Purdue Hydrogen Technology Program


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***National Renewable Energy Laboratory

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This presentation does not contain any proprietary or confidential information

Project ID # STP 40
Overview (storage)

Timeline
- Start – June 2006
- End – May 2007

Budget
- $825,000
  - $660,000 (DOE)
  - $165,000 (Purdue)
- Funding for FY06: expected

Barriers
- Barriers addressed
  - Cost of ammonia borane
  - Formation of harmful compounds in combustion-based methods
  - Thermal Management

Targets – storage system

<table>
<thead>
<tr>
<th>Specific Energy</th>
<th>2007</th>
<th>2010</th>
<th>2015</th>
</tr>
</thead>
<tbody>
<tr>
<td>kgH₂/kg (wt%)</td>
<td>(4.5%)</td>
<td>(6%)</td>
<td>(9%)</td>
</tr>
</tbody>
</table>

Partners
- General Motors
- General Atomics
Overview (bio-production)

Timeline
• Start – June 2006
• End – May 2007

Budget
• $415,500
  – $330,000 (DOE)
  – $85,500 (Purdue)
• Funding for FY06: expected

Barriers
• Barriers addressed
  ➢ Hydrogen production levels
  ➢ Gas Separation
  ➢ System Efficiency

Targets

<table>
<thead>
<tr>
<th></th>
<th>2006</th>
<th>2010</th>
<th>2015</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Production percentage</td>
<td>20</td>
<td>40</td>
<td>45+</td>
</tr>
</tbody>
</table>

Partners
• Cargill
• Griffith Labs
• Advanced Power Technologies
• Innovene
Objectives (storage)

• Examine the dehydrogenation of ammonia borane at lower temperatures
• New synthesis of ammonia borane to decrease the cost
• Develop a method for generating hydrogen from boron-hydrogen compounds with hydrogen yield >6 wt%, no catalyst and no harmful byproducts
• Design efficient thermal management sub-systems to facilitate dehydrogenation and fast-filling processes
Objectives (bio-production)

- Provide a renewable energy source to further DOE goals for development of a hydrogen energy economy
- Use biological organisms to produce hydrogen from waste using anaerobic process
- Use solar energy to preprocess the feed material
- Produce electricity in remote locations with the produced hydrogen used in either a fuel cell or reciprocating engine
- Consider ways to produce fertilizer
- Possibly separate/sequester carbon dioxide by use of organometallic nano catalysis
Approach (storage)

- Mixtures of boron-hydrogen compounds with metal (Al or Mg) and gelled water, upon ignition, exhibit parallel reactions:

\[
\begin{align*}
\text{NaBH}_4 + 2 \text{H}_2\text{O} & \rightarrow \text{NaBO}_2 + 4 \text{H}_2 \\
\text{Al} + 1.5 \text{H}_2\text{O} & \rightarrow 0.5 \text{Al}_2\text{O}_3 + 1.5 \text{H}_2 \\
\text{Mg} + \text{H}_2\text{O} & \rightarrow \text{MgO} + \text{H}_2
\end{align*}
\]

- The highly exothermic metal-water reaction assists hydrolysis of B-H compound, eliminating the need for catalyst.
- Water is an additional H\(_2\) source.
- Solid byproducts are environmentally friendly materials.
Approach (storage)

- Reviewed heat transfer issues in on-board hydrogen storage technologies, including compressed $\text{H}_2$, LH$_2$, chemical hydrides and metal hydrides

- Studied SBH systems
  - Heat of reaction measurement
  - Kinetics measurement
  - Sub-scale (1-kW$_e$) system design, construction and tests
  - Sub-scale (1-kW$_e$) system modeling

- Investigating high-pressure metal hydride systems
  - Sub-scale (1/50) system design, construction and tests
  - Sub-scale (1/50) system modeling
Approach (bio-production)

• Preliminary laboratory studies have verified the feasibility to use anaerobic digestion of organic waste for the production of hydrogen

• Determine the biological, chemical, and physical parameters that influence hydrogen production levels and develop a scheme to optimize production.
  – Individual organism
  – Consortium of organisms

• Develop an energy model that integrates design considerations with the research process
  – Heat flow modeling
  – Biological processes
  – Preliminary bio reactor concepts
  – Overall energy balance
Technical Accomplishments (storage)

