System Level Analysis of Hydrogen Storage Options


2009 DOE Hydrogen Program Review
May 18-22, 2009
Arlington, VA

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Project ID: ST_13_Ahluwalia
Overview

Timeline
■ Project start date:  Oct 2004
■ Project end date:  Sep 2014
■ Percent complete:  50%

Budget
■ FY08:  $525 K
■ FY09:  $725 K

Barriers
■ H₂ Storage Barriers Addressed:
  – A:  System Weight and Volume
  – B:  System Cost
  – C:  Efficiency
  – E:  Charging/Discharging Rates
  – J:  Thermal Management
  – K:  System Life-Cycle Assessments

Interactions
■ FreedomCAR and Fuel Partnership
■ Storage Systems Analysis Working Group, MH COE, CH COE
■ BNL, LANL and PNNL, LLNL, SRNL, TIAX, H2A, UH/UNB, UTRC, and other industry
Objectives

- Perform independent systems analysis for DOE
  - Provide input for go/no-go decisions
- Provide results to CoEs for assessment of performance targets and goals
- Model and analyze various developmental hydrogen storage systems
  - On-board system analysis
  - Off-board regeneration
  - Reverse engineering
- Identify interface issues and opportunities, and data needs for technology development
Approach

- Develop thermodynamic and kinetic models of processes in physical, complex metal hydride, sorbent, and chemical hydrogen storage systems
- Calibrate, validate and evaluate models
- Work closely with the DOE Contractors, CoEs, Storage Tech Team, other developers, and Storage Systems Analysis Working Group
- Assess improvements needed in materials properties and system configurations to achieve H$_2$ storage targets
Technical Accomplishments

Compressed Hydrogen (March 2009): Backup slides
- Gravimetric/volumetric capacity of compressed H₂ tanks, well-to-tank efficiency, validation with “Learning Demo” data
- Issuing a final joint report with TIAX on 350 and 700-bar systems

Metal Hydrides (August 2008): Backup Slides
- Performance of on-board system with alane slurries
- WTT efficiency for off-board regeneration of alane

Hydrogen Storage in Metal Organic Frameworks (June 2009)
- Performance of on-board system with off-board liquid N₂ cooling
  (storage capacity, charge and discharge dynamics, dormancy)
- Electricity consumed for cryogenic cooling
- Adiabatic refueling option

Hydrogen Storage in Ammonia Borane (December 2008)
- WTT efficiency of AB regeneration (CHCoE/LANL/PNNL schemes)

Hydrogen Storage in Lithium Alanate (September 2009)
- WTT efficiency of LiAlH₄ regeneration by UH/UNB Method
On-Board Storage of Hydrogen in Metal Organic Frameworks at Cryogenic Temperatures

Key System Requirements

Storage Medium
- 5.6 kg recoverable H₂
- 4-bar minimum delivery P

Containment Vessel
- 2.35 safety factor

Heat Transfer System
- 1.5 kg/min H₂ refueling rate
- 1.6 g/s H₂ min flow rate
- 0.1 (g/h)/kg H₂ loss rate
- 2 W in-leakage rate

*Reference system configuration, other layouts and options also being analyzed
# Key Assumptions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Reference Values</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sorbent</strong></td>
<td><strong>MOF-177</strong> J. Mater. Chem., 2007, 17, 3197-3204</td>
</tr>
<tr>
<td>Skeletal density</td>
<td>1534 kg/m(^3)</td>
</tr>
<tr>
<td>Crystallographic density</td>
<td>427 kg/m(^3) (1.56 cm(^3)/g pore volume)</td>
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<tr>
<td>Bulk density</td>
<td>342 kg/m(^3) (0.8 packing fraction)</td>
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<tr>
<td>Thermal conductivity</td>
<td>0.3 W/m.K</td>
</tr>
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</table>

