TECHNOECONOMIC ANALYSIS OF AREA II HYDROGEN PRODUCTION - PART II

Hydrogen from Ammonia and Ammonia-Borane Complex for Fuel Cell Applications

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Abstract

The aim of this analysis is to assess the issues of cost, safety, performance, and environmental impact associated with the production of hydrogen by so called "Area II" technologies, not presently funded by the U.S. DOE Hydrogen Program. The hydrogen (H_2) rich feedstocks considered are: water, hydrogen sulfide (H_2S) rich sub-quality natural gas (SQNG), and ammonia (NH_3). Three technology areas to be evaluated are:

1) Thermochemical H_2S reformation of methane with and without solar interface,
2) Thermochemical water-splitting cycles suitable for solar power interface,
3) Ammonia and ammonia adducts as hydrogen energy storers for fuel cell applications.

This project is a multi-year effort with following objectives:

- Analysis of the feasibility of the technology areas 1-3 from technical, economical and environmental viewpoints.
- Evaluation of the cost of hydrogen production by technology areas 1 & 2.
- Feasibility of the technology area 3 as a means of supplying H_2 to fuel cell power plants.

This paper provides the second in a series of analysis focusing on the prospects of ammonia and ammonia-borane compounds for use as hydrogen carriers for fuel cell applications. Due to extreme toxicity of ammonia, it is difficult to envision its widespread use as the future transportation fuel. This is despite the fact that ammonia is a low cost, readily available, environmentally clean and very high-density hydrogen energy storer. One approach to mitigate this problem is to complex ammonia with a suitable hydride so that the resulting material is neither toxic nor cryogenic. A class of compounds known as amine-boranes and their certain derivatives meet this requirement. The simplest known stable compound in this group is ammonia-borane, H_3BNH_3 (or borazane). Borazane is a white crystalline solid that upon heating reacts to release hydrogen in a sequence of reactions that occur at distinct temperature ranges. Ammonia-borane contains about 20 wt% hydrogen and is stable in water and ambient air.

Introduction

The use of ammonia as chemical hydrogen storage compound that can be easily dissociated and used in the fuel cells and power plants is not new and has been ongoing for more than 40 years [1-58]. In the early 1970s when the concept of "Hydrogen Energy Economy" was widely debated, it was envisioned that ammonia (NH_3) would provide a perfect storage medium for hydrogen produced by the ocean thermal energy conversion (OTEC) plantships [16,32]. In the early 1980s, Strickland at the Brookhaven National Laboratory (BNL) conducted a systems study to determine the economic prospects of using anhydrous liquid ammonia, produced by OTEC, as a hydrogen carrier for annual H_2 demand of 10-100 million standard cubic feet [28,31]. BNL study showed that OTEC NH_3 was competitive with H_2 made at the point of use via water electrolysis, steam reforming of natural gas, or OTEC liquid hydrogen (LH_2), in the upper fifth of the use range. In another BNL study, three alternative transportation fuels (ATFs) were compared with respect to the input energy required for their production from NG, their H_2 storage capacity and cost per unit of energy contained ($/million BTU)[26]. The ATFs chosen were LH_2, hydrogen produced by steam reformation of methanol (MeOH), and H_2 generated via thermocatalytic dissociation of anhydrous liquid ammonia. The BNL results showed that anhydrous liquid ammonia had considerable advantage over MeOH and LH_2, coming very close to matching gasoline performance as a motor fuel.

The work of Strickland at BNL was supported by the efforts at the Lawrence Berkeley National Laboratory (LBNL) [27,29]. In the early 1980s, Ross conducted a detailed experimental and analytical study on the use of indirect NH_3-air alkaline fuel cells (AFCs) for vehicular applications [27]. The impetus for his work was the belief that ammonia provided a feasible storage medium for H_2 produced from non-fossil sources, *e.g.* by the off-land OTEC or remote solar-thermal facilities. According to Ross, anhydrous liquid ammonia provides an excellent medium for H_2 storage, even though energy is required to evaporate and dissociate NH_3 resulting in somewhat lower efficiencies. LBNL results showed the advantages of AFCs relative to acidic electrolyte fuel cells, that is 2-3 times higher power densities and a factor of two lower component costs, resulting in 4-6 times lower total power plant costs. In addition, the ammonia dissociation reaction and power characteristics of an alkaline fuel cell operating on cracked NH_3 and air was determined. For a single cell unit, results obtained by Ross indicated that thermal efficiencies in the range of 34-44% at power densities of 1-2.2 kW/m^2 (using 1980s electrode technology) were achievable.