• Examined the transition-metal catalyzed dehydrogenation of ammonia borane in solution at lower temperatures
• Examined the transition-metal catalyzed alcoholysis and hydrolysis of ammonia borane
• Achieved several new syntheses of ammonia borane (and amine boranes) that should decrease the cost of ammonia borane
Technical Accomplishments (storage)

New Synthesis of Borane-Ammonia

\[ \text{LiBH}_4 + \text{NH}_4\text{Cl} \xrightarrow{\text{THF}, 40^\circ\text{C}, 7\text{ h}} \text{BH}_3\text{NH}_3 + \text{LiCl} + \text{H}_2 \]

\[ \text{B(OMe)}_3 + \text{LiAlH}_4 + \text{NH}_4\text{Cl} \xrightarrow{\text{THF}, 3\text{ hrs}} \text{BH}_3\text{NH}_3 + \text{Al(OMe)}_3 + \text{LiCl} + \text{H}_2 \]

\[ \text{B(OMe)}_3 + 4 \text{LiH} + \text{NH}_4\text{Cl} \xrightarrow{\text{THF, AlCl}_3, 8\text{ hrs}} \text{BH}_3\text{NH}_3 + \text{Al(OMe)}_3 + 4 \text{LiCl} + \text{H}_2 \]

*Unpublished results, patent applied*
Technical Accomplishments (storage)

Comparison of Procedures for the Synthesis of BH$_3$NH$_3$

Existing Methods:

B(OMe)$_3$ → NaBH$_4$ → LiBH$_4$ → BH$_3$NH$_3$

New Method: One-pot Reaction

B(OMe)$_3$ → BH$_3$NH$_3$  Yield: 86%, Purity: > 95%

*Unpublished results, patent applied*
Technical Accomplishments (storage)

Dehydrogenation of Borane-Ammonia

\[ 3 \text{ NH}_3\text{-BH}_3 + \text{PdCl}_2 \xrightarrow{\text{THF, reflux}} \text{B}_3\text{N}_3\text{H}_6 + 6 \text{ H}_2 \]

Other transition metal salts used: NiCl\(_2\), CoCl\(_2\), etc. Similar results were obtained with all other TM salts.

*Unpublished results, patent applied*
Technical Accomplishments (storage)

One-pot Synthesis and Dehydrogenation of Borane-Ammonia

\[
3 \text{LiBH}_4 + 3\text{NH}_4\text{Cl} \xrightarrow{\text{PdCl}_2, \text{THF, reflux}} \text{B}_3\text{N}_3\text{H}_6 + 3 \text{LiCl} + 9 \text{H}_2
\]

Other transition metal salts used: NiCl\(_2\), CoCl\(_2\), etc.
Similar results were obtained with all other TM salts.
Various other ammonium salts gave similar results.

*Unpublished results, patent applied*
Technical Accomplishments, (storage)

- Mixtures of NaBH$_4$ with water, metal (Al or Mg) and additional minor ingredients (gellant, stabilizer) were developed.

- The developed mixtures exhibit stable combustion and 7 wt% H$_2$ yield, with safe solid byproducts.
Technical Accomplishments, (storage)

Combustion of mixture

*Example:* NaBH₄ : nanoAl : H₂O = 1:2:3 (mass ratio). Sample diameter: 10 mm

- The reaction wave propagates uniformly along the sample.
- The gaseous products flow in the reverse direction through the combustion products towards the open top end of the sample.
Technological Accomplishments (storage)

Hydrogen generation

- Evolved gas: H₂ (>99%).
- Efficiency of H₂ generation:
  - Al: 74-77%
  - Mg: 88-92%

The maximum observed H₂ yield is ~7 wt%.
Technical Accomplishments (storage)

- Heat of reaction (SBH)
  - Widely cited: 75 kJ/molH₂
  - This study: 52.5 kJ/molH₂

- Kinetics (SBH)
  commercially available 3% Ru on 2mm carbon extrude

\[
r_{SBH} = -A \exp \left( \frac{-E_a}{R_u T} \right) \frac{K C_{SBH}}{1 + K C_{SBH}}
\]

Technical Accomplishments (storage)

- 1-kW_e SBH reactor measurements
  - 10% NaBH_4

\[
\rho u C_p,_{\text{eff}} \frac{dT}{dx} = k_{\text{eff}} \frac{d^2 T}{dx^2} - h_r \omega_f MW_f - h_{fg} \dot{m}_v
\]

