Low-Energy Solvents for CO$_2$ Capture Enabled by a Combination of Enzymes and Vacuum Regeneration

Sonja Salmon
Notices

- **ACKNOWLEDGEMENT OF GOVERNMENT SUPPORT.** This material is based upon work supported by the Department of Energy under Award Number DE-FE0007741.

- **DISCLAIMER.** This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

- **COPYRIGHT NOTICE.** Copyright, 2014, Novozymes North America, Inc., Pacific Northwest National Laboratory, University of Kentucky Research Foundation, and Doosan Power Systems Ltd.

The use in this report of any copyrighted data owned by any of the above parties is authorized pursuant to the relevant contract between such party and Novozymes North America, Inc., relating to the Department of Energy Award Number DE-FE0007741. For such copyrighted data, the copyright owner has granted to the Government, and others acting on its behalf, a paid-up, nonexclusive, irrevocable, worldwide license to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government, for all such data.
Agenda

- Project Overview
  - Partners, budget & objective
- Technology Background
  - Process concept
  - Fundamental mechanism
- Progress and Status
  - Project plan & accomplishments
  - Bench-scale system description
  - Parametric test plan
  - Parametric test results
- Conclusions & Next Steps
Project Overview

- Project Participants

- DOE Project Manager: Andrew Jones
- Project Number: DE-FE0007741
- Total Project Budget: $2,088,644
  - DOE: $1,658,620
  - Cost Share: $430,024

DOE Program Objectives
Develop solvent-based, post-combustion technology that
- Can achieve ≥ 90% CO₂ removal from coal-fired power plants
- Demonstrates progress toward the DOE target of <35% increase in LCOE.
Novozymes in Brief – World Leader in Bioinnovation
Producing large volume enzymes for industrial applications

1. Improving the production host
   Improving the microorganisms’ ability to produce more enzymes per m³ fermentation tank through genetic engineering

2. Optimizing industrial production
   • Process optimization
   • Equipment optimization
   • Input optimization

3. Improving the enzyme produced
   Improving the efficacy of the enzymes through protein engineering to meet application conditions and process economy requirements
Project Objective

Complete a *bench-scale study* and corresponding full technology assessment to validate the potential in meeting the DOE Program Objectives of a *solvent-based post-combustion carbon dioxide capture* system that integrates

\[ \text{CO}_2 + \text{H}_2\text{O} + \text{K}_2\text{CO}_3 \leftrightarrow 2\text{KHCO}_3 \]

- a *low-enthalpy*, aqueous potassium carbonate-based solvent
- with an *absorption*-enhancing (*dissolved*) carbonic anhydrase enzyme catalyst
- and a low temperature vacuum *regenerator*
- in a *re-circulating* absorption-desorption process configuration
**Process Concept, Advantages & Challenges**

- **Stable, benign, non-volatile** aq. $\text{K}_2\text{CO}_3$-based solvent does not require water wash.

- Enzyme-enhanced $\text{CO}_2$ mass transfer reduces absorber size to feasible height.

- $\text{K}_2\text{CO}_3$ loading capacity limit may increase solvent circulation rate.

- **Absorption**
  - 1 atm/30-40°C

- **Regeneration**
  - $\sim 0.35$ atm/76°C

- Dissolved enzyme enables liquid dosing.

- Increased compression energy to account for vacuum regen condition.

- Potential to minimize stripper size via enzyme-enhanced $\text{CO}_2$ desorption (simulation).

- Potential to use low pressure steam in combination with vacuum for low enthalpy $\text{K}_2\text{CO}_3$ regeneration.

- Enzyme temperature limits may result in high enzyme replenishment requirement.