As the 1980s drew to close and with the demise of non-fossil hydrogen production technologies as a near-term reality, ammonia disappeared as a viable hydrogen storage medium from the U.S. DOE programs [57]. The commonly held view was that OTEC would be roughly twice as expensive as the conventional energy forms due to the high capital cost of OTEC plants made under existing designs at that time. It is often stated that a $40/barrel oil cost would be necessary to spur investors into seriously considering OTEC technology [58]. The total energy efficiency is lower with ammonia as the H_2 carrier compared to methanol. Therefore, if methane is used as the primary fuel, then methanol will likely be the liquid fuel of choice for fuel cells, especially PEMFCs. Presently, the DOE fuel cell for transportation program appears to be focused on the use of fossil fuels and for that reason ammonia is not generally considered as a viable H_2 carrier. The ammonia scenario was unique to the OTEC project, where the electrical energy would be generated at a remote location and it was not feasible to install either power lines or a hydrogen pipeline to the shore. Hydrogen production and subsequent conversion to NH_3 for shipment to the shore seemed to be the most attractive way to store and transport OTEC hydrogen. Using ammonia directly in the fuel cells then appeared to be the most plausible approach. In other words, in the case of solar/renewable hydrogen production, ammonia can still be viewed as a viable chemical storage medium for supplying hydrogen to fuel cells, especially AFCs.

Karl Kordesch was one of the early advocates of the AFCs and the use of ammonia as a high density H_2 carrier for automotive fuel cell applications [10]. According to Kordesch and co-workers, using readily available, off-the-shelf materials, an ammonia cracker can be fabricated providing on demand H_2 on-board fuel cell vehicles [50,51,53,54]. In addition, ammonia is a more desirable source of hydrogen for AFCs, as the small amounts of unconverted NH_3 that may remain in the dissociated gas would not harm the fuel cell function. In other words, there is no need for complete removal of trace impurities in the output stream of an ammonia reformer connected to an AFC power plant. Traditionally, the main issue with the AFC technology has been the perceived problem with the fuel (*i.e.* hydrogen) storage. In acid fuel cells, hydrogen can be stored as methanol. Required hydrogen for operation of the acid fuel cell can be delivered by steam reformation of methanol employing an onboard MeOH reformer. The carbon dioxide generated during this process does not present a serious problem to the acid fuel cell electrolyte function. In the case of an alkaline fuel cell, the electrolyte would react with the carbon oxides, forming problematic insoluble carbonate [53].

Much effort has been expended to develop steam reformation of methanol as a process for generating hydrogen for use in fuel cells. Nonetheless, a comparison of the economics of H_2 production via ammonia decomposition for alkaline fuel cells versus methanol reformation for acid fuel cells has shown that ammonia decomposition is economically more favorable [40,41,55]. Commercial ammonia is prepared at 99.5% purity (the impurity is mainly water which is harmless), whereas the higher alcohol impurities present in commercial methanol can result in production of contaminants during reforming that can lead to poisoning of the catalyst. Thus, the decomposition of ammonia appears to be an excellent choice for production of hydrogen for alkaline fuel cells as well as acid fuel cells if the unreacted NH_3 in the hydrogen stream is removed to below the admissible level [59].

Problems with the formation of insoluble carbonate in the electrolyte of an AFC can be expected if air is used (without CO_2 scrubbing) instead of pure oxygen (as is the case with the space-bound AFCs) at its cathode. AFCs employed in the U.S. Space Program on-board space vehicles use the porous solid matrices soaked with potassium hydroxide (KOH) electrolyte. The main reason for using matrix-type electrolyte in the space-bound vehicles is to improve system reliability by employing only passive devices that do not contain any moving parts. The use of matrix-type electrolyte in space AFCs is not problematic because high purity hydrogen and oxygen are available on-board the spacecraft. However, in terrestrial applications, air is used and therefore the use of matrix-type electrolyte will not be practical. According to Kordesch, for terrestrial AFCs, it is more advantageous to use a circulating type electrolyte. The exchangeability of circulating KOH solution allows the operation of AFC using air with less than complete CO_2 removal [53].

The system analysis studies conducted by Avery at the Johns Hopkins University and MacKenzie of the World Resources Institute in the late 1980s and throughout 1990s indicate that ammonia can play a key role in the future H_2-based transportation systems [42]. More recently, in a 1995 study by Miller at the Colorado School of Mines, ammonia has been shown to readily convert to a mixture of H_2 and N_2 by recycling the heat generated by an alkaline fuel cell, which operates in the temperature range of 70-150 °F [60]. As recently as 1999, ammonia economy has been advocated again as a way to address concerns with global warming, smog, and acid rain coupled with the slow pace of the progress and problems in the production and storage of practical commercial hydrogen-fueled and battery powered vehicles [49].

Benefits of Ammonia Use

Ammonia is the second largest synthetic, commodity product of the chemical industry with world production capacity exceeding 140 million metric tons. 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 [61]. Furthermore, anhydrous ammonia costs about $150 per short ton (f.o.b. U.S. Gulf Coast) or less than $6.25 per million BTU of hydrogen contained [62]. Besides the large volume of production and use, and relatively low cost, ammonia has many other advantages as a hydrogen- rich fuel for fuel cell applications. They are as follows [26,27,31,42,49,59,63]:

- Anhydrous ammonia contains17.8 percent by weight hydrogen.
- Technology for transportation, distribution, storage and utilization of ammonia is well established and widely available.
- Ammonia can be stored under moderate pressure (about 370 psig) and its physical properties mimic those of liquid propane.
- Anhydrous liquid NH_3 stores 30% more energy per unit volume than LH_2 (after taking into account the energy required for both evaporation and decomposition of liquid NH_3).
- Explosion span for ammonia –air (at 0°C and 1 atm) is much narrower than that for hydrogen-air mixtures (*i.e.* 16 – 27 vol % NH_3 vs. 18.3 – 59 vol % H_2).
- Autoignition temperature for ammonia vapor is much higher than that for hydrogen (*i.e.* 651°C for ammonia vs. 585°C for hydrogen).
- Using ammonia in fuel cell power plants does not generate CO_x or NO_x emission.
- Only 16% of the energy stored in ammonia is needed to break gaseous ammonia into nitrogen and hydrogen gases.
- Ammonia as fuel for AFCs requires no shift converter, selective oxidizer or co-reactants such as water as in other hydrocarbon or alcohol fuel cell power devices.
- Hydrogen produced from ammonia can be utilized in AFCs that are amongst the most efficient and least costly fuel cell power plants.
- No final hydrogen purification stage is needed. Since nitrogen is an inert gas in the fuel cell and simply passes through as a diluent.

Ammonia can be readily converted to hydrogen and nitrogen gas by thermocatalytic decomposition. NH_3 decomposition reaction is well studied and can be accomplished in a simple reactor using variety of catalysts including transition metals and alloys [64]. Among metal catalysts, ruthenium and iridium are the most active for NH_3 dissociation under mild conditions [55,65]. Other compounds that exhibit high activity for NH_3 cracking include alloys such as Fe-Al-K, Fe-Cr, La-Ni (-Pt) and La-Co (-Pt). In general, catalysts containing noble metals are not used in the commercial processes due to high cost. The widely used supported Ni catalyst requires very high temperatures (in excess of 1000°C). Transition metal nitrides and carbides, such as Mo_2N, VN, and VC_x, have also been tested for NH_3 decomposition. Catalytic action of nitrides and carbides is similar to those of noble metals with respect to the reactions involving H_2 [66]. It has also been shown that the nitrided MoN_x and $NiMoN_x$ on α-Al_2O_3 are both very active for NH_3 dissociation. For example, the ammonia conversion for $NiMoN_x/\alpha$-Al_2O_3 exceeds 99% even at 650°C, and reaches a maximum of 99.8% when the atomic ratio of Ni/(Ni + Mo) is close to 0.60 [66]. This temperature is much lower than the operating temperatures of the commercial catalysts such as the ICI's 10%-wt Ni on alumina (catalyst 47-1), Haldor Topsøe's triply promoted iron-cobalt (catalyst DNK-2R) or SÜD-Chemie 27-2, nickel oxide (NO) on alumina catalyst [67,68].

Conventional large-scale ammonia crackers (in the power ranges of up to 1200 kW) are used in metallurgical industry for metal nitriding (69). Newer, highly efficient and fully integrated ammonia dissociators are being developed for smaller and more specialized applications. One example is the system developed by the Boston-based Analytic Power Corporation (now Dais Analytic Corp.) that provides hydrogen source for small (150 W) fuel cell power supplies (45).

Another example involves the MesoSystems Technology, Inc. (MTI). MTI has developed a compact system for ammonia storage, reforming, H_2 generation and purification utilizing the microchannel reaction technology. MTI's objective was to produce a 50W power supply to deliver one kW-hr equivalent hydrogen from a 1-kilogram hydrogen source. The weight includes the microchannel cracker, ammonia precursor, and all the necessary scrubbers to purify the resulting hydrogen/ammonia stream [70,71]. MTI estimates costs of about $300 for the H_2 generator (for orders of 10,000 systems or more) and about $10-$20 for each NH_3 fuel canister delivering about 60g of H_2 (net), for orders of 100,000 units or more [72].

Somewhat larger ammonia crackers than those developed at Dais Analytic and MTI are needed for vehicular fuel cell applications. The Apollo Energy Systems, Inc. of Fort Lauderdale, Florida and researchers at the Technical University (TU) of Graz, Austria have jointly developed an 11.5 kW ammonia cracker [73]. TU team's approach was to improve the commercially available NH_3 pyrolysis catalysts such as the SÜD-Chemie 27-2 and NO on alumina by modification with noble metals (e.g. 0.3 wt% ruthenium on nickel oxide catalyst). Apollo Energy Systems (AES) plans to market 10-kW alkaline fuel cells that can use liquid ammonia as a base fuel that is converted to H_2 in their proprietary autothermal ammonia cracker [74]. To date, no cost data are available on any of the AES crackers. Autothermal NH_3 reformers are described in the next section. For the time being it suffices to say that for larger multi-kW ammonia crackers such as those developed by Kordesch and co-workers for AES, the overall efficiency of the system can reach as high as 85% [75]. For smaller NH_3 crackers for PEM fuel cell applications, the efficiency values of about 60% have been reported by Yang and Bloomfield [76], with as much as 40% of the product H_2 burned to supply dissociation energy needed for their autothermal reformer and also compensate for the heat losses.

