Purdue Hydrogen Systems Laboratory
Part II: Hydrogen Storage (ST084)

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Overview

Timeline
Start–September 2006
End–September 2011
90% complete

Barriers
Barriers addressed
• A. System weight and volume
• J. Thermal management
• R. Regeneration processes
• S. By-product/spent material removal

Accomplishments

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<tr>
<th>Reaction Technique &amp; Conditions</th>
<th>Material wt.%</th>
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<td>Hydrothermolysis, 77 wt.% AB in H₂O @ 85°C, 200 psia</td>
<td>14.3</td>
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<tr>
<td>Thermolysis under heat management 100 wt.% AB, 90°C, 1 atm</td>
<td>14</td>
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<td>Thermolysis, 100 wt.% AB @ 155°C, &lt;50 psia</td>
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<td>Thermolysis, 80 wt.% AB in BmimCl @ 120°C, 14.7 psia</td>
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<td>Catalyzed Hydrolysis, 1 wt.% AB in H₂O @ 25°C, 14.7 psia</td>
<td>8.9</td>
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Partners
• General Motors (lab infrastructure)
• General Atomics (AB synthesis)

Budget
• $3,659,403*
  – $2,875,500 (DOE)
  – $50,000 (to Wyoming)
  – $733,903 (Purdue)
• Funding received in FY09
  $951,500

* This is the overall budget for both hydrogen production and storage research. This presentation only covers the storage part.
Project Objectives - Relevance

Ammonia Borane (AB) Recycling

- Develop an energy efficient recycling protocol for AB from ammonium borate.
- Investigate the conversion of ammonium borate to B(OMe)$_3$, B(OCOR)$_3$ and B(OSO$_2$R)$_3$ (R = CH$_3$, CF$_3$, Ph etc.).
- Investigate reduction of reaction products to AB using Bu$_3$SnH or silanes.

Dehydrogenation of AB Slurry

- Analyze engineering performance of a baseline AB slurry based system.
- Analyze gravimetric and volumetric capacities, hydrogen release rates, and byproduct removal.
- Determine operational requirements for liquid, solid and slurry AB based systems.
- Demonstrate subscale reactor modules to address engineering issues.

Noncatalytic AB Hydrothermolysis

- Advance non-catalytic hydrothermolysis of AB in aqueous slurries and in liquid carriers.
- Investigate neat AB thermolysis.
- Quantify NH$_3$ formation and investigate methods for its removal.
- Demonstrate a continuous-flow hydrogen generation system.
Approach

Noncatalytic AB Hydrothermolysis
- Conduct non-catalytic hydrothermolysis of AB in aqueous solutions and slurries to investigate the effect on H₂ yield, NH₃ generation, thermal characteristics and products.
- Assess neat AB thermolysis at PEM FC operating temperature.
- Quantify NH₃ formation and investigate methods for its removal.
- Select and test suitable liquid carriers for AB dehydrogenation.
- Demonstrate a continuous-flow hydrogen generation.

Dehydrogenation of AB Slurry
- Simulate coupled heat/mass transfer and chemical reaction processes for AB systems.
- Demonstrate a neat AB batch reactor module (batch size ~2 grams).
- Apply lessons learned to demonstrate a scaled reactor module on a mobile platform.

AB Recycling
- Convert spent fuel, ammonium borate, to boron tris(triflate) or boron tris(trifluoroacetate) to provide molecules with weaker B-O bond.
- Reduce boron tris(triflate) or boron tris(trifluoroacetate) in the presence of a trialkyl amine, followed by the displacement of the amine using ammonia for efficient AB regeneration.
## Milestones

<table>
<thead>
<tr>
<th>Month/Year</th>
<th>Milestone or Go/No-Go Decision</th>
<th>Current Status [% complete]</th>
</tr>
</thead>
</table>
| Jul-11     | Milestone: Develop the optimal conditions to convert the spent borate to acylborates.  
Milestone: Reduction of acylborates using silanes in the presence of trialkyl amine. | 90 |
| Dec-10     | Milestone: Completed two-gram scale neat AB thermolysis reactor tests. | 100 |
| Mar-11     | Milestone: Complete system engineering analysis. | 100 |
| Sept-11    | Milestone: Complete vehicle demonstration with neat AB thermolysis reactor modules. | 80 |
| Dec-10     | Milestone: Investigate hydrothermolysis of AB slurries using carrier liquids. | 100 |
| Dec-10     | Milestone: Investigate and assess neat AB thermolysis. | 100 |
| Mar-11     | Milestone: Develop, construct and test a proposed continuous-flow H₂ generation system based on AB dehydrogenation. | 100 |
Previous Purdue Technical Accomplishments

Noncatalytic AB Hydrothermolysis
• **Obtained Record High H₂ yield** (~ 14 wt.%) near PEM FC operating temperatures (~90°C) along with rapid kinetics.
• Quantified ammonia formation and developed effective methods for its removal.

