

## IV.G.1 Purdue Hydrogen Systems Laboratory: Hydrogen Storage\*

Jay Gore (Primary Contact), P. Ramachandran, A. Varma, T. Pourpoint, Y. Zheng, R. Kramer, D. Guildenbecher, R. Gejji, P. Gagare, K. Deshpande, S. Basu, T. Voskuilen, A. Al-Kukhun, D. Gao, H.T. Hwang, J. Mullings, E. Ting, L. Pelter

Purdue University  
500 Central Drive  
West Lafayette, IN 47907  
Phone: (765) 496-2829  
E-mail: gore@ecn.purdue.edu

### DOE Managers

HQ: Grace Ordaz  
Phone: (202) 586-8350  
E-mail: Grace.Ordaz@ee.doe.gov

GO: Katie Randolph  
Phone: (720) 356-1759  
E-mail: Katie.Randolph@go.doe.gov

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- National Renewable Energy Laboratory, Golden, CO
- University of Wyoming, Laramie, WY

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\*Congressionally directed project

### Fiscal Year (FY) 2011 Objectives

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

### Technical Barriers

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

- (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 <sub>2</sub> wt%	4.5/7.5	11~14 (material)
Overall efficiency of off-board regeneration	%	>60	In process being optimized

### FY 2011 Accomplishments

- AB thermolysis by-product, polyborazylene, was converted to ammonium borate [NH<sub>4</sub>B(OH)<sub>4</sub>], which was subsequently converted to trimethylborate.
- Reduced trimethylborate using diethylsilane with N<sup>1</sup>,N<sup>1</sup>,N<sup>2</sup>,N<sup>2</sup>-tetramethylethane-1,2-diamine (TMEDA) to TMEDA-bisborane complex.
- TMEDA-bisborane complex was converted to AB via transamination in 80% yield.
- Reduced ammonium borate to AB using lithium aluminum hydride with ammonium chloride.
- Analyzed gravimetric and volumetric capacities, H<sub>2</sub> release rates, and byproduct removal for liquid, solid and slurry AB-based systems.
- Addressed scientific and engineering issues with reactor capacities from 0.1 to 50 grams.
- Completed system engineering analysis of a baseline AB/ionic liquid slurry H<sub>2</sub> storage system.
- Obtained high H<sub>2</sub> yield (~14 wt%) and rapid kinetics for neat AB thermolysis under effective heat management at near proton exchange membrane fuel cell (PEMFC) operating temperatures (~90°C).
- Quantified ammonia formation in AB dehydrogenation processes and developed effective removal methods.



### 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 H<sub>2</sub> production and storage and has initiated engineering systems research with goals established as per the DOE Fuel Cell Technologies Program. Hydrogen production research of this project is reported in Purdue Hydrogen Systems Laboratory: Hydrogen Production.

A task of the H<sub>2</sub> storage work has been focused on finding energy efficient ways to recycle the AB thermolysis and hydrolysis by-products to AB. With the advantage of transportability of byproduct obtained from neat thermolysis

of AB and lessons learned with a gram scale neat AB reactor, we focused on the design, build and demonstration of a vehicle scale  $H_2$  storage system. We have demonstrated that, with effective reaction heat management, high  $H_2$  can be obtained from neat AB near PEMFC operating temperatures with rapid kinetics. We also established a physical property database for solvents and five solvents were selected as potential liquid carriers and mechanistic studies of AB dehydrogenation were conducted for each carrier. It has been reported that ammonia is generated during AB dehydrogenation. For use in PEMFCs, ammonia must be removed from the  $H_2$  stream to less than  $\sim 10$  ppm level. In our work, ammonia formation for AB dehydrogenation processes was quantified and effective methods for its removal were developed. Based on a neat AB thermolysis approach, we developed the concept of a continuous-flow system, and a prototype unit for laboratory evaluation was constructed. In this unit, the AB fuel feeding, reaction and spent fuel removal steps are integrated, and the reactor has provisions for utilization of waste heat from the PEMFC.

## Approach

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

We applied lessons learned on a multi-gram laboratory scale thermolysis batch reactor to design a cartridge based, self-sustained, and well-instrumented reactor system. The system was used to power a  $H_2$  internal combustion engine (HICE) on a club car. The design uses cartridges that are pre-filled with the storage chemical before being loaded onto the vehicle. The reagent cartridges can be recycled off-board. The reactor system has the flexibility to accommodate slurries and other chemical hydrides. We analyzed a full-scale (for a 80 kW fuel cell) system using AB (80 wt%) and BmimCl (20 wt%) as the  $H_2$  storage medium. The system consists of an AB slurry tank, a slurry pump, a slurry reactor, a  $H_2$  buffer tank, a recuperator, a gas/liquid separator, a burner, and a heat transfer fluid (HTF) pump. To size these components, we used an in-house one-dimension computational fluid dynamics model to simulate thermo-chemical processes in the reactor and thermo-fluid processes in other components. The simulation was conducted to achieve a steady-state  $H_2$  flow rate of 1.6 g/s. The  $H_2$  buffer tank was sized to meet dynamic (unsteady state) requirements.

