Potential Roles of Ammonia in a Hydrogen Economy

A Study of Issues Related to the Use Ammonia for On-Board Vehicular Hydrogen Storage

U.S. Department of Energy

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EXECUTIVE SUMMARY

The objectives of this paper are to identify, evaluate and summarize the key issues and advantages and disadvantages associated with ammonia as an energy carrier for on-board vehicular hydrogen storage. These issues have been investigated by the U.S. Department of Energy (DOE) with input from various sources including members of the Hydrogen Storage Technical Team of the FreedomCAR & Fuel Partnership (a partnership among DOE, BP America, Chevron Corporation, ConocoPhillips, Exxon Mobil Corporation, Shell Hydrogen (U.S.), and the United States Council for Automotive Research (USCAR- a legal partnership among DaimlerChrysler Corporation, Ford Motor Company, and General Motors Corporation). The outcome of this investigation is a discussion of the potential roles that ammonia might play in a hydrogen economy, particularly with regard to the viability of ammonia as an on-board hydrogen carrier for fuel cell vehicles.

Ammonia has a number of favorable attributes, the primary one being its high capacity for hydrogen storage, 17.6 wt.%, based on its molecular structure. However, in order to release hydrogen from ammonia, significant energy input as well as reactor mass and volume are required. Other considerations include safety and toxicity issues, both actual and perceived, as well as the incompatibility of polymer electrolyte membrane (PEM) fuel cells in the presence of even trace levels of ammonia (> 0.1ppm).

Given the state of the art in ‘cracking’ ammonia to produce hydrogen, there are many issues in the on-board use of ammonia similar to those identified for on-board fuel processors. Specifically, these include: high operating temperature (>500° C); longevity and reliability of catalysts and other components (at high temperatures and in the presence of impurities); start-up time (to get the system up to operating temperature); purification requirements (to prevent ammonia poisoning of fuel cells); complexity of the overall system; energy efficiency (on-board ammonia would have to be burned in the cracking process); cost (currently ~\$100K for 1-3 g H_2/s stationary units); and reactor weight and volume (commercial units with sufficient throughput currently weigh about 2000-5000 kg and are about 3000-6000 liters in size). Simply stated, most of the performance parameters of ammonia reactors would need at least two orders-of-magnitude improvements in order to be used on-board commercially viable hydrogen-powered fuel cell vehicles.

Due to the above reasons, DOE does not plan to fund R&D to improve ammonia fuel processing technologies for use on board light weight vehicles at the present time. However, a distinction may be made between conventional fuel processing of ammonia (e.g. high temperature, low efficiency, slow start-up/time response crackers) versus novel approaches to store ammonia and release its hydrogen content under conditions available on-board PEM fuel cell vehicles. As DOE’s current portfolio in hydrogen storage evolves, breakthrough approaches that allow the safe, efficient and cost effective use of ammonia-based storage may be considered at a future date. While this paper describes general advantages and disadvantages of ammonia with a focus

on on-board vehicular hydrogen storage, the use of ammonia as a potential hydrogen carrier for hydrogen delivery or off-board hydrogen storage is currently under evaluation by the DOE and the FreedomCAR and Fuel Partnership's Hydrogen Delivery Technical Team.

I. INTRODUCTION

The low volumetric energy density of hydrogen—in both compressed gas and liquid forms—makes the storage of hydrogen a difficult problem for most applications. This limitation is felt most strongly in the area of onboard storage, but it is also problematic in the delivery and distribution of hydrogen. Hydrogen's low energy density is perhaps one of the greatest barriers to the implementation of hydrogen fueled fuel cell vehicles.

A number of chemical, solid state and other approaches have been examined, and are currently being investigated, that could lead to higher stored energy density. Little attention, however, has been given to the possibility of using liquid anhydrous ammonia, NH_3, as a medium for the storage of hydrogen onboard vehicles or for use as a distribution medium.

This document will consider the possible roles ammonia might play in implementation of a hydrogen economy. It is intended to explain the rationale for considering the use of ammonia and to elucidate and weigh the advantages and disadvantages associated with ammonia. Finally recommendations are given as to what role ammonia might play in the transition to a hydrogen economy or in the final implementation of that economy.

II. AMMONIA PROPERTIES

Ammonia has several desirable characteristics that suggest its use as a medium to store hydrogen. First, it can be liquefied under mild conditions. The vapor pressure of ammonia at room temperature is 9.2 bar (~121 psig). Its physical properties are similar to those of propane (see Table 2.1).[1] This means that ammonia can be stored in a simple, inexpensive pressure vessel. Second, ammonia has a large weight fraction of hydrogen. Hydrogen constitutes 17.65% of the mass of ammonia. When these two factors are combined, the result is a liquid that is simply contained, with a volumetric hydrogen density about 45% higher than that of liquid hydrogen. Ammonia can be decomposed (cracked) over a catalyst to produce the desired fuel—hydrogen (H_2) along with nitrogen (N_2) a non-toxic, non-greenhouse gas.

In addition, ammonia might be an excellent transition fuel. It can be burned directly in an internal combustion engine (ICE) with no carbon emission, converted to electricity directly in an alkaline fuel cell, or cracked to provide hydrogen for non-alkaline fuel cells (FC). Central production from hydrocarbon fuels (e.g., natural gas) would provide opportunities for CO_2 capture; transportation and distribution would be simpler and cheaper than hydrogen delivery; and final use in an internal combustion engine or fuel cell would produce no carbon dioxide.

Some of the physical and chemical properties of ammonia are listed in the following table. Additional details in the properties of ammonia are covered in subsequent sections of this report.

Ammonia Properties

Hydrogen Content					
H_2 weight fraction	17.65	wt.%	H_2 volume density	0.105	kg/liter
Solid Phase					
Melting point	-78	°C	Latent heat of fusion (1 atm at triple point)	-337.37	kJ/kg
Liquid Phase					
Vapor pressure (21°C)	8.88	bar	Liquid density (1atm @ boiling point)	682	kg/m^3
Boiling point (@ 1.0 atm)	-33.5	°C	Liquid/gas equivalent (1 atm and 15°C)	947	vol/vol
Latent heat of vaporization (1 atm @ boiling point)	1371.2	kJ/kg			
Critical temperature	132.4	°C	Critical pressure	112.8	bar
Gas Phase					
Gas density (1 atm at boiling point)	0.86	kg/m^3	Gas density (1 atm at 15°C)	.73	kg/m^3
Compressibility (Z) (1 atm at 15°C)	.9929		Specific gravity (air=1) (1 atm at 20°C)	.597	
Specific volume 1 atm at 20°C)	1.411	m^3/kg	Viscosity	.000098	Poise
Heat capacity at constant pressure (Cp) (1 atm at 15°C)	.037	kJ/(mol.K)	Heat capacity at constant pressure (Cv) (1 atm at 15°C)	.028	kJ/(mol.K)
Critical Density:	0.24	g/ml	Entropy, Gas @ 25ºC., 1 atm. :	45.97	cal/molºC
Thermal conductivity	22.19	mW/(mK)			
Misc					
Water solubility (1 atm at 0°C)	862	vol/vol	Autoignition temperature	630	°C
Lower flammable limit in air	15%	by volume	Upper flammable limit in air	28%	by volume
Molecular Weight:	17.03				

