PURDUE UNIVERSITY Discovery Park Energy Center

DOE Hydrogen Program

Purdue Hydrogen Systems Laboratory
Part II: Hydrogen Storage

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PURDUE UNIVERSITY Discovery Park Energy Center

DOE Hydrogen Program

Overview

Timeline

Start–September 2006
End–September 2009
70% complete

Barriers

Barriers addressed

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

Budget

- $2,470,006*
  - $ 1,924,000 (DOE)
  - $ 50,000 (to NERL/subcontractor)
  - $ 496,006 (Purdue)
- Funding received in FY09
  $ 984,000

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

Targets

		2007	2010	2015
Gravimetric capacity	**kgH_2/kg (wt%)**	**0.045 (4.5%)**	**0.06 (6%)**	**0.09 (9%)**
Volumetric capacity	**kgH_2/L**	**0.036**	**0.045**	**0.081**
Overall efficiency of off-board regeneration	**%**	**> 60**	**> 60**	**> 60**

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.
- Study the conversion of ammonium borate to $B(OCOR)_3$ and $B(OSO_2R)_3$ (R = CH_3, CF_3, Ph etc.).
- Study the reduction of $B(OCOR)_3$ and $B(OSO_2R)_3$ to AB using Bu_3SnH or Me_3SiH.

Dehydrogenation of AB Slurry

- Advance catalytic AB slurry dehydrogenation technique to achieve higher than 8.5 wt% hydrogen storage density and high hydrogen purity.
- Design, test, model and analyze a benchmark continuous flow AB slurry reactor module.
- Address barriers in system weight and other engineering considerations, especially by-product/spent material removal.

Investigation of Noncatalytic AB Hydrothermolysis

- Advance non-catalytic hydrothermolysis of AB in aqueous solutions and slurries, over a wide range of AB concentrations, at different temperatures (70-135ºC) and pressures (1-10 atm).
- Determine reaction mechanisms and kinetics of hydrogen generation from AB hydrothermolysis in aqueous solutions and slurries.
- Design, test and analyze a continuous-flow reactor for hydrogen generation, based on AB hydrothermolysis.

Approach

AB Recycling

- The spent fuel, ammonium borate will be converted to boron tris(triflate) or boron tris(trifluoroacetate), which will provide molecules with weaker B-O bond.
- The further reduction of boron tris(triflate) or boron tris(trifluoroacetate) in the presence of triethyl amine, followed by the displacement of the amine using ammonia will lead to efficient ammonia borane regeneration.

Dehydrogenation of AB Slurry

- Enhance the AB powder, water and catalyst mixing process using ultrasonic mixing and high shear mixing to obtain high hydrogen yields near stoichiometry (material based gravimetric hydrogen density of 9%).
- Characterize transportability of AB slurry and its hydrolysis byproduct by viscoelastic property measurements.
- Use a reactor module to provide engineering studies of AB and other materials that have potentials for off-board recyclable chemical hydrogen storage.

Approach (cont'd)

Investigation of Noncatalytic AB Hydrothermolysis

- Conduct isotopic experiments to understand reaction mechanism of H_2 release from aqueous AB solutions/slurries.
- Investigate solubility of AB in water at temperatures 25 – 70 ^{o}C.
- Study H_2 yield over a wide concentration range (5 – 80 wt% AB).
- Characterize reaction by-products.
- Initiate development of continuous-flow reactor for hydrogen generation.

Milestones

Month/Year	Milestone or Go/No-Go Decision
Sep-09	Milestone: Develop the optimal conditions to convert the spent borate to acylborates.
Mar-09 Sep-09	Go/No-Go: Measured hydrogen storage capacity should be higher than 8.5 wt%. Milestone: complete AB Slurry dehydrogenation reactor module construction
Mar-09 Jun-09 Sep-09	Milestone: Determine reaction mechanisms and H_2 yield from AB hydrothermolysis in aqueous solutions and slurries over wide ranges of process parameters. Milestone: Characterize reaction by-products. Milestone: Develop continuous-flow reactor setup. Milestone: Test and analyze continuous-flow reactor setup.

Previous Technical Accomplishments

AB Recycling

- Conversion of the spent fuel, ammonium borate, to boric acid, followed by conversion to trimethylborate was achieved.
- Trimethyl borate was reduced to sodium borohydride, which was further converted to ammonia borane in high yield and purity using ammonium salts.
- Demonstrated the regeneration of AB from ammonium borate in 64% overall yield.

Dehydrogenation of AB Slurry

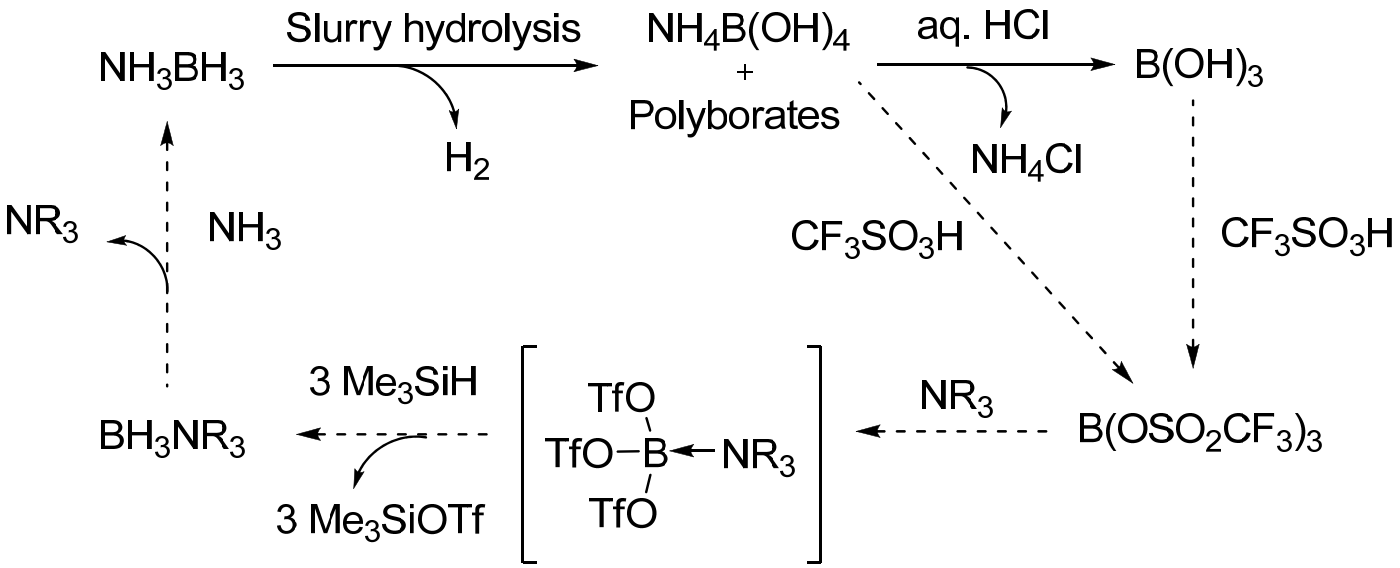
- Using catalytic AB slurry hydrolysis, we demonstrated a slurry-based hydrogen storage capacity of 7.5 wt% at room temperature.
- AB slurry dehydrogenation provided excellent reaction kinetics (0.038gH_2/s/kgfuel).