Dehydrogenation of AB Slurry
• Completed a full scale AB slurry reactor simulation using measured AB/BmimCl slurry thermolysis kinetics data.
• Achieved 92% (8.2 wt.%) hydrogen yield in a (1:2) AB/water slurry hydrolysis.
• Improved “flowability” of AB and SBH hydrolysis spent products by using first time quantitative measurements of rheological properties.
• Expanded the temperature range (373 to 430 K from the previous 373 to 393 K) of reaction kinetic measurements for neat AB thermolysis.

AB Recycling
• Reduction of trimethyl borate using diethyilsilane in the presence of TMEDA to obtain TMEDA-bisborane complex.
• Regeneration of AB from TMEDA-bisborane complex via transamination.
### Material Challenges Addressed

- **Synthesis**
- **H₂ Yield & Purity**
- **Foam**
- **Regeneration**

### System Challenges Faced

- **Weight & Volume**
- **Thermal Management**
- **Spent Material Management**

### Hydrothermalysis
- **77 wt.% AB in H₂O**
  - **@ 85°C, 13.6 atm**
  - **Material wt.%** 14.3

### Thermolysis
- **100 wt.% AB**
  - **@ 155°C, < 4 atm**
  - **Material wt.%** 12

### Catalyzed Hydrolysis
- **1 wt.% AB in H₂O**
  - **@ 25°C, 1 atm**
  - **Material wt.%** 8.9

### Room temperature
- **Improved yield @ temperature**

### Thermolysis under heat management
- **100 wt.% AB, 90°C, 1 atm**
  - **Material wt.%** 14

### Thermolysis
- **80 wt.% AB in BmimCl**
  - **@ 120°C, 1 atm**
  - **Material wt.%** 11.2

### Degradation of ionic liquid
- **Need for catalyst**

### Byproduct recycling
- **Spent fuel regeneration to be investigated**

### Highest reported yield
- **Hydrothermalysis**
  - **77 wt.% AB in H₂O**
  - **@ 85°C, 13.6 atm**

### High yield, near PEM FC operating temperature
- **Material wt.%**
  - 14.3
Technical Accomplishments and Progress (cont’d)

Large scale preparation of AB: Optimization of reaction condition

**Large-scale synthesis of AB in ammoniated-THF** (Collaborator: General Atomics)

\[
2 \text{NaBH}_4 + (\text{NH}_4)_2\text{SO}_4 \xrightarrow{5\% \text{NH}_3 \text{THF}} 2 \text{NH}_3\text{BH}_3 + \text{Na}_2\text{SO}_4 + 2 \text{H}_2
\]

- AB is hydrolyzed in the presence of \(\text{RuCl}_3\) to form ammonium tetrahydroxyborate

\[
\text{NH}_3\text{BH}_3 + 4\text{H}_2\text{O} \xrightarrow{\text{RuCl}_3 \text{(cat)} \text{rt}} \text{NH}_4\text{B(OH)}_4 + 3\text{H}_2
\]

- AB hydrolysis by-product converted to trimethylborate via methanolysis in high yield

\[
\text{NH}_4\text{B(OH)}_4 + 3\text{MeOH} \xrightarrow{\text{reflux} \text{12 h}} \text{B(OMe)}_3 + 4\text{H}_2\text{O} + \text{NH}_3
\]

- Reduction of \(\text{B(OMe)}_3\) to an amine borane, \((\text{BH}_3)_2\)-TMEDA using diethylsilane

\[
\text{B(OMe)}_3 \xrightarrow{\text{TMEDA} \text{H}_2\text{SiEt}_2 \text{H}_2 200 \text{Psi, } 145 \text{ °C} \text{24 h}} (\text{BH}_3)_2\text{-TMEDA} + \text{Et}_2\text{Si(OMe)}_2
\]

- AB regenerated via transamination of \((\text{BH}_3)_2\)-TMEDA using ammonia

\[
\text{BH}_3\text{-NH}_{3} \xrightarrow{\text{NH}_3 \text{80%}} \text{NH}_3\text{BH}_3 + \text{NH}_2\text{N}
\]

Results:
- AB was prepared in 92% yield and ≥ 98% purity
- Performed reaction on 10 mole scale
- Processes scalable to kilogram scale of AB
AB hydrolysis cycle: Recycling of ammoniumborate

• AB regenerated in overall 57% yield
Technical Accomplishments and Progress (cont’d)