Generating Bench-scale Test Data
CO₂ Absorption Mechanism

Gas Side

Liquid Side (pH > 9)

\[ \text{CO}_2(aq) + \text{HO}^- \leftrightarrow \text{HCO}_3^- \]

\[ \text{CO}_2(aq) \]

\[ \text{CO}_2(aq) + 2\text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}_3\text{O}^+ \]

\[ \text{KHCO}_3^- \]

\[ \text{K}_2\text{CO}_3 \]

\[ \text{KHCO}_3^- \]
Enzyme Enhanced CO₂ Absorption Mechanism

Gas Side

\[ CO_2(g) \leftrightarrow CO_2(aq) \]

Liquid Side (pH>9)

\[ CO_2(aq) + HO^- \leftrightarrow HCO_3^- \]

\[ CO_2(aq) + 2H_2O \leftrightarrow HCO_3^- + H_3O^+ \]

\[ KHCO_3^- \]

\[ K_2CO_3 \]

Overall Mass Transfer Coefficient (Kₜ) Enhanced by Enzyme in WWC

Enzyme adds value because, without catalyst, liquid side reaction kinetics are overall mass transfer rate limiting
Approach to Kinetic Model

- Improve existing Aspen kinetic model for $\text{CO}_2 + \text{OH}^- \rightarrow \text{HCO}_3^-$
  - Include data representing a wider temperature range than prior model
  - Include the effects of ionic strength on rate
  - Correct existing reverse kinetics to provide agreement with equilibrium model predictions at temperatures $<70^\circ\text{C}$.

- Include a parallel rate expression for $\text{CO}_2 + 2\text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{HCO}_3^-$
  - Model enzyme effect by accelerating this reaction, not hydroxide reaction

Comparison of equilibrium constants predicted by equilibrium model and pre-correction kinetic model.
# Project Plan & Accomplishments

<table>
<thead>
<tr>
<th>Task</th>
<th>Status/Result</th>
<th>Reporting</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1 – Management &amp; Administration</strong></td>
<td>Within budget; Project focused on vacuum stripping when flow thru ultrasonics gave &lt; needed results</td>
<td>Current per requirements</td>
</tr>
<tr>
<td><strong>2- Process Optimization</strong></td>
<td>Preliminary targets met&lt;br&gt; • Batch-mode ultrasonics tests conducted&lt;br&gt; • Enzyme-solvent absorption kinetics met target in WWC&lt;br&gt; • Bench-scale system designed, incl. vacuum regen</td>
<td>CCTM 2012 29th IPCC</td>
</tr>
<tr>
<td><strong>3 - Initial Technical &amp; Economic Feasibility</strong></td>
<td>Versus DOE Base Case 10, identified opportunities for&lt;br&gt; • 55% lower parasitic load with ultrasonics&lt;br&gt; • 43% lower parasitic load with vacuum stripping</td>
<td>BP2 Continuation</td>
</tr>
<tr>
<td><strong>4 - Bench Unit Procurement &amp; Fabrication</strong></td>
<td>Prototype flow-through ultrasonic unit built &amp; tested; Constructed bench-scale absorber with vacuum stripper</td>
<td>12th CCUS CCTM 2013</td>
</tr>
<tr>
<td><strong>5 - Bench-scale Integration &amp; Shakedown Testing</strong></td>
<td>Shakedown testing w/vacuum stripping completed&lt;br&gt; • Bench-scale system build completed &amp; operational&lt;br&gt; • 90% capture achieved with 30°C absorber; 30 SLPM gas flow; 78°C reboiler; 20 wt% K$_2$CO$_3$; 3 g/L Enzyme</td>
<td>BP3 Continuation</td>
</tr>
<tr>
<td><strong>6 - Bench-scale Testing</strong></td>
<td>Parametric testing completed&lt;br&gt; • Selected baseline conditions for 500 hr test &amp; obtained data for kinetic model&lt;br&gt; Rate-based simulation for vacuum stripping&lt;br&gt; • Framework for the kinetic model established&lt;br&gt; 500 h testing currently in progress</td>
<td>CCTM 2014 AIChE 2014</td>
</tr>
<tr>
<td><strong>7 - Full Technology Assessment</strong></td>
<td>TEA and EH&amp;S in progress&lt;br&gt; • Bench-scale results provide input to the assessment</td>
<td>Completion 1Q15</td>
</tr>
</tbody>
</table>
Bench-scale Unit Description

- **Flow Rates**
  - Gas: 30 SLPM (15% CO₂, humidified)
  - Liquid: 300-600 ml/min

- **Liquid Temperature**
  - Absorber Inlet: 30-40°C
  - Stripper Inlet: ~65°C
  - Reboiler Oil Inlet: 90-95°C

- **Stripper Pressure:** 0.35 atm absolute
- **K₂CO₃ Concentration:** 23 wt%
- **Enzyme Concentration:** 0 – 4 g/L
PFD of Integrated Bench-scale System