Investigation of Noncatalytic AB Hydrothermolysis

- Completed hydrothermolysis experiments with AB-lean aqueous solutions.
- Investigated the mechanistic basis of AB hydrothermolysis using isotopic labeling.
- Determined the optimum conditions where maximum H_2 can be obtained for AB lean aq. solution.

Technical Accomplishments and Progress

Proposed AB Recycling



Technical Accomplishments and Progress (cont'd)

- The conversion of the strong B-O bond to the B-H bond is crucial.
- We believe that conversion of B-N bond to B-OCOR or B-OSO_2R will weaken the B-O bond.
- The pKa of the following acids and the literature ΔH value support our hypothesis.

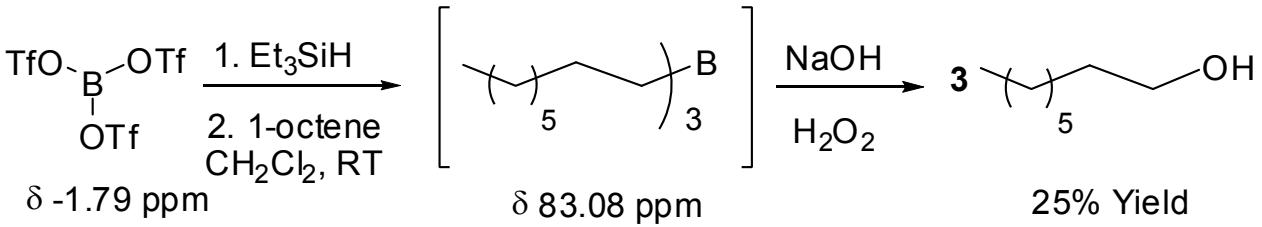
Acid	p*Ka*
HF	3.17
HCl	-8.0
HBr	-9.0
HSPh	6.6
$HOCH_3$	15.5
HOH	15.7
$HOOCCH_3$	4.8
$HOOCCF_3$	0.0
HO_3SCH_3	-2.6
HO_3SCF_3	-14.0

	ΔH (298K)
$B(OH)_3 + 3MeOH \rightarrow B(OMe)_3 + H_2O$	6.7
$HSi(CH_3)_3 + BF_3 \rightarrow FSi(CH_3)_3 + HBF_2$	-2.0[a]
$HSi(CH_3)_3 + BCl_3 \rightarrow ClSi(CH_3)_3 + HBCl_2$	-7.6[a]
$HSi(CH_3)_3 + BBr_3 \rightarrow BrSi(CH_3)_3 + HBBr_2$	-10.4[a]
$HSi(CH_3)_3 + B(OH)_3 \rightarrow (OH)Si(CH_3)_3 + HB(OH)_2$	8.3[a]
$HSi(CH_3)_3 + B(OCH_3)_3 \rightarrow (OCH_3)Si(CH_3)_3 + HB(OCH_3)_2$	7.9[a]
$HSi(CH_3)_3 + B(SPh)_3 \rightarrow (SPh)Si(CH_3)_3 + HB(SPh)_2$	-2.0[a]
$HSi(CH_3)_3 + B(O_2CCH_3)_3 \rightarrow (CH_3CO_2)Si(CH_3)_3 + HB(CH_3CO_2)_2$	6.3
$HSi(CH_3)_3 + B(O_2CCF_3)_3 \rightarrow (CF_3CO_2)Si(CH_3)_3 + HB(CF_3CO_2)_2$	-7.7
$HSi(CH_3)_3 + B(SO_3CF_3)_3 \rightarrow (CF_3SO_3)Si(CH_3)_3 + HB(CF_3SO_3)_2$	*b*
$HSi(CH_3)_3 + B(SO_3CH_3)_3 \rightarrow (CH_3SO_3)Si(CH_3)_3 + HB(CH_3SO_3)_2$	*b*

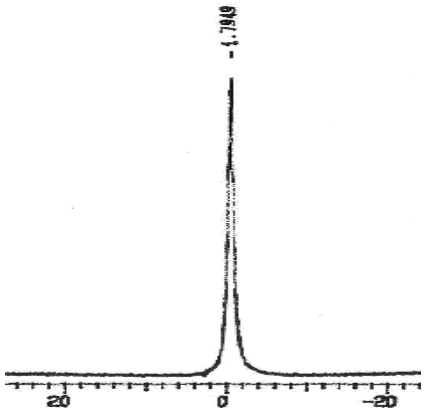
[a]literature value

[b]calculation in progress

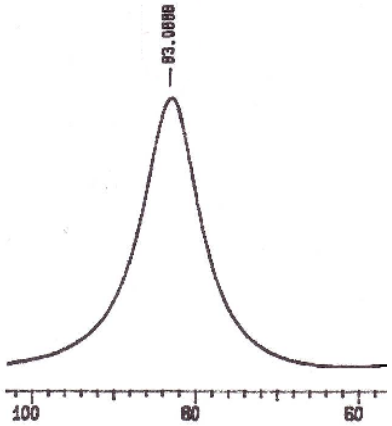
Technical Accomplishments and Progress (cont'd)



- Boron tris(triflate) was reduced using Et_2SiH_2 to BH_3 in the presence of 1-octene.
- The formation of BH_3 was proved by the hydroboration of 1-octene and α- pinene.
- The yields of borane and 1-octanol are being optimized.

