Purdue Hydrogen Technology Program

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This presentation does not contain any proprietary or confidential information

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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></th>
<th>2007</th>
<th>2010</th>
<th>2015</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Energy</td>
<td>kgH₂/kg (wt%)</td>
<td>(4.5%)</td>
<td>(6%)</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>Hydrogen Production percentage</th>
<th>2006</th>
<th>2010</th>
<th>2015</th>
</tr>
</thead>
<tbody>
<tr>
<td></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 \( \text{H}_2 \) source.
- Solid byproducts are environmentally friendly materials.
Approach (storage)

• Reviewed heat transfer issues in on-board hydrogen storage technologies, including compressed \( \text{H}_2 \), \( \text{LH}_2 \), 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
New Synthesis of Borane-Ammonia

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

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

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

Unpublished results, patent applied
Technical Accomplishments (storage)

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

Existing Methods:

$$\text{B(OMe)$_3$} \rightarrow \text{NaBH}_4 \rightarrow \text{LiBH}_4 \rightarrow \text{BH}_3\text{NH}_3$$

New Method: One-pot Reaction

$$\text{B(OMe)$_3$} \rightarrow \text{BH}_3\text{NH}_3 \quad \text{Yield: 86\%, Purity: > 95\%}$$

*Unpublished results, patent applied*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

Dehydrogenation of Borane-Ammonia

\[ 3 \text{NH}_3\cdot\text{BH}_3 \xrightarrow{\text{PdCl}_2} \text{B}_3\text{N}_3\text{H}_6 + 6 \text{H}_2 \]

THF reflux

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 NaBH₄ with water, metal (Al or Mg) and additional minor ingredients (gellant, stabilizer) were developed.

- The developed mixtures exhibit stable combustion and 7 wt% H₂ 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.
Technical 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

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

Technical Accomplishments (storage)

- 1-kW<sub>e</sub> SBH reactor measurements

- 1-kW<sub>e</sub> SBH reactor modeling

\[
\rho u C_{p,eff} \frac{dT}{dx} = k_{eff} \frac{d^2T}{dx^2} - h_r \omega_f MW_f - h_{fg} \dot{m}_v
\]
Technical Accomplishments (storage)

- High-pressure metal hydride sub-scale system modeling

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

\[ F = \frac{x}{x_m} \quad x = \frac{[H]}{[M]} \]

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

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

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

Heat Transfer Efficiency

Heat release is dominant at very beginning
Technical Accomplishments (storage)

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

\[ P_{\text{charging}} = 400 \text{ bar}, \]
\[ T_{\text{max}} = 82 \, ^\circ\text{C}, \text{ } t_{\text{ss}} = 6 \text{ min}, \]
\[ \kappa_{\text{eff}} = 1 \, \text{W/mK} \]
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>H$_2$ (µmol)</th>
<th>Digestion fraction</th>
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<tbody>
<tr>
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<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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<tr>
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<tr>
<td>21</td>
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<tr>
<td>41</td>
<td>Uninoc</td>
<td>5.8</td>
<td>5.74</td>
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<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
Future Work (bio-production)

### Timeline
- **Major Milestones**
  - 6/1/2006: Start
  - 6/30/2006: Initiate Interface With Industry Contacts
  - 6/15/2006: Complete Initial Plan Details
  - 7/21/2006: Complete Literature Search
  - 11/1/2006: Complete Test Device Development and Construction
  - 6/1/2007: Conduct Evaluation of Innoculum and Conditions to Maximize H Production
  - 6/1/2007: Conduct Energy Evaluation
  - 6/30/2007: Submit Final Report

### Task Schedule

<table>
<thead>
<tr>
<th>ID</th>
<th>Task Name</th>
<th>Start</th>
<th>Finish</th>
<th>Duration</th>
<th>2006</th>
<th>2007</th>
</tr>
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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>
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<td></td>
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<tr>
<td>4</td>
<td>Construct Test Device</td>
<td>7/3/2006</td>
<td>11/1/2006</td>
<td>88d</td>
<td></td>
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</table>
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