Purdue Hydrogen Systems Laboratory

Part II: Hydrogen Storage (ST084)

P. Gagare, K. Deshpande, R. Gejji, S. Basu, T. Voskuilen, A. Al-Kukhun, D. Gao
H. T. Hwang, D. Guildenbeger, T. Pourpoint
P. V. Ramachandran, A. Varma, J. Gore

Purdue University, West Lafayette, IN

J. Mullings, Y. Zheng

University of Wyoming, Laramie, WY

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DOE Hydrogen Program

Overview

Timeline

Start–September 2006
End–September 2011
90% complete

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.

Barriers

Barriers addressed

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

Accomplishments

Reaction Technique & Conditions	Material wt.%
Hydrothermolysis, 77 wt.% AB in H_2O @ 85°C, 200 psia	14.3
Thermolysis under heat management 100 wt.% AB, 90°C, 1 atm	14
Thermolysis, 100 wt.% AB @ 155°C, <50 psia	12
Thermolysis, 80 wt.% AB in BmimCl @ 120°C, 14.7 psia	11.2
Catalyzed Hydrolysis, 1 wt.% AB in H_2O @ 25°C, 14.7 psia	8.9

Partners

- General Motors (lab infrastructure)
- General Atomics (AB synthesis)

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 $B(OSO_2R)_3$ (R = CH_3, CF_3, Ph etc.).
- Investigate reduction of reaction products to AB using Bu_3SnH 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.

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Approach

Noncatalytic AB Hydrothermolysis

- Conduct non-catalytic hydrothermolysis of AB in aqueous solutions and slurries to investigate the effect on H_2 yield, NH_3 generation, thermal characteristics and products.
- Assess neat AB thermolysis at PEM FC operating temperature.
- Quantify NH_3 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

Month/Year	Milestone or Go/No-Go Decision	Current Status [% complete]
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 90
Dec-10 Mar-11 Sept-11	Milestone: Completed two-gram scale neat AB thermolysis reactor tests. Milestone: Complete system engineering analysis. Milestone: Complete vehicle demonstration with neat AB thermolysis reactor modules.	100 100 80
Dec-10 Dec-10 Mar-11	Milestone: Investigate hydrothermolysis of AB slurries using carrier liquids. Milestone: Investigate and assess neat AB thermolysis. Milestone: Develop, construct and test a proposed continuous-flow H_2 generation system based on AB dehydrogenation.	100 100 100

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Previous Purdue Technical Accomplishments

Noncatalytic AB Hydrothermolysis

- **Obtained Record High H_2 yield** (~ 14 wt.%) near PEM FC operating temperatures (~90^{o}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 diethylsilane in the presence of TMEDA to obtain TMEDA-bisborane complex.
- Regeneration of AB from TMEDA-bisborane complex via transamination.

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Purdue Accomplishments Summary

Material Challenges Addressed

- Synthesis
- H_2 Yield & Purity
- Foam
- Regeneration

Process	Material wt.%
Catalyzed Hydrolysis 1 wt.% AB in H_2O @ 25°C, 1 atm	8.9
Thermolysis 80 wt.% AB in BmimCl @ 120°C, 1 atm	11.2
Thermolysis 100 wt.% AB @ 155°C, < 4 atm	12
Thermolysis under heat management 100 wt.% AB, 90°C, 1 atm	14
Hydrothermolysis 77 wt.% AB in H_2O @ 85°C, 13.6 atm	14.3

Process	+	-
Catalyzed Hydrolysis	Room temperature	Need for catalyst
Thermolysis (80 wt.% AB in BmimCl)	Improved yield @ temperature	Degradation of ionic liquid
Thermolysis (100 wt.% AB)	High weight & volume capacity	High temperatures
Thermolysis under heat management	High yield, near PEM FC operating temperature	Spent fuel regeneration to be investigated
Hydrothermolysis	Highest reported yield	Byproduct recycling

System Challenges Faced

- Weight & Volume
- Thermal Management
- Spent Material Management

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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)

$$2\ NaBH_4 + (NH_4)_2SO_4 \xrightarrow[\text{THF, 0-10°C, 3 h; RT, 8 h}]{5\%\ NH_3} 2\ NH_3BH_3 + Na_2SO_4 + 2\ H_2 \quad (92\%)$$

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 ammonium borate

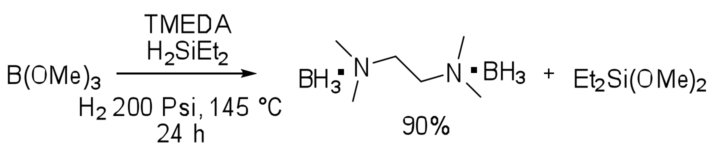
- AB is hydrolyzed in the presence of $RuCl_3$ to form ammonium tetrahydroxyborate

$$NH_3BH_3 + 4H_2O \xrightarrow[\text{rt}]{RuCl_3\ (cat)} NH_4B(OH)_4 + 3H_2$$

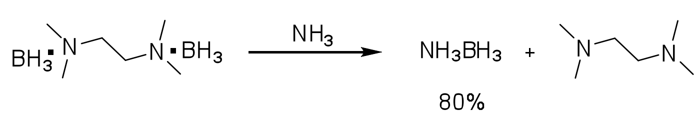
- AB hydrolysis by-product converted to trimethylborate via methanolysis in **high yield**

$$NH_4B(OH)_4 + 3MeOH \xrightarrow[\text{12 h}]{\text{reflux}} B(OMe)_4 + 4H_2O + NH_3 \quad (84\%)$$

- Reduction of $B(OMe)_3$ to an amine borane, $(BH_3)_2$-TMEDA using diethylsilane

