Development of a Novel Biphasic CO$_2$ Absorption Process with Multiple Stages of Liquid–Liquid Phase Separation for Post-Combustion Carbon Capture

(DOE/NETL Agreement No. DE-FE0026434)

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2016 NETL CO$_2$ Capture Technology Meeting
Pittsburgh PA • August 11, 2016
Project Overview

- Project objectives
  - Developing new biphasic solvents
  - Demonstrate phase separation-coupled CO$_2$ absorption process
  - Generate and assess engineering and scale-up data

- Project duration
  - 10/1/15 – 9/30/18 (36 months for two BPs)

- Funding profile

<table>
<thead>
<tr>
<th></th>
<th>DOE funding</th>
<th>Cost share (Cash &amp; In-kind)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP1</td>
<td>1,079,663</td>
<td>269,920</td>
</tr>
<tr>
<td>BP2</td>
<td>920,333</td>
<td>231,132</td>
</tr>
<tr>
<td>Total</td>
<td>1,999,996</td>
<td>501,052</td>
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Project Participants

- University of Illinois
  - Illinois State Geological Survey
    - Solvent screening & development
    - Solvent equilibria, kinetics & properties measurements
    - Absorption and desorption column testing
  - Illinois Sustainable technology Center
    - Evaluation of solvent stabilities and corrosion impact
  - Applied Research Institute
    - Molecular dynamics simulation study for solvent screening

- Trimeric Corporation
  - Process feasibility and TEA analysis
Conventional Monophasic Absorption Approach

Conventional CO₂ Absorption Process (e.g., MEA)
Advantages of Biphasic CO$_2$ Absorption Processes

Conceptual of Biphasic Absorption Processes by Other Developers

**Impacts on stripper:**

- Reduced equipment size due to reduced mass of solvent to be regenerated in stripper
- Reduced energy use and compression cost due to increased CO$_2$ loading capacity (concentrated feed), reduced mass, and increased stripping pressure
**Biphasic CO$_2$ Absorption Process with Multi-Stages of Liquid-Liquid Phase Separation (BiCAP)**

- **Cleaned flue gas**
- **Solvent makeup**
- **Solvent tank**
- **Lean solvent**
- **Cooler**
- **Rich solvent**
- **Cross heat exchanger**
- **Rich solvent tank**
- **Inter-stage cooler**
- **Phase separator**
- **Absorption column**
- **CO$_2$-lean phase**
- **CO$_2$-rich phase**
- **Flue gas**
- **Condenser to cooling tower**
- **CO$_2$ (1)**
- **CO$_2$ (2) to compressor**
- **LP steam**
- **Water separator**
- **High-pressure stripper**
- **Reboiler**
- **Condensate to power plant cooling tower**

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**Adds impacts on absorber to the impacts on stripper:**

- Reduced viscosity with separation of rich, viscous phase improves mass transfer rate
- Lean phase to next packed bed improves kinetics
- Reduced mass of solvent to next packed packed bed
Advantages of Multi-Stage Phase Separation (LLPS) during CO\textsubscript{2} Absorption

Illustration of operating & equilibrium curves with 3 stages of CO\textsubscript{2} absorption-LLPS (the equilibrium curve that may change after each LLPS is not displayed in this illustration)

- Modified operating curve allows for a higher mass transfer driving force and thus a faster absorption rate
Biphasic processes vs MEA

- Biphasic solvents have larger loading capacity for CO₂ stripping due to absorbed CO₂ concentrated in one phase as feed solution to the stripper.
- Reduced mass and elevated P for CO₂ stripping:
  - Reduced heat duty (low sensible heat and stripping heat)
  - Reduced compression work requirement.

BiCAP vs other biphasic processes

- **Absorption process:**
  Multi-LLPS in BiCAP allows for low CO₂ loading and low viscosity throughout the absorber, resulting in a faster absorption rate and reduced absorber size.

- **Solvent:**
  Phase transition behavior of BiCAP solvents are tunable, facilitated with the use of a unique solubilizer(s), allowing for a wide range of solvent component selection.

