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RESEARCH REPORT
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Ammonia As an Alternative Energy Storage Medium for Hydrogen Fuel Cells:

Scientific and Technical Review for Near-Term Stationary Power Demonstration Projects

Final Report

Caltrans/UC Berkeley Contract #22A0418, Task Order 1

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Acknowledgments

This report summarizes activities carried out by researchers at the Institute of Transportation Studies at the University of California – Berkeley under a research technical agreement with the California Department of Transportation (Caltrans). We thank Caltrans for their support of this research effort. In particular, we would like to thank Steve Prey for his assistance with the administration and conduct of this project. We also thank the many people who provided useful information for this project, especially those that we were able to personally interview. Their contributions are referenced throughout the report.

The project research team alone is responsible for the contents of this report.

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Executive Summary

This report documents the research efforts of a task order under a research technical agreement between the California Department of Transportation (Caltrans) and the University of California – Berkeley (UC Berkeley). The focus of this research is to understand the scientific and technical aspects of the potential use of ammonia and other related carbon-free energy carriers for hydrogen fuel cell applications. Caltrans has a range of potential applications for fuel cell technology, including various field operations and for providing emergency backup power, power “demand response” flexibility, and power “peak shaving” for its facilities. Ammonia is also a potential onboard hydrogen storage medium for vehicles, but we do not explicitly investigate that here.

The interest in hydrogen and fuel cell technologies at Caltrans and other California government agencies is being driven by a confluence of policy-related events the emergence of new and improved hydrogen and fuel cell technologies. The specific policy drivers for hydrogen and fuel cells include the California Hydrogen Highway Network Initiative (Executive Order S-07-04), a statewide greenhouse gas (GHG) emission reduction effort (AB 32 and the AB 1493 “Pavley Law”), and the State’s Zero-Emission Vehicle (ZEV) mandate. Also important are various drivers related to the use of electrical power in the wake of California’s failed electricity sector deregulation effort, and the continued pressures of meeting the demands of growth in California’s electricity needs.

This research effort consisted of three primary tasks:

1) An extensive scientific and technical literature review for the use of ammonia and related compounds as a fuel/energy carrier, especially for stationary hydrogen fuel cell applications;

2) An assessment of the current state of technical performance and economics of existing commercial and pre-commercial technologies for ammonia supply for fuel cell applications; and

3) A suggested demonstration plan for a physical demonstration of an ammonia/hydrogen/fuel cell system in the context of Caltrans operations.

<u>Ammonia as an Energy Carrier</u>

Ammonia has several desirable characteristics that make it potentially attractive as a medium to store hydrogen. It is non-flammable and non-explosive, it can be liquefied under mild conditions, and it has a large weight fraction of hydrogen (17.65% of the mass of ammonia). Ammonia actually has a volumetric hydrogen density about 45% higher than that of liquid hydrogen.

Ammonia can be decomposed (or “cracked”) over a catalyst to produce the desired fuel — hydrogen (H_2) — along with nitrogen (N_2) a non-toxic, non-greenhouse gas byproduct. The basic formula for ammonia decomposition is as follows:

$$2\,NH_3 \rightarrow 3\,H_2 + N_2 \qquad \Delta H^\circ = 46\ \text{kJ/mol}$$

Ammonia poses a low risk of ignition in the presence of sparks or open flames. A flammability limit is given for ammonia but generally it is considered to be a non-flammable gas (Ammonia MSDS; Air Liquide, 2002). Although injury from ammonia is most commonly the result of inhalation, it may also follow direct contact with eyes and skin or ingestion.

Ammonia is classified by U.S. DOT and OSHA as a hazardous material. A mitigating safety factor in favor of ammonia is that its specific smell makes it very easy to detect in cases of leaks so preventative measures can be taken.

Ammonia is produced commercially via the well-known Haber–Bosch process. This process first produces “synthesis gas” as a mixture of hydrogen and nitrogen gases, in the correct ratio of 3:1, and then produces ammonia in the presence of an iron oxide catalyst. This is typically done at pressures of 100-250 atmospheres and at temperatures of 300-500° C. (Hacker and Kordesch, 2003). Ammonia production is distributed worldwide, and in the U.S. is primarily centered in the Midwest. Ammonia is used in many applications but fertilizer manufacture is the largest source of demand. In fact, ammonia is the second most widely produced commodity chemical, after sulphuric acid.

The thermodynamic properties of ammonia make it an attractive fuel for fuel cell applications. Ammonia can be easily stored as a liquid at room temperature when a pressure of 8.6 bars is applied, while in the case of hydrogen an extremely low temperature of 20K and high cost tanks are required to keep it in liquid form. The usable hydrogen per kilogram of ammonia is relatively high compared to other hydrogen storage approaches. Furthermore, only 16% of the energy stored in ammonia is needed to break gaseous ammonia into nitrogen and hydrogen gases (T-Raissi, 2002). Using ammonia in fuel cell power plants does not generate COx or NOx emissions. Unlike natural gas and methanol reforming, which can lead to various impurities in the hydrogen gas stream that need to be removed, hydrogen production mainly results in water as an impurity with small amounts of un-reacted ammonia that may needs to be reduced.

Production of Hydrogen from Ammonia

The ammonia decomposition reaction is well studied and can be accomplished in a simple reactor using variety of catalysts including transition metals and alloys (Tamaru, 1988).

Figure 1 below shows the design of a small-scale catalytic ammonia-cracking unit.

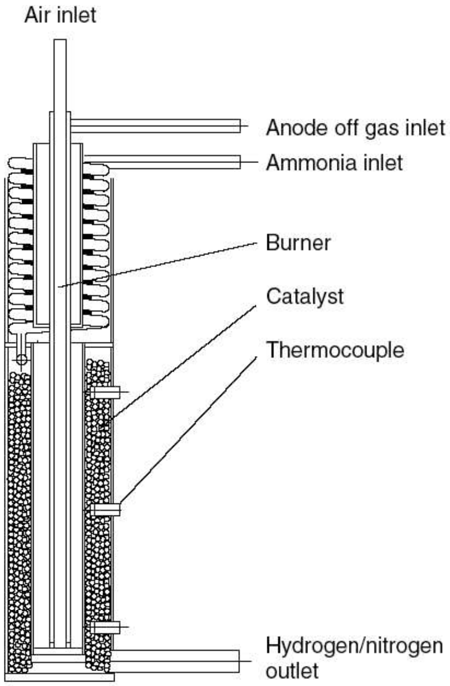

Figure 1: Schematic for a Catalytic Ammonia Cracking Unit
Source: Hacker and Kordesch, 2003

Autothermal ammonia decomposition provides an effective way to supply hydrogen for use in the fuel cell applications. This technique combines the endothermic heterogeneous ammonia decomposition reaction (into H_2 and N_2 on a catalyst) with the exothermic homogenous oxidation of ammonia (into N_2 and water) in the gas phase (Thompson, 2003). This direct coupling of ammonia dissociation and oxidation within the same reactor improves heat transfer greatly.

One approach to mitigate ammonia's shortcomings is to complex it with other hydrides so that the resulting compound is stable but not toxic. The prospective process must produce a compound that contains hydrogen at densities comparable to that of anhydrous ammonia. A class of compounds with a generalized formula of BxNxHy, known as amine-boranes and their derivatives, satisfy this requirement. However, a major drawback of this approach is the potentially high cost of these compounds.

More recently, Christensen et al. (2006) have developed a new type of compound to store ammonia using metal ammine salts. These offer a safe, reversible, high density, and potentially low-cost solution to ammonia storage (Johannessen, 2006). These systems are currently being investigated in laboratory settings and are not yet commercially available.