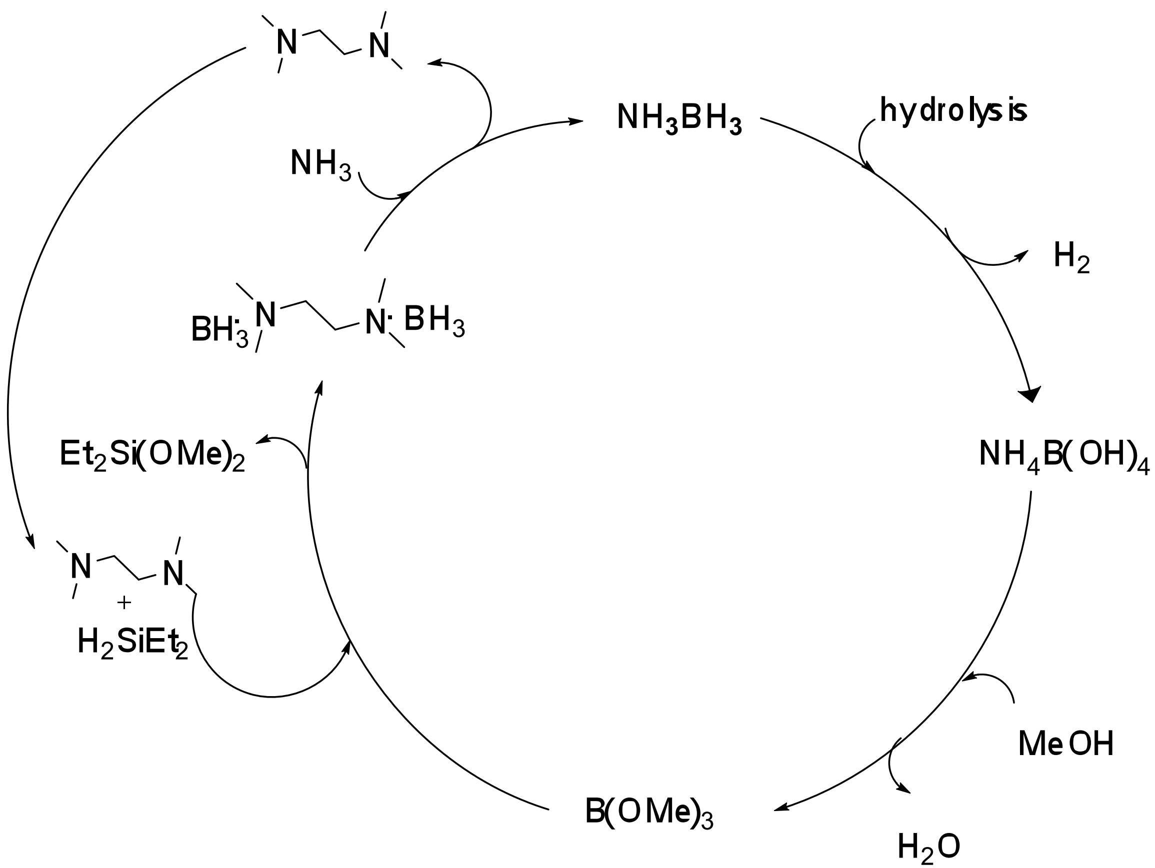


- AB regenerated via transamination of $(BH_3)_2$-TMEDA using ammonia



Technical Accomplishments and Progress (cont'd)

AB hydrolysis cycle: Recycling of ammoniumborate



- **AB regenerated in overall 57% yield**

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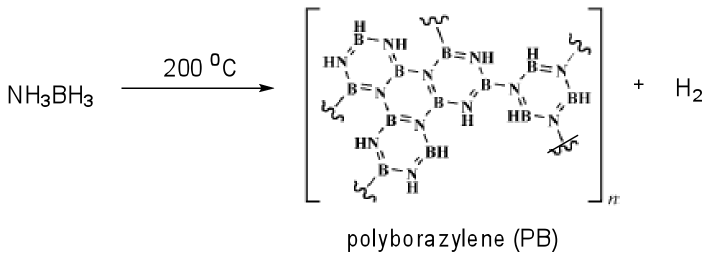
Technical Accomplishments and Progress (cont'd)

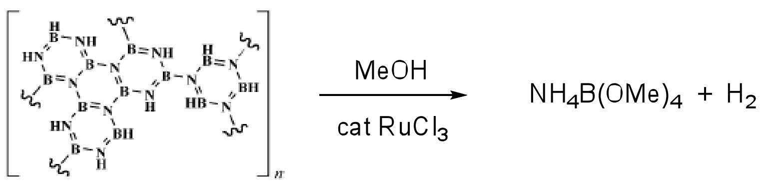
AB thermolysis cycle: Recycling of polyborazylene

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

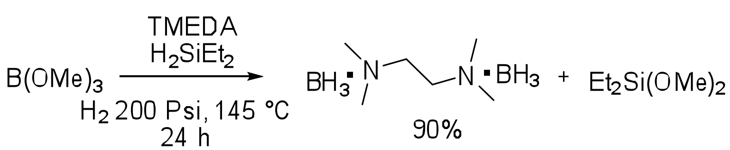


- **Recycling of polyborazylene via a common intermediate $B(OMe)_3$**

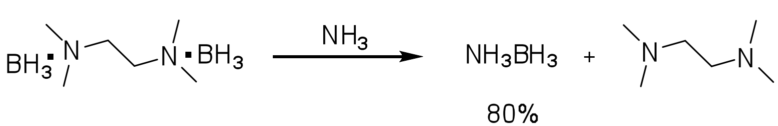
- Polyborazylene was converted to the trimethylborate by digesting with methanol



