

IV.H.2 Purdue Hydrogen Systems Laboratory: Hydrogen Storage*

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- University of Wyoming, Laramie, WY

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*Congressionally directed project

Objectives

- Develop an energy efficient recycling protocol for ammonia borane (AB) from spent borate.
- Develop AB slurry-based subscale onboard hydrogen storage systems.
- Develop a new noncatalytic method for hydrogen generation from AB and water.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3.4) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan (Revision 2007):

- (A) System Weight and Volume
- (B) System Cost
- (J) Thermal Management
- (R) Regeneration Process
- (S) By-Product/Spent Material Removal

Technical Targets

On-board Storage	Units	2010/Ulimate	Purdue 2010
System Gravimetric Capacity	H ₂ wt%	4.5/7.5	11~15 (material)
Overall Efficiency of Off-Board Regeneration	%	>60	The process is still being optimized

Accomplishments

- AB was prepared in kilogram-scale from sodium borohydride and ammonium sulfate in the presence of ammoniated tetrahydrofuran (THF) at room temperature in 92% yield and ≥98% purity.
- Trimethylborate was reduced using diethylsilane in the presence of Nⁱ,Nⁱ,N²,N²-tetramethylethane-1,2-diamine (TMEDA) to TMEDA-Bisborane complex.
- TMEDA-Bisborane complex was converted to AB via transamination in 80% yield.
- For the first time, characterized rheological properties of AB spent fuels.
- For the first time, captured the details of fast hydrogen evolution at the initial stage of the AB thermolysis process.
- Designed, constructed and tested a 10 g capacity batch reactor for neat AB thermolysis. Reactor capable of operating at up to 200°C and 8 bar.
- Investigated noncatalytic AB hydrothermolysis at near proton exchange membrane fuel cell (PEMFC) operating temperatures over a wide range of AB concentrations and pressure. The maximum hydrogen yield, obtained at 77 wt% AB and T_{reactor} ~85°C along with rapid kinetics, was 11.6 and 14.3 wt% at pressure 14.7 and 200 psia, respectively.
- Using the neat AB thermolysis process, ~15 wt% H₂ yield was obtained at 14.7 psia and T_{reactor} 90 °C with rapid kinetics also near the PEM fuel cell operating conditions.



Introduction

This project allows the creation of a Hydrogen Research Laboratory in a unique partnership between Purdue University's main campus in West Lafayette and the Calumet campus. This laboratory is engaged in basic research in hydrogen production and storage and has initiated engineering systems research with goals established as per the U.S. DOE Fuel Cell Technologies Program. Hydrogen production research of this project

is reported in Purdue Hydrogen Systems Laboratory: Hydrogen Production.

The hydrogen storage research has been focused on improving the engineering performance of AB-based onboard hydrogen storage and finding energy efficient ways to recycle the byproducts. To that end, a task is focused on finding energy efficient ways to recycle the ammonium borate to AB. The AB slurry dehydrogenation work was dedicated to measuring engineering properties of onboard hydrogen discharge and fresh/spent fuel transfer and developing a subscale reactor module to provide a platform for the studies of AB and other potential off-board recyclable hydrogen storage materials. With the advantage of transportability of byproduct obtained from neat thermolysis of AB, a scaled AB dehydrogenation batch reactor capable of handling at least one gram AB per batch was designed. The lessons learned in designing, testing, and analyzing the data obtained with the neat AB reactor system are guiding the modeling and future design of a slurry-based reactor. A third task was devoted to developing a new approach to release hydrogen by noncatalytic hydrothermolysis of AB in aqueous solutions and slurries. It is known that the release of hydrogen from AB via both thermolysis and hydrolysis is exothermic. In AB hydrothermolysis process, it was found that the heat generated by hydrolysis initiates thermolysis near PEMFC operating temperature (85°C) along with rapid heat evolution. On the other hand, for neat AB thermolysis, the sharp evolution was not observed at 85°C, indicating that water (hydrolysis) drives the sharp heat evolution resulting in high H₂ yield. Nevertheless, since the release of hydrogen from AB via thermolysis (release of first and second H₂ moles) is exothermic, it was expected that with effective heat management, the sharp heat evolution could be observed near PEMFC operating temperatures during neat AB thermolysis as well.

Approach

The spent fuel, ammonium borate will be converted to triacyl- or trialkyl borates, which will provide molecules with the weaker B-O bond. The reduction of triacyl- or trialkyl borates in the presence of TMEDA, followed by the displacement of TMEDA using ammonia will lead to efficient ammonia borane regeneration.

