from Zamfirescu and Dincer (2009a)]

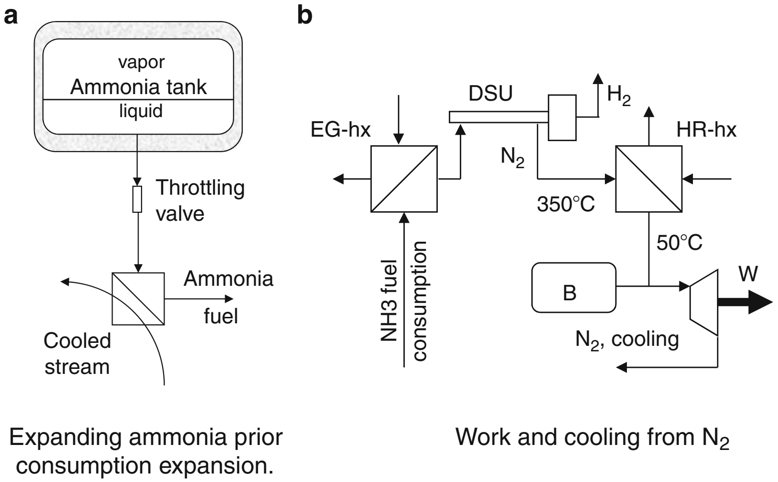


Fig. 7.14 Ways of exploiting the cooling effect of NH_3 onboard (*DSU* decomposition and separation unit, *HX* heat exchangers, *HR-hx* heat-recovery heat exchanger, *B* buffer, *W* work recovery)

profile is linear with a positive slope. This fact is explained by variations in the decomposition heat, which decreases with the decrease in temperature.

Two complementary arrangements to exploit the refrigeration effect of ammonia while it is supplied as fuel to the power plant are suggested in Fig. 7.14. With reference to Fig. 7.14a, one assumes that the saturated liquid is extracted from the thermally insulated fuel tank. The liquid stream can be throttled such that the fuel evaporation is conducted at the desired temperature (e.g., 5–10°C will suffice either for engine cooling or for obtaining some air-conditioning). After throttling, the fluid passes through a heat-recovery heat exchanger (HR-hx) where the engine coolant is cooled with ammonia. If air-conditioning is desired, the heat recovery will have two steps: first the air and subsequently the engine's coolant are cooled with ammonia.

To give an example, let us assume that the temperature in the fuel tank is 25°C, the evaporation temperature is 5°C, and the ammonia temperature at the evaporator is 15°C (superheated vapor). With these figures, the cooling effect is quantified as 6.3% from the LHV of ammonia. This means that for a medium-sized car equipped with a 70-kW engine, while the engine runs on ammonia fuel at full load, the obtained refrigeration effect to be used in the form of air-conditioning amounts to ~4.4 kW. In addition, up to 15% of LHV, meaning 10.3 kW, is available for the purpose of engine cooling. Alternatively, ~15 kW can be made available for engine cooling only.

Note that the engine effectiveness can be further improved if the refrigeration effect of ammonia is used while it is consumed as fuel. The improvement can be quantified based on the typical coefficient of performance (COP) of the vehicular cooling systems. The gain in work at the engine shaft due to the available cooling from ammonia (i.e., which comes from fan, pump, and compressor power savings) is

$$w_{\mathrm{NH_3}} = \frac{\Delta h_{\mathrm{c,NH_3}}}{\mathrm{COP}}, \tag{7.13}$$

and induces an engine performance improvement that can be quantified by the effectiveness:

$$\varepsilon_{\mathrm{r,NH_3}} = \frac{w_{\mathrm{NH_3}}}{\mathrm{LHV}} = \frac{\varepsilon_{\mathrm{c,NH_3}}}{\mathrm{COP}}. \tag{7.14}$$

For an assumed (typical) COP of 2 (COP of the engine cooling system and the air-conditioning system at the average), the maximum gain in efficiency is about 10%.

Some additional work and cooling can be recovered if ammonia is fully decomposed according to the arrangement illustrated in Fig. 7.14b. Preheated ammonia fuel is directed toward the DSU that produces the hydrogen and nitrogen as two separate streams. While the hydrogen is directed toward the consumption point (ICE or fuel cell), the hot stream of nitrogen is cooled in the HR-hx at a temperature close to ambient, say 50°C, and it can in principle be buffered at high pressure in a small tank (B). When needed, the nitrogen is expanded in a turbine for work recovery. The resultant cold stream of nitrogen can be used for some low-temperature cooling needs before being exhausted to the atmosphere.