Table 2.1: Selected Ammonia Properties

III. AMMONIA PRODUCTION

Technical Description

Ammonia is normally produced by the catalytic reaction of nitrogen and hydrogen. Although process technology has improved over the years, the basic chemistry is identical to the process developed by Haber and Bosch in the early 20th century[2] :

N_2 (g) + 3 H_2 (g) → 2 NH_3 (g) $\Delta H = -92$ kJ/mole (-46 kJ/mole for 1 mole of NH_3)

The reaction is typically carried out over iron catalysts at temperatures around 400-600°C and pressures ranging from 200 to 400 atmospheres.

In practice, ammonia synthesis is usually coupled with hydrogen production to increase efficiency. The hydrogen is typically produced from natural gas, but it can also be produced from other fuels, such as petroleum coke or biomass. These feedstocks are generally gasified to form synthesis gas (CO and H_2), which can then be reacted with water and nitrogen to produce ammonia. In a USGS Mineral Commodity Profile for nitrogen[3], world production of ammonia in 2002 was given at around 108 million metric tons (Mt) of contained nitrogen (131 million Mt ammonia) with around 8.8 million Mt contained nitrogen (10.7 Mt ammonia) produced in the U.S. At the time of the report (2004), ammonia production capacity in North America and Europe was projected to decline, with production capacity shifting toward world regions that have abundant natural gas resources.

As natural gas prices have increased, more emphasis has been placed on process efficiency. Figure 3.1 shows estimates from an August 2000 report by the Fertilizer Institute showing the effects of natural gas price on ammonia production costs (note-may not include all capital costs).[4] Currently (September 2005), spot prices for natural gas are in the range of $10-11/MMBtu. Extrapolating the trend shown in the figure, the estimated cost of ammonia production would then be $377/ton for a natural gas price of $10.50/MMBtu. At this ammonia production cost, a rough estimate for the cost of hydrogen available in the ammonia (assuming a cracking efficiency of about 75%) is ~$3.00/kg (gge).

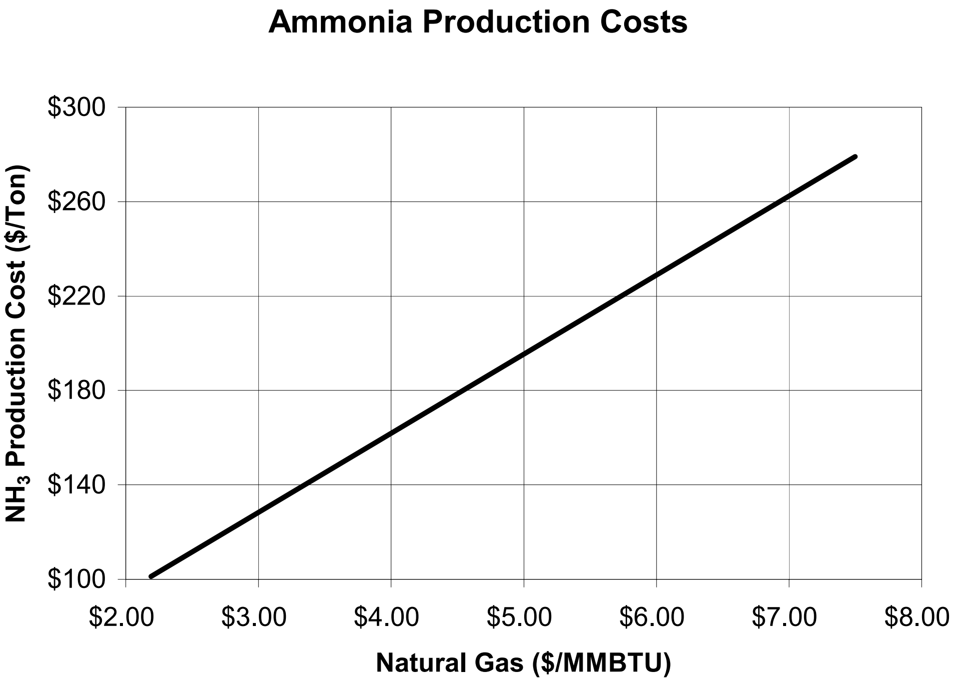

Figure 3.1 Estimated Ammonia Production Costs

As U.S. natural gas prices have risen, ammonia production has decreased due to competition from imports produced with cheaper natural gas. Higher natural gas prices have also lead to increased production from other sources. China has several plants producing ammonia from coal, coke, and petroleum fractions. In the U.S, a Coffeyville, Kansas refinery produces ammonia from petroleum coke,[5] and the Great Plains Synfuels produces around 400,000 tons of ammonia per year from coal.[6]

Energy Usage

Current technology based on natural gas as the feedstock produces ammonia with an energy input as low as 6.8 Gcal (LHV)/Mt,[7] or in non-metric units, 24.7 MMBTU/ton. Given the energy content of ammonia, conversion of natural gas to ammonia then is about 60-65% energy efficient; that is, 60-65% of the energy input to the process (mostly methane) is contained in the ammonia product.

As stated earlier, ammonia can be produced from other feedstocks, although production is not expected to be as efficient or as cheap as natural gas-based production. The alternate feedstocks are typically gasified to form CO, and the water gas shift reaction is used to produce hydrogen from the CO. Table 3.2 shows estimates from the European Fertilizer Institute of energy consumption and cost of production relative to production of ammonia from natural gas. These numbers might improve as alternate production technologies mature and gas prices go higher.

	Natural gas	*Heavy oil*	*Coal*
Energy consumption	1	1.3	1.7
Investment cost	1	1.4	2.4
Production cost	1	1.2	1.7

Source: European Fertilizer Manufacturer's Association[8]

Table 3.2 NH_3 Production from Alternate Sources

An excellent review of ammonia production—as well as other ammonia data can be found at the web site of the U.S. Geological Survey.[9]

IV. AMMONIA DECOMPOSITION

Ammonia decomposition (cracking) is simply the reverse of the synthesis reaction.

$$NH_3\ (g) \rightarrow \tfrac{1}{2}\ N_2\ (g) + \tfrac{3}{2}\ H_2\ (g) \qquad \Delta H = +46\ \text{kJ/mol}$$

Note that the reaction is endothermic. The temperature required for efficient cracking depends on the catalyst. There are a wide variety of materials that have been found to be effective, but some (e.g., supported Ni catalysts) require temperatures above 1000°C. Others have high conversion efficiency at temperatures in the range of 650-700°C. As these temperatures are well above PEM fuel cell operating temperatures, some of the fuel or, perhaps, the fuel cell purge gas, would need to be burned to maintain an efficient reaction.