Technical Readiness of Small-Scale Ammonia Crackers

With regard to smaller scale ammonia crackers specialized to support fuel cell power applications, both Intelligent Energy Corporation (IE), and Apollo Energy Systems (AES) have expressed the ability to produce ammonia-cracking systems to supply hydrogen for 5-10 kW PEM fuel cell applications. These systems would require additional “clean up” systems to be compatible with the ISO 14687-2 specification (i.e., ammonia levels of 0.1 µmol/mole or 100 ppb). Technical and economic details of the IE and AES systems are discussed in the main text of this report.

Field Operation Test/Demonstration Project Concepts

Given the technological readiness of ammonia-based hydrogen storage and delivery systems that are suitable for use with fuel cell power plants, the near-term potential is for a relatively small-scale demonstration project. This could serve as a learning demonstration and "proxy" for a larger-scale installation that looks forward to lower stationary fuel costs and low-carbon means of producing ammonia or ammonia complexes.

Two initial FOT/demonstration project concepts are discussed in the main text of the report: 1) a fuel cell power "peak shaving" FOT project, and 2) a fuel cell emergency backup power FOT project. These two concepts could in theory be combined into a single FOT project that would alternately explore both concepts. Other more ambitious concepts are possible as well such as those that would also involve the ability to provide a limited amount of refueling for hydrogen fuel cell vehicles, as well as electricity production with a stationary fuel cell system.

Conclusions

Key conclusions of the study are as follows:

- Anhydrous ammonia is an attractive hydrogen carrier in terms of weight and volume energy density, but suffers from toxicity concerns;
- Industrial-scale ammonia cracking systems are relatively mature and manufactured by various companies;
- Smaller-scale ammonia cracking systems targeted at fuel cell power system applications are under development by at least two companies, and currently at prototype status;
- Ammonia cracking systems can operate at various temperatures and pressures, with resulting technical trade-offs, especially with regard to conversion efficiencies and system energy balances;
- Ammonia cracking systems are most "naturally" suitable for use with AFCs and SOFCs due to tolerance to un-reacted ammonia with medium (~650° C.) temperature level cracking system operation, but can be used with PEM and phosphoric acid fuel cells with additional cleanup systems (albeit with some concerns about effects on durability) or with higher temperature system operation (e.g. 950° C.) where levels of un-reacted ammonia are very low;
- Ammonia cracking systems can have attractive economics compared with other hydrogen supply options, particularly at small to medium scales of 10-100 nm^3/hr;
- Ammonia electrolysis is another potentially attractive method of hydrogen production, and one that is thermodynamically favored but that currently suffers from slow reaction kinetics;
- Achieving ISO specifications of hydrogen purity for fuel cell applications of un-reacted ammonia (of <100 ppb) is technically feasible but would

require an additional cleanup system at the back end of the ammonia cracking unit;

- For PEM fuel cell applications, research with Gore membranes has shown that performance is severely reduced with levels of un-reacted ammonia of 200-1,000 ppm, but that deterioration is significant even at levels of 10 ppm and 1 ppm (although slowly reversible with pure hydrogen operation);
- The costs of small-scale ammonia cracking units are high at present, based on “one off” production and significant non-recurring engineering costs; and
- At least two companies – AES and IE – are in a position (or soon will be) to supply small-scale ammonia cracking units for near-term FOT/demonstration projects.

Anhydrous ammonia and ammonia complexes offer one potentially attractive means developing low-carbon and otherwise low-emission and sustainable means of producing and delivering hydrogen fuel. Ammonia can be converted to a hydrogen rich gas stream without any inherent emissions of greenhouse gases. Depending on how the ammonia or ammonia complex is initially produced, full fuel-cycle emissions of greenhouse gases and other air pollutants can be moderate or low/zero, making further exploration of these types of systems interesting.

Introduction

This report documents the research efforts of a task order under a research technical agreement between the California Department of Transportation (Caltrans) and the University of California – Berkeley (UC Berkeley). The focus of this research is to understand the scientific and technical aspects of the potential use of ammonia and other related carbon-free energy carriers for hydrogen fuel cell applications. Caltrans has a range of potential applications for fuel cell technology, including various field operations and for providing emergency backup power, power “demand response” flexibility, and power “peak shaving” for its facilities.

Ammonia is also a potential onboard hydrogen storage medium for vehicles, but we do not explicitly investigate that here as it is outside the scope of this project. Issues with ammonia as an onboard hydrogen storage medium include potential exposure issues to consumers during refueling, the transient or dynamic response of ammonia cracking systems in relation to vehicle power demands and duty cycles, and infrastructure issues associated with large-scale ammonia delivery to consumer refueling locations.

The interest in hydrogen and fuel cell technologies at Caltrans and other California government agencies is being driven by a confluence of policy-related events the emergence of new and improved hydrogen and fuel cell technologies. The specific policy drivers for hydrogen and fuel cells include the California Hydrogen Highway Network Initiative (Executive Order S-07-04), a statewide greenhouse gas (GHG) emission reduction effort (AB 32 and the AB 1493 “Pavley Law”), and the State’s Zero-Emission Vehicle (ZEV) mandate. Also important are various drivers related to the use of electrical power in the wake of California’s failed electricity sector deregulation effort, and the continued pressures of meeting the demands of growth in California’s electricity needs.

This research effort consisted of three primary tasks:

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5) An assessment of the current state of technical performance and economics of existing commercial and pre-commercial technologies for ammonia supply for fuel cell applications; and

6) A suggested demonstration plan for a physical demonstration of an ammonia/hydrogen/fuel cell system in the context of Caltrans operations.

The following sections of this report present the key findings from these research activity tasks.

Section 1: Technical/Scientific and Economic Literature Review

There is an extensive but not enormous body of scientific and technical literature regarding the use of ammonia as a fuel/energy carrier. The following sections of this report summarize key findings from the literature, relying considerably on review papers by T-Raissi (2002) and Hacker and Kordesch (2003), as well as the recent Thomas and Parks (2006) U.S. Department of Energy (DOE) study.

Ammonia's basic properties as an energy carrier are discussed first, followed by a brief overview of ammonia production. Then various aspects are discussed of ammonia's use as a potential fuel for hydrogen fuel cells, by first "cracking" the ammonia molecule into hydrogen and nitrogen and then feeding the resultant gas stream into the fuel side of a fuel cell power generation system.

Ammonia: Basic Properties as an Energy Carrier

Ammonia has several desirable characteristics that make it potentially attractive as a medium to store hydrogen. First, it is non-flammable and non-explosive. Second, 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. This means that ammonia can be stored in a simple, inexpensive pressure vessel. Third, 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 and that has a volumetric hydrogen density about 45% higher than that of liquid hydrogen.

Ammonia can be decomposed (or "cracked") over a catalyst to produce the desired fuel — hydrogen (H_2) — along with nitrogen (N_2) a non-toxic, non-greenhouse gas byproduct. The basic formula for ammonia decomposition is as follows:

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Ammonia is classified by U.S. DOT and OSHA as a hazardous material. The U.S. EPA has identified ammonia as one of 366 "extremely hazardous substances" subject to community "right-to-know" provisions of the Superfund Act and emergency planning provisions of the Clean Air Act (Michaels, 1999). A mitigating factor in favor of ammonia is that its specific smell makes it very easy to detect in cases of leaks so preventative measures can be taken. In addition, any releases of ammonia would be immediately dispersed.