Apparently, both AES and Analytic Power ammonia reformers described above are based on a system design first developed by Ross, Jr. at LBNL [77,78]. Although the NH_3 reformer used by Bloomfield and co-workers in a 1998 demonstration by Analytic Power [76] utilized Ross' design, it is not clear why their reported H_2 efficiency (*i.e.* only ca. 60%) was so much lower than the 80% or so obtained in the Ross' laboratory unit [78]. One explanation for this may be the attempt by the Analytic Power to reduce the size of the reformer by using higher temperatures (1050°C versus 450°C in Ross' lab unit). The theoretical (adiabatic) efficiency is 85%.

Autothermal Reformation of Ammonia

As noted above, a more direct method for supplying the required energy to drive the dissociation reaction while minimizing the heat losses is by autothermal ammonia reformation. Autothermal ammonia decomposition provides an especially effective way to supply H_2 for use in the proton exchange membrane (PEM) fuel cell systems. This technique combines endothermic heterogeneous NH_3 decomposition reaction (into H_2 and N_2 on a supported catalyst) with the exothermic homogenous oxidation of ammonia (into N_2 and water) in the gas phase [79]. This direct coupling of ammonia dissociation and oxidation within the same reactor greatly improves heat transfer and process energetics. For optimum performance, ammonia reformer must approach adiabatic operation and allow cooling of the reactor effluent via feed gas preheat in a suitable heat exchanger.

There are other advantages of autothermal ammonia reformation. Ammonia conversions exceeding 99% with H_2 selectivities above 65% have been reported at space velocities as high as 10^6 hr^{-1} [80]. We used Thermfact's chemical equilibrium program FactSage 5.0 to minimize the Gibbs free energy and determine species concentration during autothermal reformation of ammonia. Results are depicted in Figure 1 for autothermal adiabatic reaction of ammonia with air (consisting of nitrogen, oxygen and carbon dioxide gases). It was further assumed that the feed gas entering the reformer is heated to the same temperature as the reactor effluent (that is equal to the reformer temperature). The reformate mole fractions are calculated for a range of temperatures and initial NH_3 to oxygen molar ratios (x_{NH3}). Figure 1 depicts calculation results obtained for x_{NH3} values in the range of 1.33 to 49.2. Results of Figure 1 indicate that autothermal NH_3 reformation can be carried out over a wide range of x_{NH3} values. Lower ratios lead to higher ammonia conversions but lower H_2 selectivities as more hydrogen is converted into water.

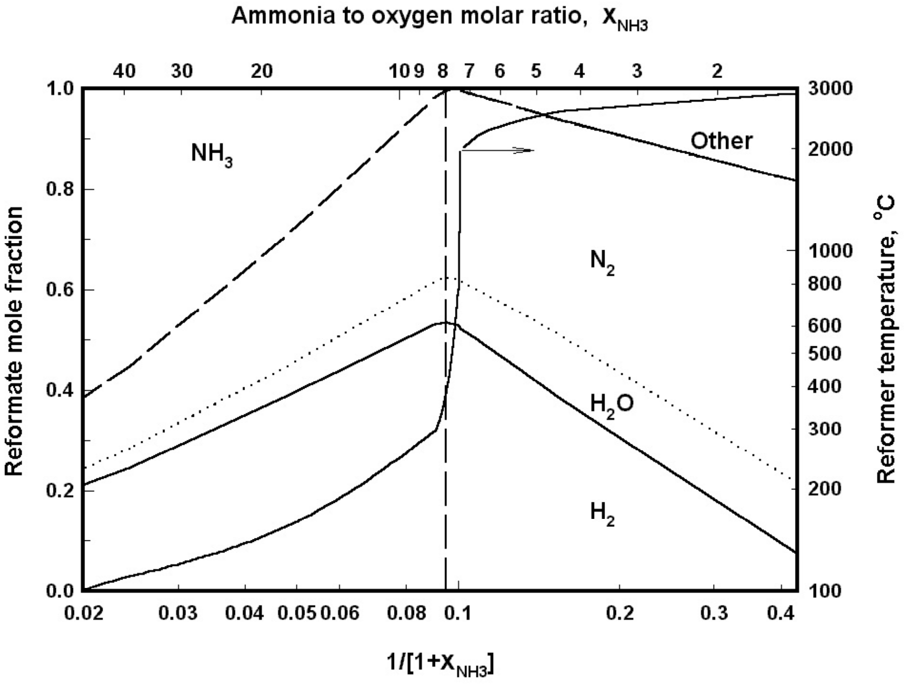

Figure 1. Autothermal reformation of ammonia in air, $[O_2+3.76N_2+0.002CO_2+x_{NH3}NH_3]_{in.}$

Figure 2 depicts the effect of reformation temperature on the reformate mole fractions for the same process conditions as that in Figure 1. It can be seen that autothermal ammonia reformation is accomplished over a wide range of reformer temperatures. Furthermore, no NO_x or any other undesirable species such as unreacted oxygen is detected in the reformer effluent for x_{NH3} values in the range of 7 to 8 and reforming temperatures from about 400°C to 1500°C.

These results are in general agreement with the experimental data of Goetsch and Schmit given in Table 1 for ammonia decomposition on ruthenium catalyst in coaxial autothermal reformer with feed gas preheating [80].

The main disadvantage of autothermal reforming of ammonia is that the effluent stream needs be cooled down to a temperature compatible with PEM 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 ppmv levels) in the effluent stream may also be necessary.