The theoretical adiabatic efficiency for the thermocatalytic reaction is about 85% relative to the energy (LHV) of the released hydrogen. If no other energy source were available, at least 15% of the available hydrogen energy content would have to be burned to supply the heat of reaction. Of course, additional energy would be required to overcome thermal losses in the cracking reactor. Since the reaction occurs at high temperature, this heat would likely come from the combustion of ammonia and/or hydrogen in onboard storage applications. The impact of this heat requirement on effective onboard storage capacity is discussed in detail in Section V. In the forecourt, one would have the option of using other energy sources (electricity, natural gas, etc.) to supply the heat of reaction.

Table 4.1 shows the equilibrium conversion of ammonia, calculated using HSC[10], as a function of temperature at reactor pressures of 1 and 10 bar. Actual decomposition conditions used in real-world operations involve tradeoffs between the costs of operations at higher temperatures and cost of removing unconverted ammonia. Since proton electrolyte membrane (PEM) fuel cells require ammonia concentrations below 0.1 ppm, significant purification will be necessary. Even at 900° C, the equilibrium calculations indicate 1500 ppm unconverted NH_3 at 10 bar.

Temperature (°C)	Unconverted NH_3 1 bar	Unconverted NH_3 10 bar
400	0.88%	7.91%
500	0.26%	2.55%
600	0.10%	1.00%
700	0.047%	0.47%
800	0.025%	0.25%
900	0.015%	0.15 %

Table 4.1: Equilibrium Ammonia Conversion[10]

As the reactor temperature is increased, other problems emerge. In particular, it becomes more difficult for the reactor materials, such as the catalyst, its supports and the reactor container, to sustain exposure to this environment. Susceptibility of the container materials to stress corrosion cracking (SCC) and high temperature hydrogen embrittlement, for example, would have to be considered in the materials choices, particularly since the unit would be subjected to temperature swings from ambient temperatures (when not used) to the highest operating temperature. Furthermore, just from a strength and stability point of view, metal alloy choices become more limited (and generally more expensive) for high temperature applications. Although a stainless steel alloy might be used below 500° C, a Ni based or other alloy would be required at higher temperatures. A higher operating temperature would perhaps also require more insulation, increasing the weight and volume of the reactor. It could also increase the time required for the reactor to start producing hydrogen from a cold start, an important parameter for on-board vehicular applications.

A potential design for an ammonia cracking reactor is schematically shown in Fig. 4.1. Liquid ammonia would be pumped from a storage tank through a heat exchanger to capture waste heat from the hot gases exiting the cracking reactor. The preheated gases would then go though a furnace or catalytic combustor to heat them to the temperatures necessary for the reaction. The stream exiting the reaction would go to a separation system which would be optimized to produce a very pure stream of hydrogen while still leaving sufficient hydrogen with the nitrogen and unreacted ammonia to provide heat for the endothermic cracking reaction. This "waste stream" would be combusted to supply heat for the reaction and to remove unreacted ammonia.

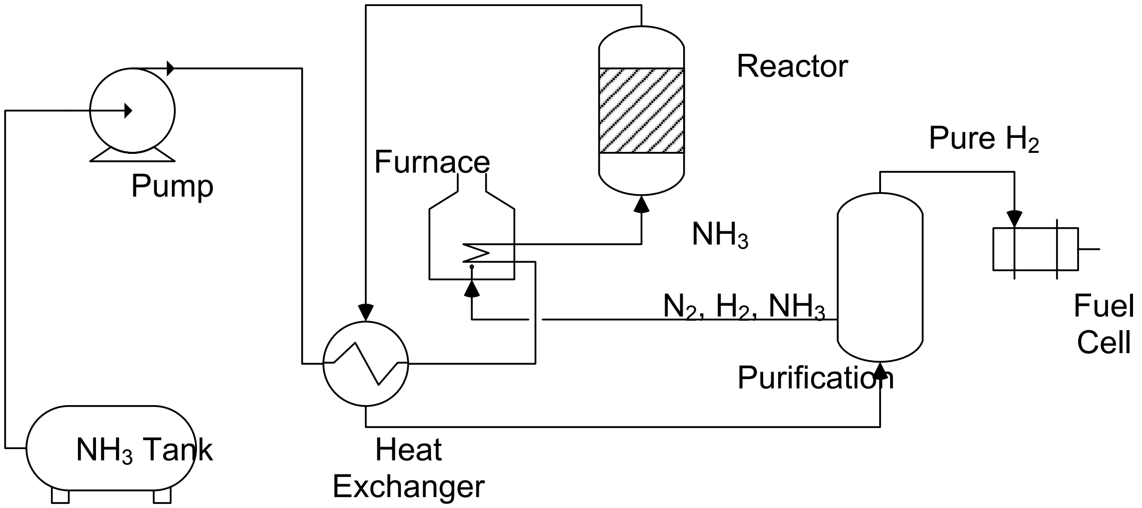

Figure 4.1 Conceptual NH_3 Fuel Processing System

For onboard storage applications, the reactor would have to operate over a very wide dynamic range and with very fast response time to supply a fuel cell or ICE under all drive conditions. It would also have to be sized based on its ability to supply enough hydrogen for full power operation. For example, the input hydrogen flow rate at full power for a 100 kW fuel cell (assuming a full power efficiency of about 45%) would be 2 g/s, or about 1,350 standard liters/min of hydrogen. At 65% overall conversion efficiency, the cracking reactor would be consuming about 1.75 liters of liquid ammonia per minute and would need to process about 23 standard liters of ammonia per second. As mentioned above, additional requirements on the cracking reactor component for on-board use would be to eliminate even trace amounts of ammonia in the outlet stream and to filter out the nitrogen. The ammonia removed from the outlet stream must be recycled into the inlet stream of the tank or used to supplement the inlet stream for source heat, since venting even small amounts of ammonia is not an option. Further details of ammonia cracking systems can be found in the literature, where a number of papers discuss the performance of different catalysts[11] and other aspects of ammonia cracking.[12]

The system above is but one of many potential designs for an integrated reactor for ammonia cracking and purification. It does, however, serve to illustrate the complexity of practical reactor systems. An onboard system would likely be very different from a system designed for use in a forecourt application, but the basic components of reactor, heat recovery, waste stream recycling and highly effective purification will be vital parts of any successful system. Potential research areas to design adequate systems include kinetics, separations methods, and reactor design and optimization. A number of potential reactors have been discussed in the patent literature.[13]

The decomposition of ammonia to produce hydrogen for use in a PEM fuel cell is a challenging problem. Advances in catalyst, high temperature materials, and separations will be necessary to produce an integrated reactor/separator that meets all the requirements.

