Accelerating the development of transformational solvent systems for CO$_2$ separations

FWP 65872

DAVID J. HELDEBRANT
NETL CO$_2$ CAPTURE TECHNOLOGY MEETING
PITTSBURGH, PA
AUGUST 11, 2016
PNNL at a Glance

Intellectual property and startups

Average ONE INVENTION per day
Average ONE PATENT per week
822 LICENSES since 1970s
170+ BUSINESSES started with PNNL IP or executives

FY15:
$955 MILLION in R&D expenditures
FY15: 4,400 STAFF
98 R&D 100 AWARDS
81 Tech transfer AWARDS

822 LICENSES since 1970s
170+ BUSINESSES started with PNNL IP or executives

Average ONE INVENTION per day
Average ONE PATENT per week

U.S. DEPARTMENT OF ENERGY
Proudly Operated by Battelle Since 1965

FY2015 R&D

ENERGY & ENVIRONMENT 20%
NATIONAL SECURITY 33%
OTHER AGENCIES 20%
DHS 6%
NONFEDERAL 2%
SCIENCE 19%
Overview: Integrating Molecular Design, Synthesis & Testing For Multiple Platforms

*Aiding DOE’s transformational solvent portfolio address the grand challenge of viscosity*
Project Goals and Objectives

Objective

▶ Enable advanced solvent designs for all water-lean solvents up DOE’s TRL readiness scale to enable large scale testing and deployment by year 2030.

Goals

▶ Develop a reduced order viscosity model that can predict key solvent physical and thermodynamic properties
▶ Down-select hundreds of candidate molecules to 2-4 viable derivatives
▶ Design testing devices for expedited testing of candidate solvents
▶ Collect necessary additional thermodynamic and kinetic data to validate models
▶ Partner with technology owners to advance the field of water-lean solvents
Project Schedule and Major Tasks

Funding: $2,561,000 / 24 months

BP 1 (May 2014-May 2015)
- 1. Project management ✓
- 2. Molecular development ✓
  - Design 200 molecules from current formulation ✓
  - Construct physical property prediction model ✓
  - Predict physical and thermodynamic properties ✓
  - Revise performance targets ✓
- 3. Synthesis and characterization of candidate molecules ✓
  - Synthesize promising candidates from Task 2 ✓
  - Measure material physical and thermodynamic properties ✓

BP 2 (May 2015-September 2016)
- 1. Project management ✓
- 4. Measure key process physical and thermodynamic data
  - Kinetics, vapor-liquid equilibria
- 5. Process performance projections
- 6. Alternative synthetic methodology identified ✓
- 7. Translation of capabilities to other solvent platforms
  - Collaboration with GE on GAP-1 aminosilicones
Case Study:
CO₂-Binding Organic Liquids (CO₂BOLs)

- "Water-lean" organic switchable ionic liquid solvent system
  - Optimal water level in circulating solvent estimated
    - (~5 wt. % water confirmed by simulation)
  - Heat of solution -80 kJ/mol (similar to amines @ -85 kJ/mol)
  - CO₂BOL material projected at ($35-70/kg)


*Nile Red Solvatochromatic Polarity Scale
Similar to aqueous amine systems except:
- Coalescing tank
- Antisolvent loop
- Water management equipment
- Commercially available equipment and infrastructure
**CO₂BOLs/PSAR Could be Energetically Viable With Lower Solvent Viscosities**

<table>
<thead>
<tr>
<th></th>
<th>MEA (Recreated NETL Case 10)</th>
<th>CO₂BOL/PSAR (356 cP)</th>
<th>CO₂BOL/PSAR (578 cP)</th>
<th>CO₂BOL/PSAR (20 cP Target)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rich solvent loading (mol CO₂/mol solvent)</td>
<td>0.49</td>
<td>0.28</td>
<td>0.34</td>
<td>0.50</td>
</tr>
<tr>
<td>Temperature Required for Regeneration (°C)</td>
<td>120</td>
<td>104</td>
<td>104</td>
<td>85</td>
</tr>
<tr>
<td>Estimated Reboiler Duty (BTU/lb CO₂)</td>
<td>1,520</td>
<td>1,107</td>
<td>965</td>
<td>870</td>
</tr>
<tr>
<td>Increase in Net Electric Power over Case 10 (%)</td>
<td>0</td>
<td>7</td>
<td>9</td>
<td>16</td>
</tr>
</tbody>
</table>

- Viscosity limits the possible *rich* solvent CO₂ loadings and reboiler duty
- If a 20 cP target were achieved:
  - Reboiler duties as low as 870 btu/lb CO₂, (57% of Case 10)
  - 16% increase in net power at an equivalent coal feed rate
Cycle-1 Showed Significant Reductions in Viscosity

