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

**Technical Targets**

<table>
<thead>
<tr>
<th>On-Board Storage</th>
<th>Units</th>
<th>2010/Ultimate</th>
<th>Purdue 2010</th>
</tr>
</thead>
<tbody>
<tr>
<td>System Gravimetric Capacity</td>
<td>H₂ wt%</td>
<td>4.5/7.5</td>
<td>11~14 (material)</td>
</tr>
<tr>
<td>Overall efficiency of off-board regeneration</td>
<td>%</td>
<td>&gt;60</td>
<td>In process being optimized</td>
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</tbody>
</table>

**FY 2011 Accomplishments**

- AB thermolysis by-product, polyborazylene, was converted to ammonium borate [NH₄B(OH)₄], which was subsequently converted to trimethylborate.
- Reduced trimethylborate using diethylsilane with N₁,N₁,N₂,N₂-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, H₂ 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 H₂ storage system.
- Obtained high H₂ 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 H₂ 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 H₂ 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 H₂ storage system. We have demonstrated that, with effective reaction heat management, high H₂ 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 H₂ stream to less than ~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 was conducted. 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 and BmimCl as the H₂ storage medium. The system consists of an AB slurry tank, a slurry pump, a slurry reactor, a H₂ 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 H₂ flow rate of 1.6 g/s. The H₂ buffer tank was sized to meet dynamic (unsteady state) requirements.

The neat AB thermolysis method for H₂ 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 H₂ to flow. Mechanistic studies (H₂ yield, thermal characteristics, NH₃ 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, NH₃ was measured by various methods including Drager tubing, mass spectrometry and titration technique. A continuous-flow H₂ generation system was designed, constructed and tested.

**Results**

We have achieved the conversion of polyborazylene, obtained via the thermolysis of AB, to ammonium tetramethoxyborate [NH₄B(OMe)₄] in the presence of methanol, followed by reduction to AB using lithium aluminum hydride and NH₄Cl 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 [NH₄B(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 tristriflate and boron tristrifluoroacetate using a variety of silanes has not been successful.

![Figure 1. AB Hydrolysis Cycle: Recycling of Ammoniumborate](image-url)
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 H₂ buffer tank is first filled to a pressure of ~6 bar from a commercial gas cylinder. Next the HICE is operated on the buffered H₂ 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.

The reaction leads to a sharp increase in the reactor temperature and increased pressure in the reactor module. The generated H₂ 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 H₂ or the system gravimetric H₂ 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°C). For neat AB thermolysis without quartz wool, H₂ gradually evolved with time and only 5 wt% H₂ yield was achieved in 90 min as shown in Figure 4a. On the other hand, under effective heat management, H₂ 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 H₂ yield. In addition, NH₃ 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 H₂ release from AB). At 85°C, similar H₂ 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 NH₃ can be effectively removed by absorption in water, followed by adsorption on impregnated carbon. Our optimization results show that the weight required for the NH₃ 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 H₂ generation system was constructed and tested. Using this system, ~13.5 wt% H₂ yield (~21 H₂ molar equivalent) was obtained along with rapid H₂ 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 diethyilsilane 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 form ammonium tetramethoxyborate in the presence of lithium aluminum hydride.

The vehicle-scale reactor system design addresses several engineering concerns with on-board chemical H₂ storage systems. It is compatible with a wide range of H₂ storage chemicals in pure or slurry form and can produce H₂ 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 target (7.5 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 H₂ yield (~14 wt%) from neat AB thermolysis at 14.7 psia and Tₚ, 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 H₂ generation system. Using this system, ~13.5 wt% H₂ yield was obtained along with rapid H₂ evolution at 120°C. The increase of required reaction temperature, from 90 to 120°C, to rapidly provide high H₂ 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