V. Onboard Storage of Anhydrous Ammonia

Anhydrous ammonia has very high gravimetric (~17 wt.% or 5.8 kWh/kg) and volumetric (~0.105 kg/liter or 3.6 kWh/liter at 25° C) hydrogen energy densities and, hence, looks appealing for use as a potential hydrogen carrier for onboard storage. Also, compared to reforming hydrocarbon fuels, the dissociation, or cracking, of hydrogen from ammonia may require a less complex process. The byproduct of the hydrogen dissociation process, nitrogen, can be vented from the vehicle with no adverse environmental effects so there is no need for a recycling process, as in some other chemical hydride systems.

However, ammonia has specific chemical and physical properties which require attention in the design and engineering of an onboard storage system. These issues are: high coefficient of thermal expansion, high vapor pressure at ambient conditions, propensity for reacting with water, reactivity with container materials and high toxicity of the vapor if released into the air. These will be discussed below. Importantly, PEM fuel cells cannot tolerate ammonia, even at very low ppm levels[14] and, hence, an onboard storage system based on ammonia would require a cracking reactor with essentially no pass-through of undissociated ammonia and/or a very effective filtration system.

Containers & Refueling

Figure 5.1 is a plot of specific gravity of liquid ammonia as a function of temperature. The plot essentially covers the expected temperature range of a storage system as defined in the DOE/FreedomCAR and Fuel Partnership storage system targets. The lowest temperature data point on the graph, -33° C, is the boiling point of ammonia at atmospheric pressure. Above this temperature, an overpressure is needed to maintain an equilibrium liquid/vapor phase system. The liquid density ranges from 0.682 at the boiling point to 0.545 at 60° C. If the tank were filled at nominal ambient temperatures (20-25° C), the volume at 60° C would be 10-12% greater. Relative to the nominal midrange temperature density, the overall range of expansion is about 23%. Thus, in practice, ammonia storage tanks at fixed sites are considered to have a usable capacity of 85% of their internal volume to allow for this expansion. It might be prudent to have somewhat more than 15% vapor space in an onboard storage system because temperature swings between filling and operating temperatures could be large. For purposes of this discussion, however, we will use a filling temperature range of 20-25° C and the 15% value for vapor space in a tank.

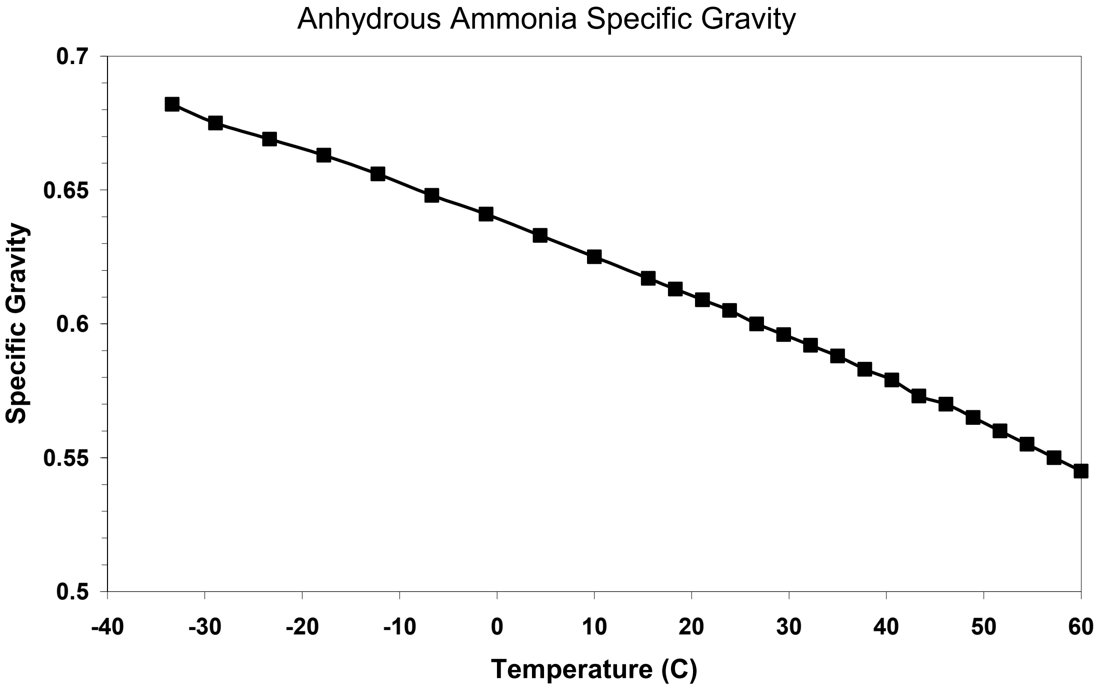

Figure 5.1 Ammonia Specific Gravity[1]

The onboard tank must also sustain a modest overpressure. The vapor pressure as a function of temperature is shown in Figure 5.2. At 60° C, the vapor pressure of anhydrous ammonia is about 365 psig (about 25 bar). With a safety factor of ~2-2.2, the tank should sustain a maximum pressure of ~800-900 psi. In order to maintain the high gravimetric density, lightweight tank fabrication would be desirable. Currently, fixed site ammonia tanks are often constructed of steel or ductile iron. Many polymers are compatible with ammonia, so it is likely that composite tanks or lightweight aluminum tanks with polymer liners could be used for onboard storage of ammonia.

