High Density Thermal Energy Storage with Supercritical Fluids (SuperTES)

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Overview

• 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

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

• 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
The project has 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

These goals will be accomplished in two 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, $\Delta H_{vap}$
  - High specific heat, $C_p$ ($C_v$)
  - High $T_c$ $T_b$
  - Low vapor pressure
### Initial Fluid Comparisons

#### Moderate Temperature Application ($T_{\text{cold}} = 373K, \Delta T = 100K$)

<table>
<thead>
<tr>
<th>Fluid Type</th>
<th>Specific Storage (kJ/kg)</th>
<th>Volumetric Storage Capacity (kJ/m$^3$) (vapor press at 200 °C)</th>
<th>$$/\text{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>Thermol (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 ($T_{\text{cold}} = 563K, \Delta T = 100K$)

<table>
<thead>
<tr>
<th>Fluid Type</th>
<th>Specific Storage (kJ/kg)</th>
<th>Volumetric Storage Capacity (kJ/m$^3$) (66 atm, $z = 0.25$)</th>
<th>$$/\text{kWh} ($/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Supercritical Fluid1</td>
<td>720</td>
<td>324,741</td>
<td>2.75 ($0.55/kg)</td>
</tr>
<tr>
<td>Supercritical Fluid2</td>
<td>541</td>
<td>387,122</td>
<td>6.50 ($1.00/kg)</td>
</tr>
<tr>
<td>Mollen Salt (NaNO$_3$, KNO$_3$)</td>
<td>145</td>
<td>129,860 (2 tanks)</td>
<td>25 – 50 ($1$-$2/kg)</td>
</tr>
</tbody>
</table>

- 400 organic fluids evaluated based on thermodynamics alone
- Factor of 10 cost reductions on fluids for high temperature applications possible
Modeling Approach

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

\[
A - A^0 = -\int_{\infty}^{V} (P - \frac{RT}{V}) dV + RT \ln \frac{V}{V^0}
\]

**Helmoltz Departure Function**

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

**Entropy Departure Function**

\[
H - H^0 = (A - A^0) + T(S - S^0) + RT(Z - 1)
\]

**Enthalpy Departure Function**

\[
H[T_2, P_2] - H[T_1, P_1] = \left( H[T_2, P_2] - H^0[T_2, P_0] \right) + \left( H^0[T_2, P_0] - H^0[T_1, P_0] \right) + \left( H^0[T_1, P_0] - H^1[T_1, P_1] \right)
\]

**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 \((T_1 = 290 \, ^\circ C, \, P_1 = 413 \, kPa/60 \, psia)\) 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)
Summary of Optimal Costs

- 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 ($/kWh₁)</th>
<th>Tank Cost ($/kWh₁)</th>
<th>Total Cost ($/kWh₁)</th>
<th>Salt Cost ($/kWh₁) (@$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)

<table>
<thead>
<tr>
<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>
</tr>
<tr>
<td>Gross Power (MW&lt;sub&gt;e&lt;/sub&gt;)</td>
<td>118</td>
<td>118</td>
<td>118</td>
</tr>
<tr>
<td>Rankine effic.</td>
<td>37.4%</td>
<td>37.4%</td>
<td>37.4%</td>
</tr>
<tr>
<td>Thermal storage (MWh&lt;sub&gt;e&lt;/sub&gt;)</td>
<td>1893</td>
<td>3786</td>
<td>5679</td>
</tr>
<tr>
<td>Temp range (500-375 °C) for supercritical fluid</td>
<td>125</td>
<td>125</td>
<td>125</td>
</tr>
<tr>
<td>Temp range (500-390 °C) for molten salt</td>
<td>110</td>
<td>110</td>
<td>110</td>
</tr>
</tbody>
</table>

**Molten Salt (HiTec Solar Salt) T<sub>1</sub> = 500 °C/T<sub>2</sub> = 390 °C**

- Cp salt (J/kg/K) | 1550 | 1550 | 1550 |
- Mass Salt (10<sup>6</sup> kg) | 52 | 104 | 156 |
- Cost of salt (SM) @ $2/kg | 104 | 208 | 312 |
- Cost of salt (SM) @ $8.80/kg | 457 | 915 | 1372 |
- Pumps+HEx (SM) | 96 | 49 | 60 |
- No pump, HEx in single tank |
- Tank cost removed |
- Tanks (SM) | 43 | 64.5 | 66 |
- Piping, Insulation, Valves, Fittings (SM) | 1.5 | 1.5 | 1.5 |
- Foundation & Support Structures (SM) | 0.5 | 0.75 | 1.5 |
- Instrumentation & Control (SM) | 6 | 6 | 6 |
- Total SM @ $2/kg | 112 | 216 | 320 |
- Tank cost removed |
- Total SM @ $8.80/kg | 465 | 923 | 1380 |
- Tank cost removed |
- Salt$/kWh, @ $2/kg | 55 | 55 | 55 |
- Total $/kWh, @ $2/kg | 59 | 57 | 56 |
- Salt$/kWh, @ $8.80/kg | 242 | 242 | 242 |
- Total $/kWh, @ $8.80/kg | 246 | 244 | 243 |

**Supercritical Fluid (Naphthalene @ T<sub>1</sub>=500°C/T<sub>2</sub>=375°C, 880 psia)**

- Fluid Cost ($/kWh) | 2 | 2 | 2 |
- Naphthalene ($0.33/kg bulk) |
- Tank material cost ($/kWh) | 33 | 33 | 33 |
- SS 316L ($1.40/kg bulk) |
- Total Fluid cost (SM) | 3.8 | 7.6 | 11.4 |
- Tank Material cost (SM) | 62 | 125 | 187 |
- Pumps + HEx (SM) | 0.0 | 0.0 | 0.0 |
- Internal HEx single tank |
- Piping, Insulation, Valves, Fittings (SM) | 1.5 | 1.5 | 1.5 |
- Foundation & Support Structures (SM) | 0.5 | 0.75 | 1.5 |
- Instrumentation & Control (SM) | 6 | 6 | 6 |
- Total SM | 74 | 141 | 207 |
- Total $/kWh | 39 | 37 | 36 |
Current Activities at JPL

5 kWh High Temp (500 °C) Testbed

Fluid: Naphthalene
Tested: 290 – 480 °C

Status: Test completed, results documented in paper to be published in ASME Sustainability Conf 2013
### Current Activities at JPL

**Moderate temperature (80-100 °C) testbed**

- **Goals:**
  - Demonstrate single tank concept in system with charge/discharge
  - Provide experience for developing 30 kWh TES to be demonstrated at SoCalGas facility

- **Status**
  - Fluid selected
  - Design complete
  - Procurements initiated
Thermal Testing of Fluids

Chemistry Evaluation

Heat and Mass Transfer

System Modeling

SunShot CSP Program Review 2013
Field demo of moderate temperature TES at SoCalGas facility at Downey, CA.
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 well integrated set of activities coordinated between UCLA and JPL covers all activities required to make this project a success.