Advanced Heat Transfer and Thermal Storage Fluids

Dan Blake, Luc Moens, Dan Rudnicki, Mary Jane Hale, Professor Ramana Reddy, and Greg Glatzmaier
Goals and Objectives

• The goal is to find a heat transfer and thermal storage fluid with a usable liquid range from near 0 to above 400 °C that will meet the cost and performance requirements of parabolic trough systems.

• The near term objective (FY03) is to identify a fluid with the potential for service up to 300 °C.
Project to Date

- Synthesis and thermal stability of imidazolium salts and identification of other possible salts — NREL FY2000-present
- Physical properties, materials compatibility, and extended thermal stability testing — The University of Alabama FY2001-present
- Production Process and Cost Study - Peak Design Subcontract FY02
The Challenge for A New Fluid

- Low freezing point - $<25 \, ^\circ C$
- Low vapor pressure - $< 1 \, \text{atm at } T_{\text{max}}$
- Low cost - $< \sim 4.50/\text{Kg}$
- Thermal stability at $> 400 \, ^\circ C$
- Compatible with alloys and materials used in solar plants
- Other physical properties compatible with the solar application
Imidazolium Salts

R
Methyl
Ethyl
Butyl
Hexyl
Octyl
Phenyl
Silyl

X

Cl

OSO₂CH₃

BF₄

PF₆
Table 1. Cost of reactants for synthesis of EmimBF\(_4\)

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Cost ($/lb)</th>
<th>Cost per lb of EmimBF(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glyoxal (50%) (ethylene glycol)</td>
<td>1.00</td>
<td>0.73 (0.12)</td>
</tr>
<tr>
<td></td>
<td>(0.38)</td>
<td></td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>0.21</td>
<td>0.03</td>
</tr>
<tr>
<td>Ammonia</td>
<td>0.10</td>
<td>0.01</td>
</tr>
<tr>
<td>Methylamine</td>
<td>0.73</td>
<td>0.11</td>
</tr>
<tr>
<td>Ethylchloride (ethylene)</td>
<td>2.00</td>
<td>0.64 (0.03)</td>
</tr>
<tr>
<td>(0.23)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetrafluoroboric acid (50%)</td>
<td>0.65</td>
<td>0.58</td>
</tr>
</tbody>
</table>
Process Changes to reduce the cost of an imidazolium salt
Peak Design (2002)
Production process for ethylmethylimidazolium Tetrafluoroborate (process 3)
### Table 3. Economic assumptions for the discount cash flow analysis

**Peak Designs (2002)**

<table>
<thead>
<tr>
<th>Economic Factor</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Internal Rate of Return</td>
<td>15%</td>
</tr>
<tr>
<td>Depreciation</td>
<td>Tab. 4</td>
</tr>
<tr>
<td>Recovery Period</td>
<td>11 years</td>
</tr>
<tr>
<td>Plant Life</td>
<td>21 years</td>
</tr>
<tr>
<td>Construction Period</td>
<td>1 year</td>
</tr>
<tr>
<td>Working Capital</td>
<td>15% of total capital</td>
</tr>
<tr>
<td>Federal Tax</td>
<td>40% of net income</td>
</tr>
<tr>
<td>State Tax</td>
<td>5% of net income</td>
</tr>
<tr>
<td>Salvage Value</td>
<td>10% of fixed capital</td>
</tr>
<tr>
<td>Debt/Equity Ratio</td>
<td>0/100</td>
</tr>
<tr>
<td>Plant size</td>
<td>10,000,000 kg/yr</td>
</tr>
<tr>
<td>Annual hours of operation</td>
<td>8,322 (95%)</td>
</tr>
<tr>
<td>Labor</td>
<td>$50/hr (loaded including supervision)</td>
</tr>
<tr>
<td>Maintenance</td>
<td>7% of fixed capital</td>
</tr>
<tr>
<td>Electricity</td>
<td>$0.06/kWhr</td>
</tr>
<tr>
<td>Reaction yields</td>
<td>100% (except glyoxal synthesis: 75%)</td>
</tr>
</tbody>
</table>
Table 7. Required costs for EmimBF$_4$

<table>
<thead>
<tr>
<th>Process</th>
<th>Reactant costs</th>
<th>Other operating</th>
<th>Capital</th>
<th>Total Cost ($/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.75</td>
<td>0.24</td>
<td>0.37</td>
<td>5.36</td>
</tr>
<tr>
<td>2</td>
<td>3.30</td>
<td>0.25</td>
<td>0.37</td>
<td>3.92</td>
</tr>
<tr>
<td>3</td>
<td>2.02</td>
<td>0.25</td>
<td>0.39</td>
<td>2.66</td>
</tr>
</tbody>
</table>

Table 8. Product cost dependence on plant size and internal rate of return

<table>
<thead>
<tr>
<th>Process</th>
<th>Plant Size ($10^8$ kg/yr)</th>
<th>Product Cost ($/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>5.57</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>5.36</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>5.16</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>4.16</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>3.92</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>3.70</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>2.90</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>2.66</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>2.43</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Process</th>
<th>IRR (%)</th>
<th>Product Cost ($/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>5.24</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>5.36</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>5.62</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>3.80</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>3.92</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>4.19</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>2.53</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>2.66</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>2.92</td>
</tr>
</tbody>
</table>
Table 9. Cost of EmimBF$_4$ as a function of reaction yield (process 3)

