Purdue Hydrogen Systems Laboratory

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Overview (storage)

Timeline
• Start – September 2006
• End – September 2007
• 40% complete

Budget
• $825,000
  – $660,000 (DOE)
  – $165,000 (Purdue)
• Funding received in FY06: $660,000

Barriers
• Barriers addressed
  – A. System weight and volume
  – J. Thermal management
  – R. Regeneration process

<table>
<thead>
<tr>
<th></th>
<th>2007</th>
<th>2010</th>
<th>2015</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravimetric capacity</td>
<td>kgH₂/kg (wt%)</td>
<td>0.045 (4.5%)</td>
<td>0.06 (6%)</td>
</tr>
<tr>
<td>Volumetric capacity</td>
<td>kgH₂/L</td>
<td>0.036</td>
<td>0.045</td>
</tr>
</tbody>
</table>

Partners
• General Motors (lab infrastructure)
• General Atomics (AB synthesis)
Overview (bio-hydrogen)

Timeline
• Start – September 2006
• End – September 2007
• 40% complete

Barriers
• Barriers addressed
  – AI. H₂ molar yield
  – AK. Feedstock cost
  – AL. Systems engineering

Budget
• $415,500
  – $330,000 (DOE)
  – $84,500 (Purdue)
• Funding received in FY06: $330,000

Targets

<table>
<thead>
<tr>
<th>Hydrogen yield percentage (%)</th>
<th>2007</th>
<th>2010</th>
<th>2015</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20</td>
<td>40</td>
<td>&gt; 45</td>
</tr>
</tbody>
</table>

Partners
• Cargill
• Griffith Labs
• Advanced Power Technologies
• Innovene
• NREL
• BP
Outline

• Ammonia Borane-based Hydrogen Storage Methods

• Thermal Management of Recyclable Chemical Hydride Systems

• Bio-hydrogen Production from Organic Wastes
Objectives
(Ammonia Borane-based Hydrogen Storage Methods)

• Improve the extent, rate and control of hydrogen release from ammonia borane (AB) by hydrolysis reactions

• Characterize the dehydrogenation products and develop new methods for AB regeneration

• Investigate a new method for hydrogen generation from water and ammonia borane using self-sustained combustion reactions
Approach

• Screening transition metal catalyst for the hydrolysis of ammonia borane

• Characterization and regeneration reactivity of BN products

• Combustion-stimulated dehydrogenation of AB in triple AB/metal/water mixtures; occurring reactions are:

\[
\begin{align*}
\text{NH}_3\text{BH}_3 & \rightarrow \text{BN} + 3 \text{H}_2; \quad \text{Thermolysis, 19.5 wt\% H}_2 \\
\text{NH}_3\text{BH}_3 + 2 \text{H}_2\text{O} & \rightarrow \text{NH}_4\text{BO}_2 + 3 \text{H}_2; \quad \text{Hydrolysis, 9 wt\%} \\
\text{Mg} + \text{H}_2\text{O} & \rightarrow \text{MgO} + \text{H}_2; \quad \text{Combustion, 5 wt\%}
\end{align*}
\]

– H\textsubscript{2} yield is the highest if AB thermolysis prevails and AB hydrolysis is negligible, thus it is necessary to find conditions favoring thermolysis
Accomplishments/Progress/Results

Hydrolysis of AB

1. Mineral acid catalyzed

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

2. Transition metal catalyzed

\[ \text{NH}_3\text{BH}_3 + 4 \text{H}_2\text{O} \xrightarrow{\text{TM cat.}} \text{NH}_4\text{B(OH)}_4 + 3\text{H}_2 \]
## Accomplishments/Progress/Results

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Catalyst (mol%)</th>
<th>React. Time, min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>RuCl$_3$</td>
<td>0.2</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>RuCl$_3$</td>
<td>0.1</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>RuCl$_3$</td>
<td>0.05</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>CoCl$_2$</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>CoCl$_2$</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>6</td>
<td>Pd/C</td>
<td>1</td>
<td>25</td>
</tr>
<tr>
<td>7</td>
<td>PdCl$_2$</td>
<td>5</td>
<td>25</td>
</tr>
</tbody>
</table>

### Transition Metal Catalyzed Hydrolysis of AB
Accomplishments/Progress/Results

- Transition metal catalyzed hydrolysis of ammonia borane generates 3 eq. of hydrogen and ammonium tetrahydroxyborate
- Ammonium tetrahydroxyborate was converted to boric acid using aq. HCl
- Boric acid was treated with methanol to form trimethyl borate
Accomplishments/Progress/Results

Combustion wave propagation

Temperature in the combustion wave exceeds 500 °C, providing conditions for full dehydrogenation of AB. The possibility of some hydrolysis, however, still exists.