One less obvious drawback to the widespread use of ammonia as vehicular fuel is that anhydrous ammonia is used, extensively, in the manufacture of the illicit drug methamphetamine. Anhydrous ammonia is used in the so-called "Nazi method" to spur methamphetamine production (NDIC, 2001). This method does not require extensive knowledge of chemistry, uses no heat, and is a simpler technique than the "Red P" method that is also used for producing methamphetamine. Ammonia storage facilities thus need to be well secured to prevent theft and vandalism.

Table 1 presents the basic physical properties of ammonia.

Table 1: Physical Properties of Ammonia

Hydrogen Content					
Hydrogen weight fraction	17.65	wt.%	Hydrogen 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 (1 atm @ 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 15°C 1 atm	.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 volume (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)			
Miscellaneous					
Water solubility (1 atm at 0°C)	862	vol/vol	Auto ignition temperature	630	°C
Lower flammable limit in air	15%	by volume	Upper flammable limit in air	28%	by volume
Molecular Weight:	17.03				

Source: (Thomas and Parks, 2006)

Overview of Ammonia Production

Ammonia is produced commercially via the well-known Haber–Bosch process. This process first produces "synthesis gas" as a mixture of hydrogen and nitrogen gases, in the correct ratio of 3:1, and then produces ammonia in the presence of an iron oxide catalyst. This is typically done at pressures of 100-250 atmospheres and at temperatures of 300-500° C. (Hacker and Kordesch, 2003).

Ammonia production is distributed worldwide, and in the U.S. is primarily centered in the Midwest. Ammonia is used in many applications but fertilizer manufacture is the largest source of demand. In fact, ammonia is the second most widely produced commodity chemical, after sulphuric acid. According to the mineral commodity data compiled by the U.S. Geological Survey, in 2000 the U.S. domestic ammonia production was about 15.8 million metric tons. During the same year, the total ammonia consumed in the U.S. exceeded 20 million metric tons, of which about 88% was for agricultural use as fertilizer (Kramer, 2000). Production in the U.S. has declined somewhat in recent years, due to an increase in natural gas input costs, and this has led to an increase in imports.

The global production capacity of ammonia approximated 170.8 million tonnes in 2004–2005 (IFDC, FSR, 2005). Ammonia production prices have fluctuated over the past several years. In 2002, ammonia prices were around $250 per tonne while current prices are approximately $350–375 per tonne (Schnitkey, 2003). This compares with current prices for hydrogen in the range from $800–3,400 per tonne (Mann and Ivy, 2004).

Natural gas is the primary input to ammonia production, although naphtha, coke, and coal are other inputs for the production plants currently in use. New ammonia plants today are built exclusively with natural gas or naphtha as inputs due to lower capital costs and lower specific energy requirements (Hacker and Kordesch, 2003). Steam and air (as a nitrogen source) are other major inputs. A "de-carbonized" ammonia production system would need to use other, non-fossil hydrogen feedstocks such as waste sources of methane (e.g. landfill gas), waste sources of hydrogen (e.g. chemical production byproduct gas), biomass gasification, or wind, solar, tidal, or hydro-powered water electrolysis.

Ammonia as a Hydrogen Storage Medium

Ammonia was initially explored as a hydrogen storage medium in the 1970s when the "Hydrogen Economy" was first being widely debated. It was envisaged that ammonia would provide a perfect storage medium for hydrogen produced by ocean thermal energy conversion (OTEC) systems, where "plant ships" could then bring the ammonia to shore as an energy carrier (Avery and Richards, 1985)

With the decline in interest in non-fossil hydrogen production technologies in the 1980s, ammonia virtually disappeared as a viable hydrogen storage medium from U.S. DOE programs. The commonly held view was that OTEC would be roughly twice as expensive as conventional energy forms due to the high capital cost of OTEC plants made under existing designs at that time. It was then estimated that a $40/barrel oil cost would be necessary to spur investors into serious consideration of OTEC technology (Tanner, 1995). The initial interest in ammonia for hydrogen production was more or less unique to the OTEC project, where the electrical energy would be generated at a remote location and where it was not feasible to install either power lines or a hydrogen pipeline to the shore.

The recent surge in oil prices and the emerging concern about climate change has led to renewed interest in OTEC (Kumm, 2005), as well as various other renewable technologies and other non-carbon based technologies such as hydrogen and nuclear power. Some of these are capable of interfacing with ammonia manufacture (Kubic, 2006), thus reviving interest in ammonia as a hydrogen storage medium.

Intermittently available or remotely situated technologies such as wind power also could potentially be "firmed up" by using ammonia as an energy storage medium (Preston, 2006). In addition ammonia can also be produced from existing coal technologies (Tse, 2006, Sheppard, 2006) or from wastewater streams (Botte and Holbrook, 2006). This and the fact that the existing fertilizer industry provides a guaranteed market, means that ammonia can potentially be used as a bridge from the existing fossil fuel based economy to the emerging renewable energy economy.

Ammonia as a Fuel for Hydrogen Fuel Cells

The thermodynamic properties of ammonia make it an attractive fuel for fuel cell applications. A direct comparison between hydrogen and ammonia properties demonstrates the benefits of using ammonia. Ammonia can be easily stored as a liquid at room temperature when a pressure of 8.6 bars is applied, while in the case of hydrogen an extremely low temperature of 20K and high cost tanks are required to keep it in liquid form. The usable hydrogen per kilogram of ammonia is relatively high compared to other hydrogen storage approaches. Furthermore, only 16% of the energy stored in ammonia is needed to break gaseous ammonia into nitrogen and hydrogen gases (T-Raissi, 2002).

Also, using ammonia in fuel cell power plants does not generate COx or NOx emissions. Unlike natural gas and methanol reforming, which can lead to various impurities in the hydrogen gas stream that need to be removed, hydrogen production from ammonia mainly results in water as an impurity with small amounts of un-reacted ammonia that may need to be reduced (depending on the level of un-reacted ammonia and type of fuel cell used). The current International Standards Organization (ISO) specification for hydrogen fuel for fuel cell applications calls for ammonia levels of 0.1 μmol/mole or 100 ppb (#ISO 14687-2).

Direct use of ammonia has recently been investigated by using high temperature proton conductor systems (Maffei et al., 2005) as well as several oxide ion-conducting systems (Wojcik et al., 2003;Dekker and Rietveld, 2004). In all cases, ammonia showed performance close to that of hydrogen at intermediate temperatures. Wojcik et al. (2003) investigated the use of ammonia in annular systems using silver and platinum as electrode materials, showing the potential of internal reforming of ammonia. Dekker and Rietveld (2004) investigated the direct use of ammonia in the high current density range for solid oxide fuel cells (SOFCs). This option is still being explored and may yield advantages if it can eliminate the need for hydrogen storage altogether.

Ammonia based hydrogen production systems are most "naturally" ideally suited to use with alkaline, molten carbonate, and solid oxide fuel cell (SOFC) systems as these are relatively tolerant to un-reacted ammonia in the product stream compared with proton-exchange membrane (PEM) and phosphoric acid fuel cells. Adsorption systems can be used to remove un-reacted ammonia from the product stream, but recent research has shown that PEM fuel cells are sensitive to ammonia levels as low as 1 ppm. Significant performance deterioration has been demonstrated in experiments with Gore membranes with 200-1,000 pppm of ammonia in the fuel stream (Soto et al., 2003), and even with levels of 10 ppm and 1 ppm (Halseid et al., 2005). This performance deterioration is slowly reversible, but to avoid a loss in performance it appears that un-reacted ammonia levels must reach sub-ppm levels, and perhaps even lower than the current ISO specification of 100 ppb.