Calculation of the additional cooling and the corresponding work recovery can be made by assuming an isentropic efficiency of the turbine, η_{S}, and computing the actual expansion enthalpy, $h_{\mathrm{a,N_2}}$, as a function of the N_2 inlet enthalpy, h_{i}:

$$h_{\mathrm{a,N_2}} = h_{\mathrm{s,N_2}} + \eta_{\mathrm{s}}\left(h_{\mathrm{s,N_2}} - h_{\mathrm{i}}\right), \tag{7.15}$$

where h_i is evaluated at the decomposition temperature and pressure (upstream turbine), and the isentropic discharge temperature, h_{s,N_2}, is calculated with the upstream entropy and discharge pressure.

It is useful to report the recovered work in terms of energy per kilogram of consumed ammonia fuel as follows (this can be done by taking into account that the number $\lambda = 0.5\,\text{kmol}_{N_2}/\text{kmol}_{NH_3}$ resulting from the NH_3 decomposition equation $NH_3 \rightarrow 1.5\,H_2 + \lambda N_2$):

$$\Delta h_{w,N_2} = \lambda \frac{\mu_{N_2}}{\mu_{NH_3}} \left(h_{a,N_2} - h_i\right). \tag{7.16}$$

The additional low-temperature cooling effect of N_2 can be quantified by considering reheating of the nitrogen stream from its low temperature T_{a,N_2} to a temperature close to ambient, T_0, featuring the flow enthalpy h_{0,N_2}:

$$\Delta h_{c,N_2} = \lambda \frac{\mu_{N_2}}{\mu_{NH_3}} \left(h_{0,N_2} - h_{a,N_2}\right). \tag{7.17}$$

Apart from ε_{c,NH_3}, one may define two additional kinds of system effectiveness, that is, one with respect to recovered work from nitrogen expansion as

$$\varepsilon_{w,N_2} = \frac{\Delta h_{w,N_2}}{\text{LHV}}, \tag{7.18}$$

and one accounting for the low-temperature cooling effect of nitrogen:

$$\varepsilon_{c,N_2} = \frac{\Delta h_{c,N_2}}{\text{LHV}}. \tag{7.19}$$

Therefore, the engine performance improvement due to nitrogen expansion can be quantified by

$$\varepsilon_{r,N_2} = \varepsilon_{w,N_2} + \frac{\varepsilon_{c,N_2}}{\text{COP}}. \tag{7.20}$$

For example, for the arrangement illustrated in Fig. 7.14b, if one assumes a turbine efficiency of 80%, $\varepsilon_{r,N_2} = 1.1\%$ or a total of 11.1% recovered power is obtained due to combined ammonia and nitrogen expansion. For a 70-kW engine, this is equivalent to 7.8 kW of saved power.

It is to be noted that the simplicity of this cooling system (which consists only of one or two heat exchangers and one throttling valve) lowers both the initial operation and maintenance costs by eliminating or downsizing the conventional mechanical cooling system (which comprises a compressor, condenser, water pump, fan, and radiator).

7.9 Performance Analysis of Ammonia-Fueled Systems

Let us investigate the impact of using ammonia as a fuel on the performance of a vehicle. Recall that, according to what has been mentioned above, there are two main approaches for using ammonia as a fuel: ICEs and fuel cells.

In an adopted power system (either an ICE or a fuel cell), for the estimation of engine performance, the cooling effect should be taken into account. In order to derive a system effectiveness that includes the cooling effect, let us consider η as the system efficiency. The system effectiveness including refrigeration and work recovery effects is

$$\varepsilon_r = \eta + \varepsilon_{r,NH_3} + \varepsilon_{r,N_2}. \tag{7.21}$$

It is obvious that the power system efficiency depends on the system, but a range of η can be estimated based on the common literature. For hydrogen fuel cells, the typical efficiency is 40% to 65%; for hydrogen ICE, efficiency of 40% to 55% was obtained; for direct ammonia fuel cell systems, the typical efficiency ranges from 30% to 45%; and for ICEs, efficiencies range from 25% to 55%. The overall range for η is from 30% to 65% (maximum values correspond to hydrogen systems, where hydrogen is supplied by onboard decomposition of ammonia). Thus, the expected range for ammonia vehicle effectiveness ε_r is 0.35 to 0.75.