The neat AB thermolysis method for  $H_2$  generation was investigated over a wide range of pressure, heating rate, AB density and insulation amount near PEMFC operating temperatures. For effective reaction heat management, some quartz wool was added at the top of the AB sample, which retains heat of exothermic thermolysis reaction while permitting product  $H_2$  to flow. Mechanistic studies

( $H_2$  yield, thermal characteristics,  $NH_3$  formation, etc.) of AB dehydrogenation for selected liquid carriers were conducted and further investigation was carried out to clarify the reaction mechanism using nuclear magnetic resonance, thermogravimetric analysis/differential scanning calorimetry, Fourier transform infrared and X-ray diffraction techniques. After cooling the reactor to room temperature at the end of the experiments,  $NH_3$  was measured by various methods including Drager tubing, mass spectrometry and titration technique. A continuous-flow  $H_2$  generation system was designed, constructed and tested.

## Results

We have achieved the conversion of polyborazylene, obtained via the thermolysis of AB, to ammonium tetramethoxyborate  $[NH_4B(OMe)_4]$  in the presence of methanol, followed by reduction to AB using lithium aluminum hydride and  $NH_4Cl$  in 81% yield. In an alternate protocol, ammonium tetramethoxyborate was converted to trimethyl borate in the presence of methanol. The reduction of trimethyl borate in the presence of TMEDA using diethylsilane resulted in the formation of bisamine borane complex in near quantitative yield (90%). The bisamine borane complex could be readily separated by filtration. The displacement of TMEDA from the amine borane complex was readily achieved using liquid ammonia to obtain 80% yield of AB (Figure 1). We have also reported the conversion of ammonium tetrahydroxyborate  $[NH_4B(OH)_4]$ , hydrolysis by-product of AB, to trimethyl borate without the conversion to boric acid. The reduction of trimethyl borate was achieved using either the silane protocol or via reduction to sodium borohydride with NaH and subsequent conversion to AB in the presence of ammonium sulfate (Figure 2). However, our attempted reduction of boron trifluoride and boron trifluoroacetate using a variety of silanes has not been successful.

