Low-Viscosity, Water-Lean CO$_2$BOLs with Polarity-Swing Assisted Regeneration (FWP-70924)

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NETL CO$_2$ CAPTURE TECHNOLOGY MEETING
PITTSBURGH, PA
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DOE/NETL Federal Project Manager: Sai Gollakota
Acknowledgment

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Project Objectives

- Rapidly scale-up and demonstrate a promising 3rd Generation CO2BOL solvent candidate from prior solvent development work (1-BEIPADIP-2-BOL)
  - Retains water-lean functionality (only 5-10% water in circulated solvent)
  - Retains shift in polarity upon loading with CO₂ (i.e. still leverages polarity swing)
  - Is a single-constituent solvent (not a blend)
  - Developed to overcome past viscosity challenges (<50cp when fully loaded)

- Leverage the capabilities in the Carbon Capture Simulation for Industry Impact (CCSI²) program.

- Engage industry – recently formed a team with RTI, EPRI, and Fluor Corporation
CO$_2$-Binding Organic Liquids (CO$_2$BOLs)

“Water-lean” organic switchable ionic liquid solvent system.

- ~5 wt. % water
- -80 kJ/mol CO$_2$
- Current projected cost: $15/kg

Project Funding & Tasks

Funding: $2,792,000 / 36 months

Solvent Scale-up

Parametric testing: O₂, SOₓ, NOₓ, H₂O

Kinetic Testing

Techno-economic Assessment

Absorber and Stripper Configurations

Industry Handoff
Project Funding & Tasks

Funding: $2,792,000 / 36 months

Solvent Scale-up

2L synthesized

Parametric testing:
\( \text{O}_2, \text{SO}_x, \text{NO}_x, \text{H}_2\text{O} \)

Kinetic Testing

Techno-economic Assessment

Preliminary TEA In Progress

Absorber and Stripper Configurations

Industry Handoff

Industrial Extension Started
## Project Plan

7/17/2017 – 12/31/2019

Extension: – 4/31/2021

### Budget Period 1 (BP1)

1. Project Management (BP1, BP2 & BP3)
2. Solvent Physical Property Measurements (1-BE/PAKP-2-BOL)
   - 2.1 Vapor-liquid equilibrium, viscosity and other properties
   - 2.2 Polarity effects on loading
   - 2.3 Degradation (oxidative & thermal)
   - 2.4 Wetted wall kinetic measurements
   - 2.5 Initial molecular dynamics modeling
3. Solvent Scale-up (1-BE/PAKP-2-BOL)
   - 3.1 Develop solvent synthesis methodology with scale-up projections
   - 3.2 Initial solvent scale-up production
4. Initial Techno-Economic Projections
   - 4.1 Complete initial process performance projections
5. Laboratory Continuous Flow System (LCFS) Redesign
6. Develop system for synthetic NOx, SOx and O2 additions
7. Retrofit PM6/LCFS based on process optimisation
8. Design and manufacture updated PSAR system
9. Initial CCS2 Engagement
10. Initial Industry Outreach

### Budget Period 2 (BP2)

8. Solvent Durability Measurements
   - 8.1 Measurement of NOx, SOx and O2 interactions
   - 8.2 Aerosol formations
   - 8.3 Corrosion
   - 8.4 Foaming
   - 8.5 Initial molecular dynamics modeling
9. Laboratory Continuous Flow System Testing
10. Parametric testing
   - 10.1 Long duration testing on realistic flue gas
11. Data analysis and reporting
12. Updated Techno-Economic Projections
13. Solvent scale up cost projections
14. Economic projections based on bench cart testing data
15. Slip Stream Testing Preparation
16. Detailed design (or retrofit) of slip stream test system
17. Final CCS2 Engagement
18. Continued Industry Outreach

### Budget Period 3 (BP3)

14. Retrofit of Slip Stream Testing System
15. Equipment/ Material Procurements
16. Equipment/ Installations/ Modifications
17. Startup/ Shakedown of System
18. Testing on Slip Stream System
19. Parametric testing
20. Long duration testing on realistic flue gas
21. Data analysis and reporting
22. Final Techno-Economic Projections
23. Solvent scale up cost projections
24. Economic projections based on slip stream testing data
25. Final Industry Outreach
CO₂BOL Evolution

3rd Generation derivatives are 98% lower in viscosity.