**Conductive Support**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Reference Values</th>
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<tr>
<td><strong>40-PPI Al 2024 Foam</strong></td>
<td>2-wt%</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>2.4 W/m.K</td>
</tr>
<tr>
<td>Contact resistance</td>
<td>1000 W/m(^2)*K</td>
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</table>

**Thermal**

<table>
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<tr>
<td><strong>U-Tube Heat Exchanger</strong></td>
<td>Al 2024 alloy</td>
</tr>
<tr>
<td>Tube ID/OD</td>
<td>9.5/11.9 mm</td>
</tr>
<tr>
<td>Tube sheet thickness</td>
<td>0.9 mm</td>
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**Insulation**

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<td><strong>Multi-Layer Vac. Super Insulation</strong></td>
<td>Aluminized Mylar(^\circledR) sheets, Dacron(^\circledR) spacer</td>
</tr>
<tr>
<td>Layer density</td>
<td>28 cm(^{-1})</td>
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<tr>
<td>Density</td>
<td>59.3 kg/m(^3)</td>
</tr>
<tr>
<td>Pressure</td>
<td>10-5 torr</td>
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<tr>
<td>Effective conductivity</td>
<td>5.2x10(^{-4}) W/m.K</td>
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</table>

**Tank**

<table>
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<tr>
<td><strong>T700S Carbon Fiber</strong></td>
<td>Toray Carbon Fiber</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>2550 MPa</td>
</tr>
<tr>
<td>Density</td>
<td>1600 kg/m(^3)</td>
</tr>
<tr>
<td>L/D</td>
<td>3</td>
</tr>
<tr>
<td>Liner</td>
<td>2.4-mm thick Al 2024 alloy</td>
</tr>
<tr>
<td>Shell</td>
<td>3-mm thick Al 2024 alloy</td>
</tr>
</tbody>
</table>

**System**

<table>
<thead>
<tr>
<th>Parameter</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Miscellaneous weight</td>
<td>30 kg</td>
</tr>
<tr>
<td>Miscellaneous volume</td>
<td>25 L</td>
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</table>
Modeled Hydrogen Adsorption Isotherms

- H Furukawa, M Miller, M Yaghi (J. Mater. Chem. 2007, 3197 – 3204)
  - MOF-177, Zn$_4$O(1,3,5-benzenetribenzoate) crystals
  - Volumetric high-P gas adsorption measurements at SWRI®
  - Gravimetric high-P gas adsorption measurements at UCLA
  - Peak 75 g-H$_2$/kg surface excess at 77 K, 70 bar; 110 g/kg absolute

- Low-T data fitted to Dubinin-Astakhov (D-A) isotherm with m=2.5

Modeled Uptake at 100 K
- 62 g-H$_2$/kg peak excess adsorption at 100 bar
- 101 g-H$_2$/kg peak absolute adsorption at 100 bar
System Storage Capacity

- MOF-177 enhances the gas density by ~50% at 100 bar, but by <12% at 250 bar
  - At 250 bar, 93% of stored H₂ recoverable with 24% on MOF and 76% within pores and void space
  - At 60% volumetric efficiency, need 75 kg/m³ medium storage density to achieve 45 kg/m³ system capacity

- System cannot reach 6-wt% and 45 kg/m³ (meets revised 2010 targets)
  - 4.5 wt% peak gravimetric capacity at ~250 bar
  - 32.4 kg-H₂/m³ peak volumetric capacity at ~425 bar
Weight and Volume Distribution

- 4.5-wt% gravimetric and 31.2 kg/m$^3$ volumetric capacity at 250 bar
  - Medium and containment contribute almost equally to the overall weight
  - 58% volumetric efficiency which can be improved by reducing insulation at the expense of dormancy
Refueling and Discharge Dynamics

- 7.2 MJ on-board cooling duty, 32.2 kW average heat transfer rate
  - 82% of the cooling duty is due to heat of adsorption
- Options for thermal management during discharge
  - Constant Q (1.8 kJ/g of H₂ discharged), 2.9 kW, 10.1 MJ heat duty
  - Variable Q, heat supplied only if tank pressure drops below 4 bar, peak heat transfer rate can exceed 20 kW (difficult to implement)
Dormancy