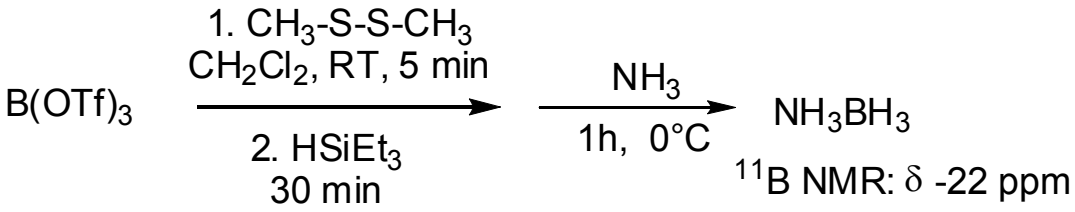


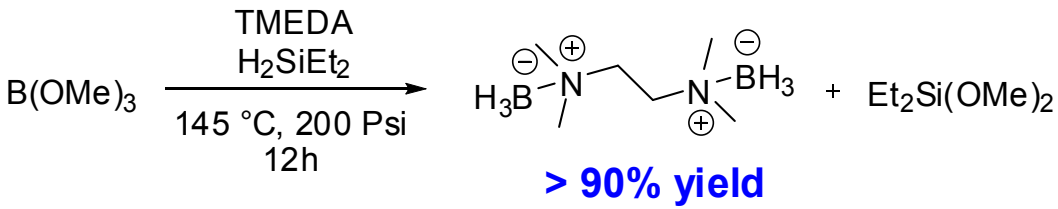
^{11}B NMR of $B(OTf)_3$

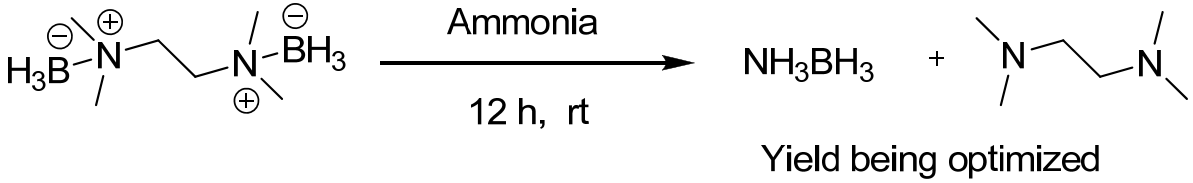


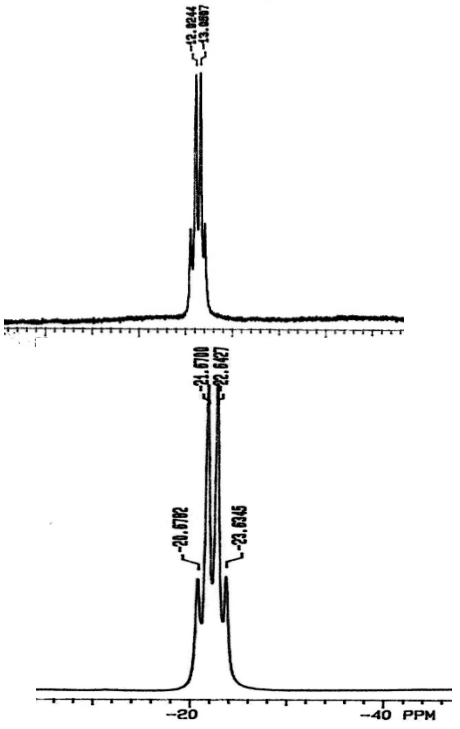
^{11}B NMR of (n-octyl)$_3$B

Technical Accomplishments and Progress (cont'd)





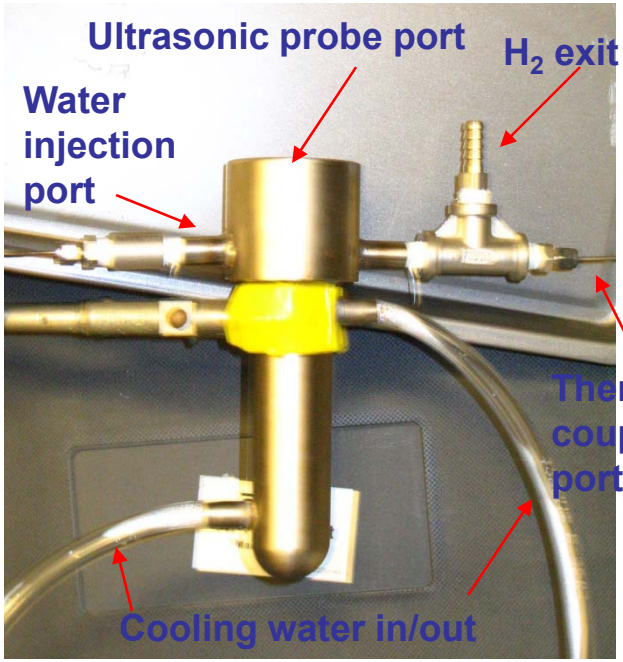




Technical Accomplishments and Progress (cont'd)