Ammonia may be particularly well suited to use with SOFCs as this can nearly eliminate the fuel pre-treatment needed for operation with hydrocarbon fuels. Additional savings in stack cost are also apparently possible when ammonia is used as a fuel in SOFCs. Patel and Petri (2006) report that total system costs can be as low as about $1,600 per kW in an ammonia-based SOFC system compared with about $2,700 per kW in a hydrocarbon fuel based system, with similar performance. This means that the allowable cost of ammonia fuel may be about $6/MMBTU higher than for propane fuel, with the same levelized cost of electricity (Patel and Petri, 2006).

Production of Hydrogen from Ammonia

A recent comparison of the economics of various methods of hydrogen production showed that catalytic cracking of ammonia, reforming of natural gas and methanol are all more economical methods of producing hydrogen than electrolysis of water (Silversand, 2002). Natural gas reforming is estimated to be the lowest cost method of production at larger scales, but at small scale production of 10 cubic normal meter per hour, ammonia cracking is estimated to be the lowest cost method. See Table 2, below, for the estimated production costs for these methods for a range of production rates of ammonia.

Table 2: Economic Comparison of Ammonia Cracking and Other Hydrogen Production Methods

Unit Size	**Electrolysis**				**Natural Gas Reforming**			
(nm^3/h)	I	R	M	**T**	I	R	M	**T**
10	$0.286	$0.64	$0.014	**$0.943**	$0.286	$0.09	$0.014	**$0.390**
100	$0.157	$0.64	$0.014	**$0.814**	$0.157	$0.09	$0.014	**$0.261**
1000	$0.082	$0.64	$0.014	**$0.739**	$0.082	$0.09	$0.014	**$0.186**
Unit Size	**Methanol Reforming**				**Ammonia Cracking**			
(nm^3/h)	I	R	M	**T**	I	R	M	**T**
10	$0.214	$0.15	$0.014	**$0.380**	$0.143	$0.19	$0.014	**$0.343**
100	$0.119	$0.15	$0.014	**$0.285**	$0.079	$0.19	$0.014	**$0.279**
1000	$0.06	$0.15	$0.014	**$0.226**	$0.041	$0.19	$0.014	**$0.241**

Source: Silversand, 2002

Note: Production costs include investment costs (I), running costs (R), maintenance costs (M), and total costs (T). All figures have been converted to U.S. dollars from Swedish Krona, using the conversion rate of 6.99 Krona per dollar, and are in units of dollars per cubic normal meter per hour (nm^3/h) of hydrogen produced.

Commercial ammonia is prepared at 99.5% purity, with the impurity mainly being water. Ammonia can be readily converted to hydrogen and nitrogen gas by thermocatalytic decomposition. The ammonia decomposition reaction is well studied and can be accomplished in a simple reactor using variety of catalysts including transition metals and alloys (Tamaru, 1988). In general, catalysts containing noble metals are not used in the commercial processes due to high costs. Some researchers have reported nickel as being a very efficient catalyst with almost complete conversion at temperatures above 773K (Choudhury et al, 2003 and Chellappa, 2002).

Figure 1 below shows the design of a small-scale catalytic ammonia-cracking unit.

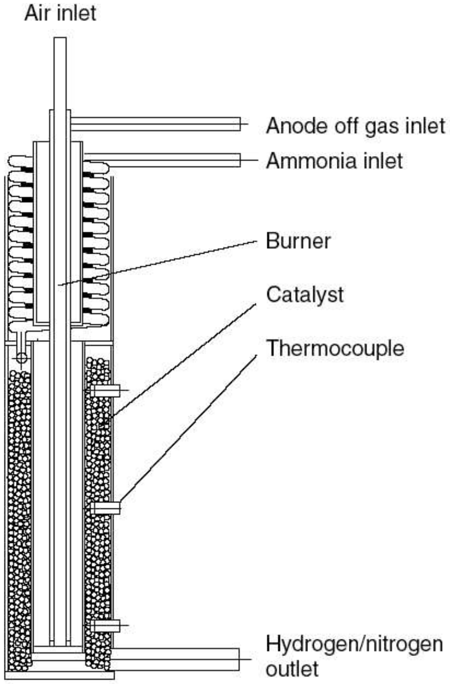

Figure 1: Schematic for a Catalytic Ammonia Cracking Unit
Source: Hacker and Kordesch, 2003

Conventional medium to large-scale ammonia crackers (in sizes of 10-300 kg per day of hydrogen output) are used in metallurgical industry for metal nitriding operations. See Table 3 (in the following section) for manufacturers and specifications for these systems. In these applications, anhydrous ammonia crackers are used to produce an active [N] radical to initiate the nitriding reaction. Ogden (2001) has comprehensively reviewed small-scale hydrogen reformers for stationary applications. She presents details on state-of-the-art (ca. 2001) small-scale hydrogen production from various R&D and commercial efforts, including ammonia reforming and other competing technologies. She presents lists of manufacturers and R&D efforts, hydrogen fueling demonstration projects, and also recent patents in the field of small-scale hydrogen production, while also reviewing promising competing technologies to ammonia reforming, such as methanol reforming.

Other studies report that Boston-based Analytic Power Corporation (now Dais Analytic Corp.) has developed an ammonia “dissociator” that provides a hydrogen source for small (~150 Watt) fuel cell power supplies (Kaye and Bloomfield, 1998). MesoSystems Technology, Inc. (MTI), and Intelligent Energy (IE) Corp. have developed a compact system for ammonia storage; reforming, H_2 generation and purification utilizing micro-channel reaction technology to produce a 50W power supply to deliver one kWh equivalent hydrogen from a 1-kilogram hydrogen source which includes the cracker, ammonia precursor, the necessary scrubbers to purify the resulting hydrogen/ammonia stream (Call et al., 2001, and Powell et al., 2004). MTI/IE estimates high-volume production costs of about $300 for the hydrogen generator (for orders of 10,000 systems or more) (T-Raissi, 2002).

For vehicular fuel cell applications, Apollo Energy Systems and researchers at the Technical University (TU) of Graz, Austria have developed an 11.5 kW ammonia cracker (Faleschini et al., 2000). TU team's approach was to improve the NH_3 pyrolysis catalysts such as the SÜD-Chemie 27-2 and nickel oxide on alumina by modification with noble metals (e.g., 0.3 wt% ruthenium on a nickel oxide catalyst). The overall efficiency of the system can reach as high as 85% (Kordesch et al, 1998). For smaller ammonia crackers for PEM fuel cell applications, the efficiency values of about 60% have been reported by Yang and Bloomfield (1998), with as much as 40% of the product hydrogen burned to supply dissociation energy needed for their autothermal reformer and also compensate for the heat losses. Both AES and Analytic Power ammonia reformers are based on a system design first developed by Ross at the Lawrence Berkeley National Laboratory (Ross, 1982).

Autothermal Reforming of Ammonia

Autothermal ammonia decomposition provides an effective way to supply hydrogen for use in the fuel cell applications. This technique combines the endothermic heterogeneous ammonia decomposition reaction (into H_2 and N_2 on a catalyst) with the exothermic homogenous oxidation of ammonia (into N_2 and water) in the gas phase (Thompson, 2003). This direct coupling of ammonia dissociation and oxidation within the same reactor improves heat transfer greatly. For optimum performance, the ammonia reformer must approach adiabatic operation and allow cooling of the reactor effluent via feed gas preheat in a suitable heat exchanger. Ammonia conversions exceeding 99% with hydrogen selectivities above 65% have been reported at space velocities[1] as high as 10^6 hr^{-1} (Goetsch and Schmit, 2001).

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[1] In chemical reactor design, space velocity represents how fast molecules move inside the reactor. It is often denoted by SV and it is related to the residence time in a chemical reactor, τ, with the relationship, $SV = 1/\tau$.

