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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2017 NETL CO$_2$ Capture Technology Project Review Meeting

Pittsburgh PA • August 22, 2017
Acknowledgements

- **DOE/NELT Project Manager:** Andrew Jones
- **University of Illinois:**
  - Kevin O’Brien (Co-PI, PhD, ISTC 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)
  - Viktoria Gomilko (MS, Assistant Research Chemist)
  - Joe Pickowitz (Environmental Engineer)
  - Santanu Chaudhuri (Co-PI, PhD, Principal Research Scientist)
  - Naida Lacevic (PhD, Lead Simulation Specialist)
- **Trimeric Corporation:**
  - Ray McKaskle (Subaward PI; P.E., Senior Chemical Engineer)
  - Darshan Sachde (PhD, Senior Chemical Engineer)
  - Kevin Fisher (VP, P.E., Senior Chemical Engineer)
  - Andrew Sexton (PhD, P.E., Senior Chemical Engineer)
Project Overview

- Project objectives
  - Develop new biphasic solvents
  - Demonstrate process concept via lab/bench column testing
  - Generate engineering and scale-up data
  - High-level process and techno-economic analysis (TEA)

- Project duration
  - BP1: 10/1/15 to 06/30/17 (21 months)
  - BP2: 07/1/17 to 12/31/18 (18 months)

- Funding profile

<table>
<thead>
<tr>
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<th>DOE funding</th>
<th>Recipient cost share</th>
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<td>BP2</td>
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<td>BP2 cost share</td>
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<td>Total</td>
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Project Participants

- **University of Illinois**
  - **Illinois State Geological Survey**
    - Solvent development
    - Solvent equilibria, kinetics, and properties measurements
    - Absorption and desorption column testing
    - Process modeling
  - **Illinois Sustainable Technology Center**
    - Assessment of solvent stability and corrosion impacts
  - **Applied Research Institute**
    - Molecular dynamics simulation study for solvent screening

- **Trimeric Corporation**
  - Process feasibility and high-level TEA
Biphasic vs. Conventional Absorption Process

Benefits of biphasic process in stripper:
- Reduced equipment size due to reduced mass of solvent to be regenerated
- Reduced energy use and compression requirement due to reduced mass of solvent, high CO₂ loading, and elevated stripping pressure

Benefits in absorber via phase separation and biphasic solvent development:
- Reduced viscosity with separation of rich, viscous phase improves mass transfer rate and allows use of viscous solvents
- Reduced equipment size
Biphasic CO₂ Absorption Process with Multi-Stages of Liquid-Liquid Phase Separation

Proposed Biphasic CO₂ Absorption Process (BiCAP)

(LLPS: Liquid-Liquid Phase Separation; LP steam: low pressure steam)
Novel Biphasic Solvents

Amine-based solvent blends:

- Tunable phase transition behavior with a new group of solvent formulations
- Consider multi-criteria (capacity, rate, CO\textsubscript{2} enrichment %, desorption pressure, stability, corrosion, viscosity, and availability/cost)
- Allow multiple steps of phase separation
- In aqueous form suitable for humid flue gas application

![Diagram of phase transition](image)

Lean solvent in a single phase

Phase transition induced by CO\textsubscript{2} loading

Two-phase system (w/ tunable phase vol.%)
Advantages of BiCAP for Post-Combustion CO₂ Capture

- **BiCAP Solvents:**
  - Phase transition behavior tunable based on a unique solvent formulation (proprietary), allowing for a wider selection of solvent blends
  - Stable with oxygen and at high temperature (e.g., 150 °C)

- **Absorption process:**
  - Multiple phase separators reduce solvent viscosity and CO₂ loading by removing the more viscous rich-phase solvent during absorption, allowing for use of relatively high viscosity solvents

- **Desorption process:**
  - High working capacity due to the absorbed CO₂ enriched in one phase as feed solution to the stripper
  - Reduced mass of solvent for regeneration and elevated CO₂ stripping pressure result in lower heat duty and compression work requirements
Project Work Plan

