Advanced Thermal Storage Fluids for Solar Parabolic Trough Systems
National Renewable Energy Laboratory

FLUIDS R&D

Alternative Solvents & Reaction Media
- aqueous
- organic
- ionic liquids
- fluorous
- supercritical
- subcritical
- biobased

Fuels
- oxidative stability
- physico-chemical properties
- purity

Functional Fluids
- heat transfer fluids
- thermal storage fluids

Bio-Lubricants
- plant oils
- carbohydrate derivatives

- synthetic chemistry
- bioreactions
- fractionation & separation
- advanced materials
- nanocatalysts

Luc Moens
Fluids R&D
National Bioenergy Center
Transfer of Solar Heat

Current System Components:
- Heat Transfer Fluid
- Heat exchanger
- High-Pressure Superheated Steam
Solar Parabolic Trough Plants

Southwest 1000 MW Strategy

Resource Availability:

<table>
<thead>
<tr>
<th>State</th>
<th>Solar Capacity (MW)</th>
<th>Land Area (Sq Mi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZ</td>
<td>1,652,000</td>
<td>12,790</td>
</tr>
<tr>
<td>CA</td>
<td>742,305</td>
<td>5,750</td>
</tr>
<tr>
<td>NV</td>
<td>619,410</td>
<td>4,790</td>
</tr>
<tr>
<td>NM</td>
<td>1,119,000</td>
<td>9,157</td>
</tr>
<tr>
<td>Total</td>
<td>4,132,715</td>
<td>32,487</td>
</tr>
</tbody>
</table>

The table and map represent land that has no primary use today, exclude land with slope > 1%, and do not count sensitive lands.

Solar Energy Resource $\geq 7.0$ kWhr/m²/day (includes only excellent and premium resource)

Current total generation in the four states is 83,500 MW.
## Current HTFs

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Application T (°C)</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic oils</td>
<td></td>
<td></td>
</tr>
<tr>
<td>e.g. Therminol VP-1</td>
<td>13 - 395</td>
<td>Flammable</td>
</tr>
<tr>
<td>(aromatic HC’s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mineral oils</td>
<td></td>
<td></td>
</tr>
<tr>
<td>e.g. Caloria</td>
<td>-10 - 300</td>
<td>Flammable</td>
</tr>
<tr>
<td>(paraffinic HC’s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silicone oils</td>
<td></td>
<td>Expensive Flammable</td>
</tr>
<tr>
<td></td>
<td>-40 - 400</td>
<td></td>
</tr>
<tr>
<td>Nitrate salts</td>
<td></td>
<td>Freezing point ≥ 120 °C</td>
</tr>
<tr>
<td>e.g. HITEC-XL</td>
<td>220 - 500</td>
<td>High T stability</td>
</tr>
</tbody>
</table>

HITEC-XL™ : Ca(NO₃)₂ + NaNO₃ + KNO₃
Goal of R&D Project:

Heat Transfer Fluid = Heat Storage Fluid

* Higher operating temperatures: low vapor pressure fluid needed
* Improved cost / performance of solar plant
* Optimized dispatch of power to meet utility peak loads (up to 12 h of storage)
Desired Properties for ‘ideal’ heat storage fluid

- High thermal stability (up to 425°C)
- Low freezing point (≤ 0 °C)
- Non-flammable
- Low vapor pressure (@ high T)
- High boiling point
- Relatively inexpensive
ROOM TEMPERATURE IONIC LIQUIDS

Imidazolium Salts

- Methyl
- Ethyl
- Butyl
- Hexyl
- Octyl
- Phenyl
- Silyl

- \( R \)
- \( X \)
- Cl
- \( \text{OSO}_2\text{CH}_3 \)
- \( \text{BF}_4 \)
- \( \text{PF}_6 \)
Ionic Liquids

Imidazolium salts
Ionic Liquids

- Organic Salt structure
- Very High Thermal Stability ($\geq 400 \, ^\circ\text{C}$ known)
- Virtually no vapor pressure
- Low Melting point (some $\leq 0 \, ^\circ\text{C}$)
- Not flammable
- Many RTILs identified among imidazolium salts
Ionic Liquids

- New to synthetic / process chemistry
- Chemical industry interest is growing
- Data on physical / engineering / toxicology growing rapidly
- Cost for production unknown
- Commercially available in research quantities, but laboratory synthesis straightforward (kilogram-scale)
## Dynamic viscosity