Adapted an ultrasound reactor for AB/water slurry hydrolysis tests

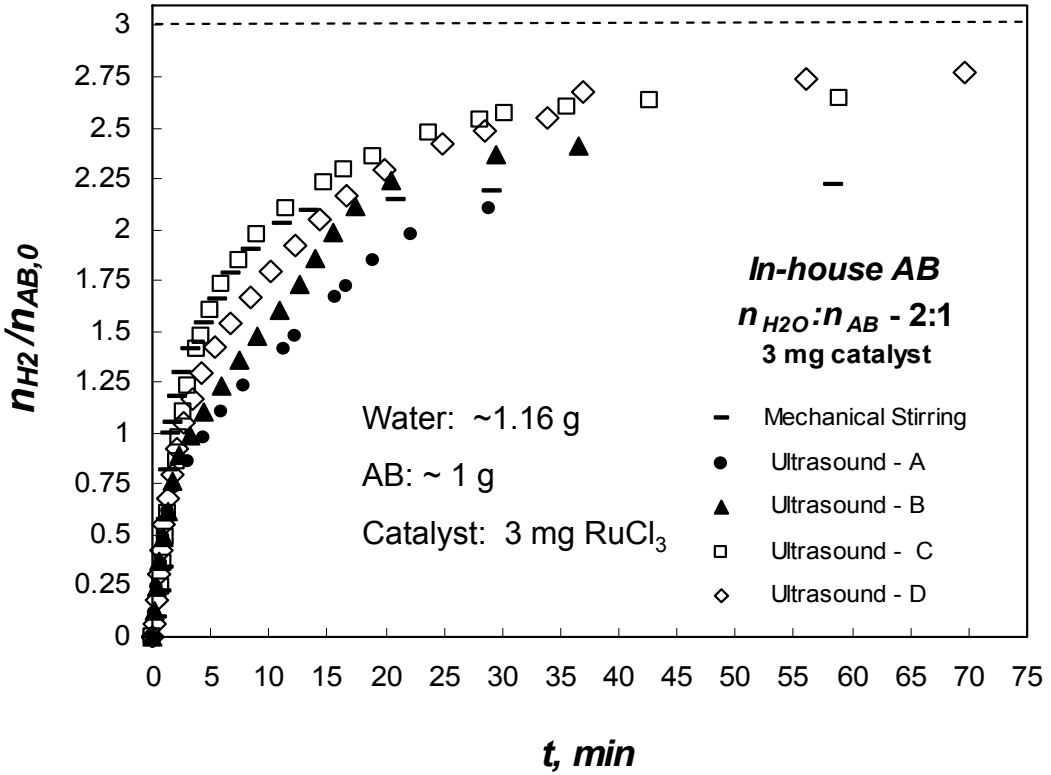
- The reactor



Sonifier: Branson 450

Power used: < 270 W

Reaction temperature: 20 °C to 45 °C

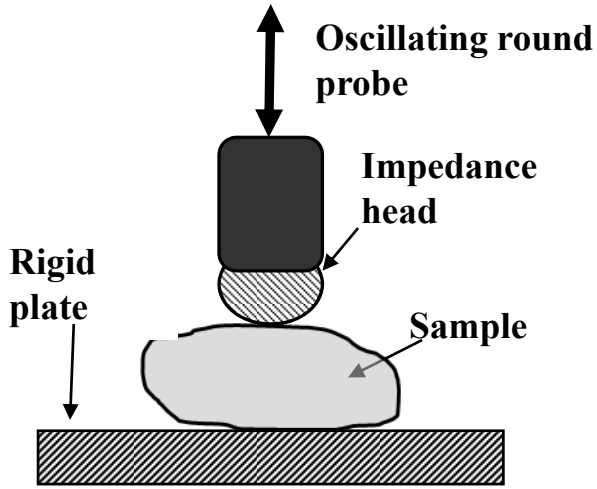


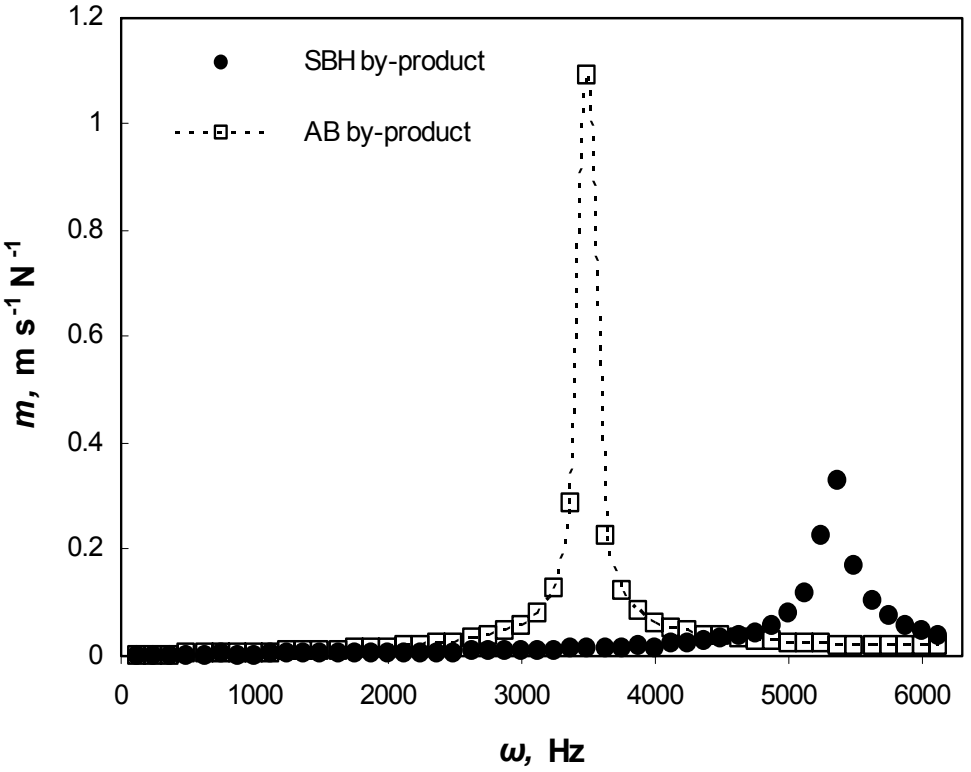
- The hydrogen yields of the four (1:2) AB/water slurry tests were 70%, 80%, 88% and 92% respectively. With a 92% hydrogen yield, the material based hydrogen storage capacity is ***8.2wt% (a new record of the AB hydrolysis approach).***

Technical Accomplishments and Progress (cont'd)