- Down-selected from >350 molecules to 13 variants for each viscosity reducing factor
  - Internal H-bond and cation charge solvation (ether) show most promise
- 60% reduction in viscosity for MEIPADM-2-BOL
- Experimental data used to validate molecular models

![Graph showing viscosity vs. loading α_CO2](image)

3,000 cP for IPADM-2-BOL @ 50 mol% CO₂ loading
1,100 cP for MEIPADM-2-BOL @ 50 mol% CO₂ loading
Technical Approach: CO$_2$BOL Solvent Class Cycle-2

*Using PNNL’s infrastructure for 2nd level refinement of CO$_2$BOLs*

- Down-select variants from Cycle-1 derivative
- Use reduced viscosity model that enables viscosity prediction off an optimized structure
- Perform comprehensive solvent property testing using ΔPVT cell
Reduced Model Is Qualitatively Predicting Viscosity From Optimized Structures

\[ X = \frac{q_N q_O}{r_{NO}} - \frac{q_O q_H}{r_{OH}} \]  

\[ P_{int} = c_1 X + c_2 \]  

\[ \eta = c_1 \ln \left( \frac{P_{int}}{1 - P_{int}} \right) \exp (c_2 L) \]

\( \eta \): viscosity  
\( P_{int} \): percent internal hydrogen bond, calculated as a function of \( X \)  
\( L \): mol percent CO\(_2\) loading  
\( c_1 \) & \( c_2 \): constants to obtain the viscosity magnitude in cP, varied to fit the experimental data for at 0 and 25 mol\% CO\(_2\)
PNNL’s Custom ΔPVT Cell Enables Rapid Screening

*Standardized Measurements on ~40 mL scale

**PT** capability matches VLE

- Flow-through viscometer measures cP as a function of CO₂ loading
- Miniaturized wetted wall contactor can extract qualitative kg·m² data

**Figure 1:**
- **Left graph:** Viscosity (cP) vs. Loading α_CO₂ (mol/mol-solvent)
- **Right graph:** Mass flow rate (kg·m²/s·Pa⁵) vs. Loading (mol-mol CO₂/mol solvent)
Applying Molecular Design Towards CO₂BOL Cycle-2

What we learned from Cycle-1:

- High degree of internal hydrogen bonding
- Ether groups for cation charge solvation
- Potential for neutral capture

Viscosity Modifying Factors:

- Fine tuned electronics for acid/base equilibria
- Steric crowding to reduce stacking

Electronic Effects

\[
\begin{align*}
R_2 & \sim N & N & - R_3 \\
X & & X_1 & \sim \text{OH}
\end{align*}
\]

X and \(X_1 = F, \text{Cl, CF}_3, \text{(EWG)}\) or \(\text{OMe, CH}_2\text{NMe}_2, \text{(EDG)}\) and \(R_2=R_3=\text{Me}, \text{CF}_3, \text{CF}_3\text{CF}_2, \text{OMe with } n=1, 2, 3\)

Steric Effects

\[
\begin{align*}
R & \sim N & N & - R_3 \\
R_1 & \sim \text{OH}
\end{align*}
\]

\(R=\text{Pr, } i-\text{Pr, Bu, } t-\text{Bu}\)
\(R_1=\text{Me, Et, } i-\text{Pr with } n=1, 2, 3\)
Reduced Model Predicts ~90% Reduction for Multiple Derivatives (@ 25 mol% CO₂)

- **Reduced Model Predicts ~90% Reduction for**
- **Multiple Derivatives (@ 25 mol% CO₂)**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Value</th>
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<tbody>
<tr>
<td>275</td>
<td>94,139</td>
</tr>
<tr>
<td>228</td>
<td>170</td>
</tr>
<tr>
<td>111</td>
<td>146</td>
</tr>
<tr>
<td>36</td>
<td>13</td>
</tr>
<tr>
<td>n/a, 14</td>
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<tr>
<td>29</td>
<td>n/a</td>
</tr>
<tr>
<td>14</td>
<td>145</td>
</tr>
<tr>
<td>198</td>
<td></td>
</tr>
</tbody>
</table>

*IPADM-2- BOL = 150 cP*
Synthesis & Testing of Cycle-2 Derivatives Confirms Significant Viscosity Reduction

- Synthesizing 4 variants of MEIPADM-2-BOL with ether and isopropyl moieties
  - 90% reduction predicted @ 25 mol% CO₂, 40 °C
- BEIPADIPA-2BOL currently being scaled up for testing