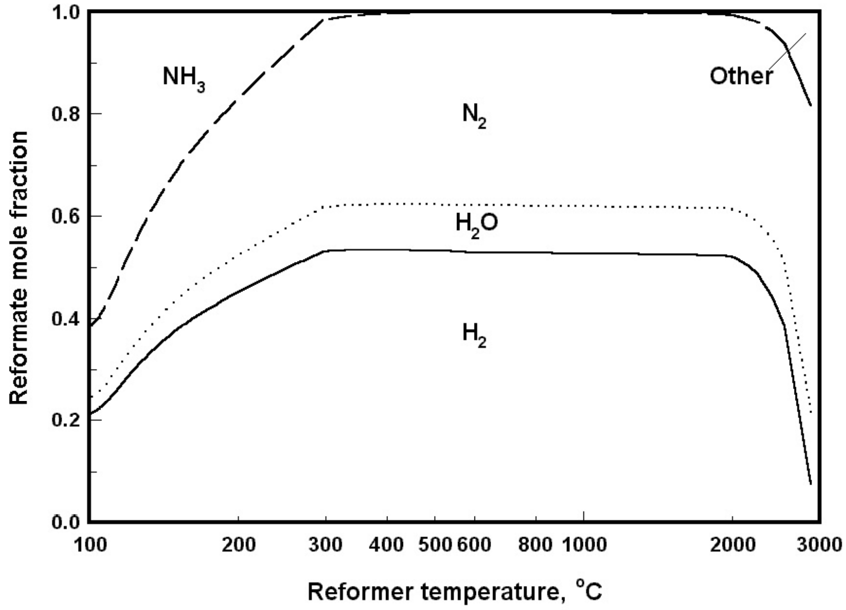

Figure 2. Effect of temperature on reformate concentration for autothermal reaction of ammonia with air.

Table 1. Autothermal reformation of NH_3 in a coaxial reactor on monolithic Ru catalyst [80].

x_{NH3}	NH_3 conversion	N_2 yield	H_2 yield	H_2 selectivity	H_2O yield	H_2O selectivity
3	0.989	0.989	0.634	0.641	0.355	0.359
4	0.976	0.976	0.707	0.725	0.268	0.275
5	0.926	0.926	0.702	0.758	0.224	0.242
6	0.826	0.826	0.607	0.735	0.219	0.265
7	0.754	0.754	0.541	0.718	0.213	0.282
8	0.645	0.645	0.445	0.689	0.201	0.311
9	0.596	0.596	0.390	0.654	0.206	0.346

Drawbacks to Ammonia Use

For vehicular fuel cell applications and for economic and performance related reasons, it is necessary to reduce the size and lower the operating temperature and cost of ammonia dissociator. Special consideration has to be also given to the safety and environmental factors resulting from the direct involvement of the public.

One major drawback to ammonia as a fuel and chemical carrier for hydrogen, especially in vehicular applications, is its extreme toxicity and adverse health effects. Permissible levels of exposure to toxic gases are defined by their time-weighted average (TWA), short-term exposure limit (STEL) and concentration immediately dangerous to life or health (IDLH). Anhydrous NH_3 has a TWA of 25 ppm, an STEL of 35 ppm and an IDLH of 500 ppm [81]. Although injury from

NH_3 is most commonly the result of inhalation, it may also follow direct contact with eyes and skin or ingestion. The EPA has identified NH_3 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 [82]. There are also other less obvious drawbacks to the widespread use of ammonia as vehicular fuel. For example, anhydrous ammonia is used, extensively, in the manufacture of illicit drug methamphetamine. Anhydrous NH_3 is used in the so-called "Nazi method" to spur methamphetamine production [83]. This method does not require extensive knowledge of chemistry, uses no heat, and is much simpler technique than the ephedrine-pseudoephedrine reduction or "Red P" method that is also used for producing methamphetamine.

Due to these and other considerations, it appears unlikely that NH_3 will find widespread use as a high-density chemical carrier for H_2 in the future transportation applications. This is despite the fact that ammonia is a superb fuel for power plants, in general, and fuel cells, in particular. Furthermore, due to economic and energy efficiency considerations, it will be advantageous if a method could be found that completely eliminated the need for or greatly simplified the function of the on-board NH_3 reformer. One approach to mitigate ammonia's shortcomings is to complex NH_3 with other hydrides so that the resulting compound is stable but not toxic or cryogenic. The prospective process must produce a compound that contains H_2 at gravimetric and volumetric densities comparable to that of anhydrous ammonia. A class of compounds (with generalized formula $B_xN_xH_y$) known as amine-boranes and some of their derivatives satisfy this requirement.