Rheology of AB slurries and spent fuels

Viscoeleastic property test apparatus



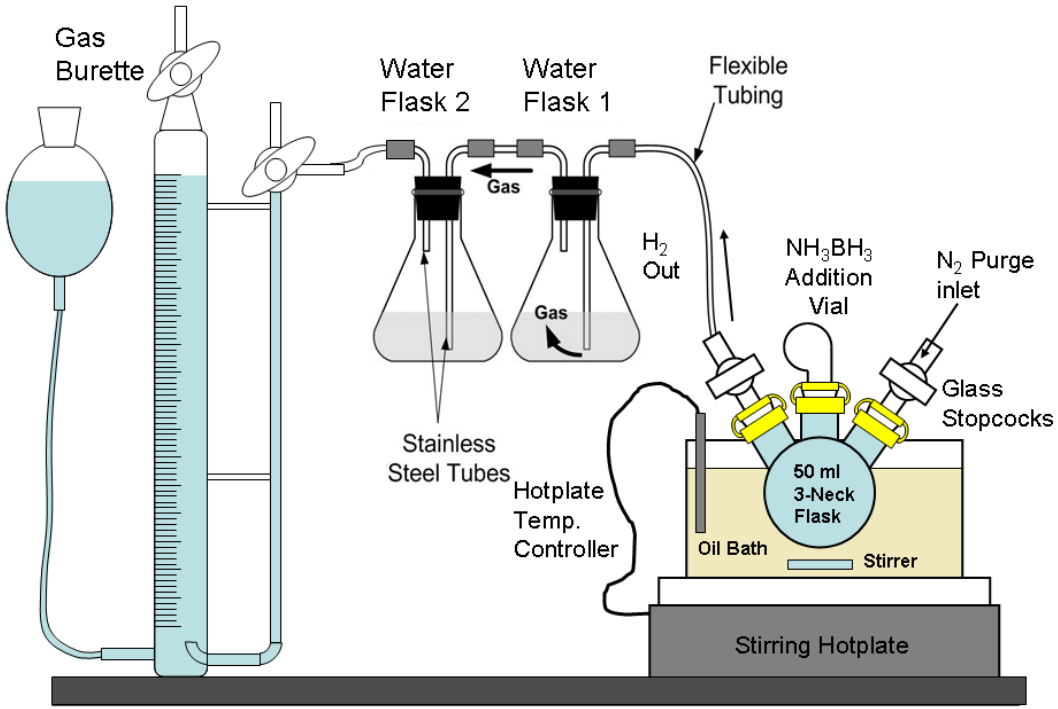


- Sample squeezed in a range of 10 Hz to 10,000 Hz.
- Complex mechanical impedance obtained by Fourier transformation of the measured force and velocity.
- Mobility (*m*), elastic stiffness and viscous damping derived from the complex mechanical impedance.
- AB hydrolysis spent fuel had lower resonance frequency and higher mobility than those of SBH hydrolysis spent fuel. This observation, ***for the first time, quantitatively*** reveals that AB spent fuel has lower elastic stiffness (softer) and smaller viscous damping than those of SBH spent fuel.

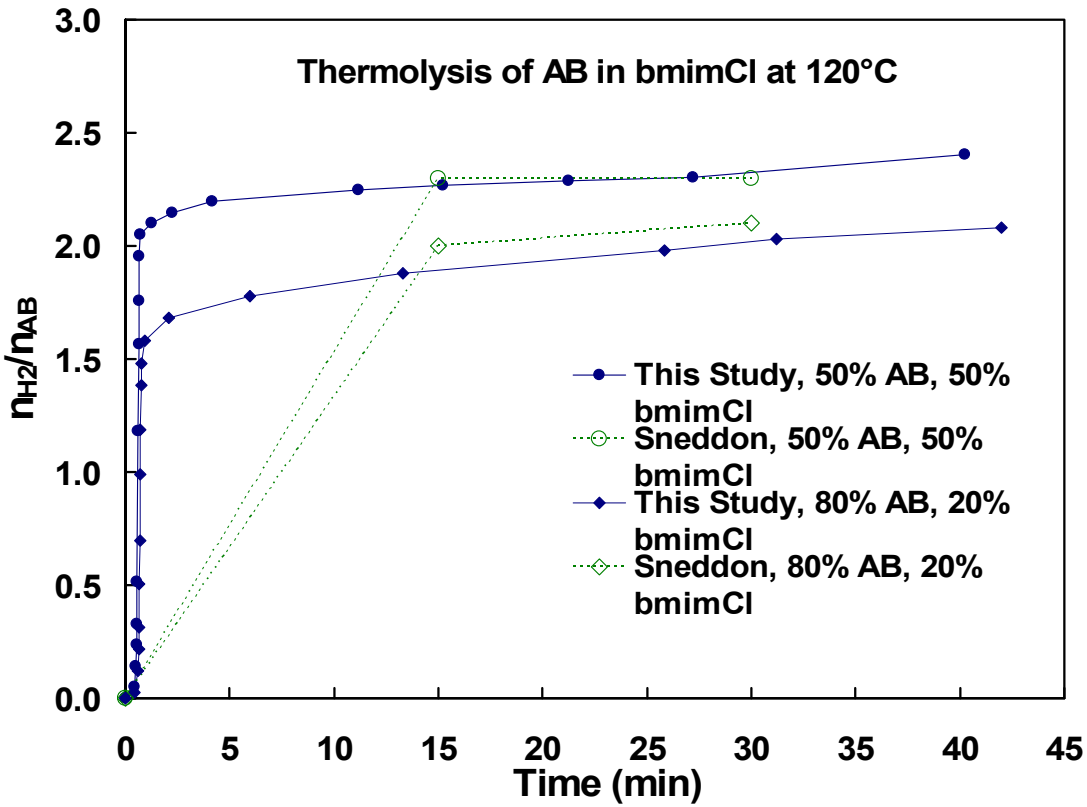
Technical Accomplishments and Progress (cont'd)

Assembled an AB ionic liquid slurry thermolysis test apparatus

- Provides continuous dehydrogenation measurements.
- Utilizes many features of the AB/water slurry hydrolysis apparatus.
- Oil bath provides desired reaction temperature
- Soluble byproducts get removed from hydrogen in the water flasks



Technical Accomplishments and Progress (cont'd)



- Observed hydrogen yields after 15 minutes and 30 minutes are very close to the literature data.
- ***To our best knowledge, very fast dehydrogenation rates in less than one minute were observed for the first time***. This observation significantly complements the literature data and provides insightful information for system design.