IPADM-2-BOL @ 40 mol% CO₂
MEIPADM-2-BOL @ 35 mol% CO₂
BEIPADIPA-2-BOL @ 42 mol% CO₂

Malhotra et al., Manuscript In Preparation
Integrating Molecular Design, Synthesis & Testing For Aminosilicone Solvents

*Collaboration with GE Global Research*
All Non-Aqueous Solvents May Have “Heterogeneous” Molecular Structure

**CO₂BOL Solvent Class: (100% Concentrated)**

- Different solution and interfacial properties
- Changes as a function of CO₂ loading

**Aminosilicone Solvent Class: (Triethylene Glycol co-Solvent)**

- TEG may not be dissolving GAP carbamates
- Potential for different co-solvent

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Heterogeneous Molecular Structure May Account for Similar Materials Performance

- CO₂BOLs and aminosilicones show similar predicted solvent structure and viscosity profiles as a function of CO₂ loading.

Mass Transfer of GAP-1/TEG is Inverse With Temperature

- Inverse $k_g$ with temperature observed
  - Similar to IPADM-2-BOL$^1$
- Follows trend of physical solubility of CO$_2$ driving liquid-stage kinetics

Mass Transfer of GAP-1/TEG is Greater Than MEA & Piperazine

- $k_g'$ of GAP-1 is twice that of 8 m PZ and 6 times that of 9 m MEA
- 100 Pa of $P^*_{CO2}$ at 40 °C
- Non-aqueous $k_g'$ values larger at higher solution viscosities

Strategies of Refinement of GAP-1 Derivatives

*GAP-1/TEG shows enhanced kinetics compared to aqueous solvents though viscosity can still be lowered*

**Near Term**
- Identify co-solvents that dissolve ionic clusters
- Identify potential diluents to breakup ionic clustering

**Long Term**
- Apply findings from CO₂BOL solvent class to refine GAP derivatives
  - Promote internal H-bonding
  - Add ether groups for charge solvation
  - Increase steric bulk
  - Optimize acid/base equilibria
Benefits of Technology to the Program

- An approach that can benefit all solvent classes
- Rapid modeling and testing of all CO₂ binding mechanisms
- Detailed understanding of molecular level interactions and how they impact performance

<table>
<thead>
<tr>
<th>Property</th>
<th>Alkylcarbonate-Derived</th>
<th>Carbamate-Derived</th>
<th>Imidazole-Derived</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(CO₂BOLs)</td>
<td>(RILs, Aminosilicones, TSILs, Phase-Change)</td>
<td>(imidazole, carbene, AHA ILs)</td>
</tr>
<tr>
<td>Internal H-Bonding</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molecular Stacking</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steric Crowding</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Optimized Thermochemistry</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quantify ( k_g )</td>
<td></td>
<td></td>
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</tbody>
</table>

**KEY**
- Current Work
- Projected Translation
Next Steps: FY17 Work Scope

Three parallel efforts at each level of testing and development

Solvent Class #3
Molecular Development
Cycle 1

Development of model
Initial solvent screen

Aminosilicone
Molecular Development
Cycle 2

Molecular-level refinement
Reduce viscosity by up to 90%

CO₂BOL/PSAR
Continuous Flow
Testing for TEA

Validate performance
$40/ton CO₂ target
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Synthesis & Scaleup

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Dr. Roger Rousseau
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Physical property projections

Dr. Feng Zheng
Process Modeling
Performance Projections

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Dr. David Cantu
Greg Whyatt
Charles Freeman
Andy Zwoster
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Abhoyjit Bhown
Revised Synthetic Pathway and Cost for Optimal Derivative May Achieve Cost Targets

- IPADM-2-BOL costs $407/kg, but projected $35/kg at tonnage scale

![Chemical reaction diagram]

- BEIPADIPA-2-BOL costs $168/kg, but projected at $12/kg at tonnage scale

*Cost target is $10/kg
Aqueous solvents have a reactive interface, a diffusion film, then bulk liquid.¹

CO₂BOLs have a diffusion film (passivated interface) followed by a reaction film, then bulk liquid.²

Potential new diffusion routes and mechanisms of CO₂ and CO₂-containing ions

Different contactor or packing may be needed New film theories needed to quantify this behavior

Utilizing A Heterogeneous Solvent
-Collaboration With CCSI

- Gradient packing to adjust to changing fluid
  - Changes in fluid properties: contact angle, surface tension and viscosity
  - Changes in packing: Structured to random, packing material

Image taken from: http://www.wes-worldwide.com