- Dormancy: Function of amount of $\text{H}_2$ stored and P/T at start of the event
  - Minimum dormancy is 15.4 W.d (7.8 days at 2 W in-leakage rate)
  - Peak $\text{H}_2$ vent rate is 0.9 g/h/W (1.8 g/h at 2 W in-leakage rate)
  - 116.7 W.d for venting of all stored $\text{H}_2$
Off-Board Refueling with LN$_2$ Cooling

- Estimated electric energy for cryogenic cooling is 10 kWh/kg-H$_2$
  - Off-board cooling duty to precool H$_2$ to 100 K: 2.8 MJ/kg-H$_2$
  - On-board cooling duty to remove heat of adsorption and cool tank internals: 1.3 kW/kg-H$_2$
  - LN$_2$ requirement: ~10 kg-LN$_2$/kg-H$_2$
  - ~1 kWh/kg-LN$_2$ electric energy for distributed LN$_2$ production by air liquefaction (FOM of 0.205)
Adiabatic Refueling Option

- Adiabatic refueling with LH₂
  - On-board heat exchanger still needed but sized for discharge
- Optimum storage temperature (115 K) for maximum recoverable $N_{ex}$
  - Allowable $\Delta T$ increases with increase in storage T, $\Delta T = 0$ at 87K
  - Excess $N_{ex}$ decreases with increase in storage T
- Optimum storage T (100 K) for maximum system capacity is $< T$ at which recoverable $N_{ex}$ is maximum
  - 4.8 wt% maximum system gravimetric capacity
  - 32 kg-H₂/m³ maximum system volumetric capacity
Sensitivity Analysis (LN₂ Cooling Option)

- Need to double the absolute adsorption for 6 wt% and 45 kg/m³ capacities at 250 bar, 100 K with 50 K temperature swing
  - 50% increase in absolute adsorption for the revised 2015 targets
Regeneration of Ammonia Borane (AB) from BNH₂

- Constructed process flowsheets for PNNL regeneration chemistry using concepts of limited reactants and excess reagents
- Digestion of spent fuel with excess t-BuOH in THF (D1); co-product B(O-t-Bu)₃ reacted with excess PhOH to form B(OPh)₃ (D3)
- Reduction of B(OPh)₃ with excess MH in an amine medium (R1)
- Add excess NH₃ to form BH₃NH₃ (A1)
- Recover MH from MXsalt using excess H₂ in the presence of a base
- Two digestion approaches
  - Preserve BH bond in spent fuel
  - Recover residual H₂

Ref: Don Camaioni, Private Communication, PNNL (2008)
Process Energy for Regenerating 1 kg $\text{H}_2$ in AB

- Analysis assumptions
  - 85% thermal efficiency
  - 2 times stoichiometric amount of reagents
  - Reflux ratio of 0.5 in distillation steps

- Recovery of residual $\text{H}_2$ approach requires significantly more energy

<table>
<thead>
<tr>
<th>Process</th>
<th>Q, MJ</th>
</tr>
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<tbody>
<tr>
<td>Digestion</td>
<td></td>
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<tr>
<td>Distill THF solvent</td>
<td>27.6</td>
</tr>
<tr>
<td>Distill t-BuOH</td>
<td>34.5</td>
</tr>
<tr>
<td>Distill PhOH</td>
<td>40.8</td>
</tr>
<tr>
<td>Reduction</td>
<td></td>
</tr>
<tr>
<td>Distill tertiary/secondary amine</td>
<td>9.9</td>
</tr>
<tr>
<td>Distill PhOH</td>
<td>40.8</td>
</tr>
<tr>
<td>MH Formation</td>
<td></td>
</tr>
<tr>
<td>Distill hexane solvent</td>
<td>50.8</td>
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<tr>
<td>Total</td>
<td></td>
</tr>
<tr>
<td>0% heat integration</td>
<td>204.4</td>
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<tr>
<td>30% heat integration</td>
<td>143.1</td>
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</tbody>
</table>