<table>
<thead>
<tr>
<th>Fluid</th>
<th>T (ºC)</th>
<th>η (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VP-1</td>
<td>15 300</td>
<td>4.98 0.22</td>
</tr>
<tr>
<td>HITEC-XL</td>
<td>120 300</td>
<td>138.99 6.37</td>
</tr>
<tr>
<td>EmimBF$_4$ (ionic liquid)</td>
<td>26 300</td>
<td>43 1.5 (calc)</td>
</tr>
</tbody>
</table>
Influence of ANION

1,3-dimethyl imidazolium Iodide
1,3-dimethyl imidazolium DBS
1,3-dimethylimidazolium chloride
1,3-dimethylimidazolium PF6
1,3-dimethylimidazolium BF4
1,3-dimethylimidazolium OMs
1,3-dimethylimidazolium NTf2
1-bu-3-methylimid NTf2
Influence of ANION

Universal V2.3C TA Instruments

Weight (%) vs. Temperature (°C)

1-ethyl-3-methylimidazolium OMs
1-ethyl-3-methylimidazolium OTf
Influence of CATION structure
Ramp 20°C/min and Isothermal decomposition over 120 min

[Graph showing weight loss vs. temperature with specific points labeled: 199.97°C (89.08%), 299.63°C (58.67%), 375.46°C (0.9011%).]

Universal V2.3C TA Instruments
Schematic of NREL’s MBMS Sampling System
MBMS study of \([\text{EtMeIm}][\text{BF}_4]\)

Proposed thermal events:
1) HF liberation at high T
2) de-alkylation of quat. amine salt
Thermal Decomposition Pathways

Demethylation

\[
\text{\text{N}} \quad \text{N} \quad \text{N} + \text{MeX} \quad \text{HH} + \text{MeX}
\]

Hofmann Type Elimination

\[
\text{\text{H}} \quad \text{H} \quad \text{N} \quad \text{N} \quad \text{N} + \text{MeX} \quad \text{N} \quad \text{Me} + \text{MeX}
\]
Determination of Half-Life of BMIM PF6
Conclusions

- Ionic Liquids are not suitable as heat storage fluids (thermally unstable at T’s required for solar trough systems)

- Synthesis straightforward (one-pot)

- Other types of fluids must be explored for use in solar troughs
New Candidate Fluids for exploratory work

• known to (petro)chemical industry

• large-scale production possible or existent

• low cost
New Candidate Fluids

- modified commercial fluids (Therminol VP-1™)
- plasticizers
- modified high-performance lubricants (esters)
New Candidate Fluids

• modified commercial fluids (Therminol VP-1™)
Explore new fluids based on modified aromatics:

- VP-1
- \( \text{C}_{12}H_{8}^- \text{M}^+ + \text{C}_{12}H_{8}O^- \text{M}^+ \)
- \( \text{C}_{12}H_{8}O^- \text{M}^+ + \text{C}_{12}H_{8}O^- \text{M}^+ \)
- \( \text{C}_{12}H_{8}O^- \text{M}^+ + \text{C}_{12}H_{8}O^- \text{M}^+ \)
- \( \text{C}_{12}H_{8}O^- \text{M}^+ + \text{C}_{12}H_{8}O^- \text{M}^+ \)
New Candidate Fluids

- modified commercial fluids (Therminol VP-1™)
- plasticizers
PLASTICIZERS

\[ R = \text{alkyl groups (linear or branched)} \]

- **Phthalate esters**
- **Trimellitate esters**
- **Pyromellitate esters**
- **Adipate esters**
### Plasticizers - US production

<table>
<thead>
<tr>
<th>Plasticizer</th>
<th>2002 (10^3 metric tons)</th>
<th>Average annual growth (%)</th>
<th>2003 price ($ / lb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diisodecyl phthalate</td>
<td>125</td>
<td>2.6</td>
<td>0.66</td>
</tr>
<tr>
<td>Dioctyl phthalate</td>
<td>120</td>
<td>1.6</td>
<td>0.66</td>
</tr>
<tr>
<td>Diisononyl phthalate</td>
<td>110</td>
<td>2.9</td>
<td>0.66</td>
</tr>
<tr>
<td>Linear C7-C11 phthalates</td>
<td>110</td>
<td>2.1</td>
<td>0.74 Š0.90</td>
</tr>
<tr>
<td>Triocetyltrimellitate</td>
<td>28</td>
<td>4.4</td>
<td>1.05</td>
</tr>
<tr>
<td>Dioctyl adipate</td>
<td>25</td>
<td>3.0</td>
<td>0.89</td>
</tr>
<tr>
<td></td>
<td>Therminol VP-1</td>
<td>Phthalates</td>
<td>Trimellitates/Pyromellitates</td>
</tr>
<tr>
<td>------------------------------</td>
<td>----------------</td>
<td>------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td><strong>Freezing point (°C)</strong></td>
<td>13</td>
<td>-58 to 0</td>
<td>-56 to 30</td>
</tr>
<tr>
<td><strong>Bp (°C)</strong></td>
<td>257</td>
<td>283 to 523</td>
<td>414 to 430</td>
</tr>
<tr>
<td><strong>Flash point (°C)</strong></td>
<td>124</td>
<td>146 to 254</td>
<td>246 to 266</td>
</tr>
<tr>
<td><strong>Viscosity (cP)</strong></td>
<td>4.98 (@ 15°C)</td>
<td>11 to 320 (@ 20°C)</td>
<td>138 to 340 (@ 22°C)</td>
</tr>
<tr>
<td><strong>Specific heat (kJ/kgK)</strong></td>
<td>1.53</td>
<td>1.57 to 1.8</td>
<td>(?)</td>
</tr>
</tbody>
</table>
### Vapor Pressure of Plasticisers at Various Temperatures

<table>
<thead>
<tr>
<th>Plasticiser</th>
<th>80°C</th>
<th>100°C</th>
<th>140°C</th>
<th>180°C</th>
<th>250°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBP</td>
<td>0.02</td>
<td>0.082</td>
<td>0.87</td>
<td>6.08</td>
<td>86.67</td>
</tr>
<tr>
<td>DOP</td>
<td>0.001</td>
<td>0.039</td>
<td>0.571</td>
<td>20.75</td>
<td></td>
</tr>
<tr>
<td>DIDA</td>
<td>0.001</td>
<td>0.023</td>
<td>0.282</td>
<td>9.697</td>
<td></td>
</tr>
<tr>
<td>L79P</td>
<td>0.025</td>
<td>0.371</td>
<td>5.144</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DIDP</td>
<td>0.009</td>
<td>0.143</td>
<td>13.74</td>
<td></td>
<td></td>
</tr>
<tr>
<td>L911P</td>
<td>0.005</td>
<td>0.087</td>
<td>4.099</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TOTM</td>
<td>0.015</td>
<td>1.005</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

DBP = di-n-butyl phthalate  
DOP = di-2-ethylhexyl phthalate  
DIDA = di-isodecyl adipate  
L79P = di-(linear C7/C8C9) phthalate  
DIDP = di-isodecyl phthalate  
L911P = di-(linear C9/C10C11) phthalate  
TOTM = tri-2-ethylhexyl trimellitate

(Source: BP Chemicals)
### VAPOR PRESSURE OF VARIOUS FLUIDS AT DIFFERENT TEMPERATURES

<table>
<thead>
<tr>
<th></th>
<th>Vapor pressures (atm) at different temperatures</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>300°C</td>
</tr>
<tr>
<td>Therminol VP-1™</td>
<td>2.4</td>
</tr>
<tr>
<td>Diphenyl ether</td>
<td>2.3 *</td>
</tr>
<tr>
<td>Di-n-butyl phthalate</td>
<td>0.4 *</td>
</tr>
</tbody>
</table>

*calculated values using equations

- Diphenyl ether: \( P_{\text{vapor}} = 10^{4.13678-[1800.415/(T-95.324)]} \)
- Di-n-butyl phthalate: \( P_{\text{vapor}} = 10^{4.30568-[2083.175/(T-131.7)]} \)
New Candidate Fluids

- modified commercial fluids (Therminol VP-1™)
- plasticizers
- modified high-performance lubricants (esters)
Known building blocks for esters used in high-performance lubricants

- Neopentyl glycol
- Trimethylolpropane
- Pentaerythritol
- Di(trimethylolpropane)
- Diphenic acid
- 4,4'-oxybis(benzoic acid)
- Dihydroxybenzophenone
Challenges for new Thermal Storage Fluids

1. Long-term stability @ 300 - 400ºC
   (~ 20-30 yrs. through kinetic modeling)

2. Thermal decomposition:
   - decomposition products
   - influence of impurities at high T
   - oxidation @ high T (antioxidants needed?)
   - kinetic data
Challenges for new Thermal Storage Fluids

3. Hydrolysis by traces of water @ high T
   (esp. for esters)

4. Vapor pressure:
   - high boiling point esters
   - negligent in case of salts
Challenges for new Thermal Storage Fluids

3. Low melting point (pref. \( \leq 0^\circ\text{C} \)) to avoid need for heat tracing for receiver tubing during cold periods

4. Low viscosity (avoid use of ‘visc. modifiers’)

5. Explore fluid formulations for optimization of physico-chemical properties

6. NEW IDEAS ?????
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Bradley Brennan

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