Compact (L)H₂ Storage with Extended Dormancy in Cryogenic Pressure Vessels

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This presentation does not contain any proprietary or confidential information
Overview

Timeline
• Start date: October 2004
• End date: September 2011
• Percent complete: 70%

Budget
• Total project funding
  – DOE: $4.5M
• Funding for FY08:
  – $1.2M
• Funding for FY09:
  – $2.25M

Barriers
• A. Volume and weight
• O. Hydrogen boil-off

Targets
• 2010 DOE volume target
• 2010 DOE weight target

Partners
• CRADA with BMW
• CRADA with Structural Composites Industries (SCI)
Relevance: Cryogenic pressure vessels offer technical potential to exceed 2010 H₂ storage goals, and approach 2015.
Approach: Build systems exceeding 2010 volume/weight targets in collaboration with industrial partners understand fundamental potential of both system & H₂ behavior

- Fabricate third generation cryotank storing \(>45 \text{ kg H}_2/\text{m}^3\) system
- Achieve \(>1\) week of dormancy
- Understand dormancy impacts of para-ortho conversion
- Investigate composite vessel impacts on vacuum quality
- Demonstrate adequate cycle life, (cryogenic shock, high pressure)
- Cryogenic vessel development and burst testing
- Explore superliquid \(H_2\) \((\rho>70 \text{ kgH}_2/\text{m}^3)\)
Collaborations:
We have entered into cooperative research & development (CRADA) agreements with an automaker and pressure vessel manufacturer

• **CRADA with BMW** collaboration has been intensifying over 3 years. CRADA finalized June 2008 to investigate vacuum stability, conduct cryogenic pressure cycling, and study conversion to *ortho*-H$_2$. BMW provides great automotive focus to our experimental and demonstration efforts.

• **CRADA with Structural Composites Industries (SCI):** Jan. 2009 CRADA formalized a longstanding relationship in high pressure and H$_2$ work of over two decades. Using LLNL’s thermal/mechanical analysis capability and H$_2$ experience as well as SCI’s in-depth composite cylinder design & manufacturing expertise to develop highly efficient and lower cost pressure vessels designed specifically for cryogenic H$_2$ storage.
We have refined our 3rd generation system to meet/exceed 2010 volume and weight targets

- Lighter, smaller vessel (4000 psi)
- Shorter, stronger boss (18,000+psi)
- Longer conduction paths (H₂ lines)
- Fewer support rings (3 to 2)
- Vacuum thickness cut by 2/3
- Less MLI layers in complex areas
- 3kW internal heat exchanger (BMW)
- LH₂ fill valve outside vacuum jacket

- Proof tested to 6600 psi
- Fabrication/integration complete
- System cryoshocked & leak tested
- Onboard dormancy test scheduled
3rd generation cryotank & vacuum jacket saves 25 kg & 70 liters
Storing 7.4 wt% H₂ at 45.2 kg H₂/m³

<table>
<thead>
<tr>
<th>Weight (kg)</th>
<th>wt%H₂</th>
<th>Volume (L)</th>
<th>kgH₂/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>4000 psi vessel+boss</td>
<td>60.9</td>
<td>14.9</td>
<td>179</td>
</tr>
<tr>
<td>Steel vacuum jacket</td>
<td>57.1</td>
<td>8.3</td>
<td>225.4</td>
</tr>
<tr>
<td>Ancillary components</td>
<td>16</td>
<td>7.4</td>
<td>11</td>
</tr>
</tbody>
</table>
3.5 day calculated dormancy of 10.7 kgLH₂ (full) in 3rd gen vessel (~7 watts, 4000 psi, H₂ heat capacity only)
6.5 day calculated dormancy if 80% full w/LH$_2$
(7 Watts, 4000 psi, H$_2$ heat capacity only)

![Graph showing internal energy vs. hydrogen density and temperature relationships.](image-url)
Vessel warming combined with (theoretical) conversion to ortho-H₂ could extend dormancy of 8.55 kg LH₂ (80% full) to 11+ days.
We will assess *para*-\(H_2\) to *ortho*-\(H_2\) conversion by experiments warming \(H_2\) outside two-phase LH\(_2\) region complemented by a surrogate test with He if warranted.

- Measure Weight, Pressure, & Temperature
- Integrated (20-100K) test and/or fixed T
- Results interpretable w/o vessel corrections
- Aggregate *para*-orth*o* conversion impact directly measured by He surrogate test
- Full scale (163 L) test & expt. range (T,P, \(\rho\))
- 10 ksi vessel w/ coolant & vacuum jacket
- Hardware capability to confirm/reverse *para*-orth*o* conversion at automotive scale
- Collaborating with BMW on experimental strategy, methodology
- Exp’t simulations use real properties of all \(L(H_2)\) states, phases
Outgassing experiments on as received 1 liter composite vessel: H$_2$O majority component, hydrocarbons not improved by baking

**Table**

<table>
<thead>
<tr>
<th>Compound (and boiling point)</th>
<th>Concentration in parts per billion by vol.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ambient</td>
</tr>
<tr>
<td></td>
<td>First test No cycling</td>
</tr>
<tr>
<td>Water (100°C)</td>
<td>80,000</td>
</tr>
<tr>
<td>Acetaldehyde (20.2°C)</td>
<td>23</td>
</tr>
<tr>
<td>Acetone, (56.5°C)</td>
<td>85</td>
</tr>
<tr>
<td>Ethanol, (78.4°C)</td>
<td>87</td>
</tr>
<tr>
<td>Isopropyl alcohol (83.6°C)</td>
<td>23</td>
</tr>
<tr>
<td>Trichloroethylene (87.2°C)</td>
<td>6.2</td>
</tr>
<tr>
<td>1-propanol (97.1°C)</td>
<td>360</td>
</tr>
<tr>
<td>Toluene (110.6°C)</td>
<td>2.7</td>
</tr>
<tr>
<td>Acetic acid butyl ester (126°C)</td>
<td>2900</td>
</tr>
<tr>
<td>Ethyl benzene (136°C)</td>
<td>4.7</td>
</tr>
<tr>
<td>Xylenes, total (140°C)</td>
<td>20</td>
</tr>
<tr>
<td>Styrene (145°C)</td>
<td>5.9</td>
</tr>
<tr>
<td>2-heptanone (151°C)</td>
<td>39</td>
</tr>
<tr>
<td>1, 3, 5 trimethylbenzene (164°C)</td>
<td>1.7</td>
</tr>
<tr>
<td>1, 2, 4 trimethylbenzene (169°C)</td>
<td>1.9</td>
</tr>
<tr>
<td><strong>Total hydrocarbons</strong></td>
<td>321</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>80,321</td>
</tr>
</tbody>
</table>

**Dormancy test cut short by valve leak into vacuum**

**Oven in pressure cell**

**1 liter vessel under vacuum in oven**
Outgassing experiments have been planned in collaboration with BMW to separate pressure cycling (Ar) from thermal effects and investigate vessel processing and surface treatments

- **Pre-bake vessels to 100°C:** Determine if H$_2$O can be essentially eliminated.

- **Cycle vessels slowly or with cooled gas:** Keeping vessels at ambient temperature (or below) better represents expected onboard conditions. Measurements after 10 & 100 pressure cycles

- **Outgassing from vacuum cured vessels with/without UV coating:** Investigate processing effects on outgassing, and potential cycling effects on coatings
A 4000 psi vessel identical to the 3rd generation storage system will be cryogenically cycle tested

- High & Low Pressure at Cryogenic T (20-100 Kelvin)
- Vacuum jacketed vessel warmed internally (2-5 kW)
- Ultrasound characterization after hundreds of cycles
We will acquire a high pressure cryogenic H$_2$ fueling capability

- **We currently fill at low pressure** from a conventional LH$_2$ storage vessel
- **A high pressure LH$_2$ pump** offers rapid single phase refueling without boiloff
- **Site Permission and Utilities granted**
  Will also serve for high pressure cryogenic H$_2$ testing (e.g. para-ortho)
- **We plan to explore densities beyond LH$_2$**
  to meet DOE’s ultimate storage goals. Pressurized LH$_2$ is up to $\sim$25% more compact and needs to be studied, tested, and ultimately demonstrated onboard
Pressure vessel designs can be improved by accounting for vessel usage

**Current automotive \( \text{H}_2 \) vessel**
- Filled with \( \text{H}_2 \) at up to 80°C
- Service pressure: 5000 psi
- Fill pressure: 6250 psi
- Burst pressure: 11,250 psi

**Future automotive cryo-\( \text{H}_2 \) vessel**
- Filled only with cold \( \text{H}_2 \)
- Service pressure: 5000 psi
- Fill pressure: 5000 psi
- Burst pressure: 9,000 psi
Cryogenics offers dramatic safety opportunities: cooling H₂ removes far more burst energy than reducing pressure.
Cryogenic pressure vessel systems will be less expensive than ambient compressed H₂ storage for fundamental reasons

- **Compact LH₂ (71 vs. 23-39 kgH₂/m³)** cuts carbon fiber (per kg H₂ stored)
- **Pressurized LH₂** even more compact (‘top off’ potential up to 88 kgH₂/m³)
- **Cryogenic H₂** in protective vacuum jacket may enable glass fibers to provide more value than carbon
- **Very low burst energy, no fast fill overpressure, secondary containment** of vacuum jacket could justify lower burst pressure ratio (Pburst/Pdormancy), improving pressure vessel mass, volume, and structural efficiency

Source: TIAAX

- SCI cryotank (350 bar) cost estimates (per kgH₂ stored):
  - 30% less vs. ambient 350 bar
  - 60% less than 700 bar
Future work: after demonstrating superior weight and volume of cryogenic pressure vessels and adequate cycle life, study a spectrum of H$_2$ states and flexible pressure vessel systems

- **Pressurized LH$_2$** offers fertile ground for achieving ultimate DOE storage goals but requires new refueling strategies.

- **Normal LH$_2$** if our *para-ortho* transition experiments measure slow kinetics then we plan to investigate “normal” LH$_2$ (25% *para*) in cryotanks, anticipating liquefaction capital cost & energy savings.

- **Multiple Volume Vessels** offer flexible blend of capacity, weight, cost, shape, and dormancy over a single state H$_2$ storage vessel, but multiple states of onboard H$_2$ adds complexity.
Summary

- **Cryogenic pressure vessels can exceed 2010 DOE storage targets** for weight and volume, with promising dormancy & cost relative to conventional LH$_2$ tanks and ambient pressure vessels.

- **In collaboration with industrial partners, we are addressing interactions between pressure, temperature, and materials.** Outgassing, cryogenic cycling, and cryogenic burst tests.

- **We are investigating fundamental operational aspects at full scale:** internal heat exchange, dormancy and dormancy recovery, para-ortho conversion, higher density (pressurized) refueling.

- **Safety advantages of cryogenic pressure vessels are yet to be assessed.** Very low burst energy, fill vs. dormancy safety factor, protective vacuum jacket, material strength at cryogenic temps.