- 1-kW_e SBH reactor modeling
  - \( \dot{m}_r = 64.3 \text{g/min}, 15\% \)
Technical Accomplishments (storage)

- High-pressure metal hydride sub-scale system modeling

\[
\rho C_p \frac{\partial T}{\partial t} = -\frac{[H]_m}{2} \Delta H_r \frac{\partial F}{\partial t} + \lambda_{\text{eff}} \nabla^2 T
\]

\[
\frac{\partial F}{\partial t} = k(1 - F)
\]

\[
k = C_a \exp\left(-\frac{E_a}{R_u T}\right) \ln\frac{P}{P_{\text{eq}}}
\]

\[
P_{\text{eq}} = P_o \exp\left(\frac{\Delta H_r}{R_u} \left(\frac{1}{T} - \frac{1}{T_o}\right)\right)
\]

\[
F = \frac{x}{x_m}
\]

\[
x = \frac{[H]}{[M]}
\]
Technical Accomplishments (storage)

- High pressure metal hydride sub-scale system modeling (3D)

\[ P_{\text{charging}} = 400 \text{ bar}, \]
\[ T_{\text{max}} = 82 \, ^\circ\text{C}, \, t_{\text{ss}} = 6 \, \text{min}, \]
\[ \kappa_{\text{eff}} = 1 \, \text{W/mK} \]
Technical Accomplishments
(bio-production)

- Preliminary laboratory studies have verified the feasibility to use anaerobic digestion of organic waste for the production of hydrogen.

<table>
<thead>
<tr>
<th>Vial #</th>
<th>Treatment</th>
<th>Initial pH</th>
<th>Final pH</th>
<th>H₂ (µmol)</th>
<th>Digestion fraction</th>
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</thead>
<tbody>
<tr>
<td>25</td>
<td>Inoc</td>
<td>6.8</td>
<td>6.17</td>
<td>933.63</td>
<td>.529</td>
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<tr>
<td>26</td>
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<td>37</td>
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<td>40</td>
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<tr>
<td>43</td>
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<tr>
<td>21</td>
<td>Uninoc</td>
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<td>6.5</td>
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<tr>
<td>41</td>
<td>Uninoc</td>
<td>5.8</td>
<td>5.74</td>
<td>0</td>
<td>.245</td>
</tr>
</tbody>
</table>

Note: Inoc = inoculated with anaerobic waste water treatment effluent
Boil = boiled for 10 minutes before start
Uninoc = not inoculated
Technical Accomplishments (bio-production)

- An initial computer simulation model of the proposed system has been developed.
- Model will be used to consider possible design and process alternatives as well as means to optimize the process.
Future Work (storage)

• New formulation of ammonia-borane (AB) doped with transition metal salts
• Thermolysis of AB in the presence of water vapor
• Thermal management for AB systems
  – Thermo-chemical property measurements
  – Hydrogen generator and AB regenerator modeling
  – Sub-scale hydrogen generator and AB regenerator tests
Future Work (storage)

- Insight into combustion mechanisms of B-H compounds mixed with metals and water.
- Optimization of mixture compositions and process conditions
- Focus on ammonia borane, with the goal to further increase hydrogen yield
- Design and construction of power system demonstration unit
### Task Schedule

<table>
<thead>
<tr>
<th>ID</th>
<th>Task Name</th>
<th>Start</th>
<th>Finish</th>
<th>Duration</th>
<th>Start</th>
<th>Finish</th>
<th>Duration</th>
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<tbody>
<tr>
<td>1</td>
<td>Develop Initial Plan Details</td>
<td>6/1/2006</td>
<td>6/15/2006</td>
<td>11d</td>
<td></td>
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<td>7/3/2006</td>
<td>11/1/2006</td>
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Summary (storage)

- All on-board hydrogen storage technologies involve heat transfer challenges
- Unknown thermo-physical properties need to be measured or modeled
- Designs of reactors and other components need to be tested and modeled at appropriate sub-scales
- Mixtures of boron-hydrogen compounds with metal and water can be used for hydrogen generation by combustion
  - high specific energy
  - no catalyst for H₂ generation
  - safe reaction byproducts, which can be recycled
Summary (bio-production)

- 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.
- Initially this approach holds promise to provide an environmentally friendly means to produce electricity in remote or third world applications.
- As the technology is developed there is the opportunity to scale up the size of the energy production.
Publications and Presentations

Patents


Archival Journal Articles


Conference Presentations