Technical Accomplishments and Progress (cont'd)

Noncatalytic AB hydrothermolysis - Experimental

Thermolysis

$$NH_3BH_3 \rightarrow NH_2BH_2 + H_2 \quad @\ 107 - 120\ ^\circ C$$

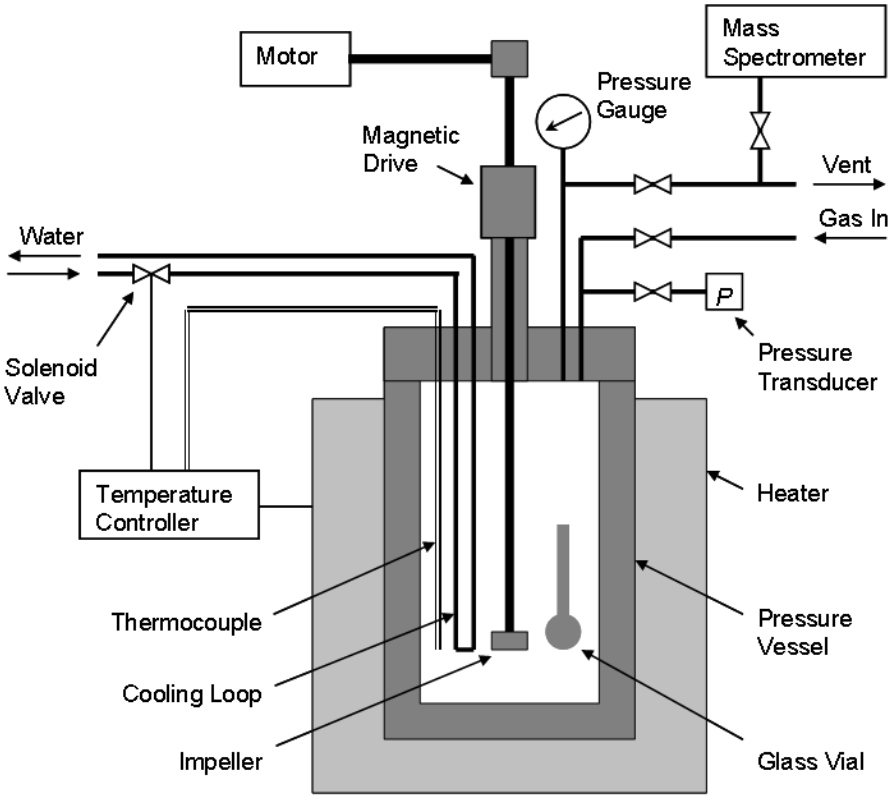
$$NH_2BH_2 \rightarrow NHBH + H_2 \quad @\ 150 - 170\ ^\circ C$$

Hydrolysis

$$NH_3BH_3 + 2D_2O \xrightarrow{Catalyst} NH_3D^+ + BO_2^- + 3HD$$

- Isotopic experiments were conducted to understand reaction mechanism in aqueous AB solutions.
- Argon gas pressure (~10 atm) prevented water boiling, thus allowing for experiments at temperatures 70-135 °C .
- It was shown that heating aqueous AB solutions and slurries over wide ranges of process parameters results in significant hydrogen release from AB and water.

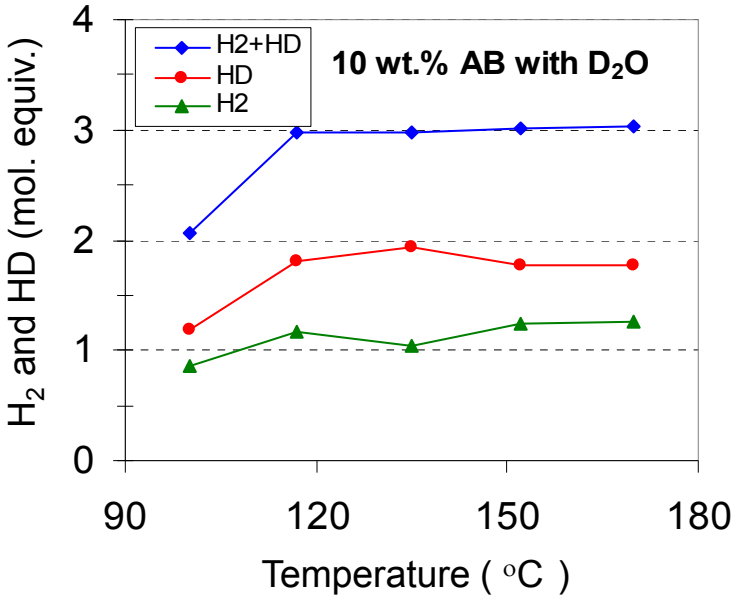
Experimental apparatus: Parr reactor



Technical Accomplishments and Progress (cont'd)