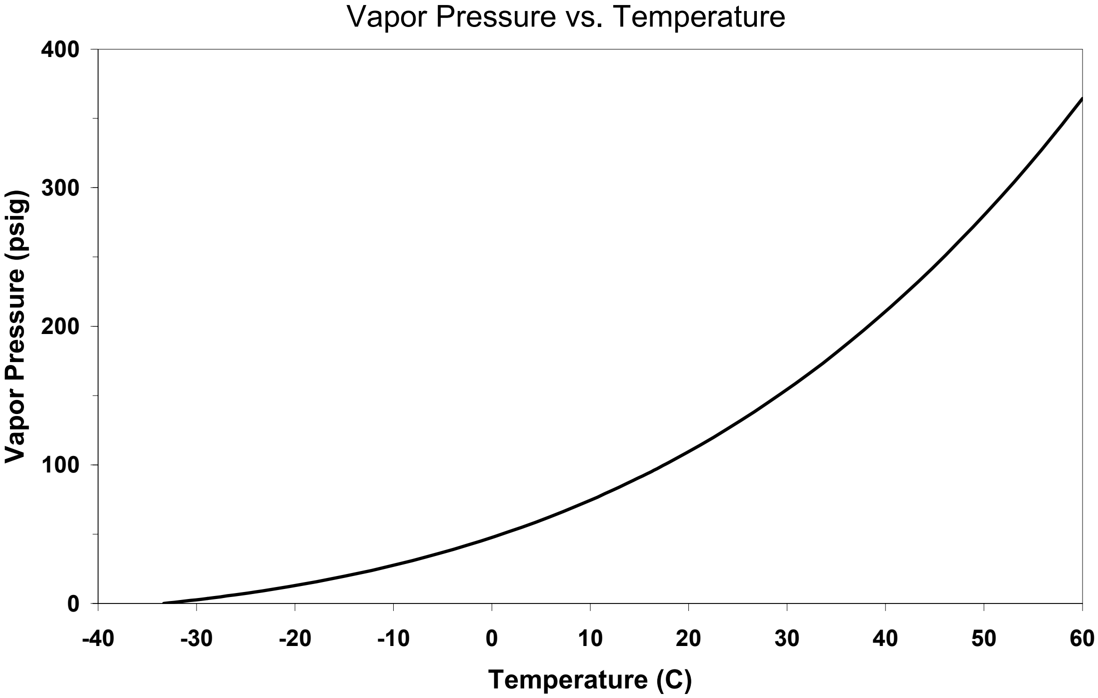

Figure 5.2 Ammonia Vapor Pressure[1]

Another issue is long term compatibility of metal tanks containing ammonia due to stress corrosion cracking (SCC). This effect could lead to failures of tanks, valves and other components in direct contact with ammonia. Large, fixed site storage tanks undergo periodic examinations, on the order of every five years, for potential SCC effects.

Filling the onboard tank from a forecourt source will require a demountable, leak-proof coupling. This is mainly due to the extreme toxicity of ammonia, but also because of the great affinity of ammonia for water resulting in the formation of ammonium hydroxide. Humidity from the air leaking into the refueling tube or coupling would, over time, lead to corrosion of the piping and tank by the hydroxide.

Meeting Storage Targets

Could an ammonia-based storage system meet the DOE/FreedomCAR and Fuel Partnership targets for onboard energy density? The answer would, of course, depend on the details of the system. However, we can gain some insight into the requirements on the cracking reactor by sizing a 5 kg delivered hydrogen system. The results are shown in Figures 5.3 and 5.4.

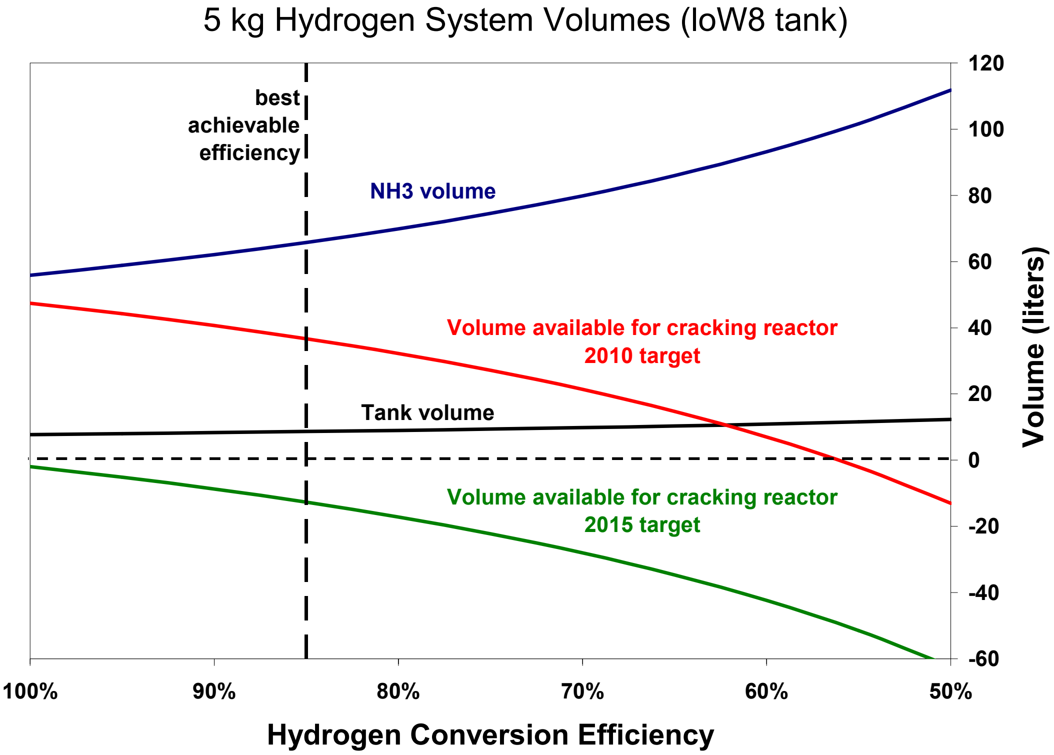

Figure 5.3 Volumetric Targets

In Figure 5.3, system volumes are plotted as a function of cracking efficiency; that is, the percentage of hydrogen delivered relative to the amount of hydrogen contained in the ammonia. On its own, ammonia has very good volumetric density — 5 kg of hydrogen is contained in 56 liters (15 gal.) of ammonia at room temperature. However, additional ammonia must be carried onboard to overcome the conversion efficiency. The dashed line at 85% is the best achievable efficiency in a system because, as mentioned earlier (Section IV), sufficient energy must be supplied to drive the endothermic decomposition reaction by burning some of the ammonia. At 50% efficiency, essentially double the amount of ammonia, 110 liters (29 gal.), is needed to supply 5 kg of hydrogen. For purposes of this analysis, we calculated the tank weight and volume based on the gravimetric and volumetric density of a light weight commercial polymer tank developed for onboard LPG containment ("loW8" tank by Advanced Lightweight Engineering BV). Subtracting the volumes of the ammonia and the tank from the total volume calculated with the DOE/FreedomCAR and Fuel Partnership energy density targets for 2010 and 2015 then yields the volume available for an ammonia cracking reactor. These volumes are shown in the red and green curves. One can see, for example, that the 2010 targets could be met if a ~20 liter sized reactor could be fabricated which had an overall conversion efficiency of 65% or greater. On the other hand, the plot also shows that the tank and ammonia volumes alone, without considering a reactor, exceed the total volume calculated for the 2015 volume density. In addition to the reactor unit, system volumes would also include a highly effective ammonia filter or scrubber and other ancillary components.