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

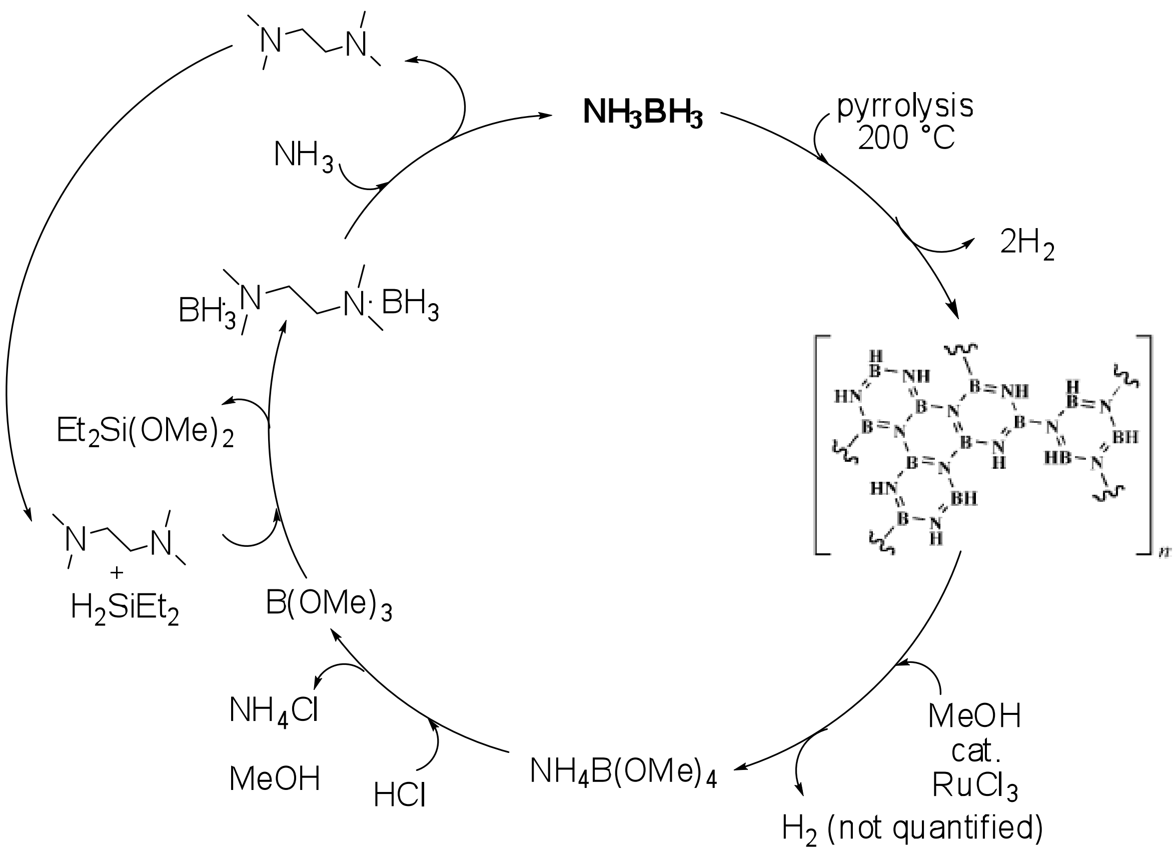


- AB regenerated via transamination of $(BH_3)_2$-TMEDA using ammonia



Technical Accomplishments and Progress (cont'd)

AB thermolysis cycle: Recycling of polyborazylene



- **The conversion of polyborazylene to AB needs optimization**

Technical Accomplishments and Progress (cont'd)