**BH Bond Preservation Approach**

**H$_2$ Recovery approach**

<table>
<thead>
<tr>
<th>Process</th>
<th>Q, MJ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Digestion</td>
<td></td>
</tr>
<tr>
<td>Distill t-BuOH</td>
<td>103.5</td>
</tr>
<tr>
<td>Distill PhOH</td>
<td>61.1</td>
</tr>
<tr>
<td>Reduction</td>
<td></td>
</tr>
<tr>
<td>Distill tertiary/secondary amine</td>
<td>14.9</td>
</tr>
<tr>
<td>Distill PhOH</td>
<td>61.1</td>
</tr>
<tr>
<td>MH Formation</td>
<td></td>
</tr>
<tr>
<td>Distill hexane</td>
<td>76.2</td>
</tr>
<tr>
<td>Ammoniation</td>
<td></td>
</tr>
<tr>
<td>Liquefy NH$_3$</td>
<td>2.3</td>
</tr>
<tr>
<td>Cool $\text{H}_2$</td>
<td>0.1</td>
</tr>
<tr>
<td>Total</td>
<td></td>
</tr>
<tr>
<td>0% heat integration</td>
<td>316.8</td>
</tr>
<tr>
<td>30% heat integration</td>
<td>221.8</td>
</tr>
</tbody>
</table>

Argonne National Laboratory
Preliminary estimate of WTT efficiency for spent AB regeneration by PNNL scheme is 25 - 47% (BH bond preserved)

Recovery of residual $H_2$ approach lowers WTT efficiency by 5 – 7 percentage points

**Primary Energy Consumption**

- MH Formation: 11%
- Reduction: 11%
- Digestion: 22%
- Production: 55%

Total = 320 MJ/kg $H_2$, WTT = 37%
Regeneration of LiAlH₄

- UH/UNB scheme for regenerating LiAlH₄ from LiH, Al and H₂ in DME solvent at 100 bar and RT

  \[3LiH + Al(Ti) + 3/2 \text{H}_2 \rightarrow \text{Li}_3\text{AlH}_6\]
  \[\text{Li}_3\text{AlH}_6 + 2Al(Ti) + 3\text{H}_2 \rightarrow 3\text{LiAlH}_4\]

- Constructed a process flowsheet without depressurizing the reactor

- Energy requirement for regeneration depends on molar ratio (α) of DME to LiAlH₄
  - Recent tests at UNB confirm regeneration for \(\alpha = 5\), 58% WTT efficiency
  - Potential to achieve 60% WTT efficiency if \(\alpha\) reduced to ~4
Future Work
As lead for Storage System Analysis Working Group, continue to work with DOE contractors and CoEs to model, validate and analyze various developmental hydrogen storage systems.

Metal Hydrides
- On-board storage system for lithium alanate
- Regeneration of LiAlH$_4$ by UH/UNB schemes
- Regeneration of alane by organometallic and electrochemical routes

Sorbent Storage
- On-board system with spillover materials
- Further analysis of MOF system

Chemical Hydrogen
- On-board system for AB class of materials
- Fuel cycle efficiency of candidate materials and processes
- Joint report with TIAX on organic liquid carriers

Physical Storage
- Update cryo-compressed storage analysis (LLNL Gen3 system)
BACKUP SLIDES
Carbon Fiber Netting Analysis

- Benedict-Webb-Rubin equation of state to calculate amount of stored $\text{H}_2$ for 5.6 kg recoverable $\text{H}_2$ and 20-bar minimum pressure

- Carbon fiber translation strength
  - 82.5% for 5,000 psi $\text{cH}_2$
  - 63% for 10,000 psi

