CO$_2$-Binding Organic Liquids, Enhanced CO$_2$ Capture Process With a Polarity-Swing-Assisted Regeneration

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Battelle Memorial Institute

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- $4 billion total revenue
- 20,400 staff (including labs)
- 30+ scientific user facilities
- Battelle has managed PNNL since 1965 and retains ability to perform commercial business
Project Overview

• Project Team:
  – BPNWD; project lead, materials development, testing
  – Fluor Corporation; process engineering, technology assessment
  – Queens University; PSAR testing, EH&S

• Project Award:
  – DOE funding: 1.99 million/ 30 months
  – Cost share (Fluor): 500k
  – Sub contract (Queens) 130k
  – Project start Oct 1, 2011

• Project Scope:
  – To advance CO$_2$BOLs from TRL 3 through 4 through bench-scale testing
Goals and Objectives

Goals
• Further develop and verify the performance of the process combining CO\textsubscript{2} binding organic liquids (CO\textsubscript{2}BOLS) with newly discovered polarity-swing-assisted regeneration (PSAR) process.

Objectives
• Develop the CO\textsubscript{2}BOLs/ PSAR solvent and process configuration against DOE’s carbon capture goals of 90% CO\textsubscript{2} capture and a Levelized-Cost of Electricity (LCOE) increase of <35%.
• Collect necessary additional thermodynamic and kinetic information to develop an optimized process configuration for the CO\textsubscript{2}BOLs/ PSAR concept that can be demonstrated at bench scale.
• Conduct a bench-scale demonstration of the technology that includes extended testing for quantifying solvent makeup requirements, by-product formation, and equipment corrosion.
• Use bench-scale testing data to make robust energy and LCOE predictions for a full-scale system, using Aspen Plus™ to model the system.
• Quantify large-scale EH&S impacts for the technology.
Project Schedule and Tasks

• **BP 1** (Oct 2011-Dec 2012)
  – 1. Project Management
  – 2. Initial techno-economic assessment
    - Full process description and analysis
    - Cost estimates
    - Measurement of missing data
    - Revise technology performance targets
  – 3. Bench-scale design and retrofits for PSAR
    - Solvent scale up of two candidate BOLs
    - Retrofit equipment for PSAR

• **BP 2** (Mar 2013-Jun 2014)
  – 4. Bench-scale testing
    - Shakedown testing
    - Bench-scale testing on liquid PSAR and solid PSAR
  – 5. Full technology assessment
Our System: CO$_2$BOLs

- “Water-lean” organic switchable ionic liquid solvent system
- Reduced heat duty from boiling and condensing less water
  - Water balance established
  - Optimal water level in circulating solvent estimated
    - (~5 wt. % water confirmed by simulation)
- Designed as a direct solvent replacement
- Heat of solution -80 kJ/mol

CO$_2$BOL Performance

- Viscosity is two orders of magnitude less than previous 2$^{nd}$ Gen CO$_2$BOLs
- Water does not precipitate bicarbonate salts
- Viscosity with 10% water (worst case loading) has a minor impact
- Further reduction in viscosity needed (20 cP maximum operating viscosity targeted)
  - Molecular refinement underway
  - Diluents under investigation

This team recognizes water-free and water-lean solvents all face this challenge of viscosity
Polarity Swing Assisted Regeneration (PSAR) Concept

- Unique to switchable ionic liquid-like systems
  - PSAR inoperable for water-based or conventional IL systems
- Anti-solvent addition enables lower temperature stripping
  - Used in combination with thermal heating to release CO$_2$

**CO₂ Loading Profiles:**
Addition of Anti-Solvent Changes Equilibrium Loading of CO₂

**Anhydrous**

- Antisolvent addition reduces CO₂ capacity at high temperatures
- No observed effect at 40 & 60 °C
- PSAR observed at 80 & 100 °C
- 0.11 mol fraction less CO₂ @ 100 °C

**With Antisolvent**

_Anergy. & Env. Sci. (2013), 6, 2233 - 2242_
Thermodynamic Model

\[ 2 \text{CO}_2 + 2 \text{BOL} \leftrightarrow \text{BOLCO}_2^+ + \text{BOLCO}_2^- \quad (1) \]
\[ \text{H}_2\text{O} + \text{BOL} + \text{CO}_2 \leftrightarrow \text{BOLH}^+ + \text{HCO}_3^- \quad (2) \]