- **Desorption process:**
  Desorption with a flash step to obtain high-pressure CO₂ and reduce compression requirements.
## Project On-Track and Initial Milestones Achieved

### WBS Lead Description Start End Q1 Q2 Q3 Q4 Q5 Q6 Q7 Q8 Q9 Q10 Q11 Q12

| 1.0 | Project management and planning | 10/01/15 | 09/30/18 |
| 1.1 | ISGS/All | Project management and planning | 10/01/15 | 09/30/18 |
| 1.2 | ISGS/All | Briefings and reports | 10/01/15 | 09/30/18 |
| 2.0 | Screening and characterization of biphasic solvents | 10/01/15 | 06/30/16 |
| 2.1 | ISGS | Solvent screening tests on CO2 absorption and phase transition behavior | 10/01/15 | 06/30/16 |
| 2.2 | ISGS | Solvent screening tests on CO2 desorption performance | 10/01/15 | 06/30/16 |
| 2.3 | ARI | Molecular simulation study for solvent screening | 10/01/15 | 06/30/16 |
| 3.0 | Measuring phase equilibria, absorption kinetics, & solvent properties | 01/01/16 | 09/30/16 |
| 3.1 | ISGS | Measurement of VLE data under absorption & desorption conditions | 01/01/16 | 09/30/16 |
| 3.2 | ISGS | Measurement of CO2 absorption kinetics | 04/01/16 | 09/30/16 |
| 3.3 | ISGS | Measurement of solvent properties | 07/01/16 | 09/30/16 |
| 4.0 | Determining thermal and oxidation stabilities of the selected solvents | 04/01/16 | 12/31/16 |
| 4.1 | ISTC | Oxidation stability of solvents under simulated absorption conditions | 04/01/16 | 12/31/16 |
| 4.2 | ISTC | Thermal stability of solvents under simulated desorption conditions | 04/01/16 | 12/31/16 |
| 5.0 | Testing CO2 absorption and phase separation in a packed-bed column | 04/01/16 | 03/31/17 |
| 5.1 | ISGS | Modification of absorption column to incorporate multi-LLPS operation | 04/01/16 | 03/31/17 |
| 5.2 | ISGS | Parametric testing of CO2 absorption and LLPS in the packed-bed column | 07/01/16 | 03/31/17 |
| 5.3 | ISGS | Rate-based modeling of CO2 absorption in the packed-bed column | 10/01/17 | 03/31/17 |
| 6.0 | Development of a process sheet and preliminary process analysis | 04/01/16 | 03/31/17 |
| 6.1 | Trimeric | Development of a conceptual process flow sheet | 04/01/16 | 12/31/16 |
| 6.2 | Trimeric | Preliminary process analysis | 07/01/16 | 03/31/17 |
| 7.0 | Testing CO2 desorption in a high-pressure flash and stripping column | 04/01/17 | 03/31/18 |
| 7.1 | ISGS | Modification of an existing packed-bed column by incorporating a flash unit | 04/01/17 | 09/30/17 |
| 7.2 | ISGS | Parametric testing of high-pressure flash and stripping | 07/01/17 | 03/31/18 |
| 7.3 | ISGS | Design modeling of CO2 desorption in the flash and stripping column | 10/01/17 | 03/31/18 |
| 8.0 | Assessing the impact of solvent corrosion on the equipment | 04/01/17 | 12/31/17 |
| 8.1 | ISTC | Assessing the impact of solvent corrosion on the equipment | 04/01/17 | 12/31/17 |
| 9.0 | Technical and economic feasibility study | 10/01/17 | 09/30/18 |
| 9.1 | Trimeric | Process simulation and mass & energy balance calculations | 10/01/17 | 06/30/18 |
| 9.2 | Trimeric | Technical and economic feasibility study | 01/01/18 | 09/30/18 |
Project Scope and Technical Approach

