Advanced Low Energy Enzyme Catalyzed Solvent for CO$_2$ Capture

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Project Overview

• Project participants

• Project duration: 24 months (initiated in Oct’2010)

• Funding:
  – Total Project: $ 3,256,759
  – DOE funding: $ 2,605,407
  – Akermin Cost share: $ 651,352
Akermin

• Founded in 2004 to commercialize patented enzyme immobilization and stabilization technology
  – Technology based on use of novel micellar polymers to immobilize and stabilize enzymes
  – Originally developed at St. Louis University, Akermin has exclusive, world-wide rights

• Akermin’s technology can be applied to a variety of enzymes for applications requiring long enzyme life under harsh conditions
  – Focused on carbon capture opportunity (since 2009)
Key Driver for Solvent-based CO$_2$ Capture:
Energy Cost Minimization

- Most amine-based post-combustion CO$_2$ capture imposes an unacceptable energy demand on power plant due to energy required for solvent regeneration

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Heat of Reaction GJ/ton CO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monoethanolamine - H$_2$O (MEA)</td>
<td>1.92</td>
</tr>
<tr>
<td>Diethanolamine - H$_2$O (DEA)</td>
<td>1.93</td>
</tr>
<tr>
<td>Methylldiethanolamine - H$_2$O (MDEA)</td>
<td>1.34</td>
</tr>
<tr>
<td>Potassium carbonate - H$_2$O</td>
<td>0.64</td>
</tr>
</tbody>
</table>

- Carbonate systems offer potential for lower regeneration energy, but exhibit slow kinetics, requiring operation at high temperatures and pressures
Akermin’s Approach

- Enable the use of low energy carbonate solvents through enzyme-catalyzed formation of bicarbonate

\[ K_2CO_3 + CO_2 + H_2O = 2 KHCO_3 \quad \Delta H_r = 640 \text{ kJ/kg CO}_2 \]

  - Achieve kinetics comparable to benchmark amine systems

- Maximize operational lifetime by using immobilized and stabilized carbonic anhydrase

  - Initial system operational life-time goal of 6 months
Technology Background

- Enzyme immobilization within thin-films of polymers with propensity to form micelles:
  - Hydrophobic polysiloxanes with reactive silicon hydride (Si-H) groups are grafted with hydrophilic chains
  - Polymer phase separates into distinct regions (micelles) in the solid state
  - Micellar polymer containing enzyme is cross-linked via remaining reactive silicon hydride (Si-H) groups
  - Polymer (containing enzyme) is cast onto an appropriate solid support
Benefits of Micellar Immobilization

- Hydrophilic domains of the micellar polymer minimize enzyme unfolding at elevated temperatures
- Encapsulation in a micellar polymer protects the embedded enzymes from high shear force
- High CO$_2$ permeability of siloxanes facilitates diffusion of CO$_2$ and products to and from enzyme active site
- Polymer films can be cast on a variety of contactor systems
- Immobilization keeps the enzyme in the absorber

Siloxane-based micellar polymer stained with PTA and coated with Au; 5000x magnification; scale bar = 5μm.
CO₂ Capture System with Immobilized CA

- **FLUE GAS** (~15% CO₂ (dry basis))
- **MAK EUP**
- **ID FAN**
- **ABSORBER**
  - "LEAN"
  - Immobilized enzyme
- **PUMP**
- **CROSS EXCHANGER**
- **STRIPPER**
  - "RICH"
- **STRIPPER**
  - "LEAN"
- **REBOILER**
  - VAPOR
  - LIQUID
- **CONDENSER**
- **ADVANCED CO₂ COMPRESSION**
- **PRODUCT CO₂**
- **TO MAKEUP**
- **MAKEUP**
- **CO₂ Capture System with Immobilized CA**

Akermin Inc. (2011)
Key Program Objectives

• Select the enzyme addressing anticipated operating conditions
• Optimize micellar polymer to achieve high enzyme loading and stabilization, minimize internal diffusion
• Develop detailed Aspen model of enzyme-catalyzed carbonate system and extrapolate to a power plant of 550 MWe (net)
  – Including mass and energy balances, electric power requirements and projected chemical and maintenance costs
• Build and test a closed loop bio-reactor capable of processing up to 500 SLPM of gas, the approximate equivalent of a 5 kWe power plant
  – Demonstrate operation over a 6 month period
Developmental Challenges

- Flexible, enzyme-independent immobilization technology
- Adaptable to a range of carbonate chemistries (K$_2$CO$_3$/KHCO$_3$, ammonium carbonate, MDEA, etc.)
- High physical enzyme retention and stabilization
  - 6-12 month lifetime under anticipated absorber conditions of 40 – 60°C, pH 9-11, high ionic strengths
- Tolerance to contaminants in flue gas
- Unique absorber design challenges
  - Heterogeneous catalysis in (3) phase system, complex mass transfer problem
  - Detailed modeling and bench-unit validation is needed
Progress and Current Status
Selection of Carbonic Anhydrase (CA) for CO₂ Capture

• CA catalyzes hydration of CO₂ to bicarbonate with $k_{\text{cat}} = 10^6 \text{ sec}^{-1}$
• CA activity is expressed ubiquitously across all life forms
  – represent a family of structurally and genetically diverse enzymes
  – active sites of all CAs contains a single divalent metal essential for catalysis
    • Zn predominates, Fe, Cd, and Co are observed.
• Enzyme selected for this project is a recombinant thermostable CA developed by Novozymes
  – Highly active (~24,000 W&A units/mg protein)
  – Good expression (sample concentrations ~38 g/l)
  – Enzyme is secreted into the medium
    • Simplifies downstream processing, and purification
Thermostability of Soluble Novozyme CA in 0.5 M K$_2$CO$_3$/KHCO$_3$ (pH ~10)

- Novozymes CA is a highly thermostable enzyme with $T_{1/2} \sim 12$ days at 60 °C pH 10
Thermostability of Soluble and Immobilized Novozyme CA in 0.5 M K$_2$CO$_3$/KHCO$_3$ (pH ~10) at 70 °C
CA Inhibition Studies

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Anticipated Conc*</th>
<th>Soluble Product</th>
<th>IC50 (mM)</th>
<th>Activity Remaining (conc.)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOx</td>
<td>~80 ppmv</td>
<td>Nitrate (NO$_3^-$)</td>
<td>----</td>
<td>49% (1 M)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Nitrite (NO$_2^-$)</td>
<td>----</td>
<td>75% (1 M)</td>
<td></td>
</tr>
<tr>
<td>SOx</td>
<td>~45 ppmv</td>
<td>Sulfate (SO$_4^{2-}$)</td>
<td>----</td>
<td>100% (250 mM)</td>
<td>Solubility limiting</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sulfite (SO$_3^{2-}$)</td>
<td>----</td>
<td>100% (2.5 mM)</td>
<td>Background limiting</td>
</tr>
<tr>
<td>Chloride</td>
<td>&lt; 1ppm</td>
<td>Chloride (Cl$^-$)</td>
<td>----</td>
<td>123% (2 M)</td>
<td></td>
</tr>
<tr>
<td>Heavy Metals</td>
<td>~1.2 ppbw</td>
<td>Mercury(II) (HgCl$_2$)</td>
<td>0.13</td>
<td>14% (3 mM)</td>
<td>Solubility limiting</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Lead(II) (Pb(NO$_3$)$_2$)</td>
<td>----</td>
<td>80% (0.002 mM)</td>
<td>Solubility limiting</td>
</tr>
</tbody>
</table>

- Sulfate, sulfite, nitrate, nitrite and chloride - little or no inhibitory potency
- Potent inhibition by divalent metals in low ionic strength buffer.
- Poor solubility of carbonates and hydroxide salts of divalent metals in carbonate solutions might obviate CA inhibition at high pH
Characterization of CA Performance in packed bed 1 L reactor (free enzyme)

- At low loading and 20 s space time >90% absorption is achieved with 0.125 g/l CA
- CO₂ absorption reaches equilibrium at ~ 80% carbonate conversion
Mass Transfer Coefficient ($K_G$) for Free CA vs. Blank

- **BLANK, 0 g/L**
- **NOVO 4 g/L**
- **NOVO 2 g/L**
- **NOVO 1 g/L**

20 wt% $K_2CO_3$
35°C; 4 s space time
Effect of CA on Mass Transfer Coefficient: Wetted Wall Measurements

- **Objective:**
  - Measure \( \text{CO}_2 \) flux (or overall mass transfer coefficient, \( K_G \)) for a range of \( P_{\text{CO}_2} \)
  - Calculate equilibrium and kinetics parameters to support system-level modeling

- **Results:**
  - Strong dependency on dissolved protein; less dependent on pH and temperature.
  - Measured value with no enzyme matched Aspen Plus

*Wetted wall information, observed and targeted \( K_G/K_{G, \text{blank}} \) data were incorporated into Aspen Plus*

Analysis: \( T, P_{\text{tot}}, P_{\text{CO}_2} \)

17 wt % \( \text{K}_2\text{CO}_3 \) solution; dissolved CA
\( \text{CO}_2 \): 0%, 5%, 10%, 20%, and 30% (balance \( \text{N}_2 \))
\( \text{CO}_2 \) loading: 13% - 80%
\( \text{K}_2\text{CO}_3 \) to \( \text{KHCO}_3 \) conversion (pH of 10.2 to 8.8)
Initial ASPEN Simulation Results for Enzyme-Catalyzed Potassium Carbonate (K₂CO₃) System
Initial Simulation Assumptions/Details