It is interesting to investigate the driving range as a function of system effectiveness. In this respect, we assume a system effectiveness and a performance indicator of the power train given in terms of shaft torque energy for each kilometer of driving range. We consider here a reasonable range for this indicator from 0.5 to 1.5 MJ/km and take three illustrative values for ε_r. The results shown in Fig. 7.15

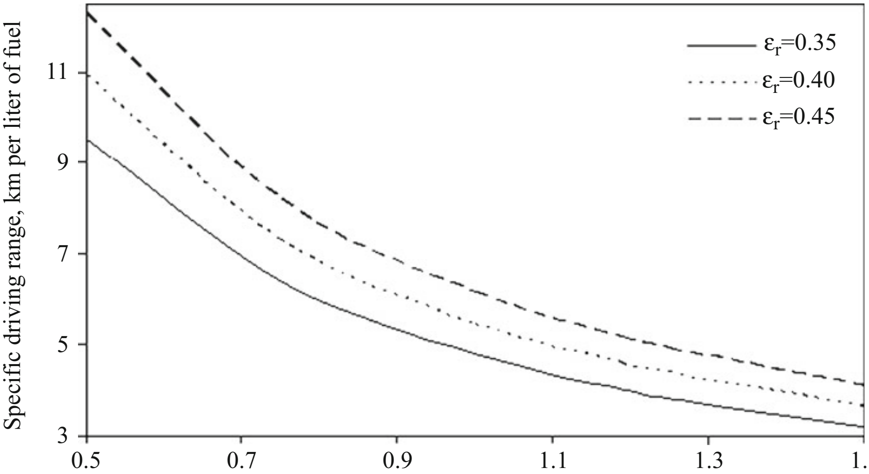
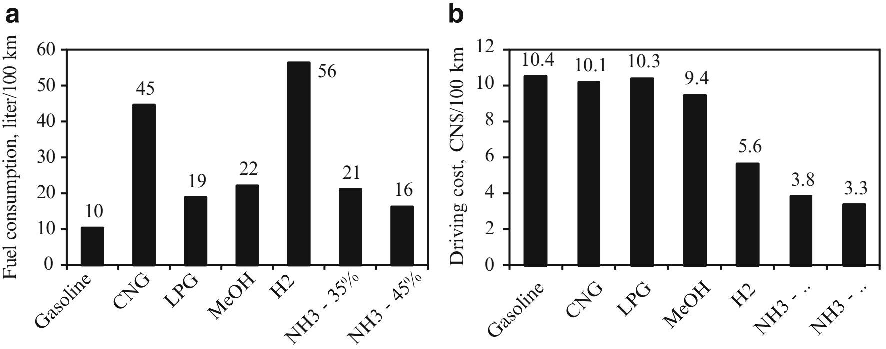


Fig. 7.15 Driving range with 1 l of fuel as a function of the shaft torque energy for 1 km driving range [modified from Zamfirescu and Dincer (2009a)]



Fuel tank compactness

Specific driving cost

Fig. 7.16 Comparative performance analysis of several power systems for vehicles [modified from Zamfirescu and Dincer (2009a)]

indicate, for instance, that with 1.0 MJ/km, the driving range may reach 7 km/l, that is, over 500 km with a 75-l NH_3 fuel tank.

Figure 7.16 compares some performance indicators for ammonia, hydrogen, and more conventional vehicles. To calculate the data shown in Fig. 7.16, it is assumed that gasoline, compressed natural gas (CNG), and liquefied petroleum gas (LPG) vehicles run with 28% efficiency. For methanol, we assumed a fuel cell system with 40% efficiency. For hydrogen, a PEM fuel cell system with hydrogen stored in metal hydride tanks has been considered, with an efficiency of 50%. For an ammonia vehicle, a liquid storage tank is assumed and the power system is not specified; thus we only considered two efficiencies (35% and 45%) that are specific for both ammonia fuel cell systems and ICEs. All efficiencies considered herein are within the current technological capabilities. Also, the parameter τ is assumed to be 1 MJ/km. The fuel costs are as listed in Table 7.1.