Another volumetric issue is that the particular composite tank design used in the analysis is a nonconformable shape. As is typical of composite pressure vessels, smooth, curved surfaces are used in their construction to allow ease of fabrication and to eliminate stress concentrator points. The actual shape of the container in this case is similar to an oblate spheroid. The wall thickness was estimated by assuming an overall density of the wall material typical of composite construction. Utilizing a tank with better volumetric efficiency for this application would certainly improve the estimates shown in Figure 5.3.

The lightweight tank construction does offer some advantages in the overall system weight. As shown in Figure 5.4, the 2015 target could be met with a cracking reactor weighing about 15 kg and operating with an overall efficiency of 85%. The less stringent 2010 system weight target could be met with even heavier cracking reactor components.

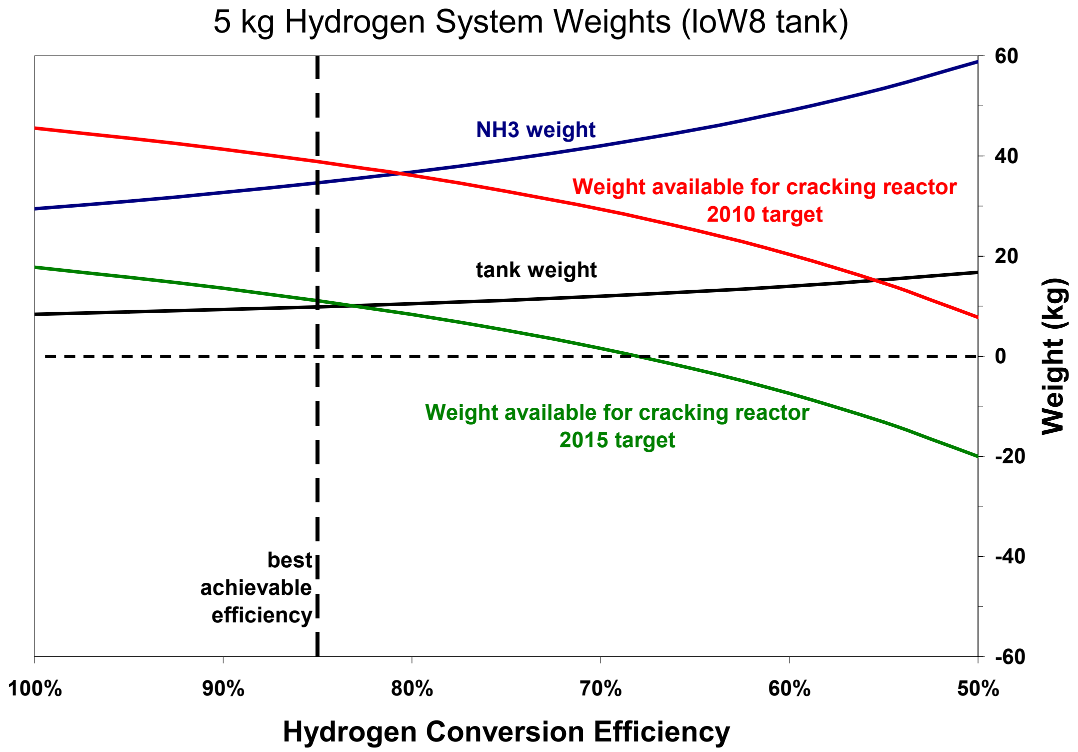

Figure 5.4: Mass Targets

At the present time, commercially available cracking reactors capable of producing hydrogen at the required flow rates (up to about 2 g H_2/s) are designed for fixed site applications. These units use external power sources and operate with conversion efficiencies in the range of ~50-65%. They are at least two orders of magnitude too heavy (2000-5000 kg vs. the tens of kg's estimated above) and too large (3000-6000 liters vs. <50 liters as shown in Fig. 5.3) for onboard use. Unit purchase prices are also quite high, typically about $100K. A significant R&D effort, similar to that pursued for onboard gasoline reformers, would be needed to develop ammonia cracking reactors with the required efficiency, size, weight and other performance characteristics required by passenger car users. The question remains, however, whether an onboard reactor approach with ammonia, as with gasoline, would be a viable approach to onboard storage in a hydrogen economy.

In summary, the viability of an ammonia-based onboard storage system would depend largely on the following factors:

1. Development of high power, small volume, lightweight and efficient integrated ammonia cracking/purification systems capable of supplying hydrogen at ~1400 slm and with ammonia pass-through of <0.1 ppm.
2. Development of lightweight tanks capable of sustaining the weight and vapor overpressure of anhydrous ammonia and with proven long-term integrity in an ammonia environment.
3. Addressing all of the safety issues associated with working with ammonia and ammonia-containing systems.

VI. AMMONIA AS A HYDROGEN CARRIER (DELIVERY)

The same constraints that cause problems in storing hydrogen onboard a vehicle arise when hydrogen is transported. Although central hydrogen production and transportation by pipeline appears to be the ultimate solution to transporting hydrogen efficiently, the high capital investment required suggests that pipelines are unlikely to be used at early stages of the transition to a hydrogen economy. During that phase, other production/ delivery options will dominate. Truck or rail transportation of compressed hydrogen is very expensive. Liquid hydrogen tankers are cheaper, but there is a considerable energy and cost penalty associated with liquefaction (currently >30% of hydrogen's energy content is required to liquefy it). Distributed production will certainly play an important role, but the capital investment associated with small reformers may limit their utility. So other more cost-effective options are also being explored.

The "wild card" option for distribution of centrally produced hydrogen is some sort of hydrogen carrier. A carrier is defined as a material, other than the H_2 molecule, that can be used to transport hydrogen. An additional requirement is that the transformation required to produce hydrogen from the material is relatively simple, uses little energy and is low in cost. Note that materials such as methane or ethanol that can be reformed at a refueling station have strong chemical bonds between carbon and hydrogen, and are thought of as raw material feedstocks for producing hydrogen rather than as hydrogen carriers.

For carriers to be effective, they need to satisfy several criteria. They should have high effective energy (hydrogen) densities (liquids or solids). The associated hydrogenation-dehydrogenation processes should be simple and energy efficient. They should be safe and environmentally benign.

Two-way carriers

A two way carrier is a material that is transported to a distribution site in a "hydrogenated" form, dehydrogenated to yield hydrogen, and the dehydrogenated material returned to a processing site where it would be re-hydrogenated for reuse. Proposed two-way carriers include complex hydrides with high hydrogen capacities (e.g., $LiBH_4$) and some hydrocarbon systems, such as decalin-napthalene ($C_{10}H_{18} \leftrightarrow C_{10}H_8$).

