Hybrid Encapsulated Ionic Liquids for Post-Combustion Carbon Dioxide (CO₂) Capture

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Effectiveness of a full scale CO2 separation/purification from flue gas process will have the challenges:

- Overall flow of the absorbing material
  - Need a “high capacity” absorbent,
  - Ideally: good ratio: mass of CO2/mass of absorbent

- Energy/heat required to reverse reaction and release the CO2
  - Higher reaction enthalpy \(\rightarrow\) higher capacity... but more energy to reverse

- Adiabatic heat rise in absorber
  - More “energetic” the absorption process, the more heat to be dissipated, but the higher capacity.
  - Either extensive internal heat removal or the absorbent must be flowing
Ionic Liquids for CO$_2$ capture

ILs are nonvolatile salts with low melting points, wide liquid phase operating ranges, and very wide range of reaction tunability.

- Potential advantages
  - Good thermal and oxidative stability
  - No evaporation into cleaned gas stream
  - One to one molar reactivity
- Potential disadvantages
  - High molar mass
  - Even our "best" ILs are more viscous than ideal
  - AProtic Heterocyclic Anion (AHA) ILs offer solutions to these issues (Gurkan et al. 2010)

http://www.bellona.org/factsheets/1191913555.13
Previous effort from our group

"Molten" PCIL (phase change ionic liquid) flowing in a 10 cm tray column used for CO$_2$ absorption

For the process, the molten IL would have been a slurry.

In principle, this process could work but the “slurry” would be scary

There is a narrow temperature window for the viscosity of the liquid PCIL to, using a slurry would shrink this substantially.
**Challenge for any new process:**

- In the CO$_2$ concentration range for flue gas, **aqueous amines** are the best commercial process
  - 10,000’s of sailors are kept alive on submarines
  - 1000’s of tons/hr of H$_2$ is produced using amine scrubbing.
- In terms of our process criteria:
  - Temperature is easily controlled even in a large absorber,
  - Continual improvements in capacity with clever chemistry, but still a ways to go.
  - Regeneration temperatures are high enough to allow heat integration with associated processes but the ΔH is large.
Microencapsulation

- Collaboration with Joshuah K. Stolaroff of LLNL:
- Encapsulate IL in a polymer coating
- Viscosity of IL is no longer directly a problem

Operate absorber as fluidized bed

Random and structured packing
Absorber: Volumetric efficiency

Diffusion and reaction in capsule

\[
\frac{\partial A_b(r, t)}{\partial t} = \frac{\alpha_1}{r^2} \left( \frac{\partial}{\partial r} \left( r^2 \frac{\partial A_b(r,t)}{\partial r} \right) \right) - k_{on} A_b(r, t) A_g(r, t) + k_{off} B(r, t),
\]

\[
\frac{\partial A_g(r, t)}{\partial t} = \frac{\alpha_2}{r^2} \left( \frac{\partial}{\partial r} \left( r^2 \frac{\partial A_g(r,t)}{\partial r} \right) \right) - k_{on} A_b(r, t) A_g(r, t) + k_{off} B(r, t),
\]

\[
\frac{\partial B(r, t)}{\partial t} = k_{on} A_b(r, t) A_g(r, t) - k_{off} B(r, t),
\]

Amine absorber: ~1 gmole/(m³ s)

For 200 μm capsules: ~1 gmole/(m³ s)
Results from past 2 years

• Several refinements in the polymer to prevent chemical reaction with different ionic liquids

• Static, batch uptake of capsules is reversible and matches what is expected for neat IL

• Capsules can be fluidized in a laboratory scale (~2 and ~4 in diameter) columns
  – CO₂ absorption and recyclability of capsules commensurate with static, batch absorption—desorption experiments.

• Modeling efforts can predict absorption rates
  – Internal mass transfer control
Laboratory Scale Unit

- Video of capsules in 6 cm column, $V = 12$ cm/s
### LSU – Mass Transfer Measurements

<table>
<thead>
<tr>
<th>Total Flow Rate (liters/min.)</th>
<th>Composition (vol % CO₂)</th>
<th>Pₐ (bar)</th>
<th>Temp (°C)</th>
<th>Absorption Time (s)</th>
<th>Regeneration Amount (L CO₂)</th>
<th>(mol CO₂)</th>
<th>Regen Temp (°C)</th>
<th>mol ratio</th>
<th>k (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3</td>
<td>45.67</td>
<td>0.547</td>
<td>71</td>
<td>1236</td>
<td>0.229</td>
<td>0.0096</td>
<td>114</td>
<td>0.65</td>
<td>1.5E-05</td>
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<tr>
<td>3.3</td>
<td>44.55</td>
<td>0.537</td>
<td>73</td>
<td>433</td>
<td>0.224</td>
<td>0.0094</td>
<td>106</td>
<td>0.64</td>
<td>2.2E-04</td>
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<tr>
<td>3.3</td>
<td>45.93</td>
<td>0.561</td>
<td>78</td>
<td>733</td>
<td>0.23</td>
<td>0.0096</td>
<td>109</td>
<td>0.66</td>
<td>3.1E-05</td>
</tr>
<tr>
<td>3.3</td>
<td>44.74</td>
<td>0.533</td>
<td>69</td>
<td>673.5</td>
<td>0.228</td>
<td>0.0095</td>
<td>108</td>
<td>0.65</td>
<td>8.8E-05</td>
</tr>
<tr>
<td>3.3</td>
<td>45.22</td>
<td>0.542</td>
<td>71</td>
<td>356</td>
<td>0.243</td>
<td>0.0101</td>
<td>114</td>
<td>0.69</td>
<td>1.0E-04</td>
</tr>
</tbody>
</table>

