Molecular Refinement of Transformational Solvents for CO$_2$ Separations (FWP-72396)

Charles Freeman (for David Heldebrant)

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DOE/NETL Federal Project Manager: Andy Aurelio
Acknowledgment

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Agenda

- CO₂BOLs Definition
- Project Objectives
- Project Details
- Technical Results to Date
- Summary
- Future Work
- Questions
What Are CO₂BOLs (Binding Organic Liquids)?

► A class of organic liquids that become zwitterionic liquids when bound with CO₂, enabling a single-constituent solvent (no blends/additives) – *simpler, lower sensible heat, higher overall loadings, less recirculation*

► Can operate with some water “water lean” (5-10 wt%) – *practical water uptake from flue gas, water wash capable*

► Change in polarity with loading – *possible use of polarity swing assisted regeneration – i.e. lower temps*

► Can exhibit viscosity increases with loading (early versions > 3000cp)

**CO₂BOL Families**

- **Alkanolguanidines**
  - e.g. 1-BEIPADIP-2-BOL

- **Aminopyridines (AP)**
  - e.g. 2-MeOEAMP

- **Diamines (DA)**
  - e.g. EEMPA: N-(2-ethoxyethyl)-3-morpholinopropan-1-Amine
Feed the pipeline of transformational post-combustion CO$_2$ capture solvents towards DOE’s $30$/tonne CO$_2$ target

- Focus on Aminopyridine and new Diamine CO$_2$BOLs
- Use PNNL’s molecular modeling/experimental solvent development approach
  - Use established understanding to optimize viscosity, loading & heat of reaction.
  - Tackle vapor pressure, surface tension, thermal conductivity and chemical degradation.
- Inform/support all solvent development across the DOE portfolio
- Disseminate all findings via peer-reviewed publications & engage industry
Project Details

- 36-month project over three budget periods:
  - Budget period 1: 5/18 – 7/19
  - Budget period 2: 7/19 – 1/20
  - Budget period 3: 2/20 – 4/21

- $2,998,000 in federal funding

- PNNL leads the project – tied to DOCCSS solvent project and CCSI²
## Milestones/ Success Criteria

<table>
<thead>
<tr>
<th>Milestone Number</th>
<th>Milestone Description</th>
<th>Completion Date</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Updated Project Management Plan</td>
<td>Jul, 2018</td>
<td>Complete</td>
</tr>
<tr>
<td>1.2</td>
<td>Go-No Go Presentation at NETL</td>
<td>Jul, 2019</td>
<td>Complete</td>
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<tr>
<td>1.3</td>
<td>Delivery of final report to NETL</td>
<td>May, 2021</td>
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### BUDGET PERIOD 1

<table>
<thead>
<tr>
<th>Milestone Number</th>
<th>Milestone Description</th>
<th>Completion Date</th>
<th>Status</th>
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<tbody>
<tr>
<td>2.1</td>
<td>Develop MD-based models for volatility and hydrolysis.</td>
<td>Jun, 2019</td>
<td>Complete</td>
</tr>
<tr>
<td>2.2</td>
<td>Assess MD-based surface energies for 20+ AP/DA solvents on both plastic and metal surfaces.</td>
<td>Jun, 2019</td>
<td>Complete</td>
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<tr>
<td>4.1</td>
<td>Synthesize &amp; characterize (e.g. VLE, viscosity, kinetics) 20+ AP/DA solvents with predicted rich viscosity &lt; 100 cP and vapor pressure &lt;1 torr at 40 °C</td>
<td>Mar, 2019</td>
<td>Complete</td>
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### BUDGET PERIOD 2

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<th>Milestone Description</th>
<th>Completion Date</th>
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<tbody>
<tr>
<td>6.1</td>
<td>Identify hydrolysis reaction mechanism (intermediates, constants, orders) for AP/DA solvents.</td>
<td>Nov, 2019</td>
<td></td>
</tr>
<tr>
<td>7.1</td>
<td>Synthesize/characterize 20+ AP/DA solvents with predicted 2-3 kcal higher hydrolysis energy barriers and half the rates.</td>
<td>Dec, 2019</td>
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### BUDGET PERIOD 3

