High Density Thermal Energy Storage with Supercritical Fluids (Super-TES)

Gani B. Ganapathi (JPL/Caltech)
Richard Wirz (UCLA)

Presented at the ASME 2012 6th International Conference on Energy Sustainability
July 23-26, 2012
San Diego, CA
• A novel high-energy density, low-cost thermal energy storage concept using supercritical fluids
  – Enhanced penetration of solar thermal for baseload power
  – Waste heat capture

• Paper presents feasibility looking at thermodynamics of supercritical state, fluid and storage system costs

• System trades
  – comparing the costs of using supercritical fluids vs molten salt systems in utility-scale applications
UCLA Solar Thermal Plant with Storage

• ARPA-E’s transformational technologies call

• Proposed key novel aspects:
  – Modular and single-tank (vs two-tank as for molten salt)
    • Internal heat exchangers (minimized heat loss)
  – Supercritical storage allowing significantly higher storage densities

• Strong team led by UCLA (Dr. Wirz) covering breadth of TRLs
  – UCLA : Low-TRL (fluid chemistry, system studies and build support)
  – JPL: Mid TRL (thermal, fluids, structural, tank design and build)
  – SoCalGas: High TRL (field demo)
  – Vendors: Chromasun (provider of solar panels)

• Prototype and field demonstrations
Project Objectives

- **Three primary goals:**
  - Demonstrate a cost-effective thermal energy storage (TES) concept for high temperature applications
  - Develop a modular single-tank TES design
  - Demonstrate a 30 kWh TES

- **Goals will be accomplished in 2 phases (Top level)**
  - **Phase 1 activities (Concept development):**
    - Fluid selection
    - System analysis
    - Development and testing with a small (5 kWh/66L) tank
  - **Phase 2 activities (Scale-up):**
    - Development of prototype (10 kWh/133L) tank
    - Performance characterization of micro-CSP with and without TES at JPL site
    - Development of full-scale (30 kWh/400L) tank for field integration at SoCalGas site
• Current sensible heat technologies
  – two-tank direct,
  – two-tank indirect,
  – single-tank thermocline
  – storage media such as concrete, castable ceramics rely on sensible heat

• PCM explored in 80’s by DOE
  – Abandoned due to complexities, life

• In 2008 restarted funding TES and HTF
  – Mostly sensible heat related
  – Or didn’t address costs $/kWh

• ARPE-E’s new program “High Energy Advanced Thermal Storage”
Supercritical Storage

- Supercritical operation permits capturing and utilizing heat taking advantage of latent and sensible heat, both in the two-phase regime as well as in supercritical regime while at the same time, reducing the required volume by taking advantage of the high compressibilities.

- Storage performance and pressures can be optimized by judicious selection of fluid with the following key properties:
  - High Latent Heat of Vaporization, $\Delta H_{\text{vap}}$
  - High specific heat, $C_p$ ($C_v$)
  - High $T_c$, $T_b$
  - Low vapor pressure
400 organic fluids evaluated based on thermodynamics alone
Factor of 10 cost reductions on fluids for high temperature applications possible

<table>
<thead>
<tr>
<th>Moderate Temperature Application ((T_{\text{cold}} = 373\text{K}, \Delta T = 100\text{K}))</th>
<th>Specific Storage (kJ/kg)</th>
<th>Volumetric Storage Capacity (kJ/m²) (vapor press at 200 °C)</th>
<th>$/kWh ($/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressed water</td>
<td>418</td>
<td>362,000 (15 atm)</td>
<td>Negligible</td>
</tr>
<tr>
<td>Therminol (VP-1)</td>
<td>229</td>
<td>228,700 (&lt;1 atm)</td>
<td>78 ($5/kg)</td>
</tr>
<tr>
<td>Fluid1</td>
<td>241</td>
<td>303,850 (&lt;1 atm)</td>
<td>8 ($0.55/kg)</td>
</tr>
<tr>
<td>Fluid2</td>
<td>200</td>
<td>216,609 (&lt;1 atm)</td>
<td>16 ($1/kg)</td>
</tr>
</tbody>
</table>

| High Temperature Application (\(T_{\text{cold}} = 563\text{K}, \Delta T = 100\text{K}\)) | | |
|---|---|---|---|
| Supercritical Fluid1 | 720 | 324,741 (66 atm, \(z = 0.25\)) | 2.75 ($0.55/kg) |
| Supercritical Fluid2 | 541 | 387,122 (66 atm, \(z = 0.219\)) | 6.50 ($1.00/kg) |
| Molten Salt (NaNO₃, KNO₃) | 145 | 129,860 (2 tanks) | 25 – 50 ($1-$2/kg) |
Modeling Approach