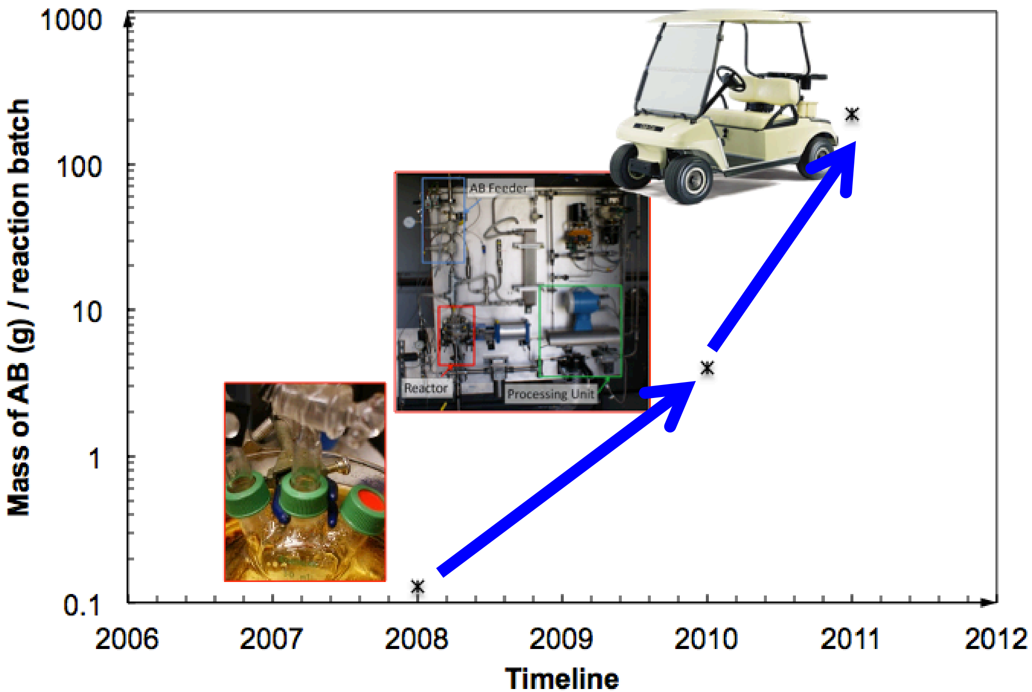
Neat AB Thermolysis Reactor Engineering

- **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**

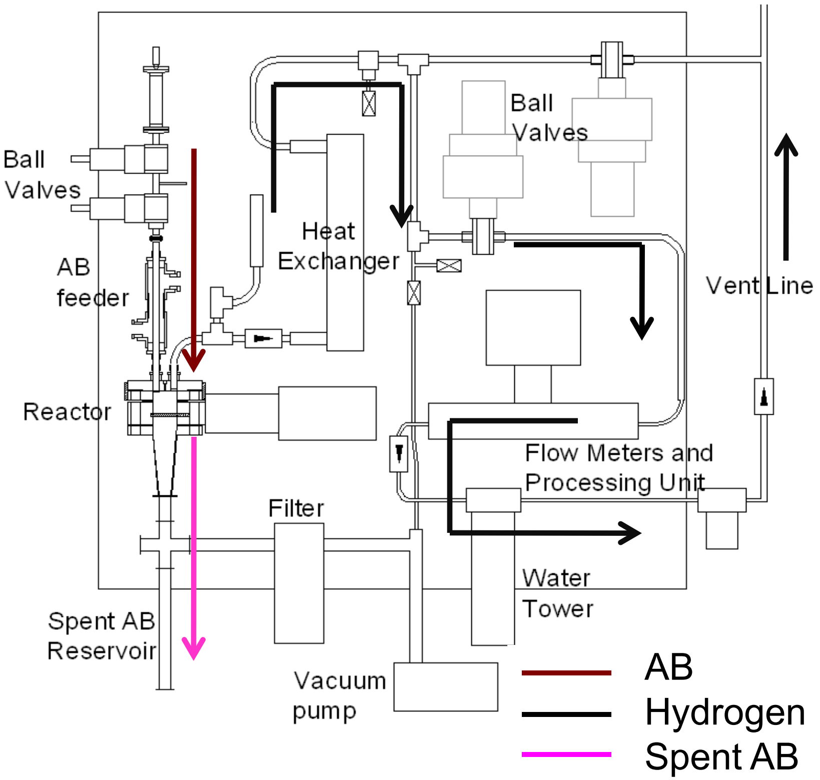
  Reactors designed to accommodate AB slurries, AB hydrolysis and other chemical hydrides.



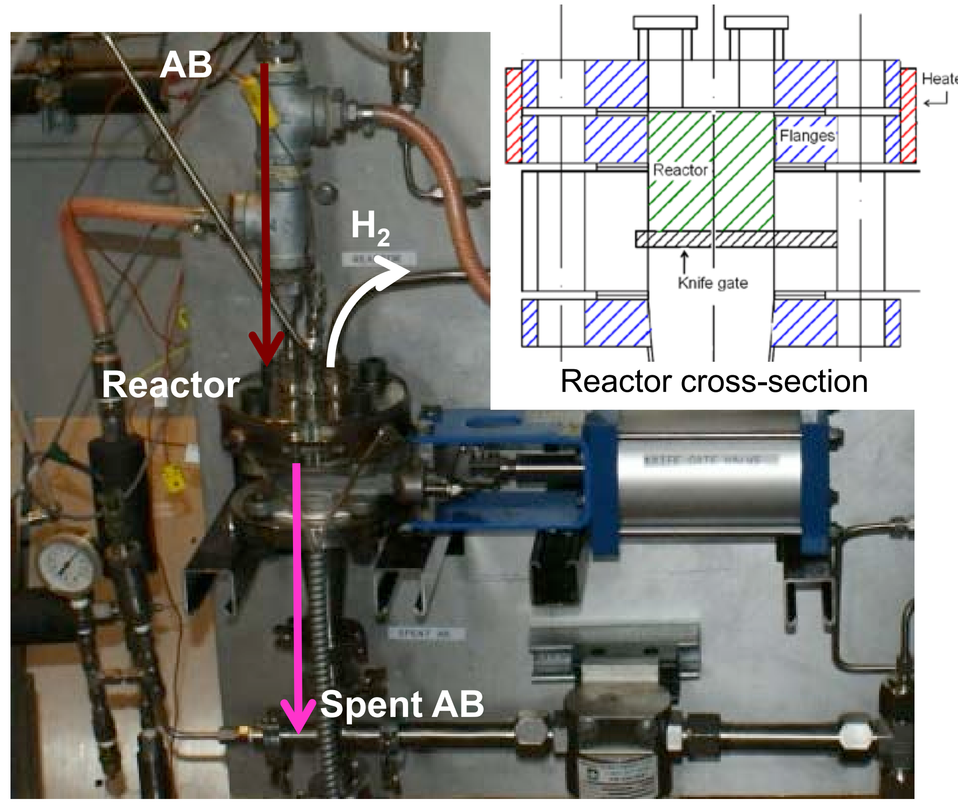
AB Reactor Scale-up Timeline

Technical Accomplishments and Progress (cont'd)

