Cryo-Compressed Hydrogen Storage: Performance and Cost Review

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Contributors to the study
- LLNL: Gen2 and Gen3 design data, Aceves and Berry
- Argonne: On-board and off-board performance modeling, bill of materials, off-board cost modeling
- TIAX: On-board cost modeling

Results
- Gravimetric and volumetric capacity
- Refueling dynamics
- Discharge dynamics
- Dormancy and boil-off losses
- WTT efficiency
- Greenhouse gas emissions
- Storage system cost
- Refueling and ownership cost
LLNL Gen3 Cryo-Compressed H₂ Storage System

Modifications from Gen2
- Reduced insulation
- Better packaging
- Vacuum valve box eliminated
- In-tank heat exchanger
- 4000-psi pressure vessel rating

- System Volume: 235 L
  - Storage: 151 L
  - Vessel: 224 L
  - Ex-Vessel: 11 L
  - V Efficiency: 64.3%

- System Weight: 144.7 kg
  - LH₂ Stored: 10.7 kg
  - CH₂ Stored: 2.8 kg
  - Vessel: 122.7 kg
  - Ex-Vessel: 22.0 kg

- System Volumetric Capacity
  - 44.5 kg/m³: 1.5 kWh/L
  - LH₂ density: 70.9 kg/m³ at 20.3 K, 1 atm
  - CH₂ density: 18.8 kg/m³ at 300 K, 272 atm

- System Gravimetric Capacity
  - 7.1 wt%: 2.3 kWh/kg
System Analysis of Physical Storage Systems

- Benedict-Webb-Rubin equation of State: REFPROP coupled to GCtool
- Carbon Fiber Netting Analysis
  - Algorithm for optimal dome shape with geodesic winding pattern (i.e., along iso-tensoids)
  - Algorithm for geodesic and hoop windings in cylindrical section
- Fatigue Analysis of Type 3 Tanks
  - Algorithm for residual compressive stresses introduced by auto-frettage, pre- and post-proof load distribution between liner and CF
  - Unloading of residual stresses under cryogenic conditions
  - S/N curves for Al 6061-T6 alloy, non-zero mean stresses
  - 5500 pressure cycles at 1.25 NWP (SAE J2579)
- Dynamic models for gaseous/liquid refueling, discharge, dormancy
- Models for off-board analysis
  - FCHtool and GREET for greenhouse gas emissions
  - H2A for pathway analysis
  - HDSAM for scenario analysis
Gravimetric and Volumetric Capacities

- 5.6-kg system meets 2015 targets
  - Gravimetric capacity > 9% with aluminum shell but higher cost
  - Maximum CF load share limited to 85% at cryogenic T, 276 bar
  - Liner heavier than CF
  - Insulation accounts for 15% of total volume

Weight Distribution

Volume Distribution

5.6-kg Recoverable H₂ System
Storage Capacity: Compressed Hydrogen Option

- Refueling with compressed H$_2$ at 300 K
- Adiabatic refueling assuming that liner, CF and gas are isothermal during refueling (maximum possible capacity)
- Tank refueled to 272-atm (4000 psi) peak pressure
- 4 atm initial pressure, variable initial temperature
- Additional storage capacity with pre-cooled H$_2$ and refueling to higher than design pressure

![Graph showing hydrogen charged vs. initial temperature with storage capacity values]
Refueling with LH2: Cryo-compressed Option

- Refueling with high-pressure LH$_2$ pump at 25% above tank pressure
- Storage capacity function of final pressure, 5.7 kg for P = 37.7 atm
- Depending on initial T and H$_2$ charged, final P may be less than 4 atm

**Initial conditions**
P=4 atm, T=50 K

- **Gas**
m < 0.4 kg
- **2-Phase**
0.4 < m < 5.4 kg
- **Sub-cooled Liquid**
5.4 < m < 6.5 kg
- **Supercritical Fluid**
m > 6.5 kg
Storage Capacity: Cryo-compressed Option

- Storage capacity is a function of initial temperature.
  - 6.4 kg recoverable for initial T = 50 K, P = 4 atm.