<table>
<thead>
<tr>
<th>Reaction Yields*</th>
<th>Total cost ($/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100%</td>
<td>$2.66</td>
</tr>
<tr>
<td>95</td>
<td>2.86</td>
</tr>
<tr>
<td>90</td>
<td>3.11</td>
</tr>
<tr>
<td>80</td>
<td>3.85</td>
</tr>
</tbody>
</table>

*Glyoxal yield is held at 75% in all cases
Summary and Conclusions

• Cost goals can be met with an organic salt
• When a viable candidate is identified the production process must be optimized
Longer term stability test of [C₈mim]PF₆

U of Alabama, 2001
Overall Observations

• We may have pushed the upper temperature limit of imidazolium salts as high as possible with anions – Further improvements may require changes in the imidazolium ring substituents
• A 300 °C salt appears to be within reach
• We will begin some work on alternative types of organic salts and mixtures
Corrosivity of Ionic Liquids
Experimental Methods

- Tafel extrapolation method was used to determine corrosion current density and calculate corrosion rates.
- Potentiodynamic polarization curves to analyze corrosion behavior of the alloys in ionic liquids.
- Experiments were performed at room temperature.
- Alloys tested:
  - 1018 carbon steel
  - 316 stainless steel
  - gray cast iron
**Typical Tafel Plot**

![Graph of Typical Tafel Plot]

- **Type 316 Stainless Steel in [C₄mim][Tf₂N], 25°C**
- **$E_{corr} = -0.138 \text{ V}$**
- **$i_{corr} = 1.10 \times 10^{-7} \text{ A/cm}^2$**

where:
- $r = \text{corrosion rate (mm/yr)}$
- $W = \text{equivalent weight (g)}$
- $d = \text{alloy density (g/cm}^3)$
- $i_{corr} = \text{corrosion current density (µA/cm}^2)$

$$r = \frac{3.27 \times 10^{-3} \cdot i_{corr} \cdot W}{d}$$
**Uniform Corrosion Rates of Solar Materials in Ionic Liquids**

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>Corrosion Rate at 25°C, in µm/yr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SS 316</td>
</tr>
<tr>
<td>[C₄mim]Cl</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>LC</td>
</tr>
<tr>
<td>[C₈mim]PF₆</td>
<td>1.2</td>
</tr>
<tr>
<td>[C₆mim]PF₆</td>
<td>0.4</td>
</tr>
<tr>
<td>[C₄mim][Tf₂N]</td>
<td>1.1</td>
</tr>
</tbody>
</table>
Conclusions

- Materials used in solar plant technology such as 316 stainless steel alloy, 1018 carbon steel and gray cast iron were found to be outstanding in corrosion resistance (corrosion rates: <20 $\mu$m/yr) against ionic liquids at RT.
- Localized corrosion was observed on the surface of the materials exposed to $[\text{C}_4\text{mim}]\text{Cl}$ ionic liquid.
- The potentiodynamic tests showed in most cases an active/passive corrosion behavior. However, the ionic liquid $[\text{C}_4\text{mim}]\text{Cl}$ prevented the formation of stable passive films.
Heat Capacities
# Properties of Heat Transfer Fluids at 25°C

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Melting point, °C</th>
<th>Density g/ml</th>
<th>Viscosity cPs</th>
<th>Cp Jg(^{-1})K(^{-1})</th>
<th>Cp, v Jcm(^{-2})K(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dowtherm HT</td>
<td>NA</td>
<td>1.01</td>
<td>953</td>
<td>1.42</td>
<td>1.41</td>
</tr>
<tr>
<td>Thermal oil</td>
<td>NA</td>
<td>0.89</td>
<td>1.9</td>
<td>1.69</td>
<td>1.90</td>
</tr>
<tr>
<td>[C(_4)mim]Cl</td>
<td>57.1</td>
<td>1.00</td>
<td>NA</td>
<td>1.58</td>
<td>&gt;1.58</td>
</tr>
<tr>
<td>[C(_2)mim][BF(_4)]</td>
<td>5.8</td>
<td>1.20</td>
<td>34</td>
<td>1.12</td>
<td>1.34</td>
</tr>
<tr>
<td>[C(_2)mim][PF(_6)]</td>
<td>60.5</td>
<td>1.10</td>
<td>NA</td>
<td>1.00</td>
<td>1.10</td>
</tr>
<tr>
<td>[C(_4)mim][PF(_6)]</td>
<td>6.5</td>
<td>1.37</td>
<td>389</td>
<td>1.14</td>
<td>1.56</td>
</tr>
<tr>
<td>[C(_6)mim][PF(_6)]</td>
<td>-80(T(_g))</td>
<td>1.30</td>
<td>688</td>
<td>1.34</td>
<td>1.75</td>
</tr>
<tr>
<td>[C(_4)mim][Tf(_2)N]</td>
<td>-5.1</td>
<td>1.44</td>
<td>53</td>
<td>1.05</td>
<td>1.50</td>
</tr>
</tbody>
</table>
A comparison of Volumetric Heat Capacity Performance

![Graph showing comparison of volumetric heat capacity performance for different fluids over temperature range.]