Hydrogen from Pyrolysis of Amine-Boranes

Review of literature prior to 1980 reveals that several methods have been investigated as a means of high capacity hydrogen storer compounds. The compounds that have been considered are primarily based on complex borohydrides, or aluminohydrides, and ammonium salts. These hydrides have an upper theoretical H_2 yield limited to about 8.5% by weight. Improvements in H_2 weight yield will not result from solid reactants based upon the interaction of metal borohydrides, or aluminohydrides, and ammonium salts, or from catalytic decomposition of the active hydride compounds. This is so because for $NaBH_4/NH_4^+$ salt systems the generation of hydrogen is the result of reaction between NH_4^+ cation and the BH_4^- anion [84]. Therefore, the counter ions only serve to stabilize these reactive species, resulting in a lower hydrogen yield because of their added weight. Thus, in order to achieve higher hydrogen yields, it is advantageous to consider those compounds that have, on a molecular basis, only moieties that react to form hydrogen. Amongst the compounds that contain only B, N, and H (both positive and negative ions), representative examples include: amine-boranes, boron hydride ammoniates, hydrazine boron complexes, and ammonium octahydrotriborates or tetrahydroborates. Of those, amine-boranes (and especially ammonia-borane) have been extensively investigated as H_2 carriers [84-91].

During 1970's and 80's, the U.S. Army and Navy funded efforts aimed at developing H_2/ deuterium gas-generating compounds for use in the HF/DF and HCl chemical lasers, and gas dynamic lasers [85-91]. Earlier H_2 gas-generating formulations were prepared using amine-boranes (or their derivatives), mixed and ball milled together with a reactive heat-generating compound, such as $LiAlH_4$ or a mixture, such as $NaBH_4$ and Fe_2O_3, until a uniform mixture was obtained [90]. Upon ignition, the heat-generating compound in the mixture reacts and the energy released pyrolyzes the amine-borane(s) forming boron nitride (BN) and hydrogen gas. A nichrome heating wire is used to initiate a self-sustaining reaction within these gas-generating compounds. Ammonia-borane or borazane (H_3BNH_3) is the simplest stable amine-borane used

in these gas-generators. Another stable amine-borane used in the gas-generators is diborane diammoniate, $H_2B(NH_3)_2BH_4$ [92].
Ammonia-borane and diborane diammoniate both pyrolyze upon heating, releasing H_2 gas. Reaction products, besides H_2, include a polymeric solid residue of poly(aminoborane) $(BH_2NH_2)_x$. With further heating, more hydrogen is released and borazine ($B_3N_3H_6$) forms, a compound that is structurally analogous to benzene. Borazine can react further releasing additional H_2 to produce boron nitride, BN. Techniques for preparation of an all amine-borane formulation consisting of hydrazine (bis)borane, $N_2H_4.2\ BH_3$ and diborane diammoniate, in the form of a compacted solid fuel is given by Grant and Flanagan [92].

In addition to the gas generating compounds discussed above that provide hydrogen yields in the range of 16 wt% and better than 99% H_2 purity, other formulations that were based on the magnesium borohydride diammoniate (MBDA), $Mg(BH_4)_2$ have also been prepared and tested [93]. Formulations based on MBDA are generally more stable and better suited for the field applications. MBDA-based compounds contain an oxidizer selected from $LiNO_3$ and KNO_3 and polytetrafluoroethylene (PTFE) as the binder. For example, a blend of 85 wt% MBDA, 7.5 wt% $LiNO_3$, and 7.5 wt% PTFE provides a H_2 yield of about 12.5 wt% with excellent pellet thermal stability (up to 75°C) and physical properties [93].

Physiochemical Properties and Synthesis of Ammonia-Borane Complex

Ammonia-borane is a white crystalline solid at normal conditions that contains about 20-wt% hydrogen. Pyrolysis of ammonia-borane is a complex process and the products of the decomposition reaction markedly depend on the conditions employed. Furthermore, the initial process is a solid-state reaction for which the onset of decomposition (T_i) is a function of heating rate of the substrate (β). In one study based on TG-FTIR and TG-DSC analysis, heating a borazane sample to 90°C at a rate of β = 0.5°C/min and then holding it at that temperature for 200 min resulted in a loss of about 10.2% of initial sample mass [94]. FTIR analysis of the evolved gases shown approximately one mol of H_2 forming per mol of BH_3NH_3 reacted. Reaction products, in addition to hydrogen, include monomeric aminoborane BH_2NH_2 and a small amount of volatile borazine ($B_3N_3H_6$) [94]. The monomeric aminoborane is unstable at room temperature oligomerizing to form a non-volatile white solid residue of poly(aminoboranes) $(BH_2NH_2)_x$ [95-99]. The inorganic analog of polyethylene, polymeric $(NH_2BH_2)_x$ is still not fully characterized [98]. Crystalline cyclic oligomers, $(NH_2BH_2)_n$ (where, n = 2, 3, 4, 5) have been prepared in the past [100] and an amorphous $(NH_2BH_2)_x$ consisting of solvated linear chains with x= 3-5 has also been produced by gas-phase pyrolysis of ammonia-borane [101].