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<tr>
<th>Milestone Number</th>
<th>Milestone Description</th>
<th>Completion Date</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.1</td>
<td>Develop MD-based models for oxidation energy and rate.</td>
<td>Jan, 2021</td>
<td></td>
</tr>
<tr>
<td>9.1</td>
<td>Synthesize/characterize 20+ AP/DA solvents with predicted 2-5 kcal higher oxidative energy barriers and order-of-magnitude lower rates</td>
<td>Mar, 2021</td>
<td></td>
</tr>
<tr>
<td>11.1</td>
<td>Identify nitrosation reaction mechanisms (intermediates, constants, orders) for 4+ AP/DA solvents, along with mitigation pathways.</td>
<td>Apr, 2021</td>
<td></td>
</tr>
</tbody>
</table>
Project Team

Project Manager
David Heldebrant

Solvent Synthesis
Chemical Degradation
Dr. Phillip Koech
Dr. Deepika Malhotra
Dr. Katarzyna Grubel

Computational Modeling
Dr. Vanda Glezakou
Dr. Roger Rousseau
Dr. Manh-Thuong Nguyen

Property Testing & Analysis
Dr. Feng Zheng
Andy Zwoster
Dr. David Heldebrant
Molecular Modeling Tools

- **Ab Initio** Electronic Structure (~$10^2$-$10^3$ atoms)
  - Accurate description of molecular properties
  - Atomic charges and intermolecular contacts
  - Reaction energetics: H-bonding, CO$_2$ absorption energy

- **Classical Molecular Dynamics** (~$10^4$-$10^5$ atoms)
  - Accurate description of molecular liquid structure
  - Universal OPLS with *ab initio* charges
  - Transport properties: diffusion and viscosity

- Reduced ordered models

- Codes, Software:
  - CP2K ([www.cp2k.org](http://www.cp2k.org))
  - NWChem ([www.nwchem.org](http://www.nwchem.org))
Viscosity Reductions Guided by Molecular Modeling

Prior work:
- Focused on alkanolguanidines and diamines
- Viscosity driver: population of internal hydrogen bonds ($P_{int}$)
- ~300 candidates evaluated/synthesized/tested
- 3 solvents identified with <30 cP at rich loading (99% reduction) – included DOCCS solvent (EEMPA)

Current project:
- Focused on aminopyridines and new diamines
- ~100 candidates evaluated/synthesized/tested to date
- 4 viable candidates identified for with low volatility & low viscosity – as low as 3 cP at rich loading

$$P_{int} = c_1X + c_2$$

$$X = \frac{q_Nq_O}{r_{NO}} - \frac{q_Oq_H}{r_{OH}}$$
Volutility Reduction for Aminopyridine (AP) Solvents

- Low viscosity (via high $P_{\text{int}}$) originally drove higher volatilities.
- New structural motifs added to reduce vapor pressure (2-order-of-magnitude reduction achieved).

Initial AP solvents:

![Initial AP solvents diagram]

<table>
<thead>
<tr>
<th>Compounds</th>
<th>MW</th>
<th>BP (°C)</th>
<th>Vapor Pressure @ 25°C (Torr)</th>
<th>CO2 Loading (wt%)</th>
<th>CO2 Loading (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-MEAP</td>
<td>166</td>
<td>239</td>
<td>0.0414</td>
<td>15%</td>
<td>57%</td>
</tr>
<tr>
<td>2-MEAP+H2O</td>
<td>192</td>
<td>304</td>
<td>0.0009</td>
<td>9%</td>
<td>41%</td>
</tr>
<tr>
<td>1-IPADM-2-BOL</td>
<td>179</td>
<td>262</td>
<td>0.0112</td>
<td>14%</td>
<td>58%</td>
</tr>
<tr>
<td>2-EAMP</td>
<td>204</td>
<td>316</td>
<td>0.0004</td>
<td>7%</td>
<td>33%</td>
</tr>
</tbody>
</table>