Reboiler duty =

\[ C_p \rho Q \left( T_{\text{hot oil inlet}} - T_{\text{hot oil outlet}} \right) \]
Capture Efficiency = \frac{{\text{inlet } CO_2 \text{ mole flowrate} - \text{outlet } CO_2 \text{ mole flowrate}}}{{\text{inlet } CO_2 \text{ mole flowrate}}}

PFD of Integrated Bench-scale System
Rich soln inlet temp is set ~10 °C lower than reboiler bulk temp
Bench-scale Operational Observations

Absorber
- Stable temp along absorber length (40°C ± 1°C)
- Antifoam dosing effectively mitigates foaming
- No visual change in packing
- Rich solvent filter removes (modest) solids

Stripper
- Water cooled condenser at top
- Tube and shell reboiler
- Bulk temp ranges from 76°C (reboiler) to 65°C (rich solvent inlet to stripper top)
Shakedown: Enzyme Dose Impacts CO$_2$ Capture

Operational parameters

- Solvent flow rate: 700 ml min$^{-1}$
- Gas flow rate: 30 LPM
- CO$_2$ inlet conc.: 15%
- Absorber: 30°C absorber
- Stripper:
  - reboiler bulk liquid: 76-80°C
  - reboiler tube surface temperature:
    - hot oil inlet: 95°C
    - hot oil outlet: 90°C
- Vacuum pressure: ~0.3 atm absolute

Each bar represents average data collected over 3 run days, with ~4.5 hours steady-state operation during each run day. System is shut down overnight. Solvent remains in reservoir and is reused for next run day.
### Parametric Test Matrix

Each condition was evaluated over 2-3 run days

<table>
<thead>
<tr>
<th>Run</th>
<th>Enz. conc. (g/L)</th>
<th>Flow rate (ml/min)</th>
<th>Hot oil inlet (°C)</th>
<th>Absorber (°C)</th>
<th>Pressure at stripper top (atm absolute)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.5</td>
<td>500</td>
<td>95</td>
<td>40</td>
<td>0.35</td>
</tr>
<tr>
<td>2</td>
<td>2.5</td>
<td>600</td>
<td>95</td>
<td>40</td>
<td>0.35</td>
</tr>
<tr>
<td>3</td>
<td>2.5</td>
<td>400</td>
<td>95</td>
<td>40</td>
<td>0.35</td>
</tr>
<tr>
<td>4</td>
<td>2.5</td>
<td>300</td>
<td>90</td>
<td>40</td>
<td>0.35</td>
</tr>
<tr>
<td>5</td>
<td>4</td>
<td>500</td>
<td>90</td>
<td>40</td>
<td>0.35</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>300</td>
<td>90</td>
<td>40</td>
<td>0.35</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>500</td>
<td>90</td>
<td>40</td>
<td>0.35</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>300</td>
<td>90</td>
<td>40</td>
<td>0.35</td>
</tr>
<tr>
<td>9</td>
<td>0</td>
<td>500</td>
<td>90</td>
<td>40</td>
<td>0.35</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>500</td>
<td>95</td>
<td>40</td>
<td>0.35</td>
</tr>
</tbody>
</table>

- **Condition for long term test**
- **No-enzyme reference condition**
### Selected Parametric Test Results

<table>
<thead>
<tr>
<th>Parameter</th>
<th>#1</th>
<th>#10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Enzyme Dosing, g/L</td>
<td>2.5</td>
<td>0</td>
</tr>
<tr>
<td>Liquid Flow Rate, mL/min</td>
<td>500</td>
<td>500</td>
</tr>
<tr>
<td>Feed Gas Temp, °C</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Reboiler Solution Temp, °C</td>
<td>77</td>
<td>76</td>
</tr>
<tr>
<td>Lean Solvent Temp, °C</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Outlet CO₂ Conc, %</td>
<td>1.9</td>
<td>12.4</td>
</tr>
<tr>
<td>Total Gas Flow, LPM</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Hot Oil Inlet Temp, °C</td>
<td>95</td>
<td>95</td>
</tr>
<tr>
<td>Q, Reboiler, KW</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>Capture Efficiency (%)</td>
<td>89%</td>
<td>19%</td>
</tr>
<tr>
<td>Energy Demand (kJ/mol CO₂ captured)</td>
<td>382</td>
<td>1611</td>
</tr>
<tr>
<td>Stripper Top Pressure, kPaa</td>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td>Rich Conversion</td>
<td>54%</td>
<td>43%</td>
</tr>
<tr>
<td>Lean Conversion</td>
<td>35%</td>
<td>39%</td>
</tr>
</tbody>
</table>