To facilitate the design of thermal management and spent fuel removal, we investigated neat and ionic-liquid aided AB dehydrogenation kinetics, especially at the initial fast hydrogen evolution stage. A neat AB batch reactor module was designed and assembled at the Hydrogen Systems Laboratory. Made of stainless steel, the cylindrical reactor is designed to handle reactions with starting temperatures of about 155±5°C and a nominal batch reaction time of 10 minutes. On-going tests with batches of up to two grams AB are providing

data and design guidance for the development of an AB-slurry based reactor.

We also developed a computational fluid dynamics (CFD) model to simulate the thermo-chemical process in an AB slurry reactor. In addition, we measured elastic stiffness and viscous damping of AB spent fuels from various reactions including hydrolysis, thermolysis and hydrothermolysis.

The AB hydrothermolysis method for H₂ generation was investigated over a wide range of AB concentration in water, pressure, and heating rate. The neat AB thermolysis was also studied near PEMFC operation temperatures. To better understand the reaction exothermicity (heat evolution), we developed a smaller size reactor (70 ml). Apart from the reactor temperature, the sample temperature (T_{sample}) was also measured by inserting a thermocouple inside the sample. In addition to mass spectrometry, ammonia was also measured by titration technique.

Results

AB was prepared in kilogram-scale from sodium borohydride and ammonium sulfate in the presence of ammoniated THF at room temperature in 92% yield and ≥98% purity. We have recycled ammonia borate to AB via conversion to trimethyl borate followed by the reduction using diethylsilane (Figure 1). We developed novel protocol for the reduction of trimethyl borate. The reduction of trimethylborate in the presence of TMEDA using diethylsilane resulted in the formation of the diamine bisborane complex in very high yield (90%). The solid bisborane complex could be readily separated by filtration. The preparation of AB from this diamine bisborane complex was achieved in 80% yield by exchange with ammonia. We have initiated energy efficient schemes to convert NH₄B(OH)₄ to AB via triacylborates. The advantage of conversion to such acylborate esters over simple alkylborate esters is that the B-O bond will be weakened enough to be reduced with mild hydride sources.

We measured the reaction kinetics of neat and 1-butyl-3-methylimidazolium chloride (bmimCl)-aided AB thermolysis under quasi-isothermal conditions in the

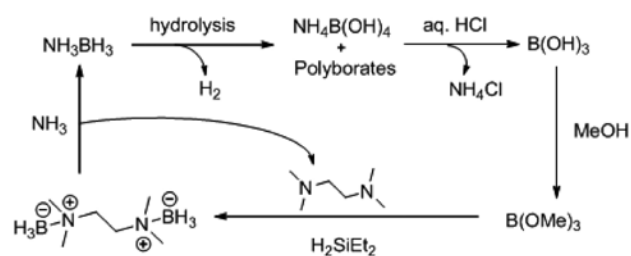


FIGURE 1. AB recycling.

temperature range from 85°C to 120°C. The measured hydrogen storage capacity of the 80/20 AB/bmimCl mixture was 11.2 wt% at 120°C and foaming during AB thermolysis was partially suppressed by the ionic liquid. Hydrogen yield reduction caused by impurity and aging of bmimCl should be further addressed. bmimCl aided thermolysis should be implemented at sufficiently high temperature (>107°C) to achieve a noticeable gain in the hydrogen storage capacity when comparing to the neat AB thermolysis.

We also quantitatively revealed the visco-elastic differences between the spent fuels obtained from the various AB dehydrogenation methods. It was demonstrated that spent fuels obtained from AB neat thermolysis and hydrothermolysis are the most transportable, followed by its hydrolysis and ionic liquid-aided thermolysis, respectively. The spent fuels obtained at higher temperatures exhibit improved transportability.

A reactor system for neat AB thermolysis of up to two gram batches of AB was designed. The system is characterized by modularity and highly repeatable batch operation. It consists of an AB feeder, a reactor and

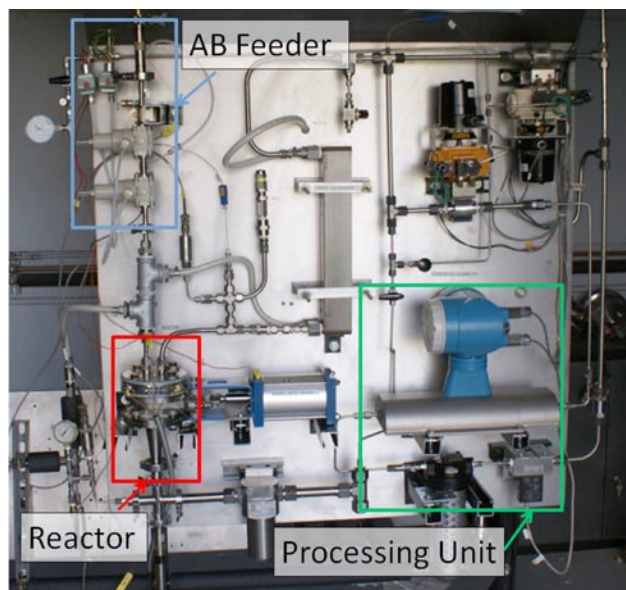


FIGURE 2. Neat AB thermolysis batch reactor.