<table>
<thead>
<tr>
<th>Composition</th>
<th>H₂ yield (wt%), experimental</th>
<th>H₂ yield (wt%), theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB:Mg:H₂O (4:4:3)</td>
<td>9.1</td>
<td>10.1</td>
</tr>
<tr>
<td>AB:Al:H₂O (2:3:3)</td>
<td>7.7</td>
<td>8.7</td>
</tr>
</tbody>
</table>

NH₃BH₃:Al:H₂O (2:3:3 mass ratio)
Sample diameter 1 cm, height 2.5 cm
Images taken at 0.20, 0.33, 0.40 and 0.85 s after ignition
Accomplishments/Progress/Results

Isotopic tests of AB under Ar/D$_2$O flow in TGA (pressure 1 atm)

TGA/MS experiments with AB under Ar/D$_2$O flow at atmospheric pressure indicate the prevalence of *thermolysis*, as the amount of released H$_2$ well exceeds that of HD.
Isotopic tests of AB with D$_2$O in Parr reactor (initial Ar pressure $\sim$14 atm)

Experiments in Parr reactor result in higher amounts of HD as compared to H$_2$, indicating that higher pressure promotes hydrolysis.
Future Work

• To achieve the conversion of methyl borate to sodium borohydride in high yield

• To accomplish ammonia borane regeneration in overall near quantitative yield and in cost effective manner
  – Go/no go: ammonia borane overall yield of $\geq 60\%$

• TGA/MS experiments
  – higher $D_2O$ vapor pressure

• Parr reactor
  – detailed elevated pressure data for the reaction with $D_2O$
  – analyze product solutions (NMR)
  – measure concentrations of impurities in generated $H_2$ (FTIR)

• Combustion stimulated hydrolysis
  – analyze both gaseous and solid byproducts (FTIR and XRD)
  – test the effect of $D_2O$ on gaseous products (MS)
Summary

- Studied different transition metal catalysts for hydrolysis and observed that RuCl₃ gives the best results.
- Isolated boric acid from the ammonium tetrahydroxyborate by aq. HCl treatment.
- Boric acid was converted to trimethyl borate in the presence of methanol.
- Self-sustained combustion was observed in mixtures of AB with water and Mg or nano-Al powder; the maximum hydrogen yield was 9 wt%.
- Isotopic tests of AB using D₂O show that thermal decomposition competes with hydrolysis; higher pressure promotes hydrolysis.
Objectives
(Termal Management of Recyclable Chemical Hydride Systems)

• To demonstrate a recyclable chemical hydride hydrogen storage system
  – Construct and test an AB hydrogen generation system up to 1-kW\textsubscript{el}
  – Construct and test a 0.2 kg AB/day regeneration system

• To increase system-based volumetric and gravimetric hydrogen densities
  – Investigate thermo-chemical properties and processes experimentally and/or numerically to guide system design and optimization
Approach

• Investigate reaction kinetics and other key thermo-chemical properties
• Utilize numerical simulations to guide system level (subscale) test apparatus design
• Study key issues in the application of AB hydrolysis onboard hydrogen storage systems, using pre-system-level test apparatus
• Construct or renovate system level apparatus
• Conduct system level tests
Accomplishments/Progress/Results

- Mobile AB or SBH hydrolysis apparatus
  - Packed reactor: 3 wt% Ru on carbon extrudate

- First system-level AB hydrolysis test
  - 5 wt% fuel aqueous solution
  - Hydrogen flow rate: ~ 2.9 SLPM

Shorter reactor can be used for AB (w/o NaOH) hydrolysis
Accomplishments/Progress/Results

• **AB hydrolysis kinetics**

![Graph showing AB hydrolysis kinetics with reaction rates at different temperatures.](image)

- Temperature, °C: 16.6, 25.6, 35.6, 55.6
- Reaction rate equation: \( t^* = \frac{m_{cat} \cdot n_{AB,o}}{m_{cat} \cdot n_{AB,o}} \)
- Volume: 9.9 ml
- Initial n_{AB}: 0.002535 mol
- Immediate m_{cat}: 15.2 mg

\[ n_{H_2} / n_{AB,O} \]