- Departure functions used with P-R EOS to determine state changes in enthalpy for fluid

\[ \Delta A = A - A^0 = -\int_{V_\infty}^V (P - \frac{RT}{V})dV + RT \ln \frac{V}{V^0} \quad \text{Helmoltz Departure Function} \]

\[ S - S^0 = \frac{\partial}{\partial T}(A - A^0) = \int_{V_\infty}^V \left[ \left( \frac{\partial P}{\partial V} \right)_V - \frac{R}{V} \right]dV + R \ln \frac{V}{V^0} \quad \text{Entropy Departure Function} \]

\[ H - H^0 = (A - A^0) + T(S - S^0) + RT(Z - 1) \quad \text{Enthalpy Departure Function} \]

\[ H[T_2, P_2] - H[T_1, P_1] = (H[T_2, P_2] - H^0[T_2, P_0]) + (H^0[T_2, P_0] - H^0[T_1, P_0]) + (H^0[T_1, P_0] - H^1[T_1, P_1]) \quad \text{Enthalpy Change between States 1 & 2} \]

- End state pressures and temperature determine the tube wall thickness
- Fixed end temperature chosen not to exceed 500 °C as allowable stress drops significantly beyond this temperature
System Cost Approach

- Fluid enthalpy changes with fixed volume
  - Fluid cost $/kWh based on fluid cost $/kg and loading
  - Tank material cost $/kWh based on tube mass which is driven by fluid pressure

- Peng-Robinson equation of state using $P_c$, $T_c$, $\omega$

- Heat transfer effects from HTF to tube negligible

- Analysis assumed Stainless Steel TP 316 for its corrosion resistance
  - Optimal tube wall thickness for different pressure ratings conforming to ASTM A213, ASTM A249 or ASTM 269 respectively
• Initial temp \((T_1 = 290 \, ^\circ C, \, P_1 = 413 \, kPa)\) for all cases

• 4 final pressure \((P_2)\) cases
  - 4.2MPa (609 psia)
  - 6.895 MPa (1000 psia)
  - 10.342 MPa (1500 psia)
  - 13.789 MPa (2000 psia)

• As loading (volume fraction) increases in 1m\(^3\) tank
  - Storage density [green] goes through peak
  - Final temperatures, \(T_2\) [blue] comes down from 800 \(^\circ C\) @ fixed \(P_2\)
  - Compressibility, \(z\), [red] changes from near ideal gas to highly non-ideal

Sample result for \(P_2 = 6.985 \, MPa\) (1000 psia)
• Pressure rating derived from Lame formula with 130 MPa (18.8 kpi) allowable stress and 4:1 FS
  - Derating of 0.6 assumed for 400°C < T₂ < 500°C
• Example for 500 °C, P₂ = 6.895 MPa [1000 psia] need to spec tube dia for 11.49 MPa [1666 psia]
  - Need thickness > 2.36E-3 m [0.093"] for 5.08E-2 m [2"] tube OD
• Total cost goes through a minimum at ~45% fill fraction
  - Minimum cost for given final fill conditions is ~$55/kWh
  - Fluid cost [green] is small fraction of total cost [cyan]

Sample result for P₂ = 6.985 MPa (1000 psia)
Optimal cost results for 4 final pressure cases when T2 <= 500 °C

<table>
<thead>
<tr>
<th>P₂ (psia)</th>
<th>T₂ (°C)</th>
<th>Storage Density (kWh/m³)</th>
<th>Load (kg/m³)</th>
<th>Fluid Cost ($/kWhₐ)</th>
<th>Tank Cost ($/kWhₐ)</th>
<th>Total Cost ($/kWhₐ)</th>
<th>Salt Cost ($/kWhₐ) (@$2/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>609</td>
<td>461</td>
<td>70.0</td>
<td>460</td>
<td>2.17</td>
<td>23.02</td>
<td>25.19</td>
<td>29.30</td>
</tr>
<tr>
<td>1000</td>
<td>498</td>
<td>84.8</td>
<td>439</td>
<td>1.71</td>
<td>28.43</td>
<td>30.14</td>
<td>24.91</td>
</tr>
<tr>
<td>1500</td>
<td>492</td>
<td>99.4</td>
<td>535.5</td>
<td>1.78</td>
<td>37.52</td>
<td>39.3</td>
<td>22.19</td>
</tr>
<tr>
<td>2000</td>
<td>499.6</td>
<td>112</td>
<td>570</td>
<td>1.68</td>
<td>44.88</td>
<td>46.57</td>
<td>22.18</td>
</tr>
</tbody>
</table>

Results indicate that though storage density increases as P2 is allowed to go higher, the penalty is higher cost as cost of metal starts making an impact.

For the lowest cost case, cost of salt alone exceeds cost of supercritical naphthalene + tank material cost.

- Assumptions
  - Bulk cost of naphthalene = $0.36/kg
  - Bulk cost of eutectic salt (KNO₃+NaNO₃) = $2/kg
  - Bulk cost of SS 316H (alibaba.com) = $1.40/kg
## Cost Comparisons for Utility-Scale

- Full analysis for comparing molten salt vs supercritical fluids for utility scale for 6-, 12- and 18-hr storage.
  - 100 MWe utility from report by Worley Parsons
- System cost using supercritical fluids is lower than molten salt
  - No external heat exchanger
  - No second pump (only HTF pump from field)