- Separate charges needed for the zwitterionic \( \text{CO}_2\text{BOL-CO}_2 \) ionic species for Aspen Plus to enable the Born term
  - Accounts for the effect of the ionic strength and the solvent dielectric constant
  - Predicts the effect of the low-dielectric-constant AS to reduce the mixed solvent’s complexation of \( \text{CO}_2 \)
  - Model under continuous revision as new data becomes available

*Energy. & Env. Sci. (2013), 6, 2233 - 2242*
Phase Behavior of CO$_2$BOL and Antisolvent

Temperatures of miscibility for 50 mol% mixtures of various ASs in CO$_2$-lean (A)

<table>
<thead>
<tr>
<th>Antisolvent</th>
<th>Chain Length</th>
<th>$T_{\text{miscibility}}$ ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heptane</td>
<td>7</td>
<td>&gt; 30</td>
</tr>
<tr>
<td>Decane</td>
<td>10</td>
<td>38</td>
</tr>
<tr>
<td>Dodecane</td>
<td>12</td>
<td>39.3</td>
</tr>
<tr>
<td>Hexadecane</td>
<td>16</td>
<td>62</td>
</tr>
</tbody>
</table>

- Miscibility between either CO$_2$-lean BOL or CO$_2$-rich CO$_2$BOL with antisolvent
- Cooling below $T_{\text{miscibility}}$ promotes phase separation

*Energy. & Env. Sci. (2013), 6, 2233 - 2242*
PSAR Conceptual Configuration

Similar to aqueous amine systems albeit with coalescing tank and antisolvent loop

Energy. & Env. Sci. (2013), 6, 2233 - 2242
Heat rate and regeneration temperature as a function of antisolvent (hexadecane) loading

- $T_{\text{regen}}$ drops with increased loadings of antisolvent (72 °C drop at 2 molar equivalents)
- Reboiler heat duty remains unchanged
- Sensitive to water

*Energy. & Env. Sci. (2013), 6, 2233 - 2242*
PSAR May Increase Net Power Output Up to 102 MWe

- For reboiler temperatures that do not require the IP steam temperatures extract power via a let-down turbine before passing the lower temperature steam to the reboiler.
- Uses more steam than directly condensing IP steam from the plant power cycle but the power generated more than compensates.

Projected net electric power output for CO₂BOL-PSAR as a function of AS (C16) loading:

<table>
<thead>
<tr>
<th>Antisolvent Loading (Molar Equivalent)</th>
<th>Regeneration Temperature (°C)</th>
<th>Net Electric Power Produced (MWe)</th>
<th>Parasitic Load</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>159</td>
<td>594</td>
<td>25%</td>
</tr>
<tr>
<td>0.5</td>
<td>132</td>
<td>603</td>
<td>23%</td>
</tr>
<tr>
<td>1</td>
<td>109</td>
<td>621</td>
<td>21%</td>
</tr>
<tr>
<td>2</td>
<td>86</td>
<td>637</td>
<td>19%</td>
</tr>
<tr>
<td>TBD¹</td>
<td>65</td>
<td>652</td>
<td>17%</td>
</tr>
</tbody>
</table>

¹Based on projections of upper critical solution temperature

Energy. & Env. Sci. (2013), 6, 2233 - 2242
Key Findings To Date

- Water management for CO$_2$BOLs is not too costly
  - High water tolerance of the candidate CO$_2$BOL determined.
  - No precipitating bicarbonate salts at water loadings as high as 1 molar equivalent (9.5 wt %)
  - Full dehumidification not required (currently assuming a small, 7MWe, refrigeration unit)

- AspenPlus models of anhydrous solvents containing ions are sensitive to the Debye Hückle term

- Separation of the CO$_2$BOL from the antisolvent is dependent on temperature & CO$_2$ loading
  - Enables antisolvent selection flexibility to tailor miscibility
  - Allows lower lean loadings of the CO$_2$BOL solvent and facile coalescing system design

