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

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Notices

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Agenda

• Project Overview
• Technology Background
• Progress and Status
  • Schedule and summary
  • Initial techno-economic assessment
  • Supporting lab results
  • Ultrasonic system testing at PNNL
  • University of Kentucky bench-scale system

• Conclusions & Next Steps
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 m$^3$ 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

www.novozymes.com
**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
- **Project Duration:** Oct. 1, 2011 – March 31, 2015

**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.
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:

- a **low-enthalpy**, aqueous potassium carbonate-based solvent
- with an **absorption**-enhancing carbonic anhydrase enzyme catalyst
- and a flow through ultrasonic-enhanced **regenerator**
- in a **re-circulating** absorption-desorption process configuration

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

- Low enthalpy, benign solvent (catalyzed aq. 20% K$_2$CO$_3$)
  - $K_2CO_3$ $\Delta H_{rxn}$ 27 kJ/mol CO$_2$
  - MEA $\Delta H_{rxn}$ 83 kJ/mol CO$_2$
- Potential for $\sim$50% regeneration energy vs. MEA

### Challenges

- Demonstrate atmospheric regeneration at 70°C enabled by ultrasonics
- Demonstrate overall techno-economic feasibility
  - energy demand
  - enzyme requirement
Background on Ultrasonic Technology

- **Rectified Diffusion Mechanism:** [1]
  - Bubbles expand and shrink in an ultrasonic field
    - Expanding bubbles = lower pressure/ higher surface area
    - Shrinking bubbles = higher pressure/ lower surface area
  - Rectified diffusion results when expanding bubbles allow for a biased transfer of dissolved gas into the bubble from solution

- **Proposed approach for solvent regeneration:**
  - Create a population of seed bubbles
  - Grow the bubbles via rectified diffusion.
    - Frequency optimization likely required
  - Rapidly remove bubbles before they can dissolve

Project Schedule & Status Summary

- Task 1 – Project Management and Planning
  - Task 2 – Process optimization
    - Batch-mode ultrasonics provided modest CO₂ release
    - Enzyme-solvent compatibility and absorption kinetics targets met
    - Integrated Bench-Scale system designed
  - Task 3 – Initial Technical & Economic Feasibility
    - Indicated opportunity for 25% net efficiency improvement vs Case 10
  - Task 4 – Bench Unit Procurement & Fabrication
    - Proto-type flow-through ultrasonic unit built & tested
    - Constructed bench-scale absorber and host rig with vacuum stripper
  - Task 5 – Bench-scale Integration & Shakedown Testing
    - Commissioning and shakedown testing w/vacuum stripping in progress
    - Long-term enzyme stability and reclamation in progress
    - Initiating kinetics-based stripping simulation
  - Task 6 – Bench-scale Testing
  - Task 7 – Full Technology Assessment

Start
10/2011

CCTM
07/2012

BP2
01/2013

CCTM
07/2013

BP3
01/2014
Preliminary Technical and Economic Feasibility

- Aspen Plus® (with Radfrac) used for Process modeling for absorption
- AspenTech’s Capital Cost Estimator® along with budget supplier quotations used for Cost Estimation of the PCC Components
- Preliminary techno-economic evaluation for the process integrated with a subcritical coal-fired power plant was carried out indicating net efficiency improvement of up to 25% versus Case 10:

<table>
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<tr>
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<th>Net efficiency, %</th>
<th>LCOE ($/MWh_e)</th>
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<tr>
<td>Case 10</td>
<td>24.9</td>
<td>119.6</td>
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<td>Power Equivalent of 0.0911 kWh/lb of steam</td>
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<tr>
<td>Ultrasonic Regeneration</td>
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</tbody>
</table>

- Key underlying assumptions were:
  - Acceptable enhancement of CO₂ absorption rate via enzyme
  - Acceptable enzyme longevity in process
  - Ultrasonic regeneration in no more than two stages (1.5 kJe/ kg of solvent)
  - Vacuum regeneration at 6psia and 70°C
Acceptable CO$_2$ Absorption Rate

- Solvent: aq. 20% K$_2$CO$_3$ + carbonic anhydrase
- Demonstrated acceptable kinetics (mass transfer) with enzyme
- Temperature (30-50°C) had minimal impact
Acceptable (Lab Scale) Enzyme-solvent Longevity

- Static incubations demonstrate high robustness at 40°C and limited robustness at 70°C.
- A more representative test (recirculating between 40-70°C) demonstrates high robustness across the temperature range.