- 2.35 safety factor

- 5-mm HDPE liner, 1-mm glass fiber, and 10-mm foam end caps

- Construct optimal dome shape with geodesic winding pattern (i.e., along isotensoids)

- Geodesic and hoop windings in straight cylindrical section

- Iterate for tank diameter, CF thickness (non-uniform in end domes), given L/D

- Commercial data for BOP components

On-board System Gravimetric Capacity

Weight Distribution (%)
5,000 psi, 5.6 kg Usable H₂
- BOP 15%
- Foam 6%
- GF 6%
- CF 55%
- H₂ 6%
- Liner 12%

System Weight = 95 kg
Gravimetric Capacity = 5.9 wt%

Weight Distribution (%)
10,000 psi, 5.6 kg Usable H₂
- BOP 12%
- Foam 3%
- GF 4%
- CF 69%
- H₂ 5%
- Liner 7%

System Weight = 119 kg
Gravimetric Capacity = 4.7 wt%
On-board System Volumetric Capacity

Volume Distribution (%)
5,000 psi, 5.6 kg Usable H₂

- Liner 4%
- CF 10%
- Foam 2%
- BOP 2%
- H₂ 81%

System Volume = 320 L
Volumetric Capacity = 17.5 g H₂/L

Volume Distribution (%)
10,000 psi, 5.6 kg Usable H₂

- Liner 4%
- CF 23%
- Foam 3%
- BOP 2%
- H₂ 68%

System Volume = 222 L
Volumetric Capacity = 25.2 g H₂/L
Comparison of ANL Analysis with “Learning Demos”

DOE 2010 Targets: 6 wt%; 45 g/L

ANL Analysis 2 to 6 kg H₂

Gravimetric Capacity (wt%)
Electricity Consumption and WTT Efficiency (Pipeline Delivery)

<table>
<thead>
<tr>
<th>Compression(^{(a)})</th>
<th># of Stages</th>
<th>Isentropic efficiency</th>
<th>Electricity (kWh/kg)</th>
<th>WTT efficiency(^{(b)})</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(_i) (bar)</td>
<td>P(_f) (bar)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>70</td>
<td>3</td>
<td>88%</td>
<td>0.6</td>
<td>Central plant, (\Delta P = 50) bar</td>
</tr>
<tr>
<td>20</td>
<td>180</td>
<td>5</td>
<td>65%</td>
<td>1.5</td>
<td>Forecourt</td>
</tr>
<tr>
<td>180</td>
<td>425</td>
<td>2</td>
<td>65%</td>
<td>0.6</td>
<td>Forecourt</td>
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<tr>
<td>180</td>
<td>850</td>
<td>3</td>
<td>65%</td>
<td>1.1</td>
<td>Forecourt</td>
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<tr>
<td>20</td>
<td>425</td>
<td>7</td>
<td>65 - 88%</td>
<td>2.7</td>
<td>58.0%</td>
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<tr>
<td>20</td>
<td>850</td>
<td>8</td>
<td>65 - 88%</td>
<td>3.3(^{(c)})</td>
<td>56.1%</td>
</tr>
</tbody>
</table>

Notes:

a) Compressor mechanical efficiency = 97%, motor efficiency = 90%
b) \(\text{H}_2\) produced by SMR central plant, electricity source from U.S. grid 2015, inclusive of 8% transmission loss
c) Includes 0.14 kWh/kg for precooling from 25\(^\circ\)C to -40\(^\circ\)C
## Life Cycle Greenhouse Gas Emissions
(Pipeline Delivery, g/kg H₂)