### Cost Comparison Table

<table>
<thead>
<tr>
<th></th>
<th>6-hr storage</th>
<th>12-hr storage</th>
<th>18-hr storage</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Net Power (MW&lt;sub&gt;e&lt;/sub&gt;)</td>
<td>103</td>
<td>103</td>
<td>103</td>
<td>Ref:</td>
</tr>
<tr>
<td>Gross Power (MW&lt;sub&gt;e&lt;/sub&gt;)</td>
<td>118</td>
<td>118</td>
<td>118</td>
<td></td>
</tr>
<tr>
<td>Rankine eff. (%)</td>
<td>37.4%</td>
<td>37.4%</td>
<td>37.4%</td>
<td></td>
</tr>
<tr>
<td>Thermal storage (MWh)</td>
<td>1893</td>
<td>3786</td>
<td>5679</td>
<td></td>
</tr>
<tr>
<td>Temp range (500-375 °C) for supercritical fluid</td>
<td>125</td>
<td>125</td>
<td>125</td>
<td></td>
</tr>
<tr>
<td>Temp range (500-390 °C) for molten salt</td>
<td>110</td>
<td>110</td>
<td>110</td>
<td>Assumes same bypass ops.</td>
</tr>
</tbody>
</table>

### Molten Salt (HITec Solar Salt) T<sub>i</sub> - 500 °C/T<sub>f</sub> = 390 °C

<table>
<thead>
<tr>
<th></th>
<th>1550</th>
<th>1550</th>
<th>1550</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co salt (J/kg/K)</td>
<td>52</td>
<td>104</td>
<td>156</td>
</tr>
<tr>
<td>Mass Salt (10⁷ kg)</td>
<td>104</td>
<td>208</td>
<td>312</td>
</tr>
<tr>
<td>Cost of salt (SM) @ $2/kg</td>
<td>457</td>
<td>915</td>
<td>1372</td>
</tr>
<tr>
<td>Cost of salt (SM) @ $5.80/kg</td>
<td>36</td>
<td>49</td>
<td>66</td>
</tr>
<tr>
<td>Pumps + HEX (SM)</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Tanks (SM)</td>
<td>0.5</td>
<td>0.75</td>
<td>1.0</td>
</tr>
<tr>
<td>Foundation &amp; Support Structures (SM)</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Total $/SM @ $2/kg</td>
<td>112</td>
<td>216</td>
<td>320</td>
</tr>
<tr>
<td>Total $/SM @ $8.80/kg</td>
<td>465</td>
<td>923</td>
<td>1380</td>
</tr>
<tr>
<td>Salt $/kWh, (@ $2/kg)</td>
<td>55</td>
<td>55</td>
<td>55</td>
</tr>
<tr>
<td>Total $/kWh, (@ $2/kg)</td>
<td>59</td>
<td>57</td>
<td>56</td>
</tr>
<tr>
<td>Sal $/kWh, (@ $8.80/kg)</td>
<td>242</td>
<td>242</td>
<td>242</td>
</tr>
<tr>
<td>Total $/kWh, (@ $8.80/kg)</td>
<td>246</td>
<td>244</td>
<td>243</td>
</tr>
</tbody>
</table>

### Supercritical Fluid (Naphthalene @ T<sub>i</sub>-500 °C/T<sub>f</sub>-375 °C, 880 psia)

<table>
<thead>
<tr>
<th></th>
<th>2</th>
<th>2</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluid cost ($/kWh)</td>
<td>33</td>
<td>33</td>
<td>33</td>
</tr>
<tr>
<td>Tank material cost ($/kWh)</td>
<td>3.8</td>
<td>7.6</td>
<td>11.4</td>
</tr>
<tr>
<td>Total Fluid cost (SM)</td>
<td>62</td>
<td>125</td>
<td>187</td>
</tr>
<tr>
<td>Tank Material cost (SM)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Pumps + HEX (SM)</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Foundation &amp; Support Structures (SM)</td>
<td>0.5</td>
<td>0.75</td>
<td>1.0</td>
</tr>
<tr>
<td>Instrumentation &amp; Control (SM)</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Total $/SM</td>
<td>74</td>
<td>141</td>
<td>207</td>
</tr>
<tr>
<td>Total $/kWh</td>
<td>39</td>
<td>37</td>
<td>36</td>
</tr>
</tbody>
</table>
Currently JPL is in process of
- Completing build of 5 kWh in readiness for testing
- Getting ready for installation of Chromasun MCT panels for 10 kWh tank

Current Activities at UCLA

**Thermal Testing of Fluids**

- Sample Temperature
- Heater Temperature
- Sample Pressure

**Chemistry Evaluation**

Before and After images showing a glass.

**Heat and Mass Transfer**

Time plots showing temperature and pressure changes over time.

- $t = 4\text{ min}$
- $t = 75\text{ min}$

**System Modeling**

Diagram of a solar field system with heat transfer components:
- Solar Field
- Thermal Storage Unit
- Steam Generator
- Charging Loop
- Discharging Loop

A novel thermal energy storage concept has been funded for development by ARPA-E that promises significant cost advantages over molten salt system.

The cost of the chosen fluid is much lower than molten salt and the difference will continue to grow as demand for nitrates grow for use as fertilizer.

A robust program to develop alternate fluids is in the process of being developed for testing. Results from the testing will be used for building larger-sized tanks as the processes get worked out.