- Biphasic solvent screening (−Q3)
  - Biphasic solvent screening tests (~50 solvents)
  - Molecular dynamics simulations for solvent screening
  - Downsize to 5-10 solvents
- Biphasic solvent characterization (−Q5 & −Q9)
  - VLE, kinetics, and properties measurements
  - Assessing solvent oxidation and thermal degradation
  - Assessing solvent corrosion impact on equipment
  - Downsize to 2-3 solvents
- Biphasic solvent-enabled process testing (−Q6 & −Q10)
  - Parametric testing of CO₂ absorption & LLPS
  - Parametric testing of high-pressure flash and stripping
- Process analysis & TEA (−Q12)
  - Process flow sheet and techno-economic analysis
Key Milestones and Success Criteria

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<tr>
<th>BP1 (by Q6):</th>
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<tr>
<td>Identify 2-3 top-performing solvents (based on phase transition &amp; CO₂ enrichment behavior, CO₂ loading capacity, absorption kinetics, and viscosity)</td>
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<td>Complete lab testing of 2-3 solvents in an absorption column with multi-LLPS (CO₂ capacity and kinetics ≥5 M MEA; each LLPS stage ≤ 5 min; ≥ 80% CO₂ enrichment in the rich liquid phase)</td>
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<td>Demonstrates reliable operability of the multi-stage absorption &amp; LLPS configuration during lab-scale testing</td>
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<th>BP2: (by Q12)</th>
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<td>Complete lab testing of 2-3 solvents in a flash / stripping system (≥5 bar stripping pressure; working capacity ≥2 times that of 5M MEA)</td>
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<td>Initial techno-economic feasibility study shows significant progress toward achievement of DOE performance goals</td>
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Task 2. Solvent Screening Experiments: Absorption Capacity

- Overall CO$_2$ capacity tested in gas impingers for 60 min of absorption under atmospheric CO$_2$ at 40°C:
  - Most solvents achieved a comparable or slightly higher CO$_2$ loading than 5M MEA for absorption
Phase Transition Behavior

- Formation of dual phases and their volumes are tunable
- CO₂ loading is highly concentrated in rich phase (91-99% of total loading)
- Loading capacity of CO₂ desorption for most solvents is improved by 37-234% over 5M MEA (as only rich phase solution is used for regeneration)
Desorption Pressure

- $P_{CO_2} = 0.7 – 10$ bar at $120 \, ^\circ C$ at lean $CO_2$ loadings of $\sim 0.3 – 0.5$ mol/mol (determined to achieve 90% $CO_2$ removal), which is much higher than that of lean MEA (pressure at $\sim 0.25$ mol/mol)
Characterization of reaction pathways and barriers
- Identified multiple reaction schemes as a function of solvent composition
- Characterized efficiency of bicarbonate protonation
- Computed energy barriers between transition states and carbonic acid via DFT
- Validated reactive molecular dynamics force field for proton transfer

Efficiency of carbon capture
- Calculated enthalpy of formation for carbamate, zwitterions, and protonated amines
- Performed stability analysis for selected ion pairs via association energy in order to construct initial configurations for phase separation simulations
- Computed Gibbs free energy change of selected reactions

Efficiency of phase separation
- Implemented steered molecular dynamics simulation to characterize phase separation process
- Computed free energy change for phase separate system for selected solvent compositions including MEA
- Developed a method to characterize chemical potential differences for species in rich and lean phases

Predicted efficiency based on Gibbs free energy of carbamate formation

Predicted efficiency based on free energy change for phase separation

Transport and mixing properties
- Computed self-diffusion coefficient of reactants and products
- Computed viscosity for selected amines

Characterized transport including diffusivity of species

Speciation completed

Experimental Input
- NMR, MS-GS, water content in each phase, pH
Molecular Dynamics Modeling for Efficiencies of Carbon Capture and Phase Separation

- Carbon capture efficiency screening is performed via thermodynamic calculations using semi-empirical molecular orbital theory (18 reactions considered). Below is one example for the carbamate formation:

\[ Am + CO_2 + Am \rightarrow AmCO_2^- + AmH^+ \]

- ΔG < 0: spontaneous reactions; ΔH < 0: exothermic reactions
- Approach is general to screen any stoichiometry & reactions of interest.