• **AB hydrolysis reactor simulations**

- Reactors using cobalt will need much more volume and weight than those using ruthenium.

\[ y = -7683.7x + 28.5 \quad R^2 = 0.9952 \]
\[ y = -7457.3x + 25.138 \quad R^2 = 1 \]

\[ m_{metal}, g \]
- Ru: 0.6
- Co: 7

\[ m_{F} = 64.3 g/min \]
- [AB]_{inlet} = 3.6 kmol/m³ @10 wt%
- P_{in} = 14.4 psi

\[ d \left( \frac{n_{H_2}}{n_{AB,o}} \right) dt = \frac{3m_{cat}}{n_{AB,o}} \exp \left( -\frac{E_a}{R_u T} \right) \frac{K[AB]}{1 + K[AB]} \]

Reactors using cobalt will need much more volume and weight than those using ruthenium.
Accomplishments/Progress/Results

- Pre-system-level test apparatus
  - To study AB hydrolysis up to saturation condition
  - To validate AB hydrolysis kinetics at high concentrations
  - To quantify possible ammonia generation
  - To study byproduct solubility

- AB aqueous solution densities

\[
y = -0.0037x + 0.993 \\
R^2 = 0.9981
\]

Reference [Ali, 2002] at Saturation
Measured Density
Linear Fit
Accomplishments/Progress/Results

- 30-Day long term storage stability test

- Samples of 10% and 25% AB aqueous solution are being studied
- Expandable bottle allows outgassing without significant pressurization
- Bottle also minimizes evaporation
Accomplishments/Progress/Results

- New AB hydrolysis reactor design
  - To keep multiple point temperature profile probe
  - To prevent leakage when operating at high pressures
  - To facilitate reactants/products sampling
Future Work

• Construction & testing of AB hydrolysis apparatus
  – Key issue: possible operation difficulties at high fuel concentrations caused by dissoluble byproduct and/or appreciable ammonia generation
  – Go: no such difficulty occurs or problem can be solved without significant cost increase
  – No-go: problem can’t be solved or can be solved but with significant cost increase

• Design, construction and testing of AB regeneration apparatus
  – Key issue: yield of AB recycling at system level
  – Go: yield > 50%
  – No-go: yield < 50%
Summary

• AB hydrolysis (w/o NaOH) is faster than SBH hydrolysis (w/ NaOH, pH 14); therefore smaller/lighter system may be used for same hydrogen output

• AB hydrolysis systems using cobalt will need much more volume and weight than those using ruthenium

• Other key issues in the application of AB hydrolysis onboard hydrogen storage systems, such as ammonia generation, byproduct solubility and long term storage stability, are being investigated
Objectives

(Bio-hydrogen Production from Organic Wastes)

• Acquiring data for the volume of hydrogen produced from food waste by fermentation

• Conduct statistical testing to determine parameters that influence hydrogen production rate and optimal configuration

• Optimize the energy balance for a modular device for supply of thermal and electric energy

• Provide data and design information consistent with the DOE objective to utilize anaerobic biological processes as a source of the Hydrogen
Approach

- Investigate methods to produce hydrogen from various organic waste streams through the use of a fermentation process.
  - The long term goal is to develop a portable unit that can process food or other waste streams locally and produce hydrogen that will subsequently be used to generate electricity in remote locations initially.
  - Current efforts are concentrating on isolating biological consortia, characterizing their hydrogen producing capabilities, and determining optimal operating parameters as well as evaluating the interrelation with potential local energy system designs.

- We have recently expanded the energy model to also consider the possibility of producing potable water as part of the process.
Approach

• Samples of food waste were collected, ground, and freeze dried to provide a homogenous substrate for testing.
• Substrate was placed in a bottles, water was added, heated to 100 C for 10 minutes, purged with nitrogen, sealed, inoculated, and placed in an incubator. Gas samples were taken over time and were analyzed in a Gas Chromatograph.
• A statistical testing approach is being developed to determine parameters that optimize hydrogen production.
• A semi continuous production test is under development.
• Energy balance for the remote energy source is being considered based upon design and hydrogen production values.
• Provide training for undergraduate and graduate students in biological hydrogen production by participating in research efforts.
Accomplishments/Progress/Results