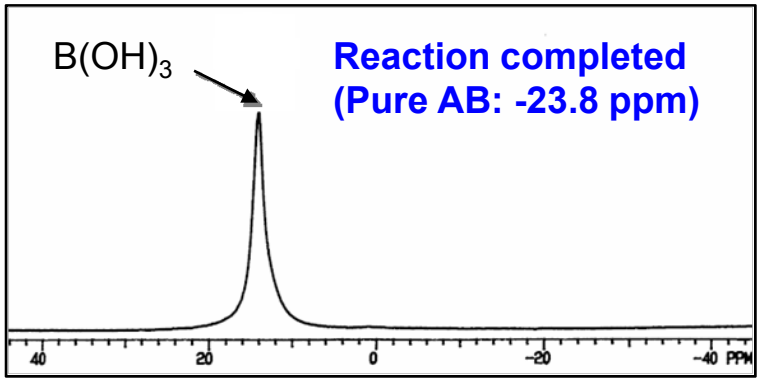
Mechanistic Studies

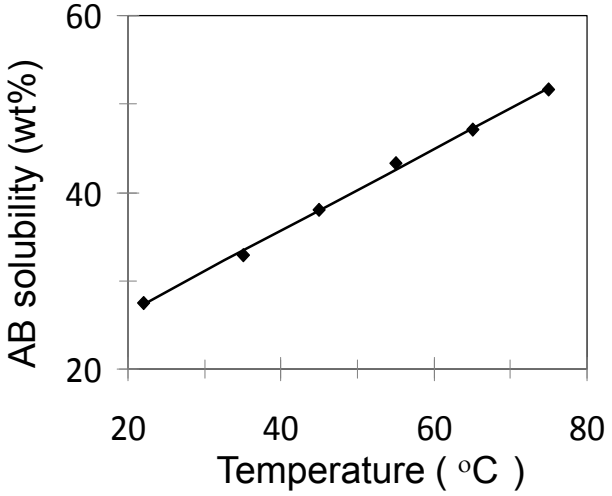
H_2 generation with varying temperature



- Heating aqueous AB solutions (10 wt% AB) to temperatures >117 °C under modest pressure (~10 atm) releases 3 mol (H_2 + HD) / mol AB.
- This is a promising non-catalytic method to release H_2 from AB.

^{11}B NMR spectrum of product (10 wt% AB)



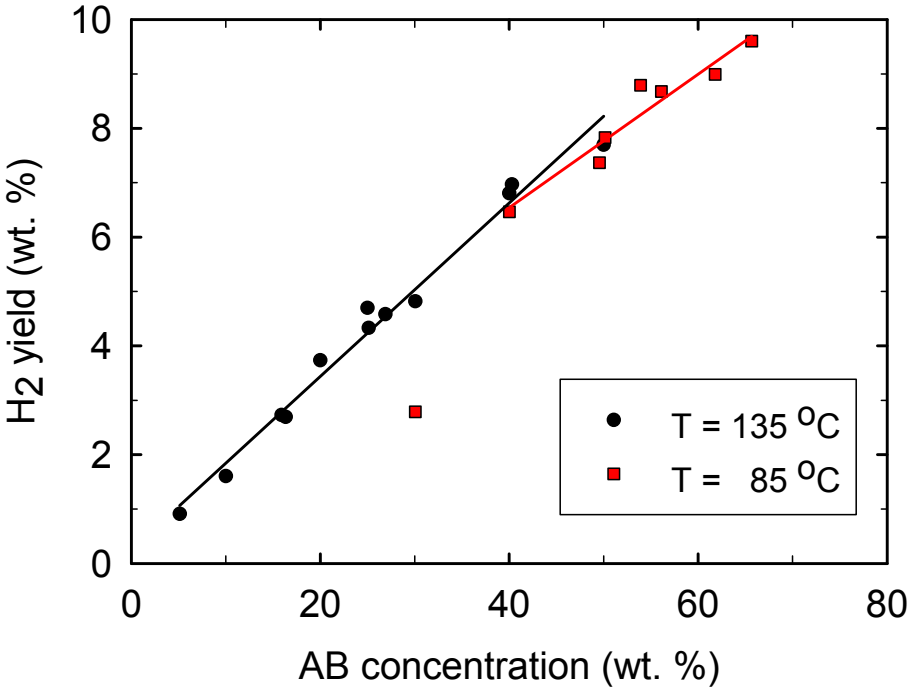


- At 70 °C, AB solubility is ~ 50 wt%.
- For T > 70 °C, H_2 generation was observed.

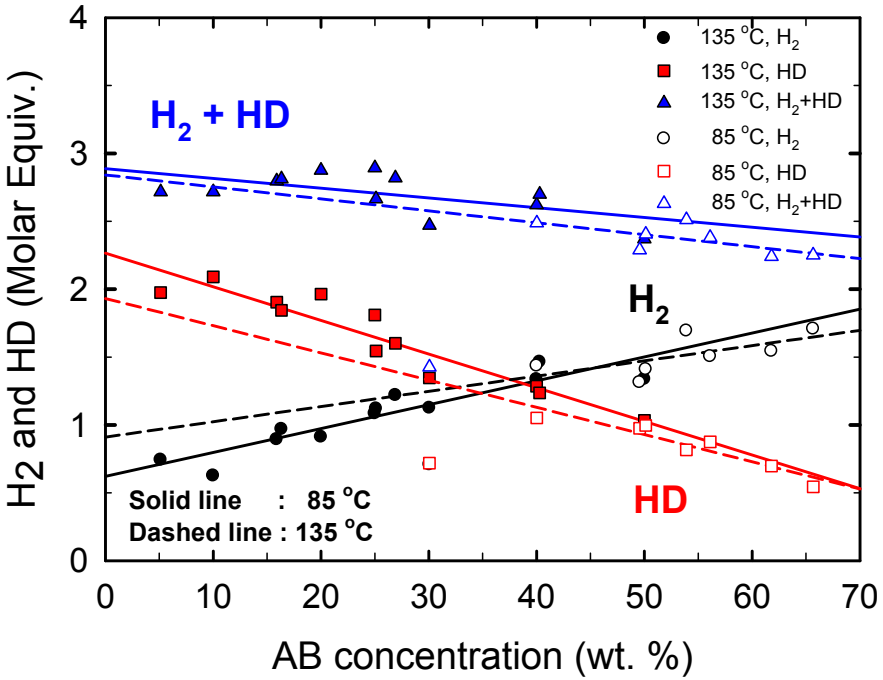
Technical Accomplishments and Progress (cont'd)