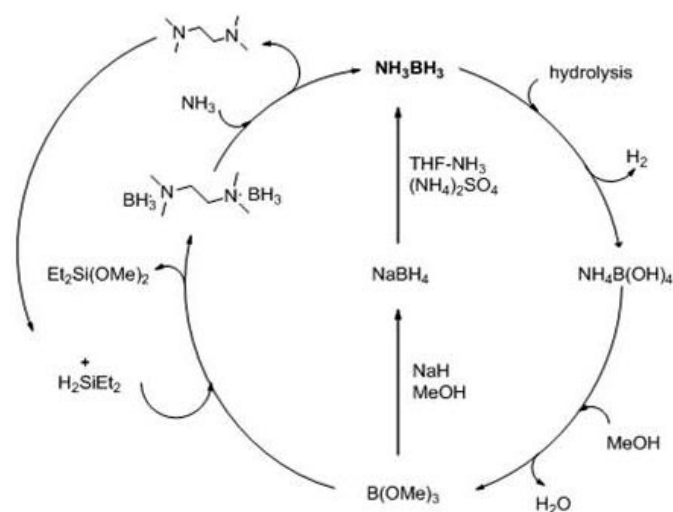


FIGURE 1. AB Hydrolysis Cycle: Recycling of Ammoniumborate

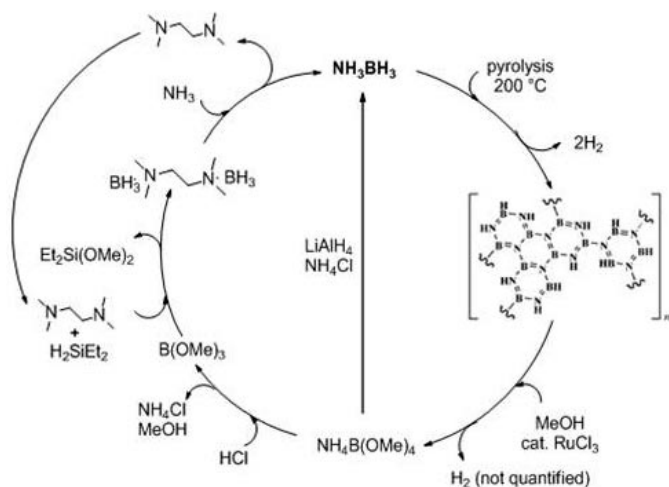


FIGURE 2. AB Thermolysis Cycle: Recycling of Polyborazylene

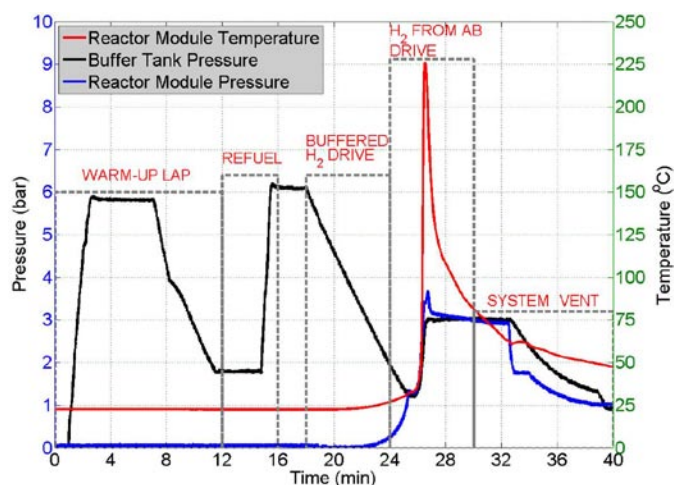


FIGURE 3. Pressure and Temperature Profile in the Club Car Vehicle Demonstration System during System Demonstration using Neat AB pellets

The vehicle-scale system consists of a HICE, four reactor modules, a modified engine exhaust, a buffer tank, and an onboard universal serial bus data acquisition system with a LabVIEW virtual interface for real time monitoring. The modified exhaust line of the HICE diverts using copper spiral tubing the exhaust to the reactor modules. Aluminum honeycomb in contact with the copper spiral further aids heat transfer to the reagent pellets. Figure 3 shows data from a typical experiment with ~50 g of AB pellets loaded in one module. The H<sub>2</sub> buffer tank is first filled to a pressure of ~6 bar from a commercial gas cylinder. Next the HICE is operated on the buffered H<sub>2</sub> and the exhaust is routed away from the reactor modules, allowing for system checks and warm-up. Once proper operation is confirmed, the buffer tank is refilled, and the engine is again operated with the exhaust routed to the first reactor module. The exhaust heat raises the AB temperature until dehydrogenation is achieved.

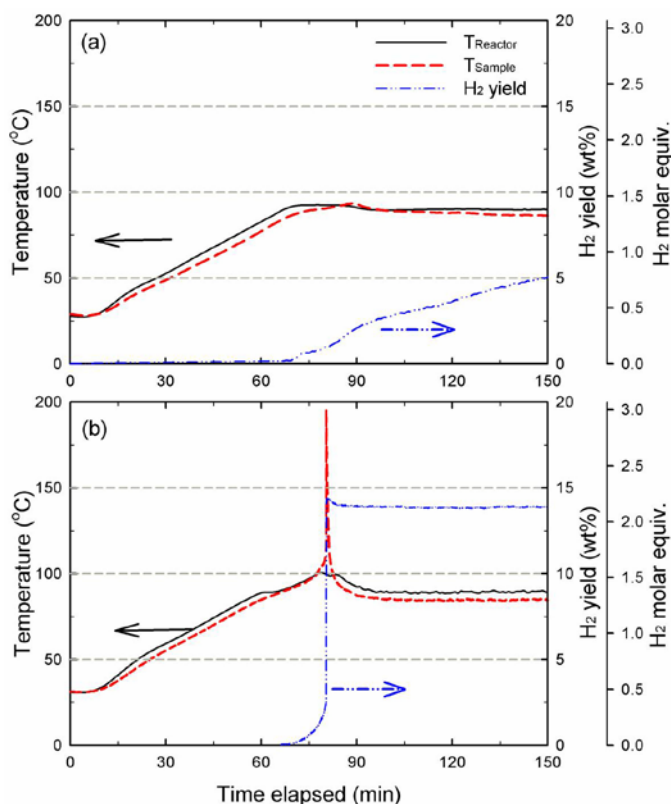


FIGURE 4. H<sub>2</sub> Yield, Temperature Profiles for Neat AB Thermolysis for  $T_{SP} = 90^{\circ}\text{C}$ ,  $P_i = 14.7$  psia and Heating Rate =  $1^{\circ}\text{C}/\text{min}$  (a) without Quartz Wool (b) with Quartz Wool