### 5,000 psi on-board storage

<table>
<thead>
<tr>
<th></th>
<th>VOC</th>
<th>CO</th>
<th>NOₓ</th>
<th>PM₁₀</th>
<th>SOₓ</th>
<th>CH₄</th>
<th>N₂O</th>
<th>CO₂</th>
<th>GHGs</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>H₂ Production</strong></td>
<td>1.55</td>
<td>3.62</td>
<td>7.34</td>
<td>2.20</td>
<td>2.71</td>
<td>29.93</td>
<td>0.06</td>
<td>14,068</td>
<td>14,774</td>
</tr>
<tr>
<td><strong>H₂ Storage</strong></td>
<td>0.12</td>
<td>0.35</td>
<td>1.33</td>
<td>1.60</td>
<td>2.91</td>
<td>1.76</td>
<td>0.02</td>
<td>1,259</td>
<td>1,567</td>
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<tr>
<td><strong>H₂ Distribution</strong></td>
<td>0.05</td>
<td>0.26</td>
<td>0.13</td>
<td>0.04</td>
<td>0.05</td>
<td>0.17</td>
<td>0.01</td>
<td>155</td>
<td>497</td>
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<tr>
<td><strong>Total:</strong></td>
<td>1.71</td>
<td>4.23</td>
<td>8.80</td>
<td>3.84</td>
<td>5.68</td>
<td>31.86</td>
<td>0.08</td>
<td>15,482</td>
<td>16,838</td>
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### 10,000 psi on-board storage

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<tr>
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<th>CO</th>
<th>NOₓ</th>
<th>PM₁₀</th>
<th>SOₓ</th>
<th>CH₄</th>
<th>N₂O</th>
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<th>GHGs</th>
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<td>29.93</td>
<td>0.06</td>
<td>14,068</td>
<td>14,774</td>
</tr>
<tr>
<td><strong>H₂ Storage</strong></td>
<td>0.19</td>
<td>0.57</td>
<td>2.17</td>
<td>2.62</td>
<td>4.76</td>
<td>2.87</td>
<td>0.03</td>
<td>2,056</td>
<td>1,953</td>
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<tr>
<td><strong>H₂ Distribution</strong></td>
<td>0.05</td>
<td>0.26</td>
<td>0.13</td>
<td>0.04</td>
<td>0.05</td>
<td>0.17</td>
<td>0.01</td>
<td>155</td>
<td>579</td>
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<tr>
<td><strong>Total:</strong></td>
<td>1.79</td>
<td>4.45</td>
<td>9.64</td>
<td>4.85</td>
<td>7.53</td>
<td>32.98</td>
<td>0.10</td>
<td>16,279</td>
<td>17,306</td>
</tr>
</tbody>
</table>
Summary

- Dome shape and carbon fiber thickness were determined by netting analysis
- Minimum tank pressure affects system gravimetric and volumetric capacities while tank geometry (L/D) affects only gravimetric capacity
- WTT efficiency is within six percentage points of DOE target of 60%
- For 5.6 kg recoverable H₂ and L/D = 3

<table>
<thead>
<tr>
<th>H₂ Tank Pressure (bar)</th>
<th>Minimum Pressure (bar)</th>
<th>Gravimetric Capacity (wt%)</th>
<th>Volumetric Capacity (g/L)</th>
<th>Electricity (kWh/kg)</th>
<th>WTT Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>20</td>
<td>5.9</td>
<td>17.5</td>
<td>2.7</td>
<td>58.0</td>
</tr>
<tr>
<td>350</td>
<td>4</td>
<td>6.2</td>
<td>18.5</td>
<td>2.7</td>
<td>58.0</td>
</tr>
<tr>
<td>700</td>
<td>20</td>
<td>4.7</td>
<td>25.2</td>
<td>3.3</td>
<td>56.1</td>
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<tr>
<td>700</td>
<td>4</td>
<td>4.8</td>
<td>26.0</td>
<td>3.3</td>
<td>56.1</td>
</tr>
</tbody>
</table>
H₂ Storage as Alane Slurry

- Investigated several methods of storing alane in powder and liquid forms and selected slurry for initial evaluation
- Pros and cons of storing alane as slurry
  - Pros: heat transfer, easier refueling, liquid infrastructure, practical
  - Cons: reduced material capacity, added difficulty in recycling spent fuel

<table>
<thead>
<tr>
<th>Component</th>
<th>Key Assumptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel Tank</td>
<td>Volume-exchange concept, 10% ullage, 5.6 kg usable H₂</td>
</tr>
<tr>
<td>AlH₃ Slurry</td>
<td>70 wt% AlH₃ in light mineral oil</td>
</tr>
<tr>
<td>Heat Transfer Fluid</td>
<td>XCELTERM®</td>
</tr>
<tr>
<td>Dehydrogenation Reactor</td>
<td>Slurry on tube side, HTF on shell side, s/d=1.1, slurry at 100 bar, HTF at 3 bar, 1.6 g/s peak H₂ consumption in FCS</td>
</tr>
<tr>
<td>AlH₃ Dehydrogenation Kinetics</td>
<td>Avrami-Erofejev rate expression</td>
</tr>
<tr>
<td>HEX Burner</td>
<td>50 kWt, non-catalytic, HTF pumped to stack P, 100°C approach T, 5% excess air</td>
</tr>
<tr>
<td>H₂ Ballast Tank</td>
<td>100 bar, 75°C, AL-2219-T81 alloy tank, 2.25 SF</td>
</tr>
<tr>
<td>Recuperator, H₂ Cooler,</td>
<td>5 - 50°C approach T</td>
</tr>
<tr>
<td>Spent Slurry Cooler</td>
<td></td>
</tr>
</tbody>
</table>
Assessment of Results

- Under optimum conditions, ~80% of H₂ stored in slurry is available for use in fuel cell system.
- Usable gravimetric capacity <4.25 wt% H₂, ~75% gravimetric efficiency
- Usable volumetric capacity ~50 g-H₂/l, 73% volumetric efficiency

Data Needs

- Preparation of 70-wt% AlH₃ slurry, effect of particle size distribution, surfactants, etc
- DeH₂ kinetics of AlH₃ slurry, fluid dynamics of slurry in micro-channel HX
- H₂ recovery from fuel tank

### Data Needs Table

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intrinsic Material Capacity</td>
<td>10.0</td>
<td>g-H₂/g-AlH₃ %</td>
<td>Variable ( T_{HTF} )</td>
</tr>
<tr>
<td>( \text{H}_2 ) Capacity in Slurry</td>
<td>7.0</td>
<td>g-H₂/g-slurry %</td>
<td>Fixed LHSV</td>
</tr>
<tr>
<td>Recoverable ( \text{H}_2 ) Capacity</td>
<td>6.9</td>
<td>g-H₂/g-slurry %</td>
<td>( \eta \text{DC} ): 82.8-93.1 %</td>
</tr>
<tr>
<td>Available ( \text{H}_2 ) Capacity</td>
<td>6.3</td>
<td>g-H₂/g-slurry %</td>
<td>( \eta \text{SU} ): 84.7-91.3 %</td>
</tr>
<tr>
<td>Usable ( \text{H}_2 ) Capacity</td>
<td>5.6</td>
<td>g-H₂/g-slurry %</td>
<td>0.5-4.2</td>
</tr>
<tr>
<td>Usable Gravimetric Capacity</td>
<td>4.2</td>
<td>g-H₂/g-system %</td>
<td>5.9-50.0</td>
</tr>
<tr>
<td>Usable Volumetric Capacity</td>
<td>49.8</td>
<td>g-H₂/L-system</td>
<td>0-0.3</td>
</tr>
<tr>
<td>Peak ( \text{H}_2 ) Loss at 25°C</td>
<td>0.3</td>
<td>g-H₂/h</td>
<td>0-7.7</td>
</tr>
<tr>
<td>Peak ( \text{H}_2 ) Loss at 50°C</td>
<td>7.7</td>
<td>g-H₂/h</td>
<td>0-7.7</td>
</tr>
</tbody>
</table>
Regeneration of Alane - ANL Reference Flowsheet

- Form AlH₃ as adduct to TMA in ether in the presence of LiAlH₄.

\[ n_1 \text{Al} + \frac{3n_1}{2} \text{H}_2 + n_2 \text{N(CH}_3\text{)}_3 \xrightarrow{\text{catalyst}} \text{AlH}_3 \cdot (\text{N(CH}_3\text{)}_3)_n \]

- Displace TMA from TMAA in ether by TEA (transamination).

\[ (\text{AlH}_3)_{n_1} \cdot (\text{N(CH}_3\text{)}_3)_{n_2} + n_2 \text{N} \xrightarrow{\text{TEA}} (\text{AlH}_3)_{n_1} \cdot \left( \text{N} \right) + n_2 \text{N(CH}_3\text{)}_3 \]

- Decompose TEAA in presence of LiAlH₄ (thermal decomposition).

\[ (\text{AlH}_3)_{n_1} \cdot \left( \text{N} \right) \xrightarrow{\text{catalyst}} n_1 (\text{AlH}_3)_x + n_2 \text{N} \]

- For high conversion, use excess amounts of reagents.
  - H₂ Stoichiometry: \( \Phi_{H_2} \)
  - TMA Stoichiometry: \( \Phi_{TMA} \)
  - TEA Stoichiometry: \( \Phi_{TEA} \)

Ref: Murib and Horvitz, U.S. Patent 3,642,853 (1972)
FCHtool Analysis: Preliminary WTT Efficiency

- Without credit for availability of low-grade heat, the WTT efficiency is 40.5% ($\Phi_{H2}=10$, $\Phi_{TMA}=1.4$, $\Phi_{TEA}=1.4$).
  - Q: 71.9 MJ/kg-H$_2$, E: 3.6 kWh/kg-H$_2$

- A single-variable parametric analysis indicates that WTT efficiency is most sensitive to the availability of low-grade waste heat.

- We are working with BNL to verify the process steps and determine the operating conditions.

Q: MJ/kg-H$_2$, E: kWh/kg-H$_2$

<table>
<thead>
<tr>
<th>Process</th>
<th>T °C</th>
<th>P bar</th>
<th>Q MJ</th>
<th>E kWh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compress H$_2$ from SMR</td>
<td>70</td>
<td>30</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>Compress circulating H$_2$</td>
<td>70</td>
<td>30</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>Distill TMA</td>
<td>65</td>
<td>5</td>
<td>28.6</td>
<td></td>
</tr>
<tr>
<td>Distill ether</td>
<td>25</td>
<td>0.3</td>
<td>22.9</td>
<td>1.1</td>
</tr>
<tr>
<td>Decompose TEAA</td>
<td>50</td>
<td>0.2</td>
<td>20.2</td>
<td>1.4</td>
</tr>
<tr>
<td>Vacuum dry AlH$_3$</td>
<td>50</td>
<td>&lt;10$^{-1}$</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>71.9</td>
<td>3.6</td>
</tr>
</tbody>
</table>
Hydrogen Storage Capacities

- Cryo-compressed option with AL shell can meet the gravimetric target (but not volumetric)
- Alane slurry option may meet the volumetric target (but not gravimetric)

- ANL modeling results for various hydrogen storage systems
- System capacities based on recoverable H₂ delivered to fuel cell
Well-To-Tank Efficiency

**Storage**
- LCH₂: Hydrogenation stages
- H₂: Hydrogen pressure
- Alane: Waste heat utilization
- LH₂: Liquefaction technology
- AB: Heat recovery
- SBH-EL: Electrolysis with/without H₂ assist
- SBH-MR: Metal reduction technology

**1-stage** 100%
**3-stage** 0%

**Current** 0%
**Future** 30%

**DOE Target**

**WTT Efficiency, %**

Option 1 vs. Option 2

Argonne National Laboratory