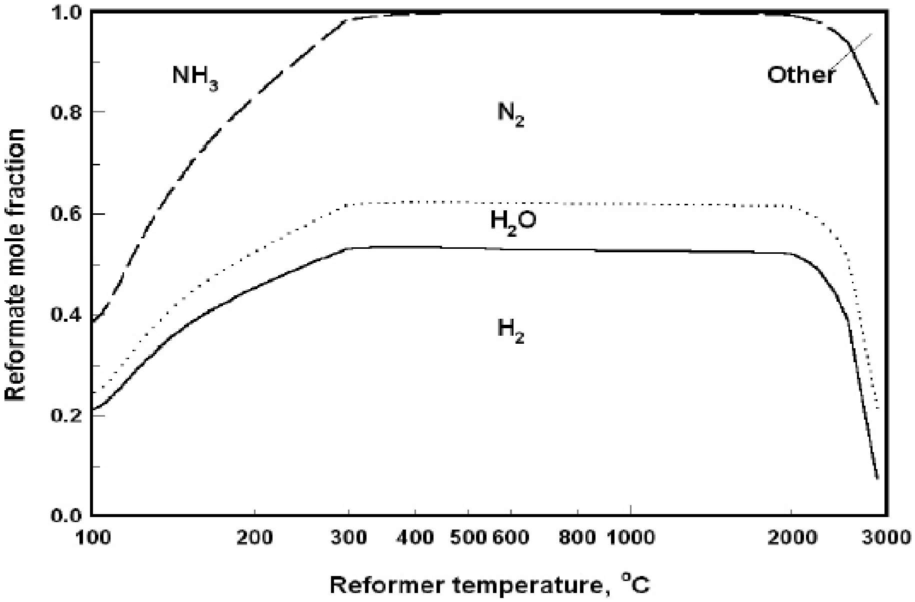


Figure 2: Effect of temperature on reformate concentration for auto-thermal reaction of ammonia with air (T-Raissi, 2002)

As seen in Figure 2, auto-thermal ammonia reformation can be accomplished over a wide range of reformer temperatures, with near complete conversion at temperatures from about 300-2,000°C. (T-Raissi, 2002). No significant NO_x or other undesirable species such as un-reacted oxygen is detected in the reformer effluent for reforming temperatures from about 400°C to 1,500°C, making reforming at high temperatures particularly attractive.

The main disadvantage of auto-thermal reforming of ammonia for use with low-temperature fuel cells is that the effluent stream needs to be cooled down to a temperature compatible with fuel cell operation. In addition, the dilution of H_2 with N_2 from air may be undesirable in some applications. The scrubbing of the residual NH_3 (at sub-ppm levels) in the effluent stream may also be necessary.

Ammonia Electrolysis

Another promising means of hydrogen production from ammonia is ammonia decomposition via electrolysis in an alkaline electrolytic cell. This method of hydrogen production has been pioneered by researchers at Ohio University (Vitse et al., 2005; Cooper and Botte, 2006). The basic concept is to couple the ammonia electro-oxidation reaction with a hydrogen evolution reaction, as follows:

$$2NH_3(aq) + 6OH^- \rightarrow N_2(g) + 6H_2O + 6e^-$$

$$6H_2O + 6e^- \rightarrow 3H_2(g) + 6OH^-$$

$$2NH_3(aq) \rightarrow N_2(g) + 3H_2(g) \quad \text{(overall reaction)}$$

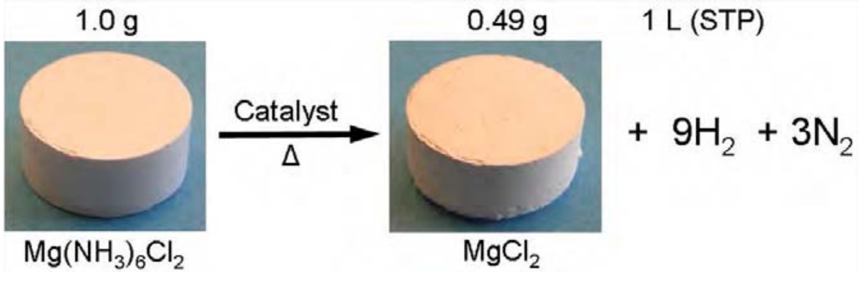
An interesting feature of this concept is that the reversible cell potential for the overall reaction is only –0.058 V, compared with –1.23 V for conventional water electrolysis (Cooper and Botte, 2006). This means that, theoretically, a kilogram of hydrogen could be produced with only a few kWh of electricity rather than the 35-50+ kWh of electricity required for water electrolysis under standard conditions. The primary limitation to the ammonia electrolysis concept is the slowness of the reaction kinetics, which has been shown to make the process financially infeasible at the present state of development (Cooper and Botte, 2006).

In an attempt to realize a more practical system based on this concept, the Ohio University team has been investigation appropriate catalysts to hasten the reaction kinetics, as well as varying the cell voltages. A recent investigation of platinum and rhodium as synergistic catalysts has been promising. The investigation demonstrated a hydrogen flow rate of 2.09×10^{-3} L/h of hydrogen per cm^2 of catalyst, at 5 mA/cm^2 and at a voltage of 0.599 V. This is equivalent to about 16 kWh per kg of hydrogen generated, or less than half the amount of electricity required for typical of water electrolysis under standard conditions (Cooper and Botte, 2006). Research is continuing with regard to the development of even more active electrocatalysts, to further reduce the potential electricity demands and speed the reaction kinetics for this method of hydrogen production.

Ammonia-Based Complexes as Hydrogen Storage Media

One approach to mitigate ammonia's toxicity is to complex it with other hydrides so that the resulting compound is stable but not toxic. The prospective process must produce a compound that contains hydrogen at densities comparable to that of anhydrous ammonia. A class of compounds with a generalized formula of BxNxHy, known as amine-boranes and their derivatives, satisfy this requirement. However, a major drawback of this approach is the potentially high cost of these compounds. There are no data available at this time for the large-scale production costs of ammonia-borane. However, the Callery Chemical Company manufactures large quantities of a similar compound known as dimethylamine borane (DMAB). Depending on the order volume, the price of DMAB is in the range of about $75-100/lb (T-Raissi, 2002). We expect the price of ammonia-borane to be also in this range, in medium to high volumes of production, and thus a large reduction in cost would be needed to be economical as a hydrogen storage medium.

More recently, Christensen et al. (2006) have developed a new type of compound to store ammonia using metal ammine salts. These offer a safe, reversible, high density, and potentially low-cost solution to ammonia storage (Johannessen, 2006). The basic chemical reaction is as follows, where nine hydrogen molecules can be evolved through thermal desorption from each gram of solid material:



Source: Christensen, 2007

The development of this new type of hydrogen storage could provide a relatively inexpensive alternative to expensive high-pressure hydrogen storage tanks, and a safer option than low-pressure ammonia tanks. Remaining questions include the economics of this type of system, how the "spent" salt would be "recharged" with hydrogen and nitrogen in an efficient manner, and the significance of other infrastructure needed to support this type of hydrogen storage. The system is also being investigated for use in combustion engine vehicles, as an ammonia delivery system for use in conjunction with a selective catalytic reduction (SCR) scrubber system for reduction of NOx emissions (Christensen, 2007).

Section 2: Technological Readiness and Business Plan Assessment

Various companies are researching ammonia cracking system technologies and producing demonstration and test units. For industrial applications, these companies include those listed in the following table. These industrial applications typically do not require very low levels of un-reacted ammonia in the resultant gas streams, as would be needed for some fuel cell applications. Additional systems to remove un-reacted ammonia would therefore be needed to support the use of these larger industrial ammonia crackers for fuel cell applications, particularly those for PEM fuel cells.