- CO$_2$BOL/PSAR allows for a higher net power output than Case 10 by either:
  - Lower $T_{\text{Regeneration}}$ enabling a let-down turbine to produce more power
    - 45% lower parasitic power than Case 10 at current 86 °C regeneration temp forecast
    - As high as 51% lower parasitic power if 65°C regeneration temp achieved
  - Or higher stripper pressure at a given $T_{\text{Regeneration}}$ resulting in reduced CO$_2$ compression power
    - Analysis underway
Benefits of Technology to the Program*

- The reboiler heat duty for the CO$_2$BOL process is 57% of NETL Case 10
- PSAR may add an estimated 20% increase in net electric power output over Case 10
- At a given pressure, PSAR lowers the temperature at which CO$_2$ is released from the rich CO$_2$BOL (demonstrated 72 °C reduction)
  - Minimizes thermal degradation and evaporative losses of the CO$_2$BOL solvent
- PSAR decreases COE 17 points compared to the Case 10 baseline (68% versus 85%)
  - Potential for a 21-26 point decrease
- PSAR allows for novel heat integration strategies unavailable to other technologies
  - Retrofit or greenfield potential

* All projections are based on an assumed loaded solvent viscosity at or below 20 cP.
Project Technical & Economic Challenges

- Refined CO$_2$BOL formulation needed to keep viscosity below 20 cP max operating limit
  - Molecular refinement desired
  - Diluents may be applicable, but may impact PSAR performance
  - Separate/ follow-on programmatic work will likely be necessary

- CO$_2$BOL material costs are too high ($35-70/kg)
  - Alternate synthesis strategies need to be developed

- Bench-scale validation of process needed for mass transfer coefficients, solvent lifetime

- Validation/optimization of PSAR process under continuous flow conditions
  - Time and efficiency of anti-solvent separation/carryover
  - Antisolvent impacts on absorber performance
  - Cheap, “green” antisolvent alternatives desired
Project Performance and Future Work

Overall Accomplishments
• All Milestones and deliverables have been completed within budget
• All risks have been addressed and mitigated to date
• Completed an initial feasibility study of the CO$_2$BOL/PSAR process and confirmed economic viability

Future Plans
• Bench-scale testing of the current best-case CO$_2$BOL solvent and PSAR antisolvent.
• EH&S study of CO$_2$BOL and degradation products
• Synthesis of less viscous CO$_2$BOL molecules already identified (as funding permits)
• Development of cheaper synthesis of CO$_2$BOL solvent
• Final technology feasibility study-facilitated by bench scale results

Beyond BP 2
• Testing at slipstream scale
BPNWD’s Testing Facilities

- BPNWD’s Carbon Capture Laboratory Completed in 2012
- $2,000,000 in internal investments
- Facilities include wetted wall column, PTx cells & Mobile Bench-Cart, viscometers, 5L synthesis reactor

**Specifications:**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column diameter</td>
<td>1.26 cm</td>
</tr>
<tr>
<td>Column height</td>
<td>9.1 cm</td>
</tr>
<tr>
<td>Gas flow rate</td>
<td>1–5 slpm</td>
</tr>
<tr>
<td>Solvent flow rate</td>
<td>300 ml/min</td>
</tr>
<tr>
<td>Absorption temperature</td>
<td>25 – 60 °C</td>
</tr>
<tr>
<td>Absorption pressure</td>
<td>1 to 5 bar</td>
</tr>
<tr>
<td>Gas/Liquid interface area</td>
<td>37.3 cm²</td>
</tr>
<tr>
<td>Reservoir capacity</td>
<td>2 liters</td>
</tr>
<tr>
<td>Gas analysis</td>
<td>Mass spectrometer</td>
</tr>
</tbody>
</table>

**Bench-scale solvent cart specifications:**

- Max. gas flow rate: 30 slpm
- Solvent flow rate: 250-300 ml/min
- Max. temperature: 200 °C
- Operating pressure: 1 to 5 bar
- Structured packing: Sulzer EX
- Packing height (absorb/strip): 83 cm / 55 cm
- Packing diameter: 3.2 cm
- Bed height: 108 cm
- Reservoir capacity: 2 liters
- Gas analysis: Mass spectrometer

Wetted Wall 5-L Synthesis Reactor Bench-Scale Portable Cart
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