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

Malhotra et al., Manuscript In Preparation.
CO₂BOL Evolution

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Malhotra et al., Manuscript In Preparation.
3rd Generation Derivative Properties

PVT testing shows physical and thermodynamic properties were retained.

Malhotra et al., Manuscript In Preparation.
3rd Generation Derivative Properties

PVT testing shows physical and thermodynamic properties were retained.

- Comparable P* at 40 °C to IPADM-2-BOL at 40 °C
- Identical mass transfer of CO₂ (kg') to IPADM-2-BOL at 40 °C

Malhotra et al., Manuscript In Preparation.
3rd Generation Derivative Properties

PVT testing shows reasonable VLE, viscosity, kg’

- Minimal impact of water on viscosity
- 2.5 and 7.5 wt% isotherms needed to fully quantify VLE with water

Malhotra et al., Manuscript In Preparation.
3rd Generation Derivative Properties

*PVT testing shows rapid *kg*’ for CO₂*

Comparative (kg’) of CO₂ compared to piperazine and MEA

Malhotra *et al.*, Manuscript In Preparation.
PVT testing shows comparable (kg') of CO$_2$ compared to piperazine, higher than MEA as a function of driving force.

5M PZ and 9M MEA data from UT Austin
3\textsuperscript{rd} Generation Derivative Scale-Up Synthesis

\textit{Synthesis of 2L of solvent for property testing}

- All reagents made in-house
  - Previous scales: 10-50g
  - Current batch size: 100-300g
3rd Generation Derivative Properties

PVT testing of scaled-up (2 L) compound is showing different properties than small-scale batches.

- Sample binds and releases CO₂ but has different VLE and viscosity
- Suggests a different compound

Malhotra et al., Manuscript In Preparation.
3rd Generation Derivative Characterization

1H and 13C NMR, IR & Mass Spec data all indicate the same compound,

Ether based amino alcohol condensed with Vilsmeier salt

Chloro-intermediate condenses losing HCl, producing 1-BEIPADIP-2-BOL

*Scale-up of custom solvents is not trivial and due diligence must be used.
Alternative 3rd Generation Derivative Scale-Up

*Currently working on alternative methods of synthesis to bypass intermediates and achieve ($10/kg) cost targets.*

\[
\begin{align*}
1) & \quad \text{NH}_2 (2.0 \text{ eq.}, \text{H}_2\text{O}, \text{RT}, 1 \text{ hr}) \\
\text{H} & \quad \text{H} \\
2) & \quad \text{NaBH}_4 (1.5 \text{ eq.}, \text{H}_2\text{O}, \text{RT}, 1 \text{ hr}) \\
\text{H} & \quad \text{H} \\
\text{N} & \quad \text{N} \\
\text{N} & \quad \text{N} \\
\end{align*}
\]

68% yield

\[
\begin{align*}
\text{N,N-Carbonyldiimidazole (1.0 eq.)} & \quad \text{CH}_2\text{Cl}_2 (2.0 \text{ M}, \text{RT}, 4 \text{ hrs}) \\
\text{N} & \quad \text{N} \\
\text{C} & \quad \text{C} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

80% yield

Then 2M HCl in H₂O

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{O} \\
n\text{Bu} & \quad n\text{Bu} \\
\end{align*}
\]

50% yield

\[
\begin{align*}
\text{NH}_3 \text{ in H}_2\text{O (10 eq.), RT, 4 hrs} \\
\text{H}_2\text{N} & \quad \text{H} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

65% yield (18% overall yield)

- Revised synthesis increased yields and potential for 50% reduced costs
Continuous Flow Cart Upgrade, Retrofit & Shakedown

*Using CCSI² toolset to redesign PNNL’s testing cart for optimal data collection. Shakedown on 1st gen solvent late August*

- All infrastructure has been sized and ordered
  - **Columns**
    - Glass for assessment of flow and phase behavior
    - Jacketed stainless for formal measurements
  - **Sampling valves** (liquid and gas on absorber/stripper/coalescer)
CO$_2$BOL/PSAR Optimal Process Configurations

*Optimal process configurations are solvent-specific.*

Preliminary assessment of solvent regeneration configurations for 1-BEIPADIP-2-BOL-1