a gas processing unit (Figure 2). Safety features such as remote operation and cooled AB reservoir make the operation very safe and reliable. Operation of the system was tested with AB batches weighing up to two grams. The average temperature for batch reactions was 160°C. Results of the batch tests are compared in Table 1 with those obtained with a bench top unit. In addition, we developed a CFD code to simulate an AB slurry reactor for on-board hydrogen storage. For 80/20 ammonia borane/ionic liquid slurry, a reactor was simulated at a H₂ release rate of 1.6 g/s with a reactor total weight of ~2.4 kg.

AB hydrothermolysis was investigated in a 70 ml stainless steel Parr reactor over a wide range of AB concentration, pressure, and heating rate. The maximum observed hydrogen storage capacity, obtained at 77 wt% AB concentration and T_{reactor} ~85°C, was 11.6 and 14.3 wt% at pressure 14.7 and 200 psia, respectively (Figure 3). For 200 psia and heating rate 1°C/min, AB converted to NH₃ (NH₃/AB) in the gaseous product decreased with increasing AB concentration. It is worth noting that even for neat AB thermolysis (in absence of water), 2-4% of AB was converted to NH₃, which must be removed for use in PEMFC. With increasing

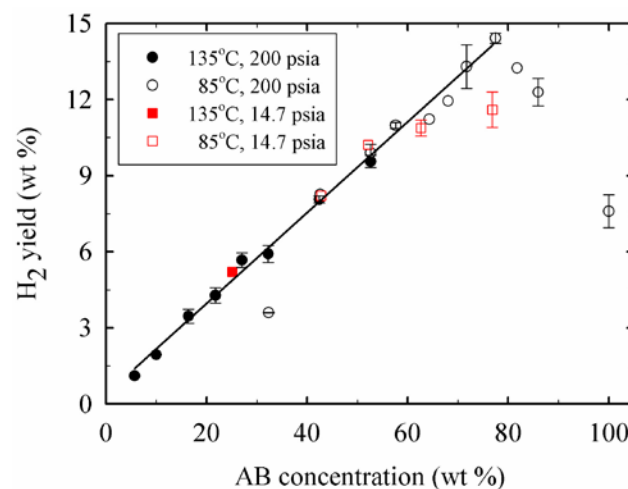


FIGURE 3. Hydrogen yield as a function of AB concentration, at different hydrothermolysis operating conditions.

TABLE 1. Results Obtained During Bench Tests and Batch Reactions

Type of reaction	Mass of AB (g)	Average Temperature (°C)	Yield of Hydrogen (mol of H ₂ per mol of AB)					
			Time (seconds)					
			10	30	50	155	510	1,800
Bench test	0.13	155	0.25	0.76	1.27	1.52	1.65	1.78
Batch #1	2.00	160	0.02	0.11	1.15	1.7	1.84	1.94
Batch #2	2.00	160	0.02	0.27	1.4	1.75	1.8	1.86

initial pressure (up to 200 psia) or heating rate (up to 1°C/min), both H₂ yield and NH₃/AB ratio increased. Further increases, however, did not influence either the H₂ yield or the NH₃/AB ratio. Using neat AB thermolysis, ~15 wt% H₂ yield (2.3 H₂ molar equiv.) was obtained at 14.7 psia and T_{reactor} 90°C with rapid kinetics under effective heat management. To our knowledge, this value is higher than by any other method using AB at near PEMFC operating temperatures.

Conclusions and Future Directions

We investigated the fundamental chemistry of AB recycling and achieved conversion of trimethyl borate to AB. The reduction of trimethyl borate using diethylsilane will be optimized with respect to temperature and pressure, silane and amines. The displacement of TMEDA from the corresponding bisborane adduct using ammonia will be further optimized for the quantitative isolation of ammonia borane. Computations of the recycling of energy efficiency will be done.