Unlike aminoborane oligomers, borazine (isoelectronic with benzene) is a volatile colorless liquid that boils at 55°C [94]. Based on the TG and DSC analysis of Geanangel and co-workers [97], pyrolysis of ammonia-borane begins with a sharp endothermic peak that appears just above the melting point of BH_3NH_3 (112-114°C depending on the sample heating rate β [94,96]. Near 117°C, a steep exothermic peak was observed, reaching a maximum at about 130°C with rapid evolution of gas. A final broad exotherm was observed to occur near 150°C. Although processes other than step-wise decomposition and hydrogen loss are involved to some degree in H_3BNH_3 and its intermediate compounds, nonetheless the following sequence of events also occur [94,96-98]:

$$H_3BNH_3\ (l) \longrightarrow H_2BNH_2\ (s) + H_2\ (g)\quad \text{at } T_i \sim 137°C\ \&\ \beta = 5\text{-}10°C/min,\quad \Delta H_r = -(21.7 \pm 1.2)\ kJ/mol$$

$$x\,(H_2BNH_2)\ (s) \longrightarrow (H_2BNH_2)_x\ (s)\quad \text{at } T_i \sim 125°C$$

$$(H_2BNH_2)_x\ (s) \longrightarrow (HBNH)_x\ (s) + x\ H_2\ (g)\quad \text{at } T_i \sim 155°C$$

$$(HBNH)_x\ (s) \rightarrow \text{borazine + other products}$$
$$(HBNH)_3 \longrightarrow 3\ BN + 3\ H_2 \quad \text{at well above } 500°C$$

and,

$$(H_2BNH_2)_x\ (s) \longrightarrow (BN)_x\ (s) + 2x\ H_2\ (g) \quad \text{at } T_i \sim 450°C\ \&\ \beta = 10°C/min$$

Due to the large amount of evolved H_2 and the exothermicity of the process, ammonia-borane appears to be a more effective chemical storer of H_2 than anhydrous NH_3 [94,102]. Other physicochemical properties of ammonia-borane complex are given in Table 2 below.

Table 2. Selected physiochemical properties of ammonia-borane complex.

<table>
<tr><th>Property</th><th>Description</th><th>Reference</th></tr>
<tr><td>Formula</td><td>NH_3BH_3</td><td>-</td></tr>
<tr><td>Molecular weight</td><td>30.86</td><td>-</td></tr>
<tr><td>X-ray structure</td><td>C_{4V} symmetry; unit cell is tetragonal</td><td>[103,104]</td></tr>
<tr><td>Odor</td><td>Ammonia-like</td><td>-</td></tr>
<tr><td>Density, g/mL</td><td>0.74</td><td>[103-105]</td></tr>
<tr><td>Melting point</td><td>112-114°C, slow decomposition at approx. 70°C</td><td>[94,96]</td></tr>
<tr><td>Heat of formation</td><td>$\Delta H_f° = -178 \pm 6$ kJ/mol</td><td>[106]</td></tr>
<tr><td>Heat of combustion</td><td>$\Delta H_c° = -1350 \pm 3$ kJ/mol</td><td>[106]</td></tr>
<tr><td>Water stability</td><td>10% solution stored at ambient temperatures:
<table>
<tr><th>Dormancy</th><th>% hydrogen loss</th></tr>
<tr><td>4 days</td><td>1.8</td></tr>
<tr><td>11 days</td><td>3.6</td></tr>
<tr><td>1 month</td><td>4.8</td></tr>
<tr><td>2.5 months</td><td>9.3</td></tr>
<tr><td>18 months</td><td>45.0</td></tr>
</table></td><td>[107]</td></tr>
</table>

Another important factor is interaction with water and other solvents. Unlike ionic hydrides, NH_3BH_3 does not react violently with water. Table 3 depicts the solubilities of borazane in water and a number of organic solvents. More information is available in reference [108].

Table 3. Solubilities of ammonia-borane complex in various solvents [107].

Solvent	Wt%	Temperature, °C	Density of saturated solution, g/mL
Water	26	23	0.89
Methanol	23	23	0.78
Ethyl Ether	0.80	24	0.71
Hexane	0.003	25	0.56
Benzene	0.03	25	0.87
Methylene Chloride	0.08	21	1.32

Borazane can be prepared through several indirect procedures [109-114] including the reaction with lithium borohydride, $LiBH_4$, in diethyl ether by either of the following two methods:

$$LiBH_4 + NH_4Cl \xrightarrow{\text{in diethyl ether}} LiCl + H_3BNH_3 + H_2$$
$$2\ LiBH_4 + (NH_4)_2SO_4 \xrightarrow{\text{in diethyl ether}} Li_2SO_4 + 2\ H_3BNH_3 + 2\ H_2$$

Alternatively, H_3BNH_3 is prepared directly from the gases by reacting diborane with ammonia in polar organic solvents (*e.g.* ether and dioxan) and in aqueous media [105,114]:

$$B_2H_6 + 2\ NH_3 \xrightarrow{\text{in ether or dioxan}} 2\ H_3BNH_3$$

A comprehensive survey of synthetic procedures applicable to most of the known boron-nitrogen compounds (except boron nitrides) including amine-boranes and their physical properties can be found in the reference [114].