<table>
<thead>
<tr>
<th>Solvent Configuration</th>
<th>MEA</th>
<th>BOL</th>
<th>BOL</th>
<th>BOL</th>
<th>BOL</th>
<th>BOL</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS/BOL (mol/mol)</td>
<td></td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Reg. Temp (°C)</td>
<td>116</td>
<td>130</td>
<td>108</td>
<td>130</td>
<td>105</td>
<td>130</td>
</tr>
<tr>
<td>Reg. Pressure (bar)</td>
<td>1.62</td>
<td>1.81</td>
<td>1.81</td>
<td>1.81</td>
<td>1.81</td>
<td>1.81</td>
</tr>
<tr>
<td>Pressure ratio</td>
<td></td>
<td>1.75</td>
<td>1.75</td>
<td>1.75</td>
<td>1.75</td>
<td>1.75</td>
</tr>
<tr>
<td>Heat rate (GJ/tonne CO$_2$)</td>
<td>3.67</td>
<td>2.11</td>
<td>2.10</td>
<td>2.48</td>
<td>2.28</td>
<td>1.98</td>
</tr>
<tr>
<td>Plant $\eta$ (% HHV)</td>
<td>25.4</td>
<td>28.7</td>
<td>29.3</td>
<td>28.1</td>
<td>29.1</td>
<td>28.9</td>
</tr>
</tbody>
</table>

Increasing antisolvent loading in PSAR has minimal effect
Lowest Heat Rate= LVC
Lowest $W_{eq}$ = IHC

*All calculations performed using ASPEN Plus.*
Thermodynamic Efficiency of the CO$_2$BOL/PSAR Configurations

*Calculated equivalent work consumption (kJ/mol CO$_2$) for varied stripper configurations using ASPEN Plus.*

<table>
<thead>
<tr>
<th>Solvent</th>
<th>MEA</th>
<th>BOL</th>
<th>BOL</th>
<th>BOL</th>
<th>BOL</th>
<th>BOL</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Configuration</strong></td>
<td>SS</td>
<td>SS</td>
<td>TSF</td>
<td>IHC</td>
<td>AFS</td>
<td>LVC</td>
</tr>
<tr>
<td><strong>Reboiler/heater</strong></td>
<td>36.7</td>
<td>21.0</td>
<td>24.8</td>
<td>19.8</td>
<td>23.1</td>
<td>19.2</td>
</tr>
<tr>
<td><strong>Cooling</strong></td>
<td>2.4</td>
<td>1.3</td>
<td>1.4</td>
<td>1.1</td>
<td>1.2</td>
<td>1.1</td>
</tr>
<tr>
<td><strong>Refrigeration</strong></td>
<td>2.1</td>
<td>2.1</td>
<td>2.1</td>
<td>2.1</td>
<td>2.1</td>
<td>2.1</td>
</tr>
<tr>
<td><strong>Pump</strong></td>
<td>0.04</td>
<td>0.14</td>
<td>0.14</td>
<td>0.14</td>
<td>0.14</td>
<td>0.14</td>
</tr>
<tr>
<td><strong>Compressor</strong></td>
<td>13.2</td>
<td>12.8</td>
<td>11.9</td>
<td>12.8</td>
<td>12.8</td>
<td>14.7**(d)**</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>52.4</td>
<td>37.3</td>
<td>40.3</td>
<td>35.9</td>
<td>39.3</td>
<td>37.2</td>
</tr>
</tbody>
</table>

(a) None of the above scenarios is optimized.
(b) A Carnot efficiency ($\eta_{stm-tb}$) of 0.9 is used.
(c) The inlet flue gas is chilled by R-134A refrigeration cycle.
(d) This value includes the work of both CO$_2$ compressor and lean vapor compressor.

*Modeling of LLE is empirical at this stage

**Identified LLE data needs for more comprehensive analysis

SS= simple stripper, TSF= two stage flash, IHC= inter-heated column, AFS= advanced flash, LVC= lean vapor compressor
Interheated Column (IHC) had the lowest total equivalent work and was used to the preliminary TEA.

Advantages: strip out CO₂ more efficiently – prevent rich feed from substantial flashing at the top of stripper

Disadvantages: additional plant complexity
Preliminary sizing and cost analysis indicates BEIPADM-2-BOL CAPEX is ~35% higher than MEA, but half of that of IPADM-2-BOL.