One-way carriers

A one way carrier would be decomposed at a distribution site to yield hydrogen and a byproduct that is environmentally benign and has no value. Its production should be cheap and efficient.

Ammonia is being considered as one of the best potential options for a one-way carrier. Ammonia is one of the only materials that can be produced cheaply, transported efficiently and transformed directly to yield hydrogen and a non-polluting byproduct. Urea is also appealing since it doesn't suffer from the toxicity problems associated with ammonia, but its hydrogen content is only 9.1 wt% - a little over half that of ammonia

The potential utility of ammonia as a carrier for hydrogen delivery needs to be investigated and is currently under analysis by the DOE and the FreedomCAR & Fuel Partnership's Hydrogen Delivery Technical Team. Since a delivery system using ammonia would use existing technology, research in ammonia delivery should focus on analysis to better understand the economics and safety issues surrounding ammonia use. Ammonia production technologies from renewable sources and from near-zero greenhouse gas emitting sources are also needed.

The ammonia cracking process needs to be improved. Better catalysts, efficient reactor designs, and inexpensive and reliable purification schemes all need to be developed if ammonia is to be used as a hydrogen carrier. It should be noted that some fuel cell technologies, such as alkaline fuel cells are ammonia tolerant, so extensive hydrogen purification would not be needed if they were fueled by hydrogen produced from ammonia.

Existing Ammonia Distribution

Ammonia is currently transported by pipeline, oceangoing tankers, rail, and truck. The different transportation modes are discussed briefly below.

Ammonia Pipelines

Figure 6.1 shows the approximately 4,950 km (3,075 miles) of ammonia pipeline operating in the U.S. today. These pipelines carry ammonia from central production sites to terminals serving distributors and end users (primarily farmers). Pipeline operation is generally safe and cost effective. Tariffs on the Kaneb pipeline average around \$0.026/ton/mile. Converting this value to a price of transporting hydrogen, the cost becomes \$0.10/kgH_2/1000km.

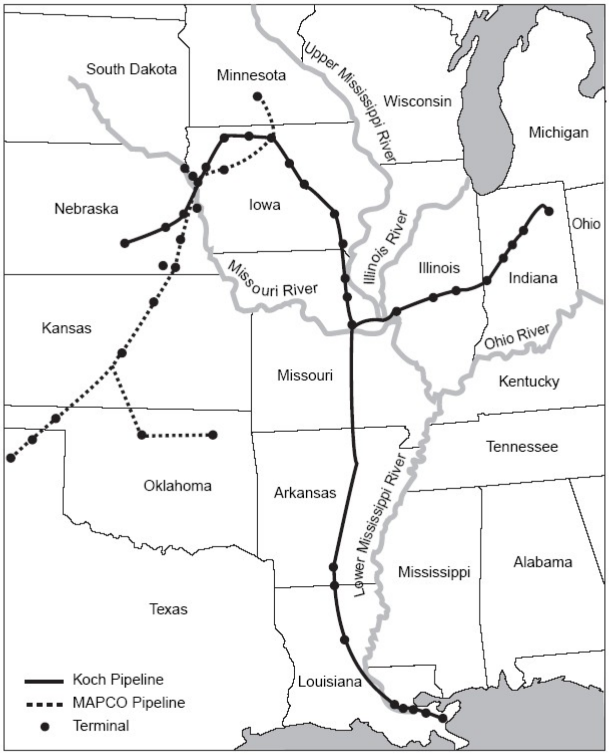

Figure 6.1 NH_3 Pipelines

Ammonia Tanker Ships
Ammonia tankers are typically refrigerated ships. In addition to ammonia, they can usually transport liquefied propane gas (LPG), propylene, vinyl chloride monomer and other condensable gases. Capacities are as high as 84,000 m^3.

Ammonia Trucking
Anhydrous ammonia is generally delivered to end users by truck or small trailers for farm use. The trucks are similar to those used to deliver liquefied propane (LPG).

Estimated Total Distribution Costs
Ammonia distribution costs should be similar to LPG costs. Ammonia distribution would require additional safety equipment, but there are likely to be cost reductions if ammonia were distributed on scales approaching those of current gasoline distribution, so it seems reasonable to assume that these effects would offset each other, yielding similar costs. A recent TIAX study estimates LPG distribution costs to be around $0.55 per gasoline gallon equivalent (gge), including retail margins.[15] Unpublished work from Oak Ridge National Lab estimates the cost at $0.54/gge including a retail margin of $0.18/gge.[16] Converting the $0.36/gge cost of distribution equates to approximately $0.62/kg H_2 when distributed as anhydrous ammonia.

VII. SAFETY, TOXICITY AND SOCIETAL ACCEPTANCE

There are significant problems associated with the use of ammonia. First and foremost is the safety hazard associated with ammonia. Ammonia is a poisonous gas with an OSHA exposure limit of 50 ppm. Its health effects are summarized in Table 7.1.[17] Nevertheless, ammonia is a commonly used industrial and agricultural chemical and can be handled safely.

Effect	**NH_3 concentration in air (by volume)**
Least perceptible odor	5 ppm
Readily detectable odor	20-50 ppm
No discomfort or impairment of health for prolonged exposure	50-100 ppm
General discomfort and eye tearing; no lasting effect on short exposure	150-200 ppm
Severe irritation of eyes, ears, nose and throat, no lasting effect on short exposure	400-700 ppm
Coughing, bronchial spasms	1,700 ppm
Dangerous, less than ½ hour exposure may be fatal	2,000-3,000 ppm
Serious edema, strangulation, asphyxia, rapidly fatal	5,000-10,000 ppm
Immediately Fatal	10,000 ppm (1%)

Table 7.1 Acute Health Effects

The table above deals with acute effects due to short exposures. Less is known about the effects of low level, long term exposures. One study reported that rats exposed continuously to 180 ppm (cited as 127 mg/m^3) for 90 days did not show any abnormalities of organs or tissues. Mild nasal irritation was observed in 12/49 rats exposed to 380 ppm (cited as 262 mg/m^3). At 655 ppm (cited as 455 mg/m^3), 32/51 animals died by day 25 of exposure and 50/51 rats had died after 65 days exposure. Rats, guinea pigs, rabbits and dogs were continuously exposed to 680 ppm (cited as 470 mg/m^3) for 90 days. Deaths occurred in 13/15 rats and 4/15 guinea pigs. At autopsy, all test animals had lung injury. No signs of toxicity were observed in rats, rabbits, guinea pigs, dogs and monkeys exposed to 60 ppm (cited as 40 mg/m^3) continuously for 114 days[18] .

Proposed safe exposure limits vary slightly between different organizations. For example, according to a 2002 position document by ASHRAE (Am. Society of Heating, Refrigeration and Air conditioning Engineers), the time weighted average exposure (over 8 hours) should be limited to 25 ppm and the short term exposure limit should be 35 ppm[19]. These limits are somewhat lower than those shown in the table above.