The results show that the driving range of gasoline vehicles is the longest, but the associated cost is the highest among all options considered here. Therefore, the gasoline tank is the most compact. The hydrogen tank is the least compact; however, the driving cost of a hydrogen vehicle is half of that of all common fuels. Regarding ammonia, the fuel tank is reasonably compact (about two times larger than the gasoline tank), and the specific driving cost is the lowest. If the considered specific cost of ammonia is 25% higher, that is, CN $0.4/kg, still the driving cost of an ammonia vehicle at 35% is lower than that of a hydrogen vehicle at 50%.

Several automakers have developed the prototypes of hydrogen-fueled vehicles in recent years. Here, for analysis purposes, we select a Ford Focus H_2ICE prototype. In Table 7.2, we list the performance parameters of the actual prototype and some calculation results for the same prototype converted to use NH_3 fuel. For the calculation, it has been assumed that the cost of ammonia is $0.30/kg. The efficiency of the ammonia engine is assumed to be the same as that of the

Table 7.1 Comparison of ammonia with other fuels including hydrogen

Fuel/storage	P [bar]	ρ, Density [kg/m^3]	HHV [MJ/kg]	HHV$'''$ [GJ/m^3]	e''' [GJ/m^3]	c [CN \$/kg]	C''' [CN \$/m^3]	c/HHV [CN \$/GJ]
Gasoline, C_8H_{18}/liquid	1	736	46.7	34.4	34.4	1.36	1,000	29.1
CNG, CH_4/integrated storage	250	188	42.5	10.4	7.8	1.20	226	28.2
LPG, C_3H_8/pressurized tank	14	388	48.9	19.0	11.7	1.41	548	28.8
Methanol, CH_3OH/liquid	1	786	14.3	11.2	9.6	0.54	421	37.5
Hydrogen, H_2/metal hydrides	14	25	142	3.6	3.0	4.00	100	28.2
Ammonia, NH_3/pressurized tank	10	603	22.5	13.6	11.9	0.30	181	13.3
Ammonia, NH_3/metal amines	1	610	17.1	10.4	8.5	0.30	183	17.5

Data from Zamfirescu and Dincer (2009a)

Table 7.2 Conversion of a Ford Focus H_2ICE to NH_3 fuel

Parameter	Unit	H_2	NH_3
Storage tank volume	Liter	217	76
Storage pressure	Bar	345	10
Energy onboard	MJ	710	1,025
Cost of full tank	CN \$	25	14
Driving range	Km	298	430
Driving cost	CN\$/100 km	8.4	3.2
Tank compactness	Liter/100 km	73	18

Data from Zamfirescu and Dincer (2009a)

hydrogen engine. In fact, ammonia can be decomposed onboard at no additional cost (using only the heat rejected by the ICE) and the engine fueled with pure hydrogen. As can be observed, the driving range of the NH_3 vehicle is much longer and hence more economical with a driving cost of \$3.2/100 km compared to \$8.4/100 km for the H_2ICE. Moreover, the tank compactness of the ammonia car is about four times better.

It is of interest to know the energy at the shaft with respect to the energy stored in the fuel tank. This is presented in Fig. 7.17, which shows the energy at the shaft per unit of fuel volume and fuel mass stored in the fuel tank. Note that because of the assumed higher efficiency at power conversion when hydrogen is generated from ammonia, the energy at the shaft per volume is the highest.

In Fig. 7.17, the situation when ammonia is used directly as a fuel (possibly with partial (3% per volume) decomposition) is also included. Fueling an ICE is a proved