Table 3: Manufacturers of Industrial Ammonia Crackers

Manufacturer	H2 Output	Electric Power Consumption	Efficiency	Weight	Footprint	Cost
	kg/day	kW	%	kg	cm X cm	$
Lindberg	273	140	63	5,800	290x240	155,000
CI Hayes	228	140	55	2,180	180x170	NA
CI Hayes	136	64	66	2,180	180x170	70,000
Koyo Thermo	96	59.5	55	N/A	280x100	NA
Borel	11.2	7.5	51	N/A	85x56	NA

Source: Leighty, 2006

With regard to smaller scale ammonia crackers specialized to support fuel cell power applications, both Intelligent Energy Corporation (IE), and Apollo Energy Systems (AES) have expressed the ability to produce ammonia-cracking systems to supply hydrogen for 5-10 kW PEM fuel cell applications. These systems would require additional "clean up" systems to be compatible with the ISO 14687-2 specification (i.e. ammonia levels of 0.1 µmol/mole or 100 ppb).

AES has stated their intention to sell their patented (US Patent# 6,936,363) ammonia cracker either as a stand-alone unit, or with the entire power plant using the Apollo alkaline fuel cell (AFC) stack. IE has expressed interest in participating in a demonstration project as well, to support PEM or other fuel cell types. Both parties have indicated a readiness to begin production as early as June 2007. Details of these systems and the production plans of the companies are presented below.

Apollo Energy Systems (information for this section from Aronsson, 2007)

Apollo Energy Systems (AES) has expressed their intention to sell their patented (US Patent# 6,936,363) ammonia cracker either as a stand-alone unit, or with the entire power plant using the Apollo AFC stack. The cracker was developed at the Technical University Graz in Austria (documented in Kordesch et al. (1998)), initially designed in conjunction with the use of AFC stacks for vehicular applications. Figure 4, below, shows a third generation unit with an integrated ammonia trace filter.

Figure 4: Third Generation AES ammonia cracking unit developed at the Technical University Graz (Source: Aronsson, 2007)

The AES patented process for producing hydrogen from gaseous ammonia comprises:

1) passing a gaseous ammonia stream to a dissociation unit of an ammonia cracker to dissociate the gaseous ammonia stream to a mixture of hydrogen and nitrogen at a temperature range of about 500° C. to 750° C., where the dissociation unit consists essentially of a catalyst bed containing aluminum oxide pellets onto which an active catalyst metal has been deposited, and the active catalyst metal is a member selected from the group consisting of nickel, ruthenium, and platinum;
2) then supplying the hydrogen and nitrogen mixture to a fuel cell system; and
3) then feeding a portion of hydrogen electrode off-gas to a heating unit of the ammonia cracker to supply heat for further dissociation reactions.

This process could initially be comprised of vaporizing liquid anhydrous ammonia to produce gaseous ammonia for the gaseous ammonia stream. The hydrogen and nitrogen mixture could be supplied to alkaline or PEM fuel cells, with appropriate removal of un-reacted ammonia for the requirements of the power production system. For alkaline fuel cells, the 99.95% cracking efficiency of the AES unit (operating at around 650° C.) would not introduce issues with un-reacted ammonia. However PEM fuel cell applications would require additional cleanup as these are much more sensitive to ammonia in the fuel stream, as discussed above.

Step 3 of the above process would consist of a heating unit comprising a catalytic burner or a lean gas combustor to convert a portion of the hydrogen electrode off-gas into heat. The power generation process could entail use of gaseous ammonia at a pressure of up to 2 bar. Dissociation of the gaseous ammonia stream in the ammonia cracker can proceed with a short start-up time, and with a low specific weight of the system per kW of hydrogen produced. The density of the un-cracked ammonia from the cracker is less than 30 ppm, and this can be reduced further using a scrubber for PEM fuel cell applications.

AES estimates that the near-term, single-unit cost of the ammonia cracking unit itself would currently be on the order of $3,000, sized to support a 5 kW fuel cell installation. The company has targeted a mass production cost of $1,250 ($250 per kW). The company will begin accepting orders when they are in production, which is not yet the case but anticipated in the near future.

Additional system costs to support a demonstration project would be ammonia supply and any manifolds needed, and an adsorption cleanup system to remove un-reacted ammonia to support PEM fuel cell applications. Another option for PEM fuel cell applications would be a higher temperature unit (operating at ca. 950° C.) where the need for ammonia cleanup would be eliminated. This higher temperature system would have considerably higher costs, and AES has not yet estimated the cost of this type of higher temperature unit.

Summary of Technical Specifications of AES' Prototype NH3 Platform

- Catalytic steam reformation technology
- Internal operating temperature 650° C.
- Output of 75% hydrogen and 25% nitrogen
- Conversion efficiency of 99.95% and residual ammonia of 100-300 ppm at 650° C. operation
- Residual ammonia can be reduced to 1-4 ppm with adsorption system
- Unit for 5 kW system measures 15"L X 15"W X 15"D and weight of 16 lbs.

Intelligent Energy Corporation (information for this section from Foster, 2007)

IE has completed demonstration of a new hydrogen generation system called 'Hestia' in collaboration with Sasol -- South Africa's largest chemical company and fast-growing fuel producer, distributor, and retailer. The Hestia system has been developed to convert Sasol's Fischer-Tropsch process fuels into hydrogen, and then into electricity and heat, using IE's fuel cell systems. IE has successfully demonstrated the system, by using it to run the company's Long Beach facilities, with excess electricity sold back to the Southern Californian Edison grid.

IE's Hestia technology platform is scalable and fuel-flexible. It can use various fuels, including anhydrous ammonia, to produce its high-purity hydrogen product gas, meaning that the platform is capable of serving a broad range of future markets and applications. The hydrogen generated by the system is sufficient to produce 10 kW of electricity, when used with IE's own stationary combined heat and power (CHP) fuel cell systems. The Hestia platform could also possibly be used for transportation applications (as a refueling station for hydrogen-fuelled vehicles, for example). With safe, low-pressure metal hydride storage technology integrated into the process, IE has demonstrated near-instantaneous fuel cell system start-up and smooth load-following capabilities.

IE's hydrogen generation technology development and desulfurization teams are located in Long Beach, California and Albuquerque, New Mexico. These two locations provide significant combined reformer development experience including competence in non-catalyzed partial oxidation (POX), catalyzed POX, auto-thermal reforming (ATR), and steam reforming (SMR). The IE team has demonstrated successful reforming of a wide variety of fuels including LPG, natural gas, ammonia, propane, diesel, synthetic diesel, soy-diesel, kerosene, methanol, and ethanol.

IE's operations in Long Beach, California include manufacturing and test facilities for the development of 1-25 kW reformer systems as well as integration of hydrogen generation systems with the fuel cell power systems. Aside from fabrication and integration capacity, the Long Beach facility has testing capabilities for hydrogen handling and fuel processing. This includes catalyst testing in micro-reactors, to full operation of hydrogen generation systems from 1-25 kW. Data collection hardware is integrated with the test cell to provide for the safe testing of hydrogen generation hardware and systems. IE ABQ or MesoFuel (a wholly-owned subsidiary of IE) has facilities that enable fabrication, testing, analysis and diagnostics for fuel processing of multiple fuel types, testing of novel hydrogen purification techniques and ultimately final integration of fuel processor systems.