Intermediate Scale Steel Reactor



System Schematic



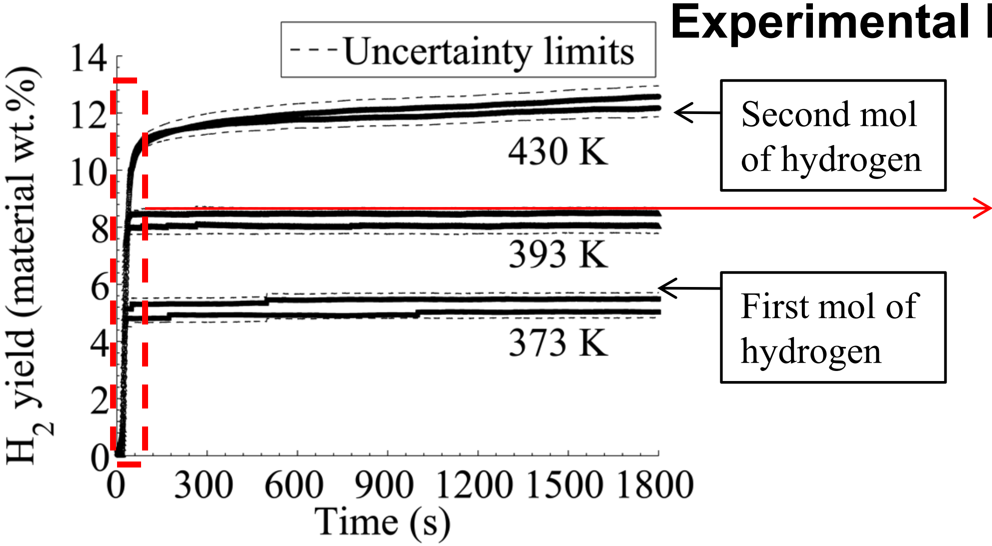
Reactor cross-section

Reactor installed in the Hydrogen Systems Laboratory

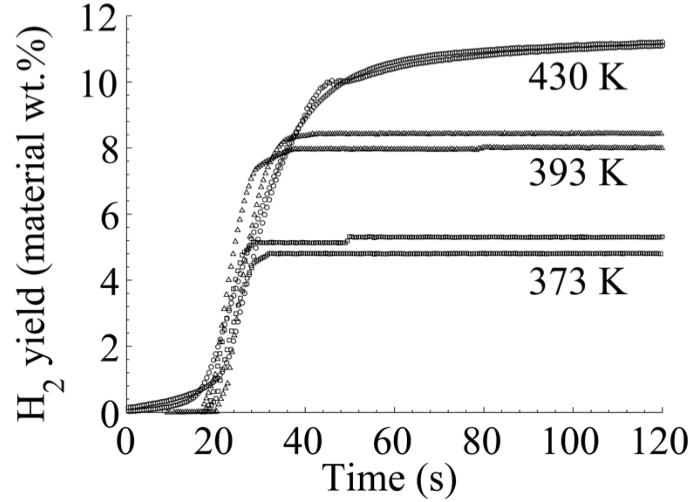
- Demonstrated an intermediate scale electric heated steel reactor system for experimental evaluation of neat AB thermolysis for automobile applications.
- Ongoing work is focused on modeling heat transfer processes and chemical kinetics of neat AB thermolysis reactions.

Technical Accomplishments and Progress (cont'd)

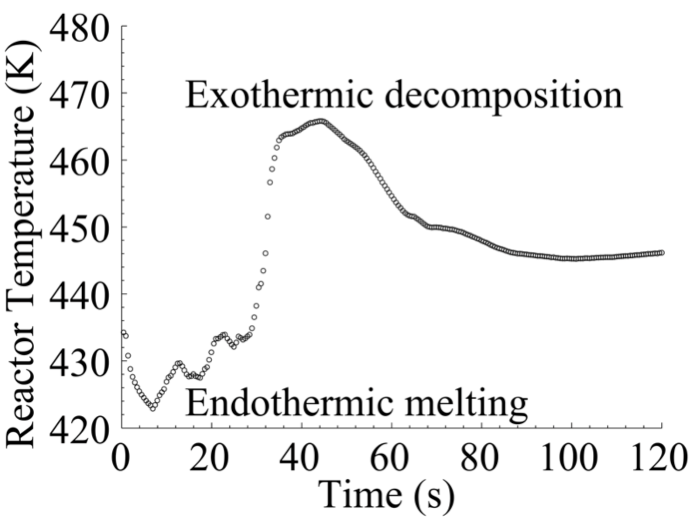
Experimental Results



Hydrogen yield with neat AB thermolysis



Hydrogen yield during initial 120 seconds



AB Temperature during initial 120 seconds

- 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).

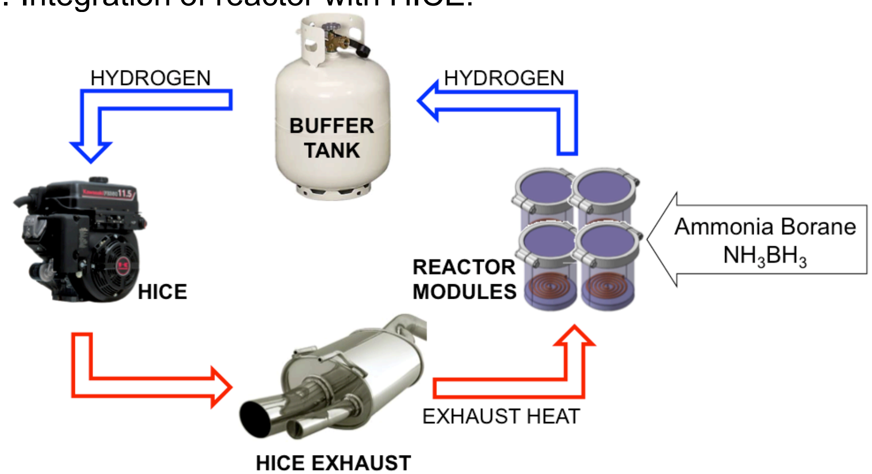
Goals:

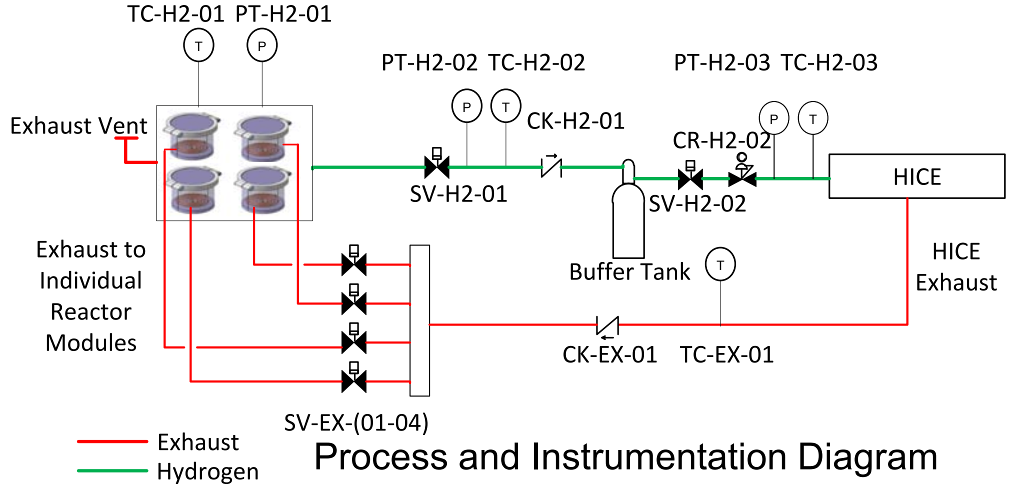
- Fixed bed cartridge based reactor. Cartridges can be replaced at re-fuelling stations for spent AB processing.
- Self sustained reactor operation utilizing waste heat from the HICE exhaust.