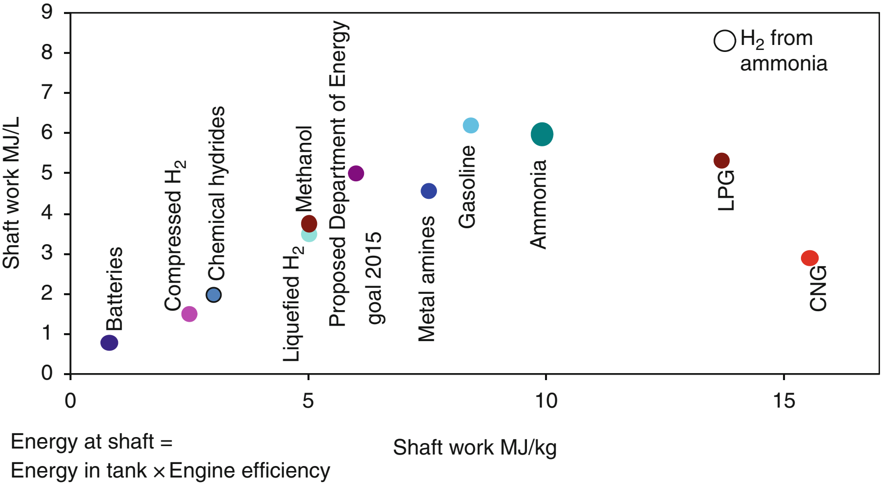


Fig. 7.17 Energy at the shaft with respect to the energy stored in the fuel tank [modified from Zamfirescu and Dincer (2009b)]

practice because an ammonia–hydrogen mixture has comparable combustion characteristics with gasoline (see Zamfirescu and Dincer 2008a,b,c). The energy developed at the shaft per unit of fuel volume is about the same for ammonia and gasoline engines, while the shaft energy developed per unit of fuel mass is in favor of ammonia. If hydrogen is produced from ammonia and work recovery is applied for improving the efficiency (as discussed above), high power conversion is achieved and this provides very promising values: ~8 MJ/l and ~14 MJ/kg shaft power.

Results regarding the life-cycle efficiency of vehicles driven with various fuels and with ammonia, and the corresponding CO_2 mitigation and cost are summarized in Fig. 7.18, which is taken from the study by Zamfirescu and Dincer (2009b). Six cases are compared in the figure:

- Reference vehicle fueled with gasoline
- Vehicle driven with hydrogen produced through sustainable methods
- Hydrogen derived from fossil fuels
- Ammonia produced by artificial biological methods (using enzymes)
- Ammonia produced from sustainable energy sources
- Ammonia produced from fossil fuels

The life-cycle efficiency includes all phases starting with primary materials and energy sources, including ammonia synthesis, storage, distribution, and power generation at remote (stationary or mobile) locations. For the reference gasoline case, the mitigation of GHG is negative, meaning that there is no mitigation in this case. When ammonia is derived from biological synthesis, the GHG mitigation is the maximum. Regarding the economics, the cheapest cost per unit of energy derived at the shaft corresponds to ammonia derived from fossil fuels.

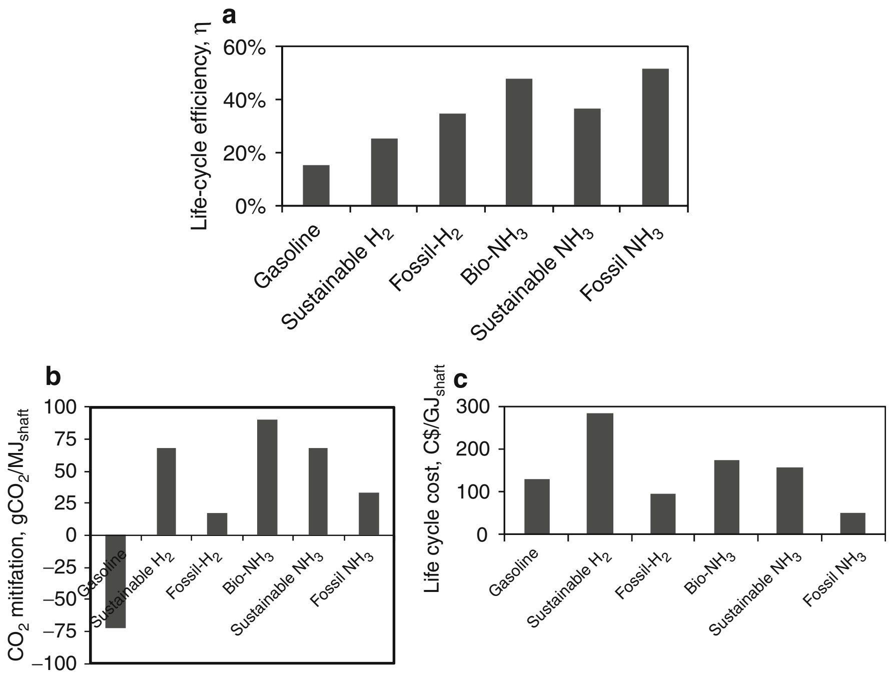


Fig. 7.18 Summary of life-cycle assessment results: (**a**), CO_2 mitigation (**b**), and unitary cost (**c**) [modified from Zamfirescu and Dincer (2009b)]