Biphasic solvent screening

- Preliminary selection of solvent components
- Biphasic solvent screening tests (≥ 50 solvents)
- Molecular dynamics simulations for solvent screening

Downsize to 5-10 solvents

Biphasic solvent characterization

- 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

- Parametric testing of CO₂ absorption & LLPS
- Parametric testing of high-pressure flash and stripping

Process analysis and techno-economic analysis

BP1: 10/1/15-6/30/17
BP2: 7/1/17-12/31/18
<table>
<thead>
<tr>
<th>Task</th>
<th>Project Tasks</th>
<th>Progress to date</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.</td>
<td>Screening &amp; characterization of biphasic solvents (~50 solvents)</td>
<td>Complete (&gt;80 formulations evaluated)</td>
</tr>
</tbody>
</table>
|      | - Screening on CO₂ absorption & phase transition  
|      | - Screening on CO₂ desorption pressure  
|      | - Molecular dynamics simulation studies | |
| 3.   | Phase equilibria, absorption kinetics, and solvent properties (5-10 solvents) | Complete  
|      | - VLE measurement  
|      | - Absorption kinetics measurement  
|      | - Solvent properties measurement | (VLE for 10 solvents; kinetics for 6 solvents; viscosity/density for ~80 solvents, heat capacity for 11 solvents; heat of absorption for 10 solvents) |
| 4.   | Determining thermal & oxidation stabilities of solvents (5-10 solvents) | Complete  
|      | - Oxidation stability  
|      | - Thermal stability | (Oxidation stability tests for 6 solvents for 2 weeks; thermal stability tests at 120-150 °C for 10 solvents for ~8 weeks) |
| 5.   | Testing CO₂ absorption & phase separation in a multi-stage packed-bed column (2-3 solvents) | Complete  
|      | - Fabrication of experimental system  
|      | - Parametric testing | (Tested 2 selected biphasic solvents) |
| 6.   | Development of a process sheet and preliminary techno-economic analysis | Complete  
|      | - Conceptual process flow sheets  
|      | - Preliminary techno-economic analysis | (Flow sheets developed and preliminary TEA completed) |
All BP1 Milestones (7) and Success Criteria (3) Succeeded

3 technical Success Criteria for BP1:

<table>
<thead>
<tr>
<th>BP1: 10/1/15 – 6/30/17 (by Q7):</th>
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<tr>
<td>Identify 2-3 top-performing solvents (based on phase transition and CO₂ enrichment behavior, CO₂ loading capacity, absorption kinetics, and viscosity)</td>
</tr>
<tr>
<td>Complete lab testing of 2-3 solvents in an absorption column with multi-phase separations:</td>
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<tr>
<td>  CO₂ capacity and kinetics ≥ 5 M MEA;</td>
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<tr>
<td>  Each LLPS stage ≤ 5 min residence time;</td>
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<tr>
<td>  ≥ 80% CO₂ enrichment in the rich liquid phase</td>
</tr>
<tr>
<td>Demonstrate reliable operability of the multi-stage absorption &amp; phase separation configuration during lab-scale testing</td>
</tr>
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</table>
Task 2: Solvent Screening

Working capacity of biphasic solvents:

- Phase separation *decouples* the absorption and desorption steps, resulting in their different solvent working capacities\(^1\)

- For comparison purposes, assuming lean and rich CO\(_2\) loadings equivalent to 0.1 and 5 kPa CO\(_2\) equilibrium pressures at 40° C:
  - Absorption working capacity: \(\geq\) MEA\(^2,3\)
  - Desorption working capacity: 2-4 times > MEA\(^2,3\)

- \(~98\%\) of absorbed CO\(_2\) concentrated in rich phase liquid for most solvents

Notes:

1) CO\(_2\) working capacity for absorption: difference between CO\(_2\) loadings at absorber top and bottom; CO\(_2\) working capacity for desorption - difference between CO\(_2\) loadings at desorber top and bottom

2) Working capacity is estimated based on maintaining lean and rich CO\(_2\) loadings equiv. to 0.1 and 5 kPa CO\(_2\) equilibrium pressures at 40 °C at the top and bottom of absorber or stripper

3) CO\(_2\) working capacity for 5M MEA equiv. to 0.1 and 5 kPa CO\(_2\) equilibrium pressures at 40 °C is estimated at 0.68 mol/kg. Practical MEA lean loading is lower (<0.1 kPa CO\(_2\)) and its practical working capacity amounts to 1-1.25 mol/kg
VLE data measured under both absorption conditions (30–50 °C) and desorption conditions (100-160 °C)
Viscosity Optimization and Reduction

- Most recent solvents have viscosity of CO₂-saturated rich-phase solution <100 cP at 40°C (< 50 cP solvents selected for further testing)
- Lean phase viscosity < 9 cP (data not displayed)

- Thermal degradation tested (1) at 150 °C for 2 weeks and (2) at 120 and 135 °C for 8 weeks

BiS4 solvent (S66, saturated in 5 kPa CO₂) as an example:
- Stability of BiS4 after 2 weeks at 150 °C
  - 4 - 19% of BiS4 components degraded vs. 56% MEA loss at 150 °C
  - Stability of BiS4 at 150 °C similar to 5M MEA at 120 °C

- Degradation at 120 and 130 °C for 8 weeks (not shown in figure) revealed a slower but otherwise similar trend to 150 °C
Biphasic Solvent Oxidative Stability

- Oxidative degradation tested (1) in 96% O₂-4% CO₂ gas (rich loading) and (2) in 96% O₂-400 ppm CO₂ gas (lean loading) in presence of metal catalysts for 10 days at 50 °C

BiS4 solvent (S66) in 96% O₂-4% CO₂ gas mixture as an example:

- <11% solvent components degraded after 10 days at 50 °C vs. 41% MEA loss (Oxidation rate is <27% of MEA)
Task 5. Laboratory Absorption System with 3-Stages of Packed Beds and LLPS Vessels Fabricated and Tested

- 3 stages (4-in ID, 7-ft packed-bed for each) arranged side by side to accommodate lab ceiling limit
- 3 stages in one vertical column envisioned for practical use
Column Testing of 2 Selected BiCAP Solvents

- CO₂ removal rate and loading capacity in the absorption step for the 2 selected solvents (BiS4 and BiS6) exceeded or comparable to 5M MEA under the same L/G and comparable CO₂ lean loading (i.e., corresponding to the same equilibrium $P^*_\text{CO}_2$ at 40°C).

- (3-stages of CO₂ absorption tests with 13 vol.% CO₂ in air at 35 - 40°C)
Effect of Inter-Stage Rich Phase Withdrawal

- Slightly higher CO₂ removal rate achieved with 1-stage LLPS compared to 3-stage LLPS
- Viscosity of CO₂-saturated rich phase solvent is 45 cP for BiS₄ and 35 cP for BiS₆; Inter-stage rich phase withdrawal expected to perform better for higher viscosity solvents (e.g., >100 cP)

(CO₂ absorption tests at L/G=4.8 L/m³, 13.6 vol.% CO₂ in air, and 35 – 40 °C)
Task 6. Preliminary Process Analysis

- Aspen Plus model developed by ISGS to simulate BICAP process and generate mass and energy balance data
- Preliminary Process Analysis conducted by Trimeric for a 550 MWe (net) power plant integrated with BiCAP process
Capture parasitic power use: 20% of gross output (142/726) for BiCAP process vs. 27% (214/802) in DOE Case 12

Total derate for CO₂ capture with BiCAP is 34% lower than Case 12
Compared with DOE Case 12, BiCAP process can achieve:

- 22% reduction in COE;
- 43% reduction in cost of CO₂ captured
- 50% reduction in cost of CO₂ avoided