Results shown are average values from duplicate runs for each test.
Impact of Enzyme Conc. and Liquid Flow Rate

Capture Efficiency (%) vs. Enzyme Dosing (g/L)

- 500 ml/min
- 300 ml/min

40°C absorber
90°C hot oil inlet
Enzyme Longevity Observations

- **Positives**
  - Even though enzyme is exposed to high temperatures in the stripper, dissolved enzyme replenishment is successful in maintaining system performance
  - Confirmed that current enzyme candidate in dissolved form could well tolerate exposure to temperatures below about 60°C

- **Challenges**
  - Current enzyme is deactivated at the higher temperatures in the stripper, especially suspect is the reboiler tube surface temp

- **Potential mitigation: Immobilized enzyme**
  - Hold in absorber (if temp in regenerator is too high)
  - Shield enzyme from direct contact with heating coil skin
Lab-scale, closed loop tests evaluate enzyme longevity during recirculation between 40°C and higher temp.

- Suggests reboiler bulk liquid (~76°C) and especially heating source skin temperature (90-95°C) results in enzyme activity loss.
Enzyme Replenishment for Parametric Tests

- Conservative 20% volume replacement used to ensure performance for parametric testing.
- Offline enzyme activity analysis and agreement among 2-3 day replicate runs on bench unit indicate stable bench unit performance.
- Both sufficient enzyme plus reboiler heat input were needed to achieve highest % capture; high enzyme activity alone could not replace heat input requirement.
- Lower enzyme activity corresponded to lower % capture performance.
- Replenishment rate refinement planned for long term testing with conditions from Parametric Run P1 – with 89% capture.
500 Hour Long Term Test

- Baseline conditions
  - 40°C absorber
  - 95°C reboiler heating source temperature
  - 0.35 atm absolute stripper top pressure
  - 500 ml/min liquid flow rate
  - 30 SLPM gas flow rate; 15% CO₂ inlet (humidified)
  - 2.5 g/L enzyme dosing

- Daily solvent replenishment
  - Enzyme replenishment: 20% solvent volume replacement (initially)
  - Antifoam dosing: 0.04% (together with above)

- Preliminary observations
  - Enzyme activity is stable at current replenishment rate
  - Pressure drop increasing in stripper due to foaming
  - Energy measurement is only relative (within the unit), not absolute
Conclusions and Next Steps

- **Conclusions**
  - 30 SLPM benchscale unit is operational and providing unique test data for low P/low T stripping with enzyme-enhanced K$_2$CO$_3$-based solvent
  - Parametric testing resulted in selection of 500 hour test conditions currently operating at 85-90% capture
  - Current enzyme longevity is significantly diminished by travel through stripper, but can be mitigated for test purposes by replenishment program

- **Next Steps**
  - Conduct 500 hour testing
  - Complete kinetics-based process simulation and ASPEN models
  - Prepare full TEA and EH&S assessment
    - 4 plant model cases defined for full TEA, based on bench-scale test results
    - Process emission and effluent streams and species identified for EH&S and preliminary risk assessment in progress

- **Potential Future Developments**
  - Improve enzyme (apparent) temp stability, guided by TEA stripper conditions
    - Immobilization or chemical modification to create physical barrier to unfolding
    - ID alternate enzyme candidates and/or protein engineering to improve T stability
  - Evaluate options for increasing liquid loading capacity
Thank You

Acknowledgements

DOE-NETL
Andrew Jones

Pacific Northwest National Laboratory
Charles Freeman (PM/TL), Mark Bearden
Greg Whyatt

UK-Center for Applied Energy Research
Kunlei Liu (PM), Kun Liu (TL), Guojie Qi
Reynolds Frimpong

Doosan Power Systems
David Fitzgerald (PM), Jonathan Slater (TL)

Novozymes
Sonja Salmon (PI/PM), Alan House (TL)
Erin Yarborough