Reducing Degradation of Carbon Capture Solvents

PROJECT NUMBER: FWP 77217
[NETL/DOE PROJECT MANAGER: Carl Laird]

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Project Overview

Total Project Funding: $1,459,000/18 months
Overall Project Performance Dates: 01/01/2021-06/30/2022

Overall Project Objectives

► Shut-down catalytic oxidative decomposition by steel interfaces by simply passivating the interface with coatings.

► Enable utilization of cheaper carbon steel (304) by surface modification

► Nitrosamine mitigation may enable abandoned economically viable CO₂ capture solvents.

► Evaluate water-lean CO₂ BOLs as active ingredients in next generation aqueous solvent systems

► Demonstrate at least for 72 hrs. of continuous flow testing achieving >95% capture from simulated coal-derived flue gas
PNNL has spent the past few years refining water-lean solvent classes, optimizing 2° and 3° physical and thermodynamic properties that may limit performance.

Potentially limiting properties of water-lean solvents

- ✓ Viscosity
- ✓ Vapor pressure
- ? Thermal conductivity
- ✓ Binding enthalpy
- ✓ Contact angle
- ○ Chemical durability
Thermal and Oxidative Solvent Degradation

- Water-lean solvents appear more stable than aqueous solvents for thermal and oxidative degradations. Due to fundamental differences in pH, charge solvation, dielectric, and H-bonding.

- Alkanolguanidines are less robust than diamines in all degradations.

Go from this: EEMPA water-lean solvent age under flue gas conditions.

To this: $N$-(2-ethoxyethyl)-3-morpholinopropan-1-amine (2-EEMPA)
Influence of Steel Interfaces on Solvent Degradation

Steel interfaces are not chemically inert to solvents, acting as catalysts for degradations.

- Stainless steel packings increase oxidation rate for CO$_2$ capture solvents.
- PNNL hypothesizes that the Chromium Oxide (CrO) or other surface oxides on the surface of 316 SS act as catalysts.
  - CrO are known oxidation catalysts for amine and alcohol moieties.
  - The CrO makes stainless steel corrosion-resistant.
  - Passivating steel interfaces increases solvent lifetime, reducing make-up rates.
    *Suggests other decomposition products (e.g. oxidation via NOx) could be controlled, potentially avoiding nitrosamines.
Project Scope

- **Task 1. Evaluation of Solvent Degradation/Byproduct Formation**
  - Subtask 1.1 – Identification of steel coating candidates
  - Subtask 1.2 – Molecular modeling
  - Subtask 1.3 – Batch testing (multi solvents, additives, coated/uncoated steels, etc.)
  - Subtask 1.4 – Small-scale continuous testing

- **Task 2. Evaluation of CO₂BOLs/Alternate Aqueous Solvent Additives**
  - Subtask 2.1 – Basic solvent property testing of CO₂BOLs at higher water contents
  - Subtask 2.2 – Preliminary Techno-Economic Analysis (TEA)
  - Subtask 2.3 – Molecular modeling
  - Subtask 2.5 – Commercial solvent cost projections
<table>
<thead>
<tr>
<th>Milestone Number</th>
<th>Milestone Description</th>
<th>Estimated Completion Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>1L of 304 and 316 stainless-steel Propak ½” packings coated by both urethane and imidazole coatings.</td>
<td>June 30, 2021</td>
</tr>
<tr>
<td>1.2</td>
<td>5-week (batch) oxidative degradation studies of 4 or more solvents completed, 50% reduction in degradation for urethane, 75% for imidazole coatings.</td>
<td>November 30, 2021</td>
</tr>
<tr>
<td>1.3</td>
<td>Molecular modeling of interfacial phenomena complete. Identification of structural motifs that are most susceptible to catalytic activation by steel interfaces.</td>
<td>November 30, 2021</td>
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<tr>
<td>2.1</td>
<td>VLE, kinetic data collected for 4 aqueous solvent blends of 2-EEMPA/commercial amines</td>
<td>November 30, 2021</td>
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<tr>
<td>2.2</td>
<td>Preliminary TEA of 4 aqueous solvent blends with total equivalent work and total costs of capture quantified for a simple-stripper configuration.</td>
<td>November 30, 2021</td>
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<tr>
<td>Fiscal Year</td>
<td>Date</td>
<td>Success Criteria</td>
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| 2021        | 9/30/2021  | 1) Identification of structural motifs that are most susceptible to oxidative catalytic activation by steel interfaces and demonstrate at least 50% reduction in nitrosation of 4 solvents comprised of diamine, aminopyridine, alkanolamine classes.  