We achieved 11.2 wt% (material) hydrogen storage capacity from the 80/20 AB/bmimCl mixture thermolysis, which is within the uncertainty limits of the highest ever reported in the literature. We measured the hydrogen yield and characterized the operation of a neat AB batch reactor. We obtained similar yield rates and chemical kinetics results for bench tests and batch reactions. However, the challenges associated with AB byproduct removal and transient mass flow rate measurement of gas yield need to be further addressed. We will apply the lessons learned with the neat AB batch reactor, the results of CFD simulations and overall engineering performance analyses to the design of the AB slurry reactor.

It was demonstrated that noncatalytic AB hydrothermolysis is a promising method for hydrogen storage. This process was studied over a wide range of AB concentrations, pressure, and heating rate. It was found that hydrogen yield, ammonia generation and thermal characteristics were influenced by these operating conditions. The maximum hydrogen storage capacity, obtained at 77 wt% AB and T_{reactor} ~85°C along with rapid kinetics, was 11.6 and 14.3 wt% at pressure 14.7 and 200 psia, respectively. The kinetics of neat AB thermolysis under various operating conditions were also investigated. For neat AB thermolysis, ~15 wt% H₂ yield (2.3 H₂ molar equivalent) was obtained at 14.7 psia and T_{reactor} 90°C with rapid kinetics under effective heat management. To our knowledge, this value is higher than by any other method using AB at near PEMFC operating temperatures. In the future, we will investigate the hydrothermolysis of AB slurry using carrier liquids. In addition, a laboratory-scale fuel cell power generation system based on AB hydrothermolysis or neat thermolysis will be developed.

FY 2010 Publications/Presentations

Archival Papers

1. Brockman, A., Zheng, Y., Gore, J.P., 2010, "A study of catalytic hydrolysis of concentrated ammonia borane solutions," *International Journal of Hydrogen Energy*, 35: 7350-7356.
2. Basu, S., Diwan, M., Abiad, M.G., Zheng, Y., Campanella, O.H., Varma, A., 2010, "Transport characteristics of dehydrogenated ammonia borane and sodium borohydride spent fuels," *International Journal of Hydrogen Energy*, 35: 2063-2072.
3. Basu, S., Zheng, Y., Varma, A., Delgass, W.N., Gore, J.P., 2010, "Catalytic hydrolysis of ammonia borane: intrinsic parameter estimation and validation," *Journal of Power Sources*, 195: 1957-1963.
4. Basu, S., Zheng, Y., Gore, J.P., 2010, "An experimental Study of Neat and Ionic Liquid-Aided Ammonia Borane Thermolysis," *Journal of Power Sources*, 196:734-740.

Conference Papers and Presentations

1. Varma, A., "New Methods to Generate Hydrogen for Fuel Cell Applications," *Dept. of Chemical Engineering, University of Texas-Austin*, September 29, 2009, Austin, TX.
2. Varma, A., "New Methods to Generate Hydrogen for Fuel Cell Applications," *Keynote Talk at the US-China Chemical Engineering Conference*, October 15, 2009, Beijing, China.
3. Diwan, M., Hwang, H., Al-Kukhun, A. and Varma, A., "High Hydrogen Yield from Ammonia Borane Hydrothermolysis for Fuel Cell Based Vehicles," *AICHE Annual Meeting*, November 10, 2009, Nashville, TN.
4. Varma, A., "New Methods to Generate Hydrogen for Fuel Cell Applications," *Engineering Distinguished Lecture, University of Western Ontario*, March 29, 2010, London, Ontario, Canada.
5. Varma, A., "New Methods to Generate Hydrogen for Fuel Cell Applications," *Dept. of Chemical Engineering, Lamar University*, April 16, 2009, Beaumont, TX.
6. Al-Kukhun, A., Hwang, H. and Varma, A., "Hydrogen Generation from Noncatalytic Hydrothermolysis of Ammonia Borane for Vehicle Applications," *NHA Hydrogen Conference & Expo*, May 4, 2010, Long Beach, CA.
7. Hwang, H., Al-Kukhun, A. and Varma, A., "Hydrogen for Vehicle Applications from Hydrothermolysis of Ammonia Borane: Hydrogen Yield, Thermal Characteristics, and Ammonia Formation," *21st International Symposium on Chemical Reaction Engineering*, June 15, 2010, Philadelphia, PA.
8. Diwan, M., Hwang, H., Al-Kukhun, A. and Varma, A., "Hydrogen Generation from Noncatalytic Hydrothermolysis of Ammonia Borane for Vehicle Applications," *AICHE Journal* (in press, DOI 10.1002/aic.12240).

9. Hwang, H., Al-Kukhun, A. and Varma, A., “Hydrogen for Vehicle Applications from Hydrothermolysis of Ammonia Borane: Hydrogen Yield, Thermal Characteristics, and Ammonia Formation,” *IEC Research* (in review).