- Dowtherm MX
- Syltherm XLT
- Dowtherm G
- [C_4mim][NTf_2]
- [C_4mim][PF_6]
- [C_6mim][PF_6]
Viscosities of Ionic Liquids
Viscosities of Ionic Liquids

\[ \text{C}_4\text{mimCl at 300K} \quad \text{C}_6\text{mimCl at 300K} \]
Long Term Thermal Stability of IL
Evaluation of Long-term Thermal Stability

◆ Experimental Procedure:
  • Hold the ionic liquid samples at a fixed temperature for 20 hours,
  • Then raise the temperature to a higher level and holding for another 20 hours until significant weight changes are observed.
Weight Changes of [C$_4$ mim][Tf$_2$ N] as a Function of Time at Different Temperatures

![Graph showing weight changes over time and temperature](image-url)
Weight Changes of $[C_6\text{mim}]PF_6$ as a Function of Time at Different Temperatures

- $T = 133.9^\circ C$
- $T = 235.3^\circ C$
- $T = 284.4^\circ C$

Rates of weight change:
- $-0.0048 \text{ Wt.}% / \text{hr.}$
- $-0.0373 \text{ Wt.}% / \text{hr.}$
- $-0.5092 \text{ Wt.}% / \text{hr.}$
Weight Changes of $[C_{8}\text{mim}]PF_6$ as a Function of Time at Different Temperatures

![Graph showing weight changes over time at different temperatures.]

- **Constant Wt.%**
- **T = 134.2°C**
- **T = 235.9°C**
- **T = 285.4°C**
- **T = 338.1°C**

- **5.365 Wt.% / hr.**
Influence of ANION

![Graph showing weight percentage versus temperature for different 1,3-dimethylimidazolium anions.]

- 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

Legend:
- R1
- R2
- X

Universal V2.3C TA Instruments
Influence of ANION

Weight (%) vs Temperature (°C) graph showing the decomposition of 1-ethyl-3-methylimidazolium OMs and 1-ethyl-3-methylimidazolium OTf.
Influence of CATION structure
Ramp 20°C/min and Isothermal decomposition over 120 min
Schematic of NREL’s MBMS Sampling System

Reactants

React with heat or photons or catalyst

Molecular Drag Pump

Turbomolecular Pump

Products and Transients

Three Stage Free-Jet Molecular Beam Source

Collisions

EI Source

\{P^+\} \rightarrow \{D^+\}

Argon Collision Gas

Turbomolecular Pump

Triple Quadrupole Mass Analyzer

Detector
Thermal Decomposition Pathways

**Demethylation**

\[
\text{Me-X} \xrightarrow{\text{Hofmann Type Elimination}} \text{MeX} + \text{NHNMe}^+ \xrightarrow{-\text{H}^+} \text{NHNMe}^+ + \text{HX}
\]

**Hofmann Type Elimination**

\[
\text{Me-X} \xrightarrow{\text{Hofmann Type Elimination}} \text{Me} + \text{NMe}^+ \xrightarrow{\text{H}^+} \text{NMe}^+ + \text{HX}
\]
MBMS study of [EtMeIm][BF₄]

Proposed thermal events:
1) HF liberation at high T
2) de-alkylation of quat. amine salt
One-Step Synthesis of Ionic Liquids

CHO  glyoxal
+  
MeNH₂  alkylamines
+  
BuNH₂  
+  
HCHO  formaldehyde
+  
HPF₆  (aq. acid)

one-pot synthesis

* avoids chloride salts as intermediates!

* 'adjustment' of melting point and thermal stability
T stability of Ionic Liquid Mixture from One-Step Synthesis

![Graph showing weight (%)](image-url)

- **Mixture**
- 1,3-dibutylimidazolium PF6
- 1,3-dimethylimidazolium PF6
- 1-butyl-3-methylimidazolium PF6
Conclusions

- Imidazolium salts offer flexibility in ‘designing’ melting point and thermal stability
- PF$_6$ salts are ‘easy’ to prepare and purify, and are probably least expensive
- Onset T for thermal decomposition must be determined carefully. Kinetic data are needed for evaluation of long-term T stability
- Reactivity of ANION has strong influence on T stability
- Structure of imidazolium CATION appears to have less influence, but more work is needed
- Influence of IMPURITIES on T stability of ionic liquids is not completely understood and is case-dependent.
- Intermediate chloride salts in synthetic route must be avoided due to residues in final ionic fluid (corrosion)
- One-Step Synthesis of ionic liquid mixtures:
  - a) no chloride residues
  - b) lower ‘complexity' of synthetic process for ionic fluids
  - c) possibly lower production cost
  - d) synthetic methods must be optimized
- Can alternative ionic liquids be developed other than the imidazolium salts?