Low-Energy Solvents for CO_2 Capture Enabled by a Combination of Enzymes and Ultrasonics

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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