Storage V: 80.8 L
Final P: 272 atm
Max H₂ Density: 71 kg/m³
Discharge Dynamics: Cryo-compressed Option

- Heat supplied to maintain 4-atm minimum delivery pressure

- Initial conditions:
  - $P = 272$ atm
  - $T = 34.3$ K
  - $m = 6.6$ kg

- 1.6 g/s full flow rate of $H_2$

- Max $Q = 3$ kW
Discharge Behavior: Cryo-compressed Option

- Total heat load is a function of initial temperature
  - 2.3 MJ for 34.3 K initial T, 6.4 kg stored H₂

![Graph showing discharge behavior](image)

- Storage V: 80.8 L
- Initial P: 272 atm
- Final P: 4 atm
- Max Q: 3 kW

- Max H₂ Density: 71 kg/m³
Dormancy and Hydrogen Loss Rate

- No loss of hydrogen after tank reaches 323 K, tank 30% full
- Difficult to always meet the targets of 0.1/0.05 g/h/kg-H₂ with 5 W reference heat in-leakage rate
- No H₂ loss with minimal daily driving (LLNL paper)
CH$_2$ to cCH$_2$ Transition

Three complete charge-discharge cycles needed to reach 71 kg/m$^3$ hydrogen density
The high volume (500,000 units/year) manufactured cost for all H₂ storage systems is estimated from raw material prices, capital equipment, labor, and other operating costs.

**BOP Bottom-up Costing Methodology**
- Develop Bill of Materials (BOM)
- Obtain raw material prices from potential suppliers
- Develop production process flowchart for key subsystems and components
- Estimate manufacturing costs using TIAx cost models (capital equipment, raw material price, labor rates)

<table>
<thead>
<tr>
<th>Tank</th>
<th>BOP (Purchased)</th>
<th>Assembly and Inspection</th>
<th>Cryo-compressed Hydrogen Storage System Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liner</td>
<td>Fill Port</td>
<td>Vacuum Processing</td>
<td></td>
</tr>
<tr>
<td>Composite Layers</td>
<td>Regulator</td>
<td>QC of finished components</td>
<td></td>
</tr>
<tr>
<td>MLVI Wrap</td>
<td>Valves</td>
<td>System assembly</td>
<td></td>
</tr>
<tr>
<td>Vacuum Shell</td>
<td>Heat Exchanger</td>
<td>QC of system</td>
<td></td>
</tr>
<tr>
<td>Bosses</td>
<td>Sensors</td>
<td></td>
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</tr>
</tbody>
</table>

We modeled material and manufacturing process costs for the cryo-compressed tank, while the BOP is assumed to be purchased.
The carbon fiber layer is the most expensive single component and accounts for about 25% and 35% of the base case 5.6 and 10.4 kg systems costs.

The BOP components account for about 30% and 25% of the base case 5.6 and 10.4 kg system costs, respectively.
### WTT Efficiency

- WTT efficiency = 41.1% (LH₂ refueling)
- Assumptions

<table>
<thead>
<tr>
<th>Process/Process Fuels</th>
<th>Nominal Value</th>
<th>Source/Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electricity production</td>
<td>32.2% thermal efficiency</td>
<td>EIA projected U.S. grid for 2015, inclusive of 8% transmission loss from power plant to user site</td>
</tr>
<tr>
<td>North American natural gas production</td>
<td>93.5% efficiency</td>
<td>GREET data</td>
</tr>
<tr>
<td>H₂ production by SMR</td>
<td>73% efficiency</td>
<td>H2A</td>
</tr>
<tr>
<td>H₂ Liquefaction</td>
<td>8.2 kWh/kg</td>
<td>HDSAM, 150 tons/day liquefier</td>
</tr>
<tr>
<td>Liquid H₂ (LH₂) delivery by truck</td>
<td>284 km round trip</td>
<td>HDSAM</td>
</tr>
<tr>
<td>Truck capacity</td>
<td>4300 kg</td>
<td>HDSAM</td>
</tr>
<tr>
<td>Boil-off losses</td>
<td>9.5%</td>
<td>HDSAM: liquefaction 0.5%, storage 0.25%/day, loading 0.5 %, unloading 2%, cryopump 3%</td>
</tr>
<tr>
<td>Vehicle refueling with LH₂</td>
<td>2 kg/min; 80% isentropic efficiency</td>
<td>BMW LH₂ pump data</td>
</tr>
<tr>
<td>Greenhouse gas emissions</td>
<td>range</td>
<td>Emission factors data from GREET</td>
</tr>
</tbody>
</table>
Off-Board Cost and Performance Summary

- Hydrogen production cost is dominated by fuel cost
  - Central SMR ~ $1.6/kg (77% fuel, 14% capital)
  - Central electrolysis ~ $3.8/kg (6 cents/kWh, 80% fuel, 15% capital)

- Hydrogen delivery cost is dominated by capital cost
  - ~ $6.1/kg for 2% market (60% capital, 10% fuel)
  - ~ $3.2/kg for > 15% market (55% capital, 18% fuel)

- Ownership cost
  - ~12 - 17 cents/mile (15%/2% market) for NG/standard grid scenario
  - ~16 - 21 cents/mile (15%/2% market) for electrolysis/renewable
  - ~10 cents/mile for conventional gasoline ICEV ($3/gal untaxed)

- WTT efficiency: 36 - 41%

- GHG emissions
  - ~ 0.31 - 0.37 kg/mile for NG/standard grid scenario
  - ~ 0 kg/mile for electrolysis/renewable scenario
  - ~ 0.35 kg/mile for gasoline ICEV (31 mpg fuel economy)
Summary and Conclusions

- Cryo-compressed: 71 kg/m³ max density or 272 atm max pressure
- Results given as single data points, consult references for range, sensitivity and background
- Metrics cover all DOE targets for on-board and off-board storage
- Some results vetted, others for developmental materials and processes

<table>
<thead>
<tr>
<th>Performance and Cost Metric</th>
<th>Units</th>
<th>ch₂ 350-T4</th>
<th>ch₂ 700-T4</th>
<th>LH₂</th>
<th>CcH₂</th>
<th>MOF-177</th>
<th>2010 Targets</th>
<th>2015 Targets</th>
<th>Ultimate Targets</th>
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</thead>
<tbody>
<tr>
<td>Tank</td>
<td></td>
<td>1-Tank</td>
<td>1-Tank</td>
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<tr>
<td>Usable Storage Capacity (Nominal)</td>
<td>kg·H₂</td>
<td>5.6</td>
<td>5.6</td>
<td>5.6</td>
<td>5.6</td>
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<tr>
<td>Usable Storage Capacity (Maximum)</td>
<td>kg·H₂</td>
<td>5.6</td>
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<td>6.6</td>
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<tr>
<td>System Gravimetric Capacity</td>
<td>wt%</td>
<td>5.5</td>
<td>5.2</td>
<td>5.6</td>
<td>5.5-9.2</td>
<td>4.0</td>
<td>4.5</td>
<td>5.5</td>
<td>7.5</td>
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<tr>
<td>System Volumetric Capacity</td>
<td>kg·H₂/m³</td>
<td>17.6</td>
<td>26.3</td>
<td>23.5</td>
<td>41.8-44.7</td>
<td>34.6</td>
<td>28</td>
<td>40</td>
<td>70</td>
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<tr>
<td>Storage System Cost</td>
<td>$/kWh</td>
<td>15.5</td>
<td>18.9</td>
<td>TBD</td>
<td>12</td>
<td>18</td>
<td>4</td>
<td>2</td>
<td>TBD</td>
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<tr>
<td>Fuel Cost</td>
<td>$/gge</td>
<td>4.2</td>
<td>4.3</td>
<td>TBD</td>
<td>4.80</td>
<td>4.6</td>
<td>2-3</td>
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<tr>
<td>Cycle Life (1/4 tank to Full)</td>
<td>Cycles</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>5500</td>
<td>5500</td>
<td>1000</td>
<td>1500</td>
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<tr>
<td>Minimum Delivery Pressure, FC/ICE</td>
<td>atm</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>3-4</td>
<td>4</td>
<td>4/35</td>
<td>3/35</td>
<td>3/35</td>
</tr>
<tr>
<td>System Fill Rate</td>
<td>kg·H₂/min</td>
<td>1.5-2</td>
<td>1.5-2</td>
<td>1.5-2</td>
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<td>1.5-2</td>
<td>1.2</td>
<td>1.5</td>
<td>2.0</td>
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<tr>
<td>Minimum Dormancy (Full Tank)</td>
<td>W·d</td>
<td>NA</td>
<td>NA</td>
<td>2</td>
<td>4-30</td>
<td>2.8</td>
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<td></td>
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<tr>
<td>H₂ Loss Rate (Maximum)</td>
<td>g/h/kg·H₂</td>
<td>NA</td>
<td>NA</td>
<td>8</td>
<td>0.2-1.6</td>
<td>0.9</td>
<td>0.1</td>
<td>0.05</td>
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<tr>
<td>WTT Efficiency</td>
<td>%</td>
<td>56.5</td>
<td>54.2</td>
<td>22.3</td>
<td>41.1</td>
<td>41.1</td>
<td>41.1</td>
<td>60</td>
<td>60</td>
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<tr>
<td>GHG Emissions (CO₂ eq)</td>
<td>kg/kg·H₂</td>
<td>14.0</td>
<td>14.8</td>
<td>TBD</td>
<td>19.7</td>
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<tr>
<td>Ownership Cost</td>
<td>$/mile</td>
<td>0.13</td>
<td>0.14</td>
<td>TBD</td>
<td>0.12</td>
<td>0.15</td>
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</tbody>
</table>
Storage Capacity

- Of all the systems built, Gen3 CcH₂ has the highest demonstrated gravimetric and volumetric capacity.
- Alane slurry shows high volumetric capacity but stable 70-wt% slurry not formulated, volume-exchange tank not developed.
- On-going studies to find AB/IL formulations that remain liquid under all conditions, volume-exchange tank not developed.
- cH₂ model capacities in agreement with Tech Val data.