- Phase separation efficiency screening is performed via steered molecular dynamics simulation

- Work done by the system or constraint is a measure of the driving force behind the phase separation process

Zwitterions and carbamates “steered” to separate inside the simulation domain

Favors phase separation

Phase separation not favored
Rate tests using both a stirred tank reactor (exemplary results displayed in plot above) and a wetted wall column reactor (work is ongoing)

Rates tunable by addition of a promoter or selection of a different solubilizer

* S18 (S17+promoter) and S31 (solubilizer different from S17)
Task 3. Viscosity Measurement and Optimization

- Lean phase viscosity < 9 cP (data not displayed)
- Rich phase viscosity was successfully decreased from ~400 cP to ~30 cP by optimizing total solvent concentration and selecting suitable amine structures
Task 5. A Lab Absorption System with 3-Stages of Packed Beds and LLPS Vessels Designed and Under Fabrication

- 3 stages (4-in ID, 7-ft packed-bed for each stage) arranged horizontally to accommodate lab ceiling limit
- 3 stages in one vertical column envisioned for practical use
Lab Prototype Phase Separation Vessel Achieved Efficient and Stable Separation

- Phase separation vessel design
  - Based on density difference (lean phase ~0.85 vs. rich phase ~1.1 g/cm$^3$)
  - Residence time ≤ 5 min (preferred at <1-2 min)

- Actual separation performance
  - Separation efficiency better than the design
  - Able to maintain constant levels of both G-L and L-L interfaces
  - Both interface levels adjustable by adjusting their weir heights
  - Very stable operation

(Liquid volume of 10 L, total volume of 15 L, liquid flow rate of 2 L/min)
Task 6. Preliminary Process Flow Diagram
Developed for BiCAP

Work underway to improve process/unit configuration, identify opportunities to minimize equipment items to reduce cost, and assess integration options into a power plant...
Future Work Plan in this Project

Biphasic solvent screening (–Q3)

❖ VLE data under absorption & desorption conditions
❖ Absorption kinetics
❖ Solvent properties (ΔHr; viscosity, diffusivity, Cp, density)
❖ Thermal & oxidation stabilities
❖ Solvent corrosion tendency

Biphasic solvent characterization (–Q5 & –Q9)

For 2-3 selected solvents:
❖ Testing CO₂ absorption and LLPS in a 3-stage packed-bed column
❖ Testing CO₂ desorption in a flash + stripping column

Biphasic solvent-enabled process testing (–Q6 & –Q10)

❖ Preliminary process analysis and TEA feasibility study

Process analysis & TEA study (–Q12)
Next-Stage Technology Development

- Current project is a laboratory development
- If process and TEA feasibility proven in the current project, next stage would be a close-loop bench or small pilot demo with simulated or actual flue gas
  - Rigorous process design and optimization modeling to enhance performance
  - Analysis of technical risks and mitigation for scale-up
  - Identify industrial partners (design, construction, and testing)
Acknowledgements

- **DOE/NETL Project Manager:** Andrew Jones
- **University of Illinois:**
  - Kevin O’Brien (Co-PI; PhD, Director)
  - Hong Lu (PhD, Chemical/Environmental Engineer)
  - David Ruhter (MS, Lab Manager)
  - Yang Du (PhD, Chemical/Environmental Engineer)
  - Qing Ye (PhD Student)
  - Wei Zheng (PhD, Senior Chemist)
  - Brajendra K Sharma (PhD, Senior Chemical Engineer)
  - Viktoriya Gomilko (MS, Assistant Research Chemist)
  - Joe Pickowitz (Environmental Engineer)
  - Santanu Chaudhuri (PhD, Principal Research Scientist)
  - Naida Lacevic (PhD, Lead Simulation Specialist)
- **Trimeric Corporation:**
  - Ray McKaskle (Subaward PI; P.E., Senior Chemical engineer)
  - Andrew Sexton (PhD, P.E., Senior Chemical Engineer)
  - Kevin Fisher (VP, P.E., Senior Chemical Engineer)