<table>
<thead>
<tr>
<th></th>
<th>No Capture</th>
<th>MEA</th>
<th>IPADM-2-BOL/PSAR</th>
<th>BEIPADM-2-BOL/PSAR (AS:BOL=2:1)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NETL Case 9</td>
<td>NETL Case 10*</td>
<td>(356 cP)</td>
<td>SS</td>
</tr>
<tr>
<td>Fuel Cost</td>
<td>1.52</td>
<td>2.20</td>
<td>2.03</td>
<td>1.91</td>
</tr>
<tr>
<td>Capital Cost</td>
<td>3.12</td>
<td>5.95</td>
<td>7.88</td>
<td>5.91</td>
</tr>
<tr>
<td>Variable Cost</td>
<td>0.51</td>
<td>1.02</td>
<td>1.03</td>
<td>0.97</td>
</tr>
<tr>
<td>Fixed Operating Cost</td>
<td>0.78</td>
<td>1.33</td>
<td>1.24</td>
<td>1.17</td>
</tr>
<tr>
<td>Tran., Seq., Mon.</td>
<td>------</td>
<td>0.59</td>
<td>0.56</td>
<td>0.53</td>
</tr>
<tr>
<td>Total ¢/kWh</td>
<td>5.94</td>
<td>11.09</td>
<td>12.75</td>
<td>10.48</td>
</tr>
<tr>
<td>Increase VS No Capture</td>
<td>------</td>
<td>86.7%</td>
<td>115%</td>
<td>76%</td>
</tr>
</tbody>
</table>

*Recreated Case 10

**CO₂ BOL processes are unoptimized, values subject to change.

***CAPEX is currently limited by heat exchanger size and solvent cost.

*COE calculation methodology from Energy & Fuels 30 (2), 1192-1203.
Preliminary sizing and cost analysis indicates BEIPADM-2-BOL Is making progress towards DOE’s $30/tonne target.

<table>
<thead>
<tr>
<th></th>
<th>NETL Case 10* – MEA</th>
<th>CO₂BOL/PSAR IPADM-2-BOL</th>
<th>CO₂BOL/PSAR BEIPADIP-2-BOL-SS</th>
<th>CO₂BOL/PSAR BEIPADIP-2-BOL-IHC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rich solvent viscosity</td>
<td>10</td>
<td>&gt;353</td>
<td>36</td>
<td>36</td>
</tr>
<tr>
<td>(40 °C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Estimated Reboiler Duty</td>
<td>3.67</td>
<td>2.67</td>
<td>2.11</td>
<td>1.97</td>
</tr>
<tr>
<td>(GJ/tonne CO₂)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Net Plant Efficiency</td>
<td>25.4%</td>
<td>27.5%</td>
<td>29.3%</td>
<td>29.5%</td>
</tr>
<tr>
<td>(HHV)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Capital Cost (M USD)</td>
<td>423.5</td>
<td>1103.3</td>
<td>599.7</td>
<td>608.1</td>
</tr>
<tr>
<td>¢/kWh</td>
<td>11.09</td>
<td>12.75</td>
<td>10.48</td>
<td>10.44</td>
</tr>
</tbody>
</table>

*Recreated Case 10
**CO₂BOL processes are unoptimized, values subject to change.
Conclusions

- Solvent scale-up challenges are not insignificant
- BEIPADM-2-BOL has comparable mass transfer to 5M PZ
- Total equivalent work calculated by Aspen Plus is 35.9 kJ/mol CO₂
  - Includes all units of operation
  - Currently unoptimized
- BEIPADM-2-BOL reboiler duties as low as 1.9 GJ/tonne CO₂
- Modeling of LLE is highly empirical at this stage
  - Identified LLE data needs for more comprehensive analysis
- No one size fits all configuration, optimal process configurations appear to be solvent-specific
- BEIPADM-2-BOL projects 50% lower CAPEX than IPADM-2-BOL, 35% higher than MEA
  - Costs still limited by heat exchanger and solvent cost
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  - Chemical Durability
  - Synthesis & Scaleup
  - Dr. Phillip Koech
  - Dr. Deepika Malhotra

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  - Dr. Roger Rousseau

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  - Dr. Feng Zheng
  - Andy Zwoster
  - Dr. David Heldebrant

- Process Modeling Performance Projections
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  - Charles Freeman

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- Dr. Marty Lail
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