Diagram to be regarded as a snapshot in time.
- Different systems not analyzed to same level of sophistication.
- Advanced materials not ready for deployment.
- Some component concepts require further development.

Consult ANL reports for complete details, assumptions and background.
Weight Distribution

- 350-bar \( \mathrm{cH}_2 \), \( \mathrm{LH}_2 \) & \( \mathrm{CcH}_2 \) systems may meet 2015 gravimetric target
- \( \mathrm{CcH}_2 \) system with Al shell approaches the ultimate gravimetric target
- CF is the main contributor to the overall weight in \( \mathrm{cH}_2 \) systems
- Metal liner is a heavy component in all Type-3 pressure vessels
- Medium weight dominates in metal hydride and chemical \( \mathrm{H}_2 \) systems

\( \mathrm{cH}_2 \): Compressed \( \mathrm{H}_2 \)
350b: 350 bar
700b: 700 bar
\( \mathrm{LH}_2 \): Liquid \( \mathrm{H}_2 \)
\( \mathrm{CcH}_2 \): Cryo-compressed \( \mathrm{H}_2 \)
\( \mathrm{MOF} \): MOF-177
\( \mathrm{SA} \): TiCl\(_3\) catalyzed NaAlH\(_4\)
\( \mathrm{LCH}_2 \): Organic liquid carrier
\( \mathrm{SBH} \): Alkaline NaBH\(_4\) solution
\( \mathrm{AB} \): Ammonia borane
Volume Distribution

- CcH₂ system meets 2015 volumetric target but not ultimate target
- Medium volume significant in all options and, by itself, exceeds the 2015 system target in CH₂ systems
- Insulation volume important in cryogenic systems
- CDS in LCH₂ is bulky because of highly endothermic reaction
- BOP in SBH (adiabatic reactor, exothermic release) is bulky because of condensers

BOP: Balance of Plant
CDS: Charge-Discharge System
Hydrogen Loss During Extended Parking

- 40% of H₂ stored in LH₂ tank vented to ambient in a typical use cycle
- Negligible H₂ loss from insulated cryogenic pressure vessels with some daily driving
- H₂ loss from alane determined by kinetics and ambient temperature, not by heat transfer
- H₂ loss from AB/IL determined by kinetics, ambient temperature, and heat transfer coefficient
Dormancy

- Shorter dormancy in LH$_2$ system if the fuel tank is partially full
- Longer dormancy in CcH$_2$ system with partially-full tank, no stranded driver syndrome
- Longer dormancy in cryogenic sorbent systems than CcH$_2$ because of heat of desorption
- Dormancy definition not meaningful for alane and AB storage
Cost of On-Board Systems at High-Volume Manufacturing

- Cost data from TIAX studies with ANL inputs, 500,000 units/year
- Fiber cost dominates in cH₂ systems, less expensive in cryogenic sorption systems
- Material cost important in sorption systems and in SA system
- Dehydrogenation catalyst cost important in LCH₂ system

Consult TIAX reports for complete details, assumptions and background
Efficiency of On-Board Systems

- Venting loss accounts for inefficiency of LH$_2$ system
- 10-30% H$_2$ consumed in alane, SA and LCH2 systems to sustain high-temperature endothermic reactions
- ~1% loss in AB system efficiency because of fuel pump, additional FCS coolant and radiator fan power
- DOE target for on-board system efficiency is 90%
Well-to-Tank Efficiency

- 350- and 700-bar CH\textsubscript{2} options have <60% WTT efficiency
- Reversible metal hydrides may have higher WTT efficiency than CH\textsubscript{2}
- LCH\textsubscript{2} regeneration is exothermic and can reach 60% efficiency
- High uncertainty in alane regeneration efficiency because of vacuum distillation steps and low-grade waste heat requirement
- Options involving cryogenic H\textsubscript{2} have < 41% WTT efficiencies
- Low efficiencies for AB and SBH regeneration
Greenhouse Gas Emissions

- Values given in kg of CO₂ equivalent per kg of H₂ delivered to the vehicle or per mile driven
  - 63.4 mpgge assumed fuel economy for 2015 advanced FC vehicle
- As reference, GHG emissions for 2015 mid-size ICE vehicle with 31 mpgge fuel economy is 0.35 kg-CO₂/mile
Refueling Cost

- H2A data for cost of unit operations, natural gas at $0.22/Nm³
- Liquefaction contributes significantly to the fuel cost in options requiring LH₂
- Regeneration is the main component of fuel cost in SBH option
- No storage option can meet the $2-3/kg cost target (untaxed)

Consult ANL and TIAX reports for complete details, assumptions and background