The reaction leads to a sharp increase in the reactor temperature and increased pressure in the reactor module. The generated H<sub>2</sub> refills the buffer tank and is used to power the HICE. As designed, this process can be repeated with multiple reactor modules, leading to a self-sustained operation. Based on our engineering analysis of a baseline full-scale AB slurry system, a system of 81.2 kg total weight is required to store 5.6 kg usable H<sub>2</sub> or the system gravimetric H<sub>2</sub> storage capacity is 6.9 wt%. Among the total weight, the weight of the AB slurry is 58.5%, the weight of the HTF pump (on-shelf) is 19.7%, the weight of the slurry pump (on-shelf) is 11.7%, and the weight of other components is 10.1%.

We evaluated neat AB thermolysis near PEMFC operating temperature ( $90^{\circ}\text{C}$ ). For neat AB thermolysis without quartz wool, H<sub>2</sub> gradually evolved with time and only 5 wt% H<sub>2</sub> yield was achieved in 90 min as shown in Figure 4a. On the other hand, under effective heat management, H<sub>2</sub> yield ~14 wt% was achieved and stabilized quickly after sharp heat evolution (Figure 4b). To our knowledge, this value is higher than by any other method using AB at near PEMFC operating temperatures. A key factor is that effective reaction heat management is required to obtain sharp heat evolution, which plays a critical role in providing high H<sub>2</sub> yield. In addition, NH<sub>3</sub> in gaseous product was trace (~1 ppm), much less than that observed in neat AB thermolysis (~400 ppm) without heat

management. The solid products of neat AB thermolysis under heat management were found to be polyborazylene-like species (after 2 H<sub>2</sub> release from AB). At 85°C, similar H<sub>2</sub> yield was obtained from AB in all glycol-type liquid carriers (ethylene glycol, propylene glycol, trimethylene glycol and 1-3-butanediol) and slightly less in dimethyl sulfoxide. However, it was found that all the selected liquid carriers react with AB during dehydrogenation reaction and produce boric acid, which is not preferable from the spent fuel regeneration viewpoint. We demonstrated that NH<sub>3</sub> can be effectively removed by absorption in water, followed by adsorption on impregnated carbon. Our optimization results show that the weight required for the NH<sub>3</sub> removal system can be significantly reduced if water is recycled from the PEMFC. Further, since borazine hydrolyzes readily in water, our proposed method removes ammonia and any volatile borazine present. Based on neat AB thermolysis approach, a continuous-flow H<sub>2</sub> generation system was constructed and tested. Using this system, ~13.5 wt% H<sub>2</sub> yield (~2.1 H<sub>2</sub> molar equivalent) was obtained along with rapid H<sub>2</sub> evolution at 120°C.

## Conclusions and Future Directions

We have developed an efficient protocol to prepare AB in large-scale from sodium borohydride and ammonium sulfate. We have developed four protocols to regenerate the spent material; (i) the AB hydrolysis by-product was converted to trimethyl borate and subsequently treated with diethylsilane in the presence of TMEDA to yield TMEDA-Bisborane complex which was converted to AB via transamination using ammonia (ii) the trimethyl borate was reduced to sodium borohydride which upon treatment with ammonium sulfate provided AB, (iii) the AB thermolysis by-product was converted to ammonium tetramethoxyborate and subsequently reduced to AB via silane protocol and (iv) AB was also regenerated from ammonium tetramethoxyborate in the presence of lithium aluminum hydride.

The vehicle-scale reactor system design addresses several engineering concerns with on-board chemical H<sub>2</sub> storage systems. It is compatible with a wide range of H<sub>2</sub> storage chemicals in pure or slurry form and can produce H<sub>2</sub> of sufficient purity for operation with a fuel cell. Future work includes design optimization with a COMSOL-based model, which incorporates reaction kinetics and heat and mass transfer and demonstration with a few other candidate chemicals for comparison. In on-going work we are (1) focusing on the experimental determination of the thermal properties of the ammonia borane pellets used in the vehicle-scale system, and (2) using the thermal property data together with the reaction kinetics data already obtained to improve the fidelity of the numerical model. The AB/BmimCl (80:20) slurry system can meet the 2015 system gravimetric H<sub>2</sub> storage capacity target (5.5 wt%) but can't meet the ultimate target (7.5 wt%). The present on-shelf pumps are too heavy and light HTF and slurry pumps

must be developed. In addition, effective spent fuel removal technologies must be developed in the near future.

Under effective reaction heat management, we obtained high H<sub>2</sub> yield (~14 wt%) from neat AB thermolysis at 14.7 psia and T<sub>sp</sub> 90°C with rapid kinetics, without the use of either catalyst or chemical additives. To our knowledge, this value is higher than by any other method using AB at near PEMFC operating temperatures. We optimized and demonstrated that a sequence of absorption in water and adsorption on impregnated carbon captures ammonia, by-product of AB dehydrogenation, effectively from the product gas stream. Based on neat AB thermolysis, we developed and evaluated a laboratory-scale continuous-flow H<sub>2</sub> generation system. Using this system, ~13.5 wt% H<sub>2</sub> yield was obtained along with rapid H<sub>2</sub> evolution at 120°C. The increase of required reaction temperature, from 90 to 120°C, to rapidly provide high H<sub>2</sub> yield occurs due to heat loss from the reaction zone, and methods to minimize this loss will be investigated in the future.

## FY 2011 Publications/Presentations

1. Deshpande, K.A., Voskuilen, T.G., Basu, S., Zheng, Y., Pourpoint, T.L., Gore, J.P., "Design, Construction and Test of a Subscale Ammonia Borane Reactor," *Proceedings of the ASME 2010 International Mechanical Engineering Congress & Exposition IMECE2010*, Nov. 2010, Vancouver, British Columbia, Canada.
2. Basu, S., Zheng, Y., Gore, J.P., "An experimental study of neat and ionic-liquid aided ammonia borane thermolysis," *Journal of Power Sources*, 196: 734-740, 2011.
3. Li, L., Zheng, Y., 2011, "An experimental study of spent fuel transport for onboard hydrogen storage," *Proceedings of the 2011 ASME International Mechanical Engineering Congress and Exposition*, in review.
4. Varma, A., "New Methods to Generate Hydrogen from Boron Compounds and Water for Fuel Cell Applications," *Invited Dept. of Chemical Engineering Seminar*, Columbia University, New York, NY, October 19, 2010.
5. Varma, A., "New Methods to Generate Hydrogen from Boron Compounds and Water for Fuel Cell Applications," *Induction Lecture*, National Academy of Engineering - Mexico, Mexico City, Mexico, November 5, 2010.
6. Hwang, H.T., Al-Kukhun, A., and Varma, A., "Hydrogen Generation From Thermolysis of Neat Ammonia Borane for On-Board Vehicle Applications," *AICHE Annual Meeting*, Salt Lake City, UT, November 8, 2010.
7. Al-Kukhun, A., Hwang, H.T., and Varma, A., "Ammonia Borane Dehydrogenation Always Generates Ammonia, How Much and How to Remove It?," *AICHE Annual Meeting*, Salt Lake City, UT, November 9, 2010.
8. Varma, A., "New Methods to Generate Hydrogen from Boron Compounds and Water for Fuel Cell Applications," *Invited Dept. of Chemical Engineering Seminar*, Georgia Institute of Technology, Atlanta, GA, December 1, 2010.

9. Varma, A., “New Methods to Generate Hydrogen from Boron Compounds and Water for Fuel Cell Applications,” *Invited Talk, Tactical Power Sources Summit*, Washington, DC, January 25, 2011.
10. Varma, A., “New Methods to Generate Hydrogen from Boron Compounds and Water for Fuel Cell Applications,” *Invited Dept. of Chemical and Biomolecular Engineering Seminar*, Vanderbilt University, Nashville, TN, February 22, 2011.
11. Hwang, H.T., Al-Kukhun, A., and Varma, A., “Hydrogen for Vehicle Applications from Hydrothermolysis of Ammonia Borane: Hydrogen Yield, Thermal Characteristics, and Ammonia Formation,” *Industrial & Engineering Chemistry Research*, Vol. 49, pp. 10994-11000, (2010).
12. Diwan, M., Hwang, H., Al-Kukhun, A. and Varma, A., “Hydrogen Generation from Noncatalytic Hydrothermolysis of Ammonia Borane for Vehicle Applications,” *AIChE Journal*, Vol. 57, pp. 259-264, (2011).
13. Al-Kukhun, A., Hwang, H.T., and Varma, A., “A Comparison of Ammonia Borane Dehydrogenation Methods for Proton-Exchange-Membrane Fuel Cell Vehicles: Hydrogen Yield and Ammonia Formation and Its Removal,” *Industrial & Engineering Chemistry Research* (in press, DOI: 10.1021/ie102157v).
14. Hwang, H.T., Al-Kukhun, A., and Varma, A., “High and Rapid Hydrogen Release from Thermolysis of Ammonia Borane near PEM Fuel Cell Operating Temperatures,” (submitted).