For vehicular fuel cell applications, the main drawback to the use of amine-boranes, in general, and H_3BNH_3, in particular, is the present high cost of these compounds and lack of a suitable reformer design for the on demand generation of hydrogen. No data could be found for the large-scale production costs of ammonia-borane. However, the Callery Chemical Co manufactures large quantities of dimethylamine borane (DMAB), which has significant use in the electroless plating industry. Depending on the volume, the price of DMAB is in the range of about $75-100/lb [115]. It can be expected that the large volume price of ammonia-borane to be also in this range. The issue of the cost of ammonia-borane can be highlighted by comparing its price to the bulk material prices for other chemical hydrides under consideration as hydrogen storer compounds. The feasibility of using various ionic hydrides as potential hydrogen storer compounds for alkaline fuel cell (AFC) applications has been investigated by Kong et al. [116]. Their application required a hydrogen storage system capable of supplying hydrogen to an AFC generator producing 1 kW of electrical power for 8 hours. The fuel cell was assumed to operate at 57% efficiency (0.7 V) requiring 231 mol of H_2 (assuming 100% utilization) to meet the target duty. Table 4 depicts the cost of several hydrogen storer compounds including H_3BNH_3.

Table 4. Required mass, volume and cost of chemical hydrides for specified targeted duty.

Storer	Mass, kg	Volume, L	Cost, US$	Reference
LiH	1.7	3.7	109	[116]
CaH_2	4.5	4.0	104	[116]
$NaBH_4$ (35 wt% aqueous)	6.21	6.21	102	[116,117]
H_3BNH_3	2.38	3.21	390-525	This study

New chemical synthesis techniques and/or processes are needed to reduce the H_3BNH_3 production costs. Some work is already underway in this area. The U.S. Army has funded Venture Scientific International to investigate new methods for the synthesis of H_3BNH_3 and its pyrolytic decomposition to hydrogen, as well as packaging this compound into a compact, high output portable power source [118]. In addition to the cost issues, new processes must also be developed to allow recycling of the by-products of ammonia-borane decomposition on-board fuel cell powered vehicles. For example, if an on-board ammonia-borane based hydrogen storage system is to be developed for maximum H_2 delivery, then it will be desirable, if not necessary, to be able to retrieve and recycle the boron nitride residue. Here, the challenge is to develop a chemical route for activating boron-nitrogen bond in a manner analogous to dinitrogen bond activation in the Haber-Bosch process for ammonia synthesis. In the modern ammonia plants, steam reformation of natural gas is used as the primary source of hydrogen. Based on pure methane, let's formulate a simple stoichiometric equation for ammonia production by steam methane reformation (SMR) as follows [63]:

$$CH_4 + \underbrace{0.3035\ O_2 + 1.131\ N_2}_{1.4345\ \text{AIR}} + 1.393\ H_2O \rightarrow CO_2 + 2.262\ NH_3$$

In real processes, a high degree of irreversibility exists and considerable amount of energy is needed to produce ammonia from methane, air and water. The stoichiometric quantity of methane required in the equation above is about 583 m^3 per ton of ammonia produced. Energetically, this corresponds to approximately 20.9 GJ per ton of NH_3 (LHV). It can be argued that this is the minimum amount of energy needed per ton of ammonia produced using SMR process. It is interesting to note that the best energy figure reported for commercial ammonia production is about 27 GJ/t NH_3 [63]. This figure corresponds to a rather high efficiency of around 75% with respect to the theoretical minimum of 20.9 GJ/t NH_3, calculated as stoichiometric methane demand discussed above.

In a like manner, an idealized process for ammonia-borane synthesis from recycled BN (or borazine) may be written as:

$$CH_4 + 1.33\ BN + 2\ H_2O \rightarrow CO_2 + 1.33\ H_3BNH_3$$

Or,

$$CH_4 + 0.667\ (HBNH)_3 + 2\ H_2O \rightarrow CO_2 + 2\ H_3BNH_3$$

If similar processes could be developed at energy conversion efficiency levels that are comparable to the present day SMR-based ammonia synthesis plants, it is then possible to realize a major reduction in the production costs of ammonia-borane complex that is useful for the vehicular fuel cell applications. We note that a concept similar to that discussed above has been developed for a new nitric acid synthesis process based on boron nitride analogous to the Haber-Bosch route for HNO_3 production from ammonia [119]. In another recent report, nano-structured hexagonal boron nitride (h-BN) was prepared by mechanical milling under hydrogen atmosphere [120]. Hydrogen uptake in the mechanically activated h-BN reached 2.6% by mass of the material after milling for 80 h. Mechanical milling may be one approach to facilitating hydrogenation and reformation of boron nitride to amine-boranes. Finally, recent results have shown that unusual parallel behavior exists between hydrocarbons and their corresponding B-N analogues [121]. Thus, hydrogenation of benzene to cyclohexane may provide a model for the reformation of borazine to other amine-boranes.

Conclusions

There are many advantages to the use of NH_3 as hydrogen source for vehicular FC applications. However, a major drawback is ammonia's extreme toxicity and adverse health effects. By complexing NH_3 with diborane, a stable, non-toxic and non-cryogenic material (H_3BNH_3) can be prepared. This ammonia-borane complex is stable in water and ambient air and when heated liberates H_2 in a sequence of reactions between 137°C and 400°C that reaches about 20% of the initial mass of H_3BNH_3. Successful implementation of ammonia-borane as a potential future transportation fuel, however, requires new chemical techniques and/or processes for its synthesis that promise substantial reduction in its production costs.

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