**AB thermolysis cycle: Recycling of polyborazylene**

• Thermolysis of AB at 200 °C liberated 2.1 equiv of hydrogen and a white residue of polyborazylene (PB)

\[
\text{NH}_3\text{BH}_3 \xrightarrow{200 \degree C} \left[ \begin{array}{c}
\text{H} \\
\text{N} \\
\text{B} \\
\vdots \\
\text{H}
\end{array} \right]_n + \text{H}_2
\]

- Polyborazylene was converted to the trimethylborate by digesting with methanol

\[
\text{MeOH} \text{cat RuCl}_3 \xrightarrow{\text{MeOH}} \text{NH}_4\text{B}(_2\text{OMe})_4 + \text{H}_2
\]

• The reduction of B(OMe)_3 to an amine borane, (BH_3)_2-TMEDA using diethylsilane was achieved.

\[
\text{B(OMe)}_3 + \text{H}_2\text{SiEt}_2 \xrightarrow{\text{H}_2 200 \text{Psi, 145 °C, 24 h}} (\text{BH}_3)_2\text{-TMEDA} + \text{Et}_2\text{Si(OMe)}_2
\]

- AB regenerated via transamination of (BH_3)_2-TMEDA using ammonia

\[
(\text{BH}_3)_2\text{-TMEDA} + \text{NH}_3 \xrightarrow{\text{NH}_3} \text{NH}_3\text{BH}_3 + \text{N} = \text{N}
\]
AB thermolysis cycle: Recycling of polyborazylene

- The conversion of polyborazylene to AB needs optimization
Technical Accomplishments and Progress (cont’d)
Neat AB Thermolysis Reactor Engineering

- **Demonstration of AB thermolysis reactors at multiple scales:**
  i. Glass milligram scale reactor (130 mg)
  ii. Steel multi-gram reactor (2 g per batch)
  iii. Vehicle demonstration (~200 g per reactor module)

- **Challenges addressed:**
  a. Heat management
  b. Foaming of AB
  c. Hydrogen purity (Ammonia sequestration)
  d. Spent product management

- **Flexibility**
  Reactors designed to accommodate AB slurries, AB hydrolysis and other chemical hydrides.

[AB Reactor Scale-up Timeline]
Demonstrated an intermediate scale electric heated steel reactor system for experimental evaluation of neat AB thermolysis for automobile applications.

Ongoing work is focused on modeling heat transfer processes and chemical kinetics of neat AB thermolysis reactions.
Technical Accomplishments and Progress (cont’d)

Experimental Results

- Determined hydrogen yield in intermediate scale reactor with high accuracy volume calibration of pressure and temperature measurements.

- Obtained 90% of hydrogen within initial 120 seconds at 373, 393 and 430 K – temperatures selected to bracket AB melting point (383 K) and study release of second mol of hydrogen (430 K).

- Quantified ammonia generated during neat AB thermolysis to be 4% by mass in the gas stream.

- Observed endothermic melting followed by exothermic decomposition of AB characterized by 30 K of temperature rise.
Technical Accomplishments and Progress

Vehicle Demonstration

Vehicle Platform
- Club Car Carryall 2; 351 cc Kawasaki single cylinder four cycle HICE (Hydrogen I.C. Engine).

Goals:
- Fixed bed cartridge based reactor. Cartridges can be replaced at re-fuelling stations for spent AB processing.
- Self sustained reactor operation utilizing waste heat from the HICE exhaust.

Reactor Details:
1. Cartridge based fixed bed reactor
   Four reactor modules, each 6" diameter x 5" height, is pre-loaded with ~200 g of AB
2. Reactor modules heated sequentially to 150°C to provide continuous hydrogen supply to the buffer tanks.
3. Integration of reactor with HICE:
Technical Accomplishments and Progress (cont’d)
Engineering analysis of an AB/BmimCl (80/20) slurry system

System weight: 81.2 kg with 5.6 kg usable H₂ or 6.9 system wt%
Noncatalytic AB hydrothermolysis

Thermolysis

\[ \text{NH}_3\text{BH}_3 \rightarrow \frac{1}{x} (\text{NH}_2\text{BH}_2)_x + \text{H}_2; \]  
\[ (90-117 \, ^\circ\text{C}) \]

\[ \frac{1}{x} (\text{NH}_2\text{BH}_2)_x \rightarrow \frac{1}{x} (\text{NHBH})_x + \text{H}_2; (150-170 \, ^\circ\text{C}) \]

Hydrolysis

\[ \text{NH}_3\text{BH}_3 + 3\text{H}_2\text{O} \xrightarrow{\text{catalyst}} \text{NH}_3 + \text{B(OH)}_3 + 3\text{H}_2 \]

- Maximum H\text{H}_2 \text{ yield} obtained with rapid kinetics at 77 wt.% AB and 85°C, was 11.6 and 14.3 wt.% at pressure 14.7 and 200 psia, respectively.
- NH\text{H}_3 concentration in gaseous product varies between 16% –2% from 50-100 wt.% AB.
- Some ammonia is observed even for neat AB thermolysis.
**Ammonia Removal**

NH₃ can be removed (<0.1 ppm in H₂) by **absorption** in water, followed by **adsorption** (carbon).