IE's hydrogen generation system utilizes highly efficient system design and components and is comprised of a catalyzed reformer chamber and an ammonia adsorption module. The design of the system is aimed at maximizing overall system efficiencies. The unit does not require any electrical source from the grid to start-up or operate. The system requires approximately 100 watts of on-board power for start up. Start up will require 20 minutes. The overall weight of the system is close to 100 lbs. The overall dimensions of the system are approximately 24"L X 36"W X 18"D. Parasitic power requirements are in the 10% to 15% range of the operational output (e.g., 500 – 750 Watts for a 5 kW output). The expected conversion efficiency of the system is 75%. The turn-down ratio relative to the highest levels of operation is targeted at 2:1 or higher.

For a potential demonstration system, an ammonia "getter" system would be incorporated to provide approximately 1 month of operation before changing of the adsorption bed would be required. The approximate mass of the adsorption material would be 15 kg. Regenerative beds can also be provided for longer run times. Final pricing on the system will be determined and finalized in a formal quotation upon request. To develop a "one-off" demonstration system to support a 5 kW fuel cell system utilizing ammonia as the feedstock and eliminating all requirements for power from a grid or distributed generation source would require several hundred hours of design, engineering and fabrication effort. IE's "best guess" pricing range is that with non-recurring engineering and labor, the system price will be between $140,000 and $210,000.

Summary of Technical Specifications of IE's Prototype NH3 Platform

- Catalytic steam reformation technology
- Supports fuel cell systems from 10 W to 10 kW
- Output of 75% hydrogen and 25% nitrogen
- Ammonia adsorption module
- Fertilizer/commercial grade ammonia supply
- Catalyst life >10,000 hours
- Internal operating temperature 700° C.
- Dimensions of 24"L X 36"W X 18"D and weight of ~100 lbs.
- Scalable design for higher volumes

Section 3: Field Operational Test Concepts

The primary finding of this research project is that ammonia-cracking units are in commercial production for larger industrial applications, and in pre-commercial (prototype) status for smaller applications to support fuel cell-based power generation. At least two U.S.-based companies – AES and IE – are in a position (or soon will be) to supply small ammonia crackers for fuel cell power demonstrations. AES has focused their technology mostly toward AFC systems, while IE is focusing more on PEM applications. However either hydrogen supply system could be adapted for either of these fuel cell types.

A field operational test (FOT) to demonstrate the use of an ammonia-based energy storage system to produce hydrogen for a fuel cell power system could be arrayed around one or more of several different potential applications. A small-scale (e.g. 5-15 kW) demonstration could be initially targeted for technology validation, with potential applicability to similar sized or larger-scale deployments. These potential applications include:

- Emergency backup power for a critical facility (e.g. telecommunications facility or small data center)
- Peak shaving for an office building or other facility, to simultaneously reduce electricity energy and demand charges
- Standalone power for remote field applications, particularly those of an intermittent or seasonal nature
- Construction site power

Figure 5, below, presents a general scheme for delivery of ammonia to a demonstration site, storage of the ammonia onsite in a cylinder array, delivery of the ammonia with a manifold delivery system to the ammonia cracking unit, delivery of hydrogen to the fuel cell system, and finally delivery of electrical power to the end-use application.

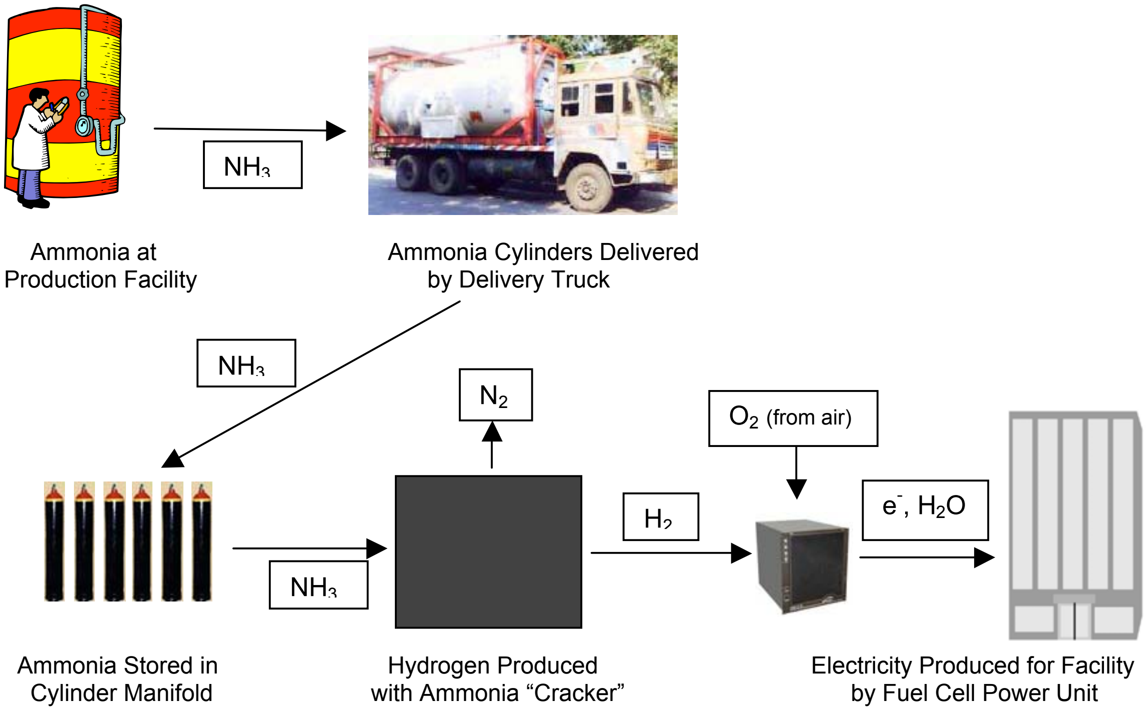


Figure 5: Schematic of an Ammonia-Based Hydrogen Fuel Cell Power System

Figure 6, below, shows a hydrogen-cylinder storage system to support a ~10 kW PEM fuel cell system application. An ammonia-based system could be similarly packaged, with additional space allowed for the ammonia-cracking unit.

Figure 6: Hydrogen Fuel Cell Cabinet with Hydrogen Supply Cylinders
Note: Picture courtesy of Altergy Corp.

Field Operational Test Technical Considerations and Process Steps

There are technical considerations for each aspect of a potential FOT project of this sort. For the ammonia supply, these include the specifications of the ammonia (e.g. anhydrous versus dilute, and laboratory versus commercial versus agricultural grade), the means of delivery and storage, and the amount of ammonia stored onsite.

Ammonia storage quantities in excess of 500 lbs. would trigger the need for a site-specific "risk management plan" under 40 CFR Part 355 and the Emergency Planning and Community Right-To-Know Act (EPCRA).[2] With typical cylinders holding 150 lbs. each, a maximum of three cylinders stored onsite would allow for the avoidance of additional regulatory/permitting complexity. An additional consideration would be security of the ammonia supply to avoid theft for illicit uses.

For the ammonia cracking unit, the key issues are: 1) sizing the unit to satisfy the demands of the application; 2) assuring that the hydrogen produced would be sufficiently free of the relevant contaminants to meet the specifications of the specific fuel cell type;[3]

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[2] Energy and Environmental Analysis, Inc. has a helpful website that documents the various regulations that govern the storage, transport, and accidental release of ammonia under various statutes and regulations. The website can be found at: http://www.eea-inc.com/rrdb/DGRegProject/Ammonia.html

[3] I.e., PEM fuel cells are more sensitive to un-reacted ammonia, CO, and sulfur compounds than AFCs, but AFCs are more sensitive to CO_2 – with carbon compounds not of much concern for ammonia-based hydrogen supply systems where they could only enter in small concentrations on the air side of the fuel cell system.

and 3) other technical details such as needs for startup power, turndown ratios, startup times, etc.