Reactor Details:

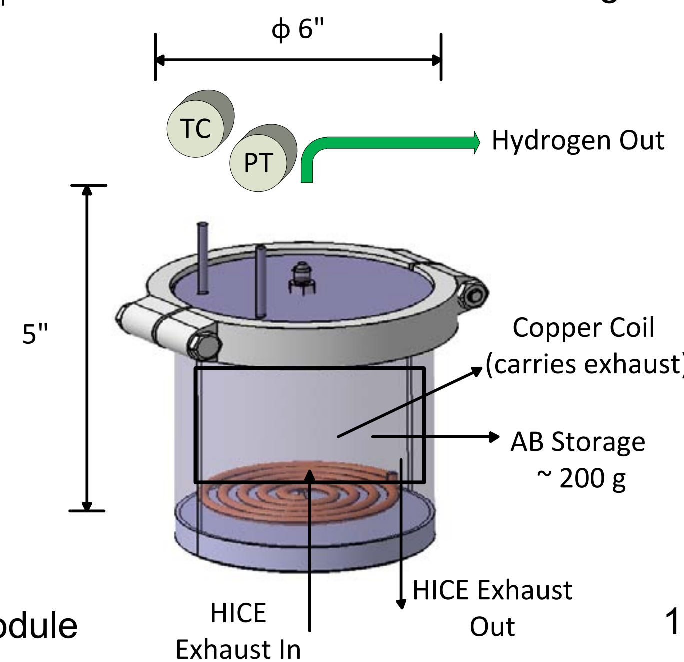
1. Cartridge based fixed bed reactor

   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:





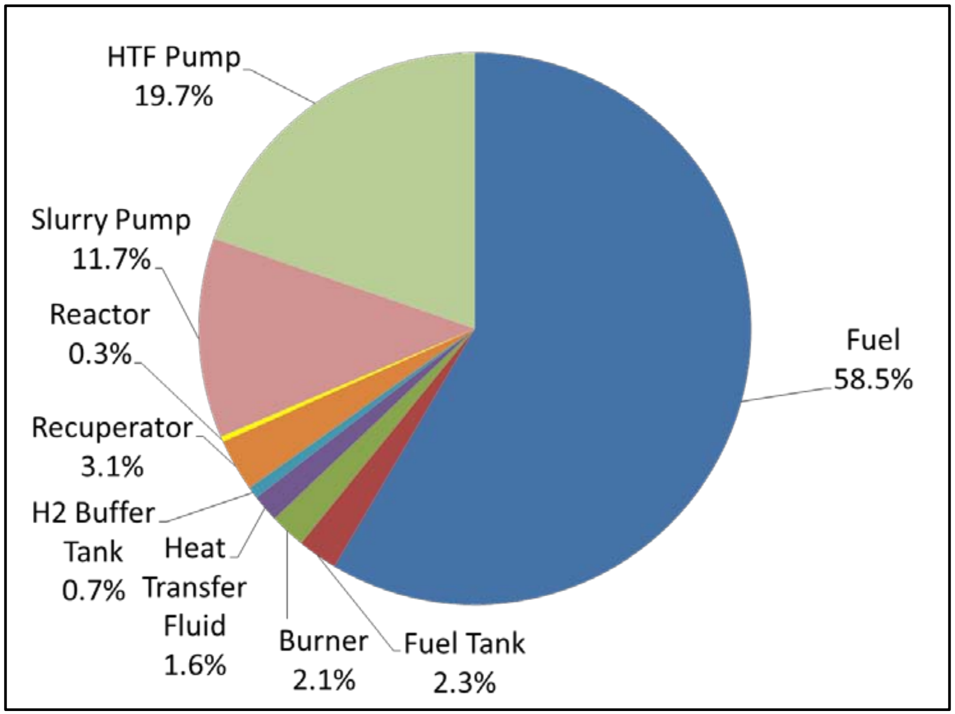
Process and Instrumentation Diagram

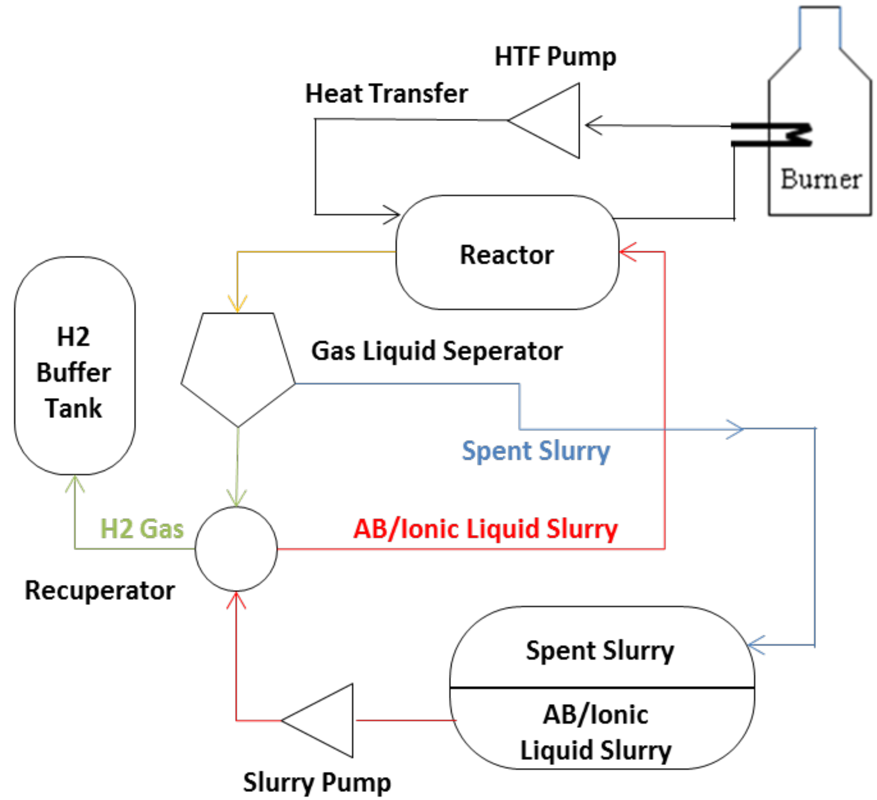


Reactor Module

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 H_2 or **6.9 system wt%**

Technical Accomplishments and Progress (cont'd)