NH₃ removal system weight decreases **significantly** with water recycle from PEM FC.

In addition to removing NH₃, this method also removes any borazine in the H₂ stream.

\[ \text{N}_3\text{B}_3\text{H}_6 + 9\text{H}_2\text{O} \rightarrow 3\text{NH}_3 + 3\text{B(OH)}_3 + 3\text{H}_2 \]
Neat AB Thermolysis

Neat AB at $T_{SP} = 90^\circ C$, $P_i = 14.7$ psia, heating rate = 1$^\circ C$/min, with heat management

- Under **effective heat management**, high $H_2$ yield (~ 14 wt %) was obtained near PEM FC operating temperatures (~ 90$^\circ C$) along with **rapid kinetics**.
- This value is **higher** than by any other method reported in the literature, using AB near PEM FC operating temperatures.
- NH$_3$ formation is **significantly** decreased.
- Main solid products of neat AB thermolysis under heat management are polyborazylene/polyiminoborane (after **2 $H_2$ release from AB**).
Technical Accomplishments and Progress (cont’d)

**Liquid Carriers**

- At 85°C, similar H₂ yield was obtained from AB in all glycols and slightly less in DMSO.
- The spent product for 60 wt.% AB in glycols was polymeric hard solid while in DMSO was powder, similar to that obtained for hydrothermolysis.

![Graph showing H₂ yield for various liquid carriers](image)

**Development of a continuous-flow hydrogen generation system**

- A reactor for AB dehydrogenation is currently under construction, where the H₂ release process consists of the following steps. First, AB fuel is loaded to the reactor, followed by H₂ generation using waste heat from PEM FC. The spent fuel is then removed from the reactor and the process repeats.
Collaborations

Purdue University

• Rheology measurements of AB slurry and its hydrolysis byproduct with Prof. O.H. Campanella, Department of Agricultural and Biological Engineering, Purdue University.
• Kinetics modeling of AB hydrolysis with Prof. W.N. Delgass School of Chemical Engineering, Purdue University.
• Development and use of Club Car Vehicle with Prof. J. M. Woodall School of Electrical and Computer Engineering, Purdue University.

Outside Purdue University

• Hydrogen Systems Laboratory facility development Chemical and Environmental Science Laboratory General Motors Research & Development Center.
• Ammonia borane synthesis General Atomics.
Future Work

Dehydrogenation of AB Slurry
- Understand the spent fuel removal process to achieve effective spent fuel removal.
- Optimize sizing and operation of vehicle demonstration reactor module(s).
- Make vehicle demonstration reactor module(s) for new and enhanced chemical hydrides and other hydrogen storage platforms.

Investigation of Noncatalytic AB Hydrothermolysis
- Test the continuous-flow hydrogen generation system based on AB dehydrogenation.

AB Recycling
- Calculation of the bond energies for the proposed AB recycling.
- The reduction of tris-acylborates using silanes is being optimized to avoid over reaction and charring.
- Isolation of ammonium borate from polyborazylene will be studied to improve the yield and the reaction to optimize the isolated yield of NH$_4$B(OH)$_4$ from B(OMe)$_3$ will be standardized.
Project Summary

AB Recycling
• 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.
• Trimethylborate was reduced using diethylsilane in the presence of TMEDA to TMEDA-Bisborane complex which was converted to AB via transamination in 80% yield.
• AB is regenerated form AB hydrolysis and thermolysis by-product

Dehydrogenation of AB Slurry
• Engineering analysis of a baseline AB/BmimCl (80/20) slurry system has been completed. To achieve the ultimate gravimetric hydrogen storage system capacity (7.5 wt.%), light heat transfer fluid (HTF) pump must be developed.
• Designed two new AB thermolysis reactors at the Hydrogen Systems Laboratory:
  • First reactor: designed for 2-gram AB batches to confirm and complement reaction kinetics data and to guide engineering of a demonstration system that addresses heat management challenges
  • Second reactor: developed for vehicle scale demonstration with HICE.

Investigation of Noncatalytic AB Hydrothermolysis
• Maximum H₂ yield 14.3 wt.% was obtained with rapid kinetics at 77 wt.% AB and 85°C for AB hydrothermolysis.
• NH₃ formation was observed for AB hydrothermolysis as well as neat AB thermolysis.
• NH₃ can be removed by absorption in water, followed by adsorption (carbon).
• High H₂ yield (~ 14 wt.%) was obtained near PEM FC operating temperatures (~90°C) along with rapid kinetics for neat AB thermolysis.