Current usage of ammonia is limited to industrial applications and in rural farming communities. Would broader usage of ammonia in high density urban environments be accepted by society? As noted above, ammonia odor is detected at concentrations as low as 5 ppm. Small leaks, spills, etc. in and around filling stations should be expected and these could have a cumulative effect on airborn ammonia levels in the immediate vicinity. Similarly, high traffic concentrations in downtown areas and on traffic-clogged urban freeways might also result in odor-detectable concentration levels in the air if ammonia were used for onboard storage. Although the low detectability level may be cited as a positive safety factor in detecting leaks, a pervasive odor in the vicinity of high use areas may be counter to the perception of a “clean” fuel.

It should also be noted that EU Directive 67/548/EEC (27 June 1967) classifies ammonia as dangerous to the environment because it is highly toxic to aquatic animals. Widespread use of ammonia as a fuel would certainly result in spills which could find their way to lakes, rivers and, in coastal areas, to the oceans.

One final comment concerns the generally known fact that anhydrous ammonia, stolen from fertilizer nurse tanks, applicator hoses, etc., has found increasing application to the production of illegal methamphetamine in clandestine labs. This has become a common problem in the upper midwest farming regions where ammonia is readily available and has prompted the Minnesota Department of Agriculture, Agronomy and Plant Protection Division to issue a brief document[20] describing the health hazards and spill response for first responders. This issue would have to be addressed on a broad scale if anhydrous ammonia were adopted for use as a primary energy carrier.

In summary, numerous safety and liability issues would have to be resolved if ammonia were to be used for onboard storage or as a distribution carrier for hydrogen.

VIII. CONCLUSIONS

Due mainly to its high hydrogen capacity, ammonia has the potential for use as a carrier for hydrogen delivery and distribution and, perhaps, as an onboard storage medium. There are, however, significant barriers to overcome before it could satisfy the requirements for either of these uses.

Safety: Safety is the first and foremost requirement for any transportation fuel. If ammonia is to play a role in the transportation system, all associated safety issues must be completely resolved. These include toxicity in the case of a sudden accidental release, small leak detection, and other hazards such as flammability.

Over the last hundred years, we have learned to mitigate and live with the hazards associated with gasoline and other petroleum-based fuels. Introduction of a new fuel in an age of increased scrutiny of all new technology will be difficult. Programs are needed to fully assess the hazards associated with ammonia and to look for appropriate technological and societal solutions. Specific areas of interest include lightweight "indestructible" tanks, cheap ammonia sensors, and better quantification of long and short term ammonia health effects.

Potential "Show Stoppers" for On-board Ammonia

Safety: ammonia leaks, tank ruptures, etc.

Ammonia crackers: cost, weight, size, efficiency, start-up, …

Purification: ammonia poisoning of PEM fuel cells

Efficiency: This paper gives a cursory estimate of the efficiency of ammonia production and distribution, but a more comprehensive well-to-wheels analysis of ammonia production, distribution, and use is needed. The analysis should include the production of ammonia from feedstocks other than natural gas, including renewables. End use options should include ammonia PEM fuel cells, internal combustion engines (ICEs), and alkaline fuel cells (direct ammonia or hydrogen).

Ammonia conversion: Current PEM fuel cells are poisoned by trace levels (>0.1ppm) of ammonia. This requirement places significant demands on an integrated ammonia decomposition reactor. The reactor and purification system must deliver ammonia-free hydrogen over a wide range of space velocities. Based on current knowledge, the reactor will probably operate at temperatures greater than 500° C and will require very efficient waste heat recovery. Cost and size will impact forecourt systems if ammonia were used as a carrier for hydrogen distribution.

Ammonia Research Priorities

High Efficiency Cracking Catalysts & Reactors

Purification Systems Coupled to Reactor Designs

"Failsafe" Ammonia Tank Designs

Systems Integration

Reactor designs need to be evaluated and the best candidates characterized experimentally. Reactor optimization must be carried out at a systems level, including the hydrogen purification system as well as some sort of combustor to provide the heat needed for the endothermic ammonia decomposition reaction.

In addition to the performance requirements listed above, compact, lightweight reactors would be needed if ammonia were to be used for onboard hydrogen storage. Indeed, from a technical point of view, the viability of ammonia as an onboard hydrogen storage medium hinges largely on the performance of onboard ammonia crackers. There are significant obstacles to overcome, however, to achieve acceptable performance levels in these units. These small reactors would require high activity catalysts to achieve the high decomposition rates needed to satisfy hydrogen flow requirements and they would also have to achieve rapid start-up and the other performance criteria needed for use with fuel cell vehicles. Current ammonia cracking systems which have sufficiently high hydrogen production rates for supplying even modest fuel cell powerplants are designed for stationary use and the analysis shown in Section V suggests that these units are two orders of magnitude too large and too heavy. Furthermore, they are too costly and do not have the dynamic response needed for onboard vehicular applications. Clearly, a significant effort would be needed to develop onboard ammonia cracker systems.

Due to the above reasons, DOE does not plan to fund R&D to improve ammonia fuel processing technologies for on-board use on light weight vehicles at the present time. However, a distinction may be made between conventional fuel processing of ammonia (e.g. high temperature, low efficiency, slow start-up/time response crackers) versus novel approaches to store ammonia and release its hydrogen content under conditions available on-board PEM fuel cell vehicles. As DOE's current portfolio in hydrogen storage evolves, breakthrough approaches that allow the safe, efficient and cost effective use of ammonia-based storage may be considered at a future date. It should also be mentioned that other systems, such as on-board dehydrogenation of organic liquids, are under consideration because they do not require the conventional fuel processors similar to those for gasoline or diesel fuels. For instance, on-board reactions of chemical hydrides that can release hydrogen at much lower temperatures (e.g., ~100° C) may be considered.

Although DOE is not currently funding conventional fuel processing of ammonia for on-board hydrogen storage, the potential use of ammonia as an energy carrier, particularly during the transition towards the hydrogen economy, is not disqualified. Ammonia may be considered as a potential hydrogen carrier for hydrogen delivery and for off-board storage, such as at refueling stations and for stationary power applications. Ammonia, delivered to refueling stations and stored onsite, would need to be reformed prior to vehicle filling and levels of trace ammonia in the hydrogen stream would need to be reduced to meet fuel purity requirements (e.g., < 0.1 ppm NH_3) for PEM fuel cells. The use of ammonia as a hydrogen carrier is being investigated further by DOE's Hydrogen Delivery Program and the FreedomCAR & Fuel Partnership's Hydrogen Delivery Technical Team.

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