We suggest the following process for defining and "scoping" a potential FOT/demonstration project to further explore and validate the use of ammonia-based hydrogen supply systems to support a fuel cell power system.

1. Identify application type (e.g. premium power, peak shaving, etc.)
2. Identify fuel cell system size and type (e.g. 10 kW PEM)
3. Define fuel cell system duty cycle
4. Determine hydrogen fuel requirement
5. Determine ammonia cracking unit size and type (e.g. higher or lower temperature and pressure, etc.)
6. Determine ammonia supply size and type (e.g. cylinder manifold or larger scale system -- assume 0.15 to 0.20 gallons of ammonia per kW of fuel cell power, per hour)
7. Establish potential cost of demonstration project
8. Obtain project funding
9. Develop detailed project plan
10. Identify suppliers/vendors/partners
11. Initiate permit process(es) (if any required)
12. Obtain permits and other permissions
13. Obtain required equipment and materials
14. Initiate construction
15. Complete construction
16. Final permit sign-off
17. Commission project
18. Operate project
19. Study/assess project performance
20. Decommission project

With regard to costs of procuring ammonia for a demonstration project, we have found through vendor quotes that anhydrous ammonia is currently available in Northern California for $0.86/lb, or $129 for a 150-lb. cylinder. Additional costs include a $200 deposit for each cylinder, plus freight charges for delivery. In order to deliver liquid ammonia from the cylinder array to the ammonia-cracking unit, a manifold piping system would be required.

Field Operational Test Demonstration Plan – Option 1: Facility Peak-Shaving Demo

Given the technological readiness of ammonia-based hydrogen storage and delivery systems that are suitable for use with fuel cell power plants, the near-term potential is for a relatively small-scale demonstration project. This could serve as a learning demonstration and "proxy" for a larger-scale installation that looks forward to lower stationary fuel costs and low-carbon means of producing ammonia or ammonia complexes.

One interesting idea is the use of fuel cell power to "peak shave" the electricity demands of a facility in order to produce power at key times when it is most highly valued, and the benefits of displacing grid power purchases are highest. This is typically the case during summer months and from early afternoon through early evening. Particularly for PEM fuel cells, which have somewhat limited "durability" at present and are not generally considered ideal for 24/7 (8,760 hour per year) operation, this can be an attractive option. Operating the fuel cell system for

With only a 5-15 kW demonstration, the actual cost savings associated with displacing peak power needs at a given facility would be pretty modest. Again, however, this could serve as a FOT "proxy" for a larger scale project in the future, with a larger ammonia/hydrogen fuel supply system and a larger fuel cell system. The cost savings from the peak shaving operation of the fuel cell system would come from both electricity energy cost savings (i.e., $/kWh peak rate multiplied by the kWh of grid power displaced) as well as electricity demand charge savings (i.e., $/kW-month times the monthly actual peak power reduced).

Field Operational Test Demonstration Plan – Option 2: Emergency Backup Power Demo

Another concept for a demonstration project, that could be developed and analyzed separately or in conjunction with "option 1" above, is the idea of using a fuel cell power systems for emergency backup of a communications center or other "critical load" facility that would be desirable to remain operational in the event of a loss of grid power. Diesel backup generators are typically used for this purpose, but they are highly polluting and also have been found in some cases to be unreliable for periods of extended outage.

Since the ammonia cracking systems need 10 to 20 minutes to warm up, an emergency backup system based on fuel cell power units and ammonia fuel would need to include a hydrogen buffer tank. The buffer storage would need to be sized adequately to allow the fuel cell system to operate on stored hydrogen while the ammonia cracking system was warming up. A demonstration project using a 5-15 kW fuel cell might or might not be sufficient to backup all of the critical electrical loads of a given facility, but again the small-scale FOT/demonstration project could be studied as a proxy for a larger scale future deployment project.

Note that these two demonstration project options could be combined into a demonstration that included peak shaving as well as emergency backup power. The system could be used during peak demand periods to reduce the needs for grid power purchases, as well as supplying emergency backup power for critical loads in the event of a loss of grid power.

Other more ambitious concepts are possible as well such as those that would also involve the ability to provide a limited amount of refueling for hydrogen fuel cell vehicles, as well as electricity production with a stationary fuel cell system. The limited size of the small-scale ammonia-cracking units being developed by IE and AES would limit the amount of hydrogen that could be made available for this dual-mode type of system, but again a small-scale demonstration could serve as a learning experiment with an eye toward a larger-scale project as a subsequent phase.

Conclusions

This report has documented the findings of a research project for Caltrans to assess the status of technologies to support a potential fuel cell system demonstration project that is based on an ammonia-based hydrogen supply system. The study has focused on potential stationary fuel cell applications, and primarily on a liquid anhydrous ammonia-based hydrogen supply.

Key findings of the study are as follows:

- Anhydrous ammonia is an attractive hydrogen carrier in terms of weight and volume energy density, but suffers from toxicity concerns;
- Natural gas and naphtha are the primary feedstocks for ammonia production today, but other non-carbon based hydrogen sources are possible in the future as a route toward “de-carbonized” ammonia as a hydrogen energy carrier;
- Industrial-scale ammonia cracking systems are relatively mature and manufactured by various companies;
- Smaller-scale ammonia cracking systems targeted at fuel cell power system applications are under development by at least two companies, and currently at prototype status;
- Ammonia cracking systems can operate at various temperatures and pressures, with resulting technical trade-offs, especially with regard to conversion efficiencies and system energy balances;
- Ammonia cracking systems are most “naturally” suitable for use with AFCs and SOFCs due to tolerance to un-reacted ammonia with medium (~650° C.) temperature level cracking system operation, but can be used with PEM and phosphoric acid fuel cells with additional cleanup systems (albeit with some concerns about effects on durability) or with higher temperature system operation (e.g. 950° C.) where levels of un-reacted ammonia are very low;
- Ammonia cracking systems can have attractive economics compared with other hydrogen supply options, particularly at small to medium scales of 10-100 nm^3/hr;
- Ammonia electrolysis is another potentially attractive method of hydrogen production, and one that is thermodynamically favored but that currently suffers from slow reaction kinetics;
- Achieving ISO specifications of hydrogen purity for fuel cell applications of un-reacted ammonia (of <100 ppb) is technically feasible but would require an additional cleanup system at the back end of the ammonia cracking unit;
- For PEM fuel cell applications, research with Gore membranes has shown that performance is severely reduced with levels of un-reacted ammonia of 200-1,000 ppm, but that deterioration is significant even at levels of 10 ppm and 1 ppm (although slowly reversible with pure hydrogen operation);
- The costs of small-scale ammonia cracking units are high at present, based on “one off” production and significant non-recurring engineering costs; and

- At least two companies – AES and IE – are in a position (or soon will be) to supply small-scale ammonia cracking units for near-term FOT/demonstration projects.

In conclusion, achieving the promise of hydrogen as a fuel source and expanded use of fuel cells in stationary and mobile power applications depends on ultimately developing low-carbon and otherwise low-emission and sustainable means of producing and delivering hydrogen fuel (or hydrogen-rich fuels for high temperature fuel cells). Anhydrous ammonia and ammonia complexes offer one potentially attractive means of doing this as ammonia can be converted to a hydrogen rich gas stream without any inherent emissions of greenhouse gases. Depending on how the ammonia or ammonia complex is initially produced, full fuel-cycle emissions of greenhouse gases and other air pollutants can be moderate or low/zero, making further exploration of these types of systems interesting.

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