7.10 Concluding Remarks

In this chapter, it was shown that ammonia is a potential substance for sustainable energy systems because it uniquely offers the opportunity to store hydrogen at high density; it produces power when used as fuel, hydrogen source, and working fluid, and is simultaneously used as a refrigerant and an NO_x-reducing agent. Some specific conclusions from this chapter are as follows:

- Thermo-catalytic membrane reactors are the most promising devices for H_2 generation from NH_3.
- If ammonia is used simultaneously as a working fluid and a fuel, the efficiency increases by >2%.
- NH_3 can be stored seasonally as opposed to H_2, which must be consumed within a few days after production.
- Ammonia delivered and converted into shaft energy is cheaper than hydrogen, although in the production phase ammonia could be up to ~25% more expensive than hydrogen from which it is synthesized.
- The energy generated at the shaft is 25% higher in hydrogen-from-ammonia cases; with respect to gasoline, per unit of fuel volume, and per unit of mass, it is 30% higher.

- Some additional advantages of ammonia are commercial availability and viability, global distribution network, and easy handling experience, while its toxicity may be seen as a challenge. This can easily be overcome with the current control and storage technologies.

Nomenclature

c	Specific cost, currency per mass
ex	Specific exergy, kJ/kg
g	Gravitational acceleration, m/s^2
h	Specific enthalpy, kJ/kg
H	Formation enthalpy, J/mol
LHV	Lower heating value, MJ/kg
P	Pressure, Pa
s	Specific entropy, KJ/kg K
T	Temperature, K
w	Mass specific work, J/kg
x_d	Dissociation fraction
z	Elevation, m

Greek Letters

ε	Effectiveness
η	Efficiency
μ	Molar mass, kg/kmol
ρ	Density, kg/m^3

Subscripts

0	Reference state
c	Cooling effect
d	Dissociation
i	Inlet
r	Refrigeration
S	Isentropic
w	Expansion

Superscript

$( )'''$ Per unit of volume

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Study Questions/Problems

7.1 How much hydrogen is embedded in 1 mol of ammonia, 1 m^3 of ammonia, and 1 kg of ammonia?

7.2 Determine the quantity of hydrogen present in a 1-m^3 ammonia tank containing 20% per volume of ammonia vapor, and ammonia liquid. Consider that the tank is kept at (a) standard temperature, (b) negative 40°C, and (c) positive 45°C.

7.3 Consider the system presented in Fig. 7.1 for ammonia synthesis. Using energy and mass balance equations and appropriate assumption, determine the ammonia production efficiency according to the first and second law of thermodynamics.

7.4 According to Fig. 7.2, determine the amount of energy needed to synthesize one molecule of ammonia using nitrogenase enzyme.

7.5 Consider the ammonia storage system presented in Fig. 7.3. Make reasonable assumptions and determine the efficiency and the cost of storage for a period of 6 months.

7.6 Calculate the reaction heat associated with NO_x decomposition on zeolites using ammonia, according to Eq. (7.3), for two cases: (a) cold start at ambient temperature, and (b) steady operation at 300°C.

7.7 Demonstrate through calculation of the cost the advantage of the "hydrogen from ammonia route" compared with the "hydrogen-only route." Use the diagram in Fig. 7.8 for the calculations.

7.8 Determine the reaction heat of an ammonia decomposition reaction for a reasonable range of temperatures and pressures.

7.9 By minimizing Gibbs energy, determine the equilibrium concentration of the ammonia decomposition reaction for pressures of 0.1 bar, 1 bar, 10 bar, and 100 bar and temperatures in the range of $-40°C$ to 1,000°C.

7.10 Make reasonable assumptions and determine the efficiency of the power-generation system presented in Fig. 7.10.

7.11 Consider the system in Fig. 7.14a and determine the refrigeration effect associated with a 100-kW engine.

7.12 Redo through your own calculation the plot in Fig. 7.17.

7.13 Based on a literature study, determine the energy density per mass and volume of ammonia borane and compare it with that of an ammonia-only system.

7.14 Calculate the life-cycle carbon dioxide emissions when ammonia is produced from coal and then used as fuel for motor engines.