Solvent: aq. 22% K$_2$CO$_3$/KHCO$_3$ with 3 g/L enzyme and adjusted to lean pH.
Basis for Ultrasonic Regeneration Energy Projections

► Commercial water sterilization = 0.24 to 0.79 kJe/ kg of water
  ▪ Based on developed applications for ship ballast treatment [2]

► Initial batch testing for CO₂ regeneration = 4.9 kJe/ kg of solvent
  ▪ Laboratory horn used. Poor CO₂ removal (significant re-dissolution)
  ▪ Demonstrated value = 10.3 kJe /mol of CO₂, 0.021 kg of CO₂ removal
    per kg of recirculated solvent recirculation assumed.

► Full-scale CO₂ regeneration system estimate = 1.5 kJe/ kg of solvent
  ▪ Based on (conservative) tube sonication configuration
  ▪ Equates to just over 11 MWe of parasitic power for the ultrasonic
    system in the 500 MWe reference system)

Ultrasonic Testing Platforms

**Batch System**

*Can introduce ultrasonic power while maintaining temperature to within 2°C.*

**Semi-Continuous System**

*Large reservoir of solvent recirculated. Gas separated after sonication via hydroclone.*
Initial Batch Ultrasonic Experiments

- Pure Water at 70°C – With Sonication
- Loaded Solvent at 70°C – No Sonication
- Loaded Solvent at 70°C – With Sonication

- Significant agitation/ bubbling observed when ultrasonic power added to loaded K₂CO₃ solution at 70°C
Batch Test Results for Ultrasonic Regeneration

- Testing with 20 wt% K$_2$CO$_3$ solvent loaded to 4.6 wt% CO$_2$
- ASPEN (equilibrium) projections of CO$_2$ release at 6 psia = 0.96%
- Total CO$_2$ release observed = 0.67% (0.25% from ultrasonic effect) – likely impacted by re-dissolution of CO$_2$
- Slow CO$_2$ release rates observed – also likely impacted by re-dissolution of CO$_2$
Comparison of Batch-mode Regeneration

- All tests with 20 wt% K$_2$CO$_3$ – temp tests at ~82% (converted to bicarbonate), vacuum and ultrasonic tests at 72%
- Similar kinetic rates (initial part of curves) but higher with enzyme – kinetic limitation?
- Total CO$_2$ release low for ultrasonic test – CO$_2$ re-dissolution suspected
Ultrasonic Flow-Through Results

- CO₂ release rate similar to batch studies – can be explained by temperature increase alone
- Enzyme additions unexpectedly decreased release rate – likely due to foaming
Summary of Regeneration Testing Results

- Multiple passes (5+) required for significant CO₂ release from both vacuum and ultrasonic flow through tests – kinetic limitation suspected
- Ultrasonic flow through results within temperature-driven projections; not in line with 70°C, 6psia vacuum target
- Current ultrasonics configuration delivers insufficient CO₂ release
Bench-scale Demonstration Unit Status

- **Design capabilities:**
  - Dual regeneration sources (vacuum and ultrasonic)
  - Able to assess long-term enzyme stability
  - Able to assess mass transfer

- **Construction complete:**
  - Host rig framework
  - Absorber
  - Vacuum regeneration
  - Heat transfer
  - Instrumentation check and calibrations

- **Unit commissioning for vacuum process in progress**
Key Bench-scale Operational Parameters

- Flow rates
  - Gas: 10-30 SLPM
  - Liquid: 100-300 ml/min
- Liquid temperature
  - Absorber inlet: 30-40 °C
  - Stripper outlet: 70-80 °C
- Stripper pressure: 0.25-0.4 atm
- Enzyme dose: 3-5 g/L

Optimized parameters yield process energy

Add ultrasound, Maintain lean loading

Comparative energy for ultrasound advantage
Conclusions and Next Steps

- Target absorption kinetics and enzyme robustness measured
- Visual evidence of ultrasonic effect shown in batch system
- Preliminary techno-economic evaluation indicated potential for net efficiency improvement of up to 25% versus Case 10
- Construction of bench-scale absorption column with vacuum regeneration completed and commissioning in progress
- Flow-through bench-scale ultrasonic regeneration system was assembled and tested
  - CO₂ release rates below single-pass stripping target for the project
  - Low CO₂ release rates may point toward a kinetic limitation in stripping; enzyme catalyst could help overcome this limitation
  - Ultrasonics in current configuration delivers insufficient CO₂ release
- Project now focuses on validating the potential for low temperature regeneration by developing a rate-based simulation for vacuum stripping corroborated by data from bench-scale testing
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