AP solvents optimized in BP1:
CAPEX Reduction Opportunity via Plastic Packings

- Plastic process components could offer a number of advantages:
  - Cheaper than steel – $5/tonne CO2 savings via packing only
  - More durable than steel (reduced corrosion and metals leaching)
  - More easily manufactured into unique structures (e.g. gyroids)

- The challenge is wettability – an attribute of water-lean solvents
Connections to DOCCSS and CCSI² Programs

- Contact angle measurements, surface tensions and interfacial properties are feeding absorber modeling and packing designs.
Experimental Contact Angle Results

Key Observations:

- CO$_2$BOLs wet both steels and plastics better than water and MEA
- EEMPA wet some plastics (HMPE and PEEK) better than steel
Molecular Modeling Insights: Wetting

- Unloaded CO2BOL solvent (non polar) migrates to non polar air & plastic surface
  - Drives wetting of plastics
  - Could explain high mass transfer observations

- Loaded solvent (polar) migrates to polar steel surfaces
  - Possibly creates a stagnant layer, which is why steel and plastic contact angles are similar.
These were extreme measurements (e.g. pure O₂)

Higher degradation observed in steel vessels vs plastic or glass

Lower degradation compared to MEA

Reaction Conditions: 16.5 h @ 100 °C
Over time solvent ligand predicted to slowly pull iron off surface (expected to be similar for aqueous amines).

Experimental data suggests that leached metals are catalyzing degradations.

Therefore, plastics may reduced solvent degradation along with reducing CAPEX.
Summary of Results to Date

- Comprehensive MD analysis and screening of ~100 solvent identified 4 new AP/DAs for future study
  - Low volatility (<0.0004 torr)
  - Low viscosity (<5 cP fully loading)
  - Energetics potentially better than EEMPA (currently at 2.1 GJ/tonne).

- DA solvents shown to wet some plastics better than steel.
  - Potential CAPEX saving of $5/tonne CO₂ (packing only).

- For all solvents (incl. aqueous amines) steel interfaces not chemically inert
  - Could lead to both corrosion and solvent decomposition
Future Work

- BP2 (current): Focus on oxidative degradation and hydrolysis
- BP3: Focus on nitrosation
- Continue to engage commercial partners on the newest CO$_2$BOL solvents (i.e. feed the pipeline)
Accepted Manuscripts:

Manuscripts in Process:
1. “Molecular-Level Overhauling of GAP-1/TEG Post Combustion Carbon Capture Solvents” This manuscript covers the molecular design, synthesis and characterization of the new DA compounds that were finalized in Tasks 3 and 4.
2. “Interfacial phenomena of water-lean solvents on carbon capture infrastructure.” This manuscript covers the interfacial phenomena and observed speciation and potential catalytic degradations of water-lean solvents on varied interfaces in Task 2.

Awarded United States Patents:
1. PNNL filed US patent application with Dr. Robert Perry, entitled “NOVEL DIAMINE SOLVENT SYSTEM FOR CO₂ CAPTURE - IPID 31486-E” filed on March 25, 2019. This patent application covers the molecular design of the new DA compounds that were finalized in Tasks 2 and 3.
Acknowledgements

► Office of Fossil Energy and NETL: Andy Aurelio (NETL PM), Lynn Brickett, and John Litynski

► PNNL Team: Dave Heldebrant (PM) Phillip Koech, Deepika Malhotra, Kat Grubel, Vanda Glezkou, Roger Rousseau, Mahn-Thuong Nguyen, Richard Zheng, and Andy Zwoster

► CCSI2 Team: Mike Matuszewski, et al.
Questions?