Noncatalytic AB hydrothermolysis

AB hydrothermolysis

Thermolysis

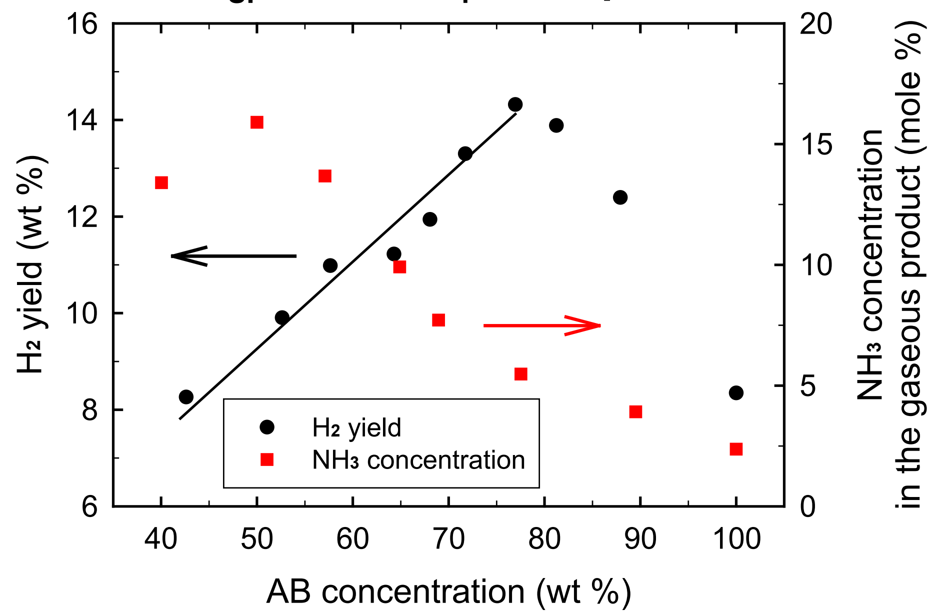
$$NH_3BH_3 \rightarrow \frac{1}{x}(NH_2BH_2)_x + H_2; \qquad (90\text{-}117\,^{\circ}C)$$

$$\frac{1}{x}(NH_2BH_2)_x \rightarrow \frac{1}{x}(NHBH)_x + H_2; (150\text{-}170\,^{\circ}C)$$

Hydrolysis

$$NH_3BH_3 + 3H_2O \xrightarrow{catalyst} NH_3 + B(OH)_3 + 3H_2$$

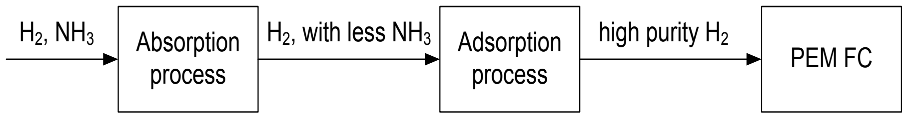
T_{SP} = 85°C, P_i = 200 psia

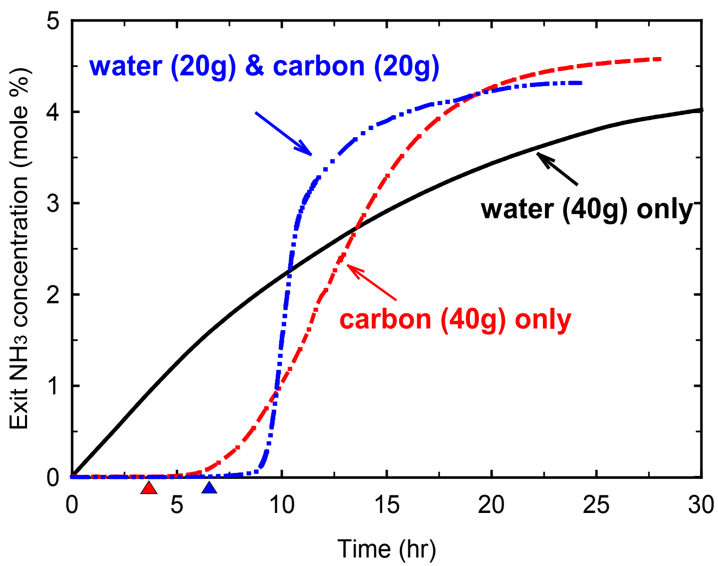


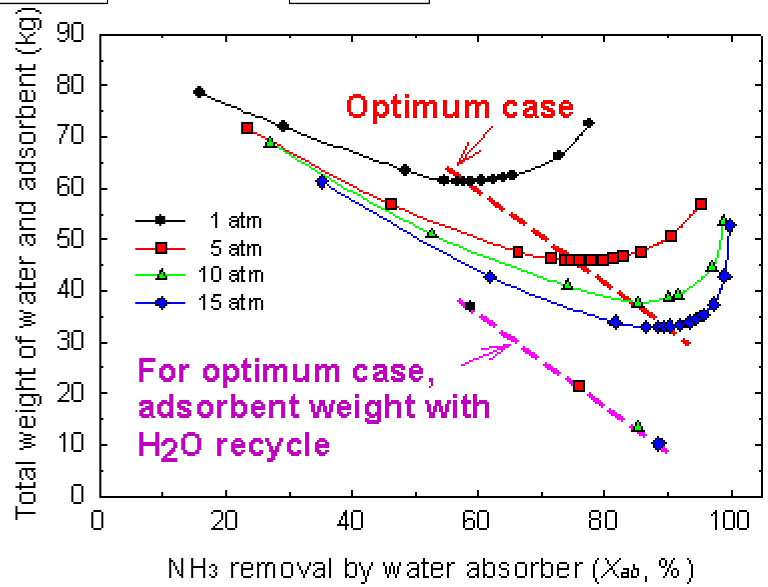
- Maximum **H_2 yield** obtained with **rapid kinetics** at 77 wt.% AB and **85°C**, was 11.6 and **14.3 wt.%** at pressure 14.7 and 200 psia, respectively.
- NH_3 concentration in gaseous product varies between 16% –2% from 50-100 wt.% AB.
- Some **ammonia** is observed even for **neat AB thermolysis**.