System Overview
Accomplishments/Progress/Results

• It has been possible to produce up to ~20 volume % hydrogen from initial non optimized tests.
• A statistical optimization testing scheme is currently being implemented.
• Initial work started on multiple testing device to conduct automated testing.
• Energy balance calculations are being modified to accommodate testing results and input from industrial advisors.
• Semi continuous testing device is under construction.
• Progress is consistent with project milestones and objectives.
Accomplishments/Progress/Results
### Accomplishments/Progress/Results

**Example of Test Data**

<table>
<thead>
<tr>
<th>Microbiology Research Data Sheet</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Name:</strong> Sarah Sauerer</td>
</tr>
<tr>
<td><strong>Date:</strong> March 29-30 2007</td>
</tr>
<tr>
<td><strong>Title:</strong> Comparison of Hydrogen Composition from 3 Different Sludge Samples</td>
</tr>
<tr>
<td><strong>Objectives:</strong> To determine which sludge inoculum contains microorganisms able to produce the greatest % H2.</td>
</tr>
<tr>
<td><strong>Medium:</strong> pH 6.5 (actual pH 6.15, phosphate buffer retested at 6.5 - food waste caused drop in pH) (1X) food waste medium, NO cysteine.</td>
</tr>
<tr>
<td><strong>Gassing:</strong> Nitrogen</td>
</tr>
<tr>
<td><strong>Incubation:</strong> 35°C</td>
</tr>
</tbody>
</table>

#### Result:

<table>
<thead>
<tr>
<th></th>
<th>VOL 48 H % H2 (AVG)</th>
<th>VOL 48 H % H2 (AVG)</th>
<th>VOL 48 H % H2 (AVG)</th>
<th>VOL 72 H % H2 (AVG)</th>
<th>VOL 72 H % H2 (AVG)</th>
<th>VOL 96 H % H2 (AVG)</th>
<th>VOL 96 H % H2 (AVG)</th>
<th>FINAL pH</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1. ANDI</strong></td>
<td>53</td>
<td>55</td>
<td>14</td>
<td>11</td>
<td>8</td>
<td>10</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td><strong>2. ML</strong></td>
<td>40</td>
<td>41</td>
<td>19</td>
<td>19</td>
<td>3</td>
<td>2</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td><strong>3. NRG</strong></td>
<td>51</td>
<td>57</td>
<td>21</td>
<td>14</td>
<td>1</td>
<td>0</td>
<td>16</td>
<td>6</td>
</tr>
<tr>
<td><strong>4. ANDIph</strong></td>
<td>54</td>
<td>55</td>
<td>12</td>
<td>11</td>
<td>8</td>
<td>6</td>
<td>0</td>
<td>19.1052</td>
</tr>
</tbody>
</table>

| pH1            | 5.00                 | 5.06                 | 5.05                 | 5.04                 | 5.12                 | 5.11                 | 5.12                 | 5.04     |

| GC%H2          | Run 1 | Run 2 | Run 1 | Run 2 | Run 1 | Run 2 | Run 1 | Run 2 | Run 1 | Run 2 | Run 1 | Run 2 | Run 1 | Run 2 | Run 1 | Run 2 | Run 1 | Run 2 | Run 1 | Run 2 | Run 1 | Run 2 | Run 1 | Run 2 | Run 1 | Run 2 |
|----------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|

Two bottles were run for each inoculum. VOL indicates how many extra ml were produced each day. For example, VOL 24 H #1 for ANDI inoculum is 53 ml.
Accomplishments/Progress/Results

- Energy Balance Calculations

![Graph showing energy balance calculations](image)

![Graph showing tank length required](image)
Future Work

• Determination of optimal parameters for hydrogen production from fermentation of food waste will continue.
• Multiple testing device is being developed.
• Energy balance will continue to be developed.
• Feasibility of production of potable water as a byproduct will be considered.
• Concept for capture of carbon dioxide to produce marketable chemical product will be considered.
Summary

- Anaerobic production of hydrogen holds promise as a viable source of energy.
- Waste streams provide a low cost source of feed for the energy production process.
- This approach holds promise to provide an environmentally friendly means to produce electricity in remote or third world applications.
- Identification of optimal operating parameters and consortia for hydrogen production is producing positive results.
- Statistical experimental design testing is underway.
- Energy balance is being refined to accommodate information from testing and commercialization concerns of industry advisors.
- New concepts to maximize value as a local energy source, consistent with DOE goals, are being considered such as production of potable water as a by product. CO2 capture is being considered using organometallic nanocatalyst.
- As the technology is developed there is the opportunity to scale up the size of the energy production.