H_2 yield vs. AB concentration

H_2 yield



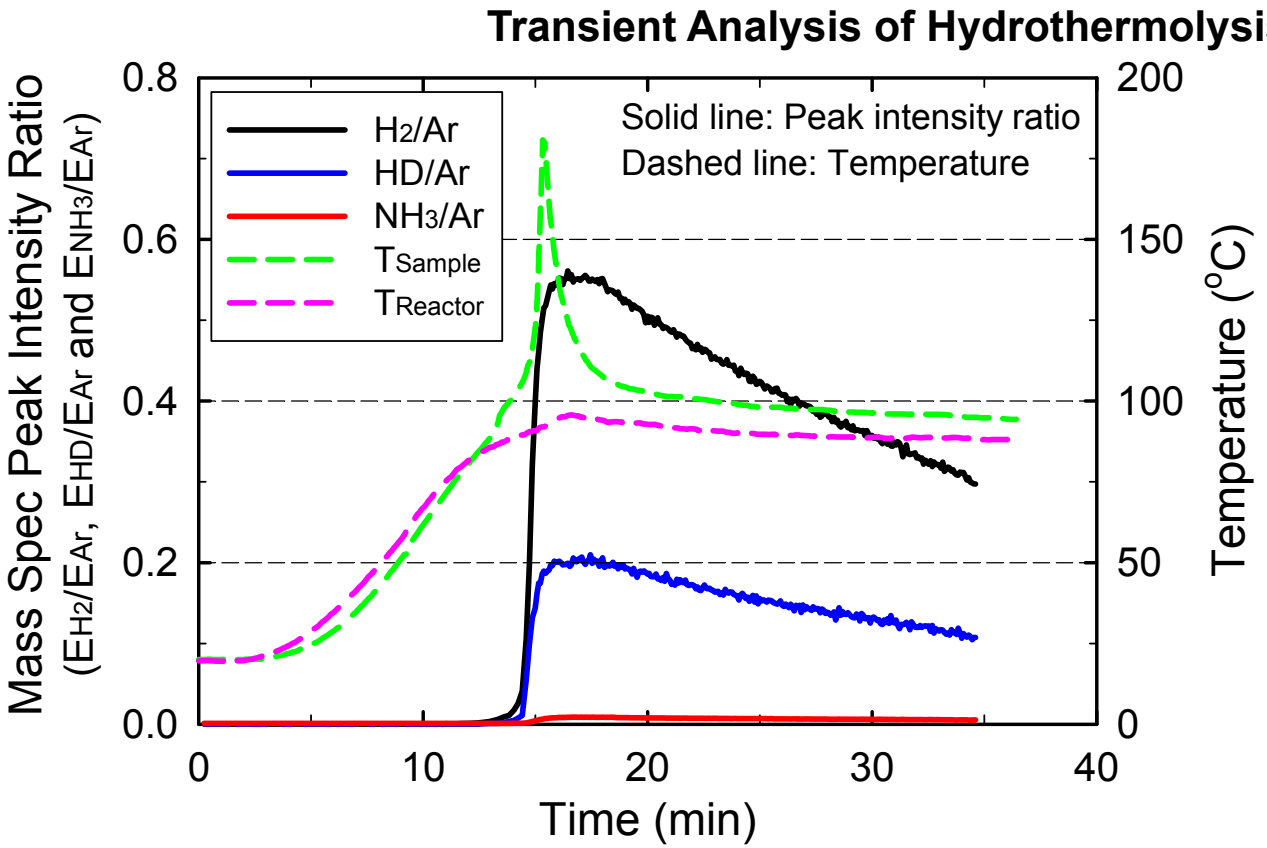
H_2 and HD molar equivalent



- Hydrogen yield increases with AB concentration (for < 65 wt% AB).
- Maximum hydrogen yield determined to be ~ 9.6 wt%.

- Although H_2 and HD yield vary with AB concentration, the total hydrogen yield (H_2+HD) remains at 2.25 -2.75 molar equivalent.
- Temperature of 85 °C is sufficient to obtain hydrogen yield ~ 6 wt % for AB concentration > 40 wt%.

Technical Accomplishments and Progress (cont'd)



Reaction Conditions:

- 40 wt% AB in D_2O
- $T_{reactor}$ = 85 °C
- $P_{initial}$ = 200 psia

- Transient analysis was conducted to understand gas evolution with time.
- At $T_{reactor}$ ~ 80 °C , T_{sample} increased sharply up to 180 °C with simultaneous evolution of H_2 and HD (begins at T_{sample} ~ 105 °C).
- The sample temperature rises sharply due to heat evolution during hydrothermolysis reaction (both AB hydrolysis and the first step of AB thermolysis are exothermic).

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.

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

AB Recycling

- The calculation of the bond energies for the proposed AB recycling is under way.
- The conversion of ammonium borate or boric acid to boron tris(triflate) is being examined.
- The optimization of the reduction of tris-acylborate to borane-ammonia will be carried out.

Dehydrogenation of AB Slurry

- Continue kinetics study of AB ionic liquid slurry thermolysis.
- Design, construct and test a AB slurry dehydrogenation reactor module.

Investigation of Noncatalytic AB Hydrothermolysis

- Determine reaction mechanisms and yield of hydrogen generation from AB hydrothermolysis in aqueous solutions and slurries.
- Quantify reaction by-products.
- Develop smaller size reactor and understand the heat evolution effects

Project Summary

AB Recycling

- The reduction of B-OTf bond in dibutyl boron triflate, followed by hydroboration of 1-octene supports our hypothesis.
- The reduction of boron tris(triflalte) was achieved using diethylsilane in 25% yield. The reaction is being optimized to 100% yield.
- The calculation for the energy efficiency of the complete regeneration cycle is in progress.

Dehydrogenation of AB Slurry

- 92% hydrogen yield in a (1:2) AB/water slurry hydrolysis test was observed, which provided a material based hydrogen storage capacity of 8.2wt%.
- The rheology properties of AB and SBH hydrolysis spent fuels were compared quantitatively for the first time.
- Continues monitoring of the AB/bmimCl slurry thermolysis process revealed extremely fast dehydrogenation rate.

Investigation of Noncatalytic AB Hydrothermolysis

- AB solubility is ~ 50 wt% @ T = 70 ^{o}C; for T> 70 ^{o}C, hydrogen generation is observed.
- While varying AB concentration from 5 to 65 wt% (P = 200 psia), the total hydrogen yield remains in the narrow range of 2.25 - 2.75 equivalent per mole of AB.
- Hydrogen yield increases with AB concentration. For 40 and 65 wt% AB, hydrogen yields of 6 and 9.6 wt% respectively, are achieved at T ~ 85 ^{o}C.