2) Obtain VLE, and kinetic data for 4 aqueous solvent blends of 2-EEMPA/commercial amines and perform preliminary TEA with total equivalent work and total costs of capture quantified for a simple-stripper configuration. Key metrics include viability towards $30/tone CO\textsubscript{2} and reboiler duties ~2.0 GJ/tone CO\textsubscript{2}. |
| 2022        | 9/30/2022  | 1) Perform continuous flow parametric testing on LCFS with coated steels and show reduction in nitrosation by >50% using coated steels  

2) Demonstrate steady-state continuous flow testing of CO\textsubscript{2}BOLs based aqueous solvents for at least 72 hrs., achieving >95% capture from simulated coal-derived flue gas and complete final TEA. Key metrics include at or near $30/tonne CO\textsubscript{2} and reboiler duties <2.0 GJ/tonne CO\textsubscript{2}. |
Coated Steel Packing Material

Identified coatings for steel with potential to be thermally and chemically stable under both absorber and stripper conditions

Synthesis of Imidazolium Salt

Surface Modification of Steel

<table>
<thead>
<tr>
<th>Contact Angle (deg)</th>
<th>Uncoated</th>
<th>Coated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>36, 35, 34, 34, 35, 31, 36</td>
<td>20, 14, 13, 14, 14, 16, 12</td>
</tr>
<tr>
<td>Average of six (discarded)</td>
<td>35 (31)</td>
<td>14 (20)</td>
</tr>
</tbody>
</table>
**Ab initio Molecular Dynamics Simulations: Effects of NO\textsubscript{x} on 2-EEMPA**

AIMD simulations for 2-EEMPA with and without NO\textsubscript{x} show that NO is less likely to react with EEMPA under anhydrous conditions.

- NO is stable as a dimer it is likely to form clusters in a box of anhydrous 2-EEMPA.
- NO\textsubscript{2} is less stable as a dimer in dry 2-EEMPA.
- NO/NO\textsubscript{2} show weak interactions with 2-EEMPA with N-N distribution centered at about 2Å.
**Evaluation of CO$_2$BOLs as Alternate Aqueous Solvent Additives**

**Basic solvent property testing of CO$_2$BOLs at higher water content using PNNL’s custom PVT cell**

- A PTx instrument consisting of Pressure, Volume & Temperature cell, internal wetted conductor and an in-line viscometer.
- Measure VLE, absorption rate, viscosity and vapor pressure at different CO$_2$ loadings and temperature.
- This instrument requires only 50 mL of solvent.
CO₂ uptake capacity increase with water loading.
Rate of reaction $K_g$ is consistent with that water-lean solvent, that is decreasing with CO₂ loading.
Viscosity increase with water content up to 20 wt.% in 2-EEMPA.
2-EEMPA as an Alternate Aqueous Solvent Component

2-EEMPA is a potential substitute ingredient for an unstable component of a leading proprietary aqueous amine (a-amine) solvent formulation.

- Equilibrium partial pressure VLE shows a-amine/2-EEMPA formulation is stronger CO$_2$ capture solvent than pure EEMPA.
- Rate (mass transfer coefficient) is comparable to that of 2-EEMPA.
- A-amine/2-EEMPA has lower viscosity at higher loading than pure 2-EEMPA.
Summary and Future Work

Key Findings

- Identified and synthesized imidazole coatings for steel with potential to be thermally and chemically stable.
- Developed AIMD simulations models for evaluating amine interactions with NO$_x$.
- VLE data shows that 2-EEMPA is a stronger solvent in water and optimal water content for minimum viscosity is 50 wt.%.
- Preliminary results showing that 2-EEMPA has potential to be an additive in aqueous solvent.

Future work

- Completed solvent degradation studies for 2-EEMPA and others with NOx.
- Utilized molecular simulations to identify and degradation pathways and propose mitigation strategies.
- Complete comprehensive property testing for 2-EEMPA as an additive in aqueous solvents.
- Perform preliminary TEA for the best 2-EEMPA/ aqueous solvent formulation.
## Project Management

### 1. Solvent Degradation/Byproduct Formation

1.1 Identification of steel coating candidates

1.2 Molecular modeling

1.3 Batch testing (multi solvents, additives, coated/uncoated steels, etc.)

1.4 Small-scale continuous testing

1.5 Task 1 reporting

### 2. Evaluation of CO2BOLs as Aqueous Solvent Additives

2.1 Basic solvent property testing of CO2BOLs at higher water contents

2.2 Preliminary Techno-Economic Analyses (TEA)

2.3 Molecular modeling

2.4 Batch testing for degradation/byproduct formation

2.5 Commercial solvent cost projections

2.6 Small-Scale Continuous Testing

2.7 Final TEA & Task 2 Reporting

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### Gantt Chart

| Project Management                    |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
| 1. Solvent Degradation/Byproduct Formation |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
| 1.1 Identification of steel coating candidates |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
| 1.2 Molecular modeling                 |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
| 1.3 Batch testing (multi solvents, additives, coated/uncoated steels, etc.) |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
| 1.4 Small-scale continuous testing     |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
| 1.5 Task 1 reporting                   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
| 2. Evaluation of CO2BOLs as Aqueous Solvent Additives |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
| 2.1 Basic solvent property testing of CO2BOLs at higher water contents |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
| 2.2 Preliminary Techno-Economic Analyses (TEA) |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
| 2.3 Molecular modeling                 |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
| 2.4 Batch testing for degradation/byproduct formation |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
| 2.5 Commercial solvent cost projections |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
| 2.6 Small-Scale Continuous Testing    |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
| 2.7 Final TEA & Task 2 Reporting      |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |