An Advanced Catalytic Solvent for Lower Cost Post-combustion CO$_2$ Capture in a Coal-fired Power Plant

Award # DE-FE0012926

Cameron Lippert, James Landon, Kun Liu, Moushumi Sarma, Rafael Franca, Reynolds Frimpong, Guojie Qi
And Kunlei Liu

University of Kentucky, Center for Applied Energy Research

http://www.caer.uky.edu/powergen/home.shtml
Email: cameron.lippert@uky.edu
**Overall Objective:** Address technical hurdles to developing an integrated process focused on a catalyzed solvent utilizing homogeneous catalyst.

**Project Details**
- Benefit from multiple CAER technologies: solvent; catalyst, membrane, process
- Project cost:
  - DOE share: $2.97M
  - Cost share: $742K
- Period performance: 10/1/2013 – 9/30/2016

**Project Objectives**
- Build towards low-cost CO₂ capture system via Integration of multiple CAER technologies
- To verify an advanced catalytic solvent with integrated membrane dewatering for solvent enrichment in our 0.1MW pilot plant (Proof of concept)

---

**CAER**
- Project management
- Catalytic solvent testing
- ASPEN modeling

**CMRG**
- Technical support

**SMG**
- PPE recommendation
- EH&S analysis

**WorleyParsons**
- Front-end engineering support
- TEA

---

2015 NETL CO₂ Capture Technology Meeting
### Project Schedule and Milestones

#### Laboratory Validation and Scale-up

- **Solvent Optimization**
  - **Milestone**: VLE and model regression

- **Membrane Enrichment**
  - **Milestone**: 5% enrichment over 5hr

- **Catalyst Scale-up**
  - **Milestone**: Develop method to produce 50g/batch

- **Milestone**: PPE recommendation & front-end engineering analysis

#### Parametric Testing on 0.1 MWth Unit

- **Catalyst Production**
  - **Milestone**: 500g produced

- **Parametric Testing**
  - **Milestone**: 100hr runs with and without catalyst completed

- **Membrane Enrichment**
  - **Milestone**: 10% enrichment over 100hr and module design

### Previous work

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>BP</td>
<td>-</td>
<td>1</td>
<td>1/2</td>
<td>2/3</td>
<td>3</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

- **Slipstream ~2 MWth**
- **~20 MWe**

- **Verification Testing on 0.1 MWth Unit**
  - **Verification Run**
    - **Milestone**: 500hr verification run
  - **Membrane Enrichment**
    - **Milestone**: Unit integrated and 20% dewatering observed
  - **Techno-Economic Analysis**
    - **Milestone**: TEA showing at least 20% reduction in energy cost compared to Case 12
  - **EH&S**
    - **Milestone**: Favorable EHS assessment

#### 2015 NETL CO₂ Capture Technology Meeting

June 23 – 26
Design and Work Plan

3-Prong Approach

- Process/Economics
- Membrane Enrichment
- Catalytic Solvent

Parametric Baseline
Parametric: Catalytic Solvent
Long-term Verification Run

Increase Performance Lifetime
Scale-up Design
Pilot Plant Integration and Testing

Increase catalyst/solvent thermal stability
Bench-scale Optimization
ASPEN modeling

Technology Scale-Up

2015 NETL CO₂ Capture Technology Meeting
Pre-absorber CO₂ enrichment and dewatered CAER-B3 used to lower the energy cost of CO₂ capture.
Catalytic Solvent CO₂ Capture

Advantages
- Potential for reduced capital cost for post-combustion CO₂ capture
  - Increased scrubber kinetics (smaller absorber)
- Potential for reduced energy consumption compared to reference case (MEA)
  - High $\alpha$; cyclic capacity
  - High stripper temperatures/pressure
  - Less solvent make-up rate

Challenges
- Transition from lab- to bench-scale process under real flue gas conditions
- Solvent oxidation via catalyst addition
- Integration of multiple technologies
- $k_{obs}$ impacts PFO calculation

$$k_{obs} = k[amine] + k'[cat]$$

Pseudo first order approximation

$$k_{g,PFO}' = \frac{\sqrt{D_{CO2} \cdot k_{obs}}}{H_{CO2}}$$

$$k_{g,PFO}' \propto \sqrt{k_{obs}}$$

Higher the value of $k_{obs}$ higher the mass transfer rate

Achieve rate enhancement at higher carbon loadings
**Development Efforts: Catalysts**

**Improved Catalyst**

- 10% rate enhancement in CAER-B3
- Retains activity after heating at 145 °C for 150h
- Simple catalyst preparation; suitable for scale-up

---

![Graph showing thermal stability and mass transfer enhancement for different catalyst iterations.](image)
BP2 Activities

<table>
<thead>
<tr>
<th>Task Number</th>
<th>Title</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>Updated Project Management Plan for budget period 2.</td>
<td>Review and update PMP/SOPO</td>
</tr>
<tr>
<td>8</td>
<td>CAER catalyst Production</td>
<td>Production of at least 500 g of CAER catalyst</td>
</tr>
<tr>
<td>9</td>
<td>Parametric CAER-B3 investigation</td>
<td>100 hour parametric study on conventional PCC using CAER solvent without catalyst at bench-scale completed</td>
</tr>
<tr>
<td>10</td>
<td>Parametric catalytic CAER-B3 investigation</td>
<td>100 hour parametric study with catalyst and gas pre-concentration membrane at bench-scale completed</td>
</tr>
<tr>
<td>11</td>
<td>Membrane dewatering</td>
<td>Membrane shown to dewater CAER-B3 solvent by at least 10% over 100 hours in lab-scale single element testing</td>
</tr>
<tr>
<td>11</td>
<td>Zeolite membrane bench-scale test module design</td>
<td>Completed design for dewatering membrane test module for integration in 0.1 MWth bench-scale test unit</td>
</tr>
</tbody>
</table>

- BP2 has focused on testing in our 0.1 MWth unit
  - baseline testing, parametric catalytic solvent testing
  - short term degradation analysis
- Membrane improvement and module design for pilot integration
## BP2 Milestones

<table>
<thead>
<tr>
<th>Task #</th>
<th>Milestone</th>
<th>Description</th>
<th>Deliverable Date</th>
<th>Completion Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>Updated PMP for BP 2</td>
<td>Review and update PMP/SOPO</td>
<td>10/30/14</td>
<td>12/18/14</td>
</tr>
<tr>
<td>8</td>
<td>CAER catalyst production</td>
<td>Production of at least 500 g of CAER catalyst</td>
<td>12/31/14</td>
<td>12/17/14</td>
</tr>
<tr>
<td>9</td>
<td>Parametric CAER-B3 investigation</td>
<td>100 hr parametric study on conventional PCC using CAER solvent without catalyst at bench-scale completed</td>
<td>2/28/15</td>
<td>1/29/15</td>
</tr>
<tr>
<td>10</td>
<td>Parametric catalytic CAER-B3 investigation</td>
<td>100 hr parametric study with catalyst and pre-concentration membrane at bench-scale completed</td>
<td>8/15/15</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Membrane dewatering</td>
<td>Membrane shown to dewater CAER-B3 by at least 10% over 100 hr in lab scale testing</td>
<td>5/31/15</td>
<td>2/24/15</td>
</tr>
<tr>
<td>11</td>
<td>Zeolite membrane bench-scale test module design</td>
<td>Completed designs for dewatering membrane test module for integration into 0.1 MWth bench-scale unit</td>
<td>6/30/15</td>
<td>6/8/15</td>
</tr>
</tbody>
</table>

### Success Criteria

- A minimum process energy operating condition established based on 100 hour parametric testing for the CAER catalyzed advanced amine solvent showing at least a 20% reduction in stripping energy compared to uncatalyzed CAER-B3 solvent. **80%**

- The validation to show the advantages of the CAER catalyzed amine to the uncatalyzed CAER advanced amine solvent verifying at least a 10% increase in overall mass transfer or 5% more rich solution at the CAER bench-scale evaluation. **80%**

- Zeolite membrane performance at the lab-scale maintains chemical and mechanical stability for 100 hour run verified. **100%**
## Previous Work

<table>
<thead>
<tr>
<th>Scale (g)</th>
<th>Ligand Yield (%)</th>
<th>Ligand Purity (%)</th>
<th>Catalyst Yield (%)</th>
<th>Catalyst Purity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>&gt; 90</td>
<td>&gt; 90</td>
<td>50</td>
<td>&gt; 90</td>
</tr>
<tr>
<td>5</td>
<td>&gt; 90</td>
<td>&gt; 90</td>
<td>86</td>
<td>&gt; 90</td>
</tr>
<tr>
<td>20</td>
<td>70</td>
<td>&gt; 90</td>
<td>77</td>
<td>&gt; 90</td>
</tr>
<tr>
<td>50</td>
<td>&gt; 90</td>
<td>&gt; 90</td>
<td>81</td>
<td>&gt; 90</td>
</tr>
<tr>
<td>100</td>
<td>&gt; 90</td>
<td>&gt; 90</td>
<td>92</td>
<td>&gt; 90</td>
</tr>
</tbody>
</table>

**Zeolite layer**

**Mullite support**

Uniform zeolite layer deposited on mullite support

Zeolite layer *ca.* 50 - 60 μm
Zeolite Membrane Characterization

Y Zeolite crystals
Successful creation of ~25 µm crystalline zeolite layer

Characteristic Y zeolite peaks

Y Zeolite layer ca. 25-30 µm

Pore size ca. 7 Å
Supercages ca. 12 Å
Long term dewatering operation

Membrane: TMAOH/ 1.0 % seed solution /3 s deposition / 10h crystallization (100°C)

Conditions: CAER-B3 solvent α=0.4 , 100°C, 70 PSI, 20 mL/min
Zeolite Membrane Module

High packing density of separation area
Values based on permeate flux of 10kg/m²h and flow rate of 40 mL/min

\[ l = 10 \text{ cm} \]
Active area of each membrane = 23.5 cm²
Target Permeate flow rate = 200ml/min
Assuming 20% rejection= 91 membrane tubes

\[ l = 18 \text{ cm} \]
Active area of each membrane = 48.7 cm²
Target Permeate flow rate = 200ml/min
Assuming 20% rejection= 44 membrane tubes

6 Tubes/Module
Long Membrane Synthesis

Y zeolite peaks

Intensity (cps)

deg

Intensity (cps)

Intensity (cps)
Membrane Improvements

- Use of nanoseeds (OSU) towards the production of a defect-free membrane

- Ideal thickness 5-10 μm to produce higher flux
Bench-Scale CAER-B3 Testing

- Different L/G ratio from variation in liquid circulation
- Absorber inlet temperature (30, 40°C)
- Stripper pressure – (45, 55 psia)
Experiments at liquid load of ~19 m³/(m².h) and stripper pressure of 45 psia, absorber inlet temperature of 40 °C.

### Baseline – No Catalyst Added

<table>
<thead>
<tr>
<th></th>
<th>Total amine wt%</th>
<th>Alkalinity (mol/kg)</th>
<th>Viscosity @ 40 °C (cP)</th>
<th>% Capture</th>
<th>Energy (Btu/lb CO₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>April</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>29.7</td>
<td>5.34</td>
<td>4.67</td>
<td>81</td>
<td>2006</td>
</tr>
<tr>
<td></td>
<td>66.5</td>
<td>7.04</td>
<td>12.84</td>
<td>76</td>
<td>1980</td>
</tr>
<tr>
<td></td>
<td>40.2</td>
<td>4.88</td>
<td>3.76</td>
<td>81</td>
<td>2114</td>
</tr>
<tr>
<td>May</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>38.8</td>
<td>4.87</td>
<td>3.85</td>
<td>81</td>
<td>2007</td>
</tr>
<tr>
<td></td>
<td>40.66</td>
<td>4.98</td>
<td>4.04</td>
<td>75</td>
<td>2135</td>
</tr>
<tr>
<td></td>
<td>36.61</td>
<td>5.05</td>
<td>4.28</td>
<td>79</td>
<td>2107</td>
</tr>
<tr>
<td></td>
<td>42.45</td>
<td>5.10</td>
<td>4.46</td>
<td>79</td>
<td>2085</td>
</tr>
<tr>
<td></td>
<td>35.3</td>
<td>5.18</td>
<td>5.06</td>
<td>77</td>
<td>2034</td>
</tr>
<tr>
<td></td>
<td>36.41</td>
<td>5.03</td>
<td>3.98</td>
<td>78</td>
<td>2005</td>
</tr>
</tbody>
</table>

Maintained similar capture for a range of varying relative concentrations of amines in blend.
CAER-B3 Performance Tests

- Slow decrease in [amine]
  - most likely from aerosol emissions
• Slow increase in alkalinity and viscosity
Membrane Integration

Established process intensification (e.g., pump around) needed with membrane to realize potential energy savings from reduced solvent circulation from the pre-concentration using CAER-B3
Membrane Installed

- Membrane successfully integrated with bench unit with accompanying vacuum pump and blower
  - Modified process

- Demonstrated CO₂ pre-concentration by a factor of ~2 obtainable in system
Energy savings of ~25% could be obtained from the reduced L/G runs with the membrane.

<table>
<thead>
<tr>
<th>Run</th>
<th>L/G wt/wt</th>
<th>Liquid load m³/(m².h)</th>
<th>Absorber LMTD (°C)</th>
<th>Stripper bottom temp. (°C)</th>
<th>Capture efficiency %</th>
<th>Energy (Btu/lb CO₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref 1</td>
<td>5.1</td>
<td>19</td>
<td>50</td>
<td>134</td>
<td>77</td>
<td>2091</td>
</tr>
<tr>
<td>Ref 2</td>
<td>5.3</td>
<td>19</td>
<td>47</td>
<td>135</td>
<td>81</td>
<td>2006</td>
</tr>
<tr>
<td>Membrane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>4.9</td>
<td>17.8</td>
<td>43</td>
<td>137</td>
<td>82</td>
<td>1650</td>
</tr>
<tr>
<td>2</td>
<td>3.8</td>
<td>13.6</td>
<td>41</td>
<td>138</td>
<td>80</td>
<td>1473</td>
</tr>
<tr>
<td>3</td>
<td>3.7</td>
<td>13.4</td>
<td>42</td>
<td>140</td>
<td>82</td>
<td>1515</td>
</tr>
<tr>
<td>4</td>
<td>3.1</td>
<td>10.8</td>
<td>42</td>
<td>140</td>
<td>88</td>
<td>1412</td>
</tr>
<tr>
<td>5</td>
<td>2.9</td>
<td>10.6</td>
<td>43</td>
<td>140</td>
<td>86</td>
<td>1465</td>
</tr>
</tbody>
</table>
Acknowledgements

The work presented here was made possible through funding by:

- The U.S. DOE/ National Energy Technology Laboratory
  - Project Award # DE-FE-0012926


<table>
<thead>
<tr>
<th>CMRG</th>
<th>SMG</th>
<th>WorleyParsons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lynn Brickett, José Figueroa</td>
<td>Heather Nikolic, Kun Liu, Jesse Thompson, Brad Irvin</td>
<td>John Moffet, David Link, Michael Manahan, Doug Durst, Talina Matthews, Abhoyjit Bhown, Curtis Sharp</td>
</tr>
<tr>
<td>Clayton Whitney, Sarah Carty</td>
<td>Mike Bartone, Vlad Vaysman</td>
<td></td>
</tr>
</tbody>
</table>
Thank You