<table>
<thead>
<tr>
<th>2007$ (x1,000$)</th>
<th>BiCAP</th>
<th>DOE Case 12</th>
<th>Difference vs. Case 12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Plant Cost</td>
<td>$1,130,000</td>
<td>$1,600,000</td>
<td>-29%</td>
</tr>
<tr>
<td>CO₂ Capture and Compression</td>
<td>$378,000</td>
<td>$469,000</td>
<td>-19%</td>
</tr>
<tr>
<td>Total Fixed Operating Costs</td>
<td>$39,900</td>
<td>$53,200</td>
<td>-25%</td>
</tr>
<tr>
<td>Total Variable Operating Costs</td>
<td>$30,300</td>
<td>$35,700</td>
<td>-15%</td>
</tr>
<tr>
<td>Solvent Make-Up Costs Due to Degradation</td>
<td>$2,061</td>
<td>$1,017</td>
<td>103%</td>
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<tr>
<td>Total Fuel Costs</td>
<td>$72,800</td>
<td>$80,400</td>
<td>-10%</td>
</tr>
<tr>
<td>Coal Flowrate (lb/hr)</td>
<td>512,000</td>
<td>566,000</td>
<td>-10%</td>
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<tr>
<td>COE(^1) (mills/kWh, 2007$)</td>
<td>83</td>
<td>107</td>
<td>-22%</td>
</tr>
<tr>
<td>Cost of CO₂ Captured(^1) ($/tonne, 2007$)</td>
<td>$28</td>
<td>$49</td>
<td>-43%</td>
</tr>
<tr>
<td>Cost of CO₂ Avoided(^1) ($/tonne, 2007$)</td>
<td>$35</td>
<td>$70</td>
<td>-50%</td>
</tr>
</tbody>
</table>

\(^1\) Includes Transportation, Storage, and Monitoring;
\(^2\) DOE/NETL-2010/1397, Revision 2, Nov. 2010; Revision 2a, Sep. 2013
Future Work Plan for This Project

- **Task 7. Testing CO₂ desorption in a high pressure flash and stripping column (2 - 3 solvents)**
  - Fabrication of a flash and stripper system
  - Parametric testing of CO₂ flash and stripping
  - Modeling of CO₂ flash and stripping

- **Task 8. Assessing the impact of solvent on equipment corrosion (2 - 3 solvents)**
  - Under absorption conditions
  - Under desorption conditions

- **Task 9. Final Techno-Economic Analysis**
  - Updated process simulation and mass and energy balance calculations
  - High-level cost and sensitivity analysis

**Timeline**

- Parametric testing of high-pressure flash and stripping (by 6/30/18)
- Assessing solvent corrosion impact on equipment (by 3/31/18)
- Process analysis and techno-economic analysis (by 12/31/18)
**BiCAP Technology Development Vision**

Currently

- **10 kWe test Laboratory / Abbott Power plant Champaign, IL**
  - **Funding:** University of Illinois (UI)

- **Solution test Laboratory**
  - **Funding:** DOE / UI

- **Separate Absorber / Stripper**
  - **Funding:** DOE / UI

- **Integrated Closed-Loop System**
  - **Funding:** DOE / UI / Corporate partners / State

- **Parametric Test**
  - **Funding:** DOE / UI / Corporate partners / State

- **0.1 MWe Abbott Power Plant Champaign, IL**

- **1 MWe Abbott Power Plant Champaign, IL**

- **Small Pilot**
  - **Funding:** DOE / UI / Corporate Partners / State

- **Large Pilot**
  - **Funding:** DOE / UI / Corporate Partners / State

- **10 MWe Abbott Power Plant Champaign, IL**
Summaries

Biphase Solvents
- Phase transition behavior tunable with unique solvent formulation
- Working capacity for CO\textsubscript{2} desorption: >2 times > MEA process
- Desorption pressure: 3-4 times > MEA process
- Stable with O\textsubscript{2} and at high temperature
- Acceptable viscosity of CO\textsubscript{2}-loaded rich-phase solvent (≤ 50 cP)

BiCAP Process
- Reduces total parasitic power use for CO\textsubscript{2} capture by 34% compared with DOE Case 12
- Reduces COE by 22% and cost of CO\textsubscript{2} capture by 43% compared with DOE Case 12
Thank you!

Questions / Comments?