Recyclability (5 cycles) shows consistent CO₂ capacity of 0.66 +/- 0.02 moles CO₂/mol PCIL
Rate Based Model

- Comparison of measured vs. predicted mass transfer flux in a fluidized bed of microcapsules containing NDIL0309

<table>
<thead>
<tr>
<th>Measured mass transfer flux (mol/(m²·s))</th>
<th>Predicted mass transfer flux (mol/(m²·s))</th>
<th>True prediction (no adjusted parameters)</th>
<th>Excellent agreement</th>
<th>Confidence in model</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.84 × 10⁻⁴</td>
<td>3.33 × 10⁻⁴</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Absorption temperature = 70 °C; Capsule diameter = 560 µm; Exposure time = 100 s
New results

• Recyclability of capsules in the presence of water
• Additional modeling comparisons with mass transfer rates for fluidized capsules
• Preliminary results for effect of NO and SO$_2$ on CO$_2$ absorption
• Overall conclusion of optimal heat of absorption.
Task 21: Recyclability and uptake is excellent even with water present.

Corrected for physical CO$_2$ uptake by shell material.

Meets CO$_2$ uptake criterion.
CO$_2$ uptake recyclability of NDIL0230 capsules in the presence of water.
Task 22: Additional comparisons of experimentally measured and predicted CO$_2$ flux data for NDIL0309 microcapsules in laboratory-scale fluidized bed

- Particle size = 586 microns. Total surface area = 0.774 m$^2$. IL content = 65 wt% IL, assuming perfect drying.

<table>
<thead>
<tr>
<th></th>
<th>Run 1</th>
<th>Run 2</th>
<th>Run 3</th>
<th>Run 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>74.5</td>
<td>77.6</td>
<td>72.7</td>
<td>71.7</td>
</tr>
<tr>
<td>Inlet Pressure (bar)</td>
<td>0.41</td>
<td>0.19</td>
<td>0.25</td>
<td>0.26</td>
</tr>
<tr>
<td>Inlet CO$_2$ (vol%)</td>
<td>13.44</td>
<td>13.49</td>
<td>13.33</td>
<td>13.70</td>
</tr>
<tr>
<td>Gas flow (L/min)</td>
<td>34.16</td>
<td>31.33</td>
<td>32.16</td>
<td>32.27</td>
</tr>
</tbody>
</table>
absorber temperature = 293.15 K, absorber pressure = 1 bar, stripper pressure = 1 bar, heat of chemical absorption = $-50\text{ kJ/mol}$, entropy of chemical absorption = $-130\text{ J/(mol K)}$, IL viscosity = 100 cP, weight fraction IL in capsule = 0.5, and microcapsule diameter = 200 micron. The IL cost was taken to be $20/kg and the microcapsule shell material cost $20/kg.
Task 19: Effect of Contaminants

- The fluidized absorber was used for multiple runs where the CO2-N2 mixture was spiked 10 PPM of NO or SO$_2$
- As would be expected from experiments with “neat” IIs, there was some degradation of absorption performance.
Recovery after NO runs

NDIL0309 Absorption

Estimated mol Ratio (CO₂/IL)

Cycle

1  2  3  4  6  7  9  15

NDIL0309 Absorption with Contaminants

Estimated mol Ratio (CO₂/IL)

10 PPM: NO

9 PPM: SO₂

Cycle

10 11 12 13 14 16 17 18 19 20
Concluding remarks

- We have shown that polymer-encapsulated ionic liquids and phase change ionic liquids
  - Can be made chemically compatible in the presence of CO2 and water.
  - That these capsules can be fluidized and used to efficiently absorb CO2 in on a laboratory scale
  - That the mass transfer resistance is controlled by diffusion within the capsule (the polymers have a higher diffusivity than the ILs)
  - That we can model the absorption process and predict an optimal heat of reaction and an optimal stripper temperature
  - That this combination can be used successfully in the presence of water

- Experiments so far indicate that as with a neat IL, NO and SO2 compete for reaction sites, and hence reduce absorption performance.
  - Some of the degradation is reversible.
Acknowledgments

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