Technical Accomplishments and Progress (cont'd)

Ammonia Removal







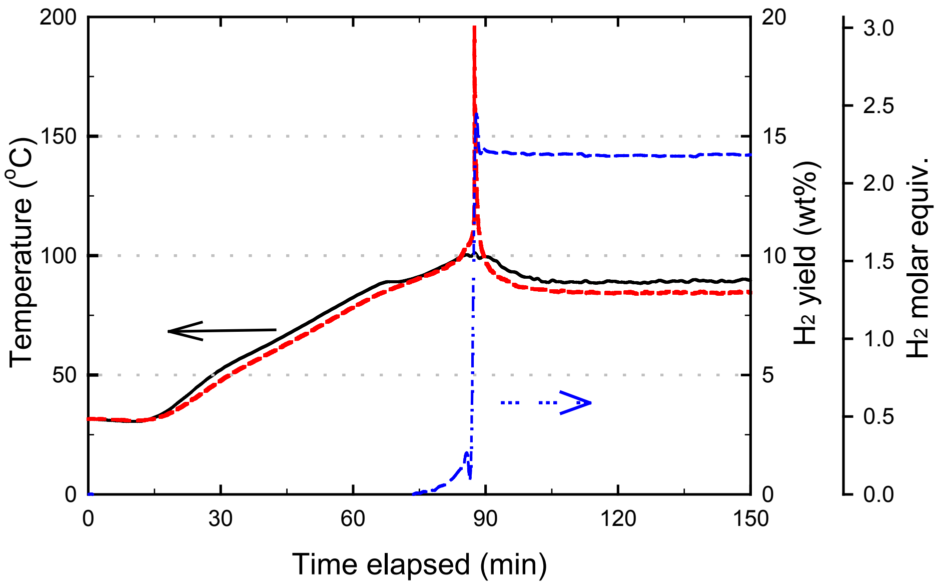
- NH_3 can be removed (<0.1 ppm in H_2) by **absorption** in water, followed by **adsorption** (carbon).
- NH_3 removal system weight decreases **significantly** with water recycle from PEM FC .
- In addition to removing NH_3, this method also **removes** any **borazine** in the H_2 stream.

$$N_3B_3H_6 + 9H_2O \rightarrow 3NH_3 + 3B(OH)_3 + 3H_2$$

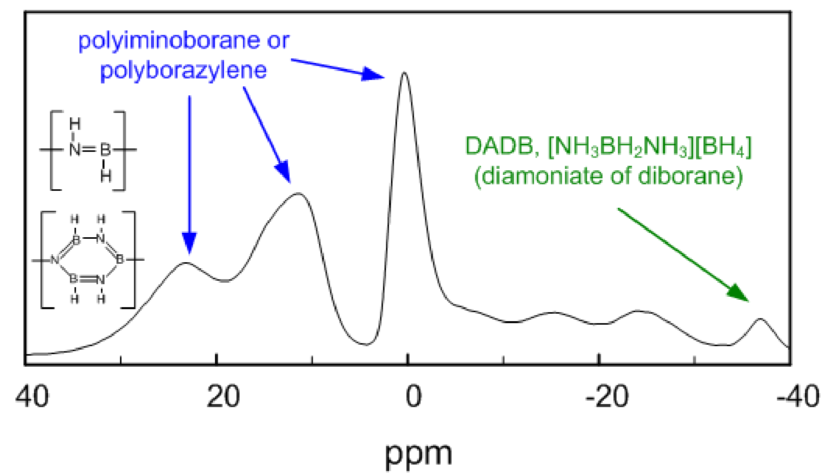
Technical Accomplishments and Progress (cont'd)

Neat AB Thermolysis

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



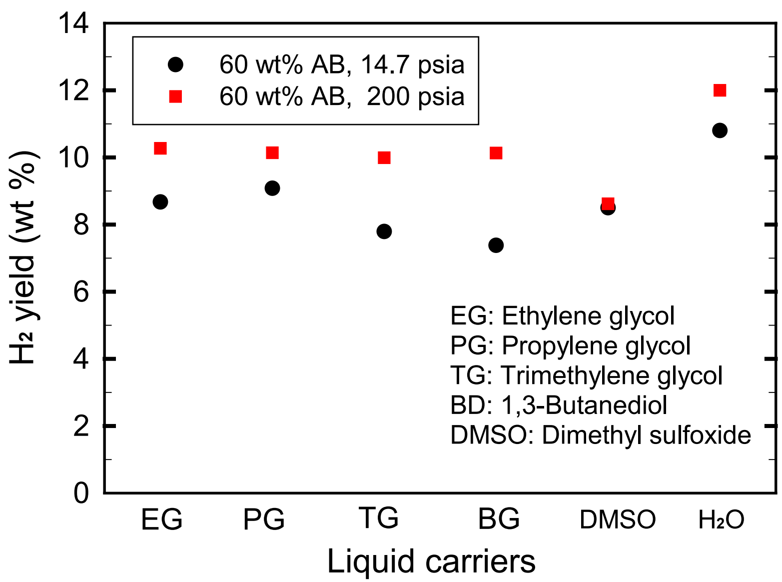
Solid-state ^{11}B NMR characterization



- Under **effective heat management,** high H_2 yield (**~ 14 wt %**) was obtained near PEM FC operating temperatures (**~ 90°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 H_2 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.

Development of a continuous-flow hydrogen generation system

- A reactor for AB dehydrogenation is currently under construction, where the H_2 release process consists of the following steps. First, AB fuel is loaded to the reactor, followed by H_2 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 $NH_4B(OH)_4$ 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 H_2 yield 14.3 wt.% was obtained with rapid kinetics at 77 wt.% AB and 85^{o}C for AB hydrothermolysis.
- NH_3 formation was observed for AB hydrothermolysis as well as neat AB thermolysis.
- NH_3 can be removed by absorption in water, followed by adsorption (carbon).
- High H_2 yield (~ 14 wt.%) was obtained near PEM FC operating temperatures (~90^{o}C) along with rapid kinetics for neat AB thermolysis.