- NETL Case 12 flue gas rate and composition downstream of a wet limestone flue gas desulfurization unit & direct contact water cooler (same as MEA)

<table>
<thead>
<tr>
<th>Flowrate (lbmol/hr)</th>
<th>210,160</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flowrate (lbs/hr)</td>
<td>6,323,430</td>
</tr>
<tr>
<td>Temperature (F)</td>
<td>90.1</td>
</tr>
<tr>
<td>Pressure (psia)</td>
<td>15.2</td>
</tr>
</tbody>
</table>

**Composition:**

- N₂ (mol%) 76.4%
- H₂O (mol%) 4.9%
- CO₂ (mol%) 15.1%
- O₂ (mol%) 2.7%
- Ar (mol%) 0.9%

- 90% CO₂ capture
- ISO ambient conditions (sea level, 15 °C, 14.7 psia, 60% RH)
- Absorber: packed tower gas liquid contacting system
- Equilibrium simulation in stripper
- Compression of separated CO₂ to 2215 psia
- ASPEN model components: cooling tower, steam cycle, absorber/stripper, and CO₂ compressor.

- Enzyme effect simulated by adjusting activation energy for bicarbonate reaction:

\[
CO_2(aq) + OH^- \leftrightarrow HCO_3^- + H_2O
\]
Initial Simulation Data Comparison – Net Electric Power

Key Observations:

- To exceed the net electric power of MEA the lean loading is increased, and stripper pressure is reduced.
- Initial set of conditions was identified for potassium carbonate system exhibiting a 21% parasitic load compared to 31% for MEA (including CO₂ compression energy).
- Increase of carbonate concentration from 20 wt% to 25 wt% had little impact on net electric power.
- Absorber kinetics had little or no effect on net electric power (equilibrium effect only).

<table>
<thead>
<tr>
<th>Condition</th>
<th>Net Electrical Power (MWe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 wt% MEA</td>
<td>650</td>
</tr>
<tr>
<td>20 wt% K₂CO₃</td>
<td>550</td>
</tr>
<tr>
<td>1.0 to 0.83 bar Stripper</td>
<td>450</td>
</tr>
<tr>
<td>K₂CO₃; 0.41 bar Stripper</td>
<td>350</td>
</tr>
</tbody>
</table>

NETL Case 12
(30 wt% MEA)
K₂CO₃, 20 wt%
Xₐₙ lean = 0.24
15 psia stripper
K₂CO₃, 20 wt%
Xₐₙ lean = 0.45
15 psia stripper
K₂CO₃, 20 wt%
Xₐₙ lean = 0.45
12 psia stripper
K₂CO₃, 20 wt%
Xₐₙ lean = 0.45
6 psia stripper
K₂CO₃, 20 wt%
Xₐₙ lean = 0.375
6 psia stripper...
K₂CO₃, 20 wt%
Xₐₙ lean = 0.40
6 psia stripper
Solvent Recirculation to Achieve 90% Capture

**Key Observations:**

- Solvent recirculation increased with increases in lean loading
- Increased solvent concentration reduces solvent recirculation rate
- Recirculation rate is not affected by improved kinetics
**Key Observations:**

- Predicted absorber tower height for MEA is 40 ft; 100 ft is reasonable from an economic perspective.
- A 10-15X multiplier in $K_G$ (vs. blank) reduces absorber to ~100 ft for $K_2CO_3$.
- Tower height is roughly proportional to the multiplier in overall mass transfer coefficient; impacts capital cost.
Conclusions Based on Initial Modeling

• A positive impact on net electric energy was predicted with higher lean loading levels.

• Operating the stripper under mild vacuum conditions yielded energy efficiencies that outperformed MEA. Combined efficiency ~33% better than MEA.

• $K_2CO_3$ with no kinetic enhancements would require an absorption tower 30 times taller than NETL’s MEA reference case.

• $K_2CO_3$ with a kinetic enhancement of ~10X on an overall flux basis reduces the absorber tower height considerably, placing it within a competitive range.
Future Activities

• Optimize micellar polymer
• Perform the long-term enzyme stability studies
• Design and commission a bench-scale closed loop carbon capture system
• Refine CAPex and OPex calculations
• Experimentally determine regeneration energy for $\text{K}_2\text{CO}_3$ under various operating conditions of the desorber
• Operate unit for 6 months to establish robust data set for system operating costs
# Key Team Members

**AKERMIN:**
- Dr. Paul Gifford, PM, VP, Development
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- Mark Bearden, PI
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- Dale King, PI

**BATTELLE:**
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**U.S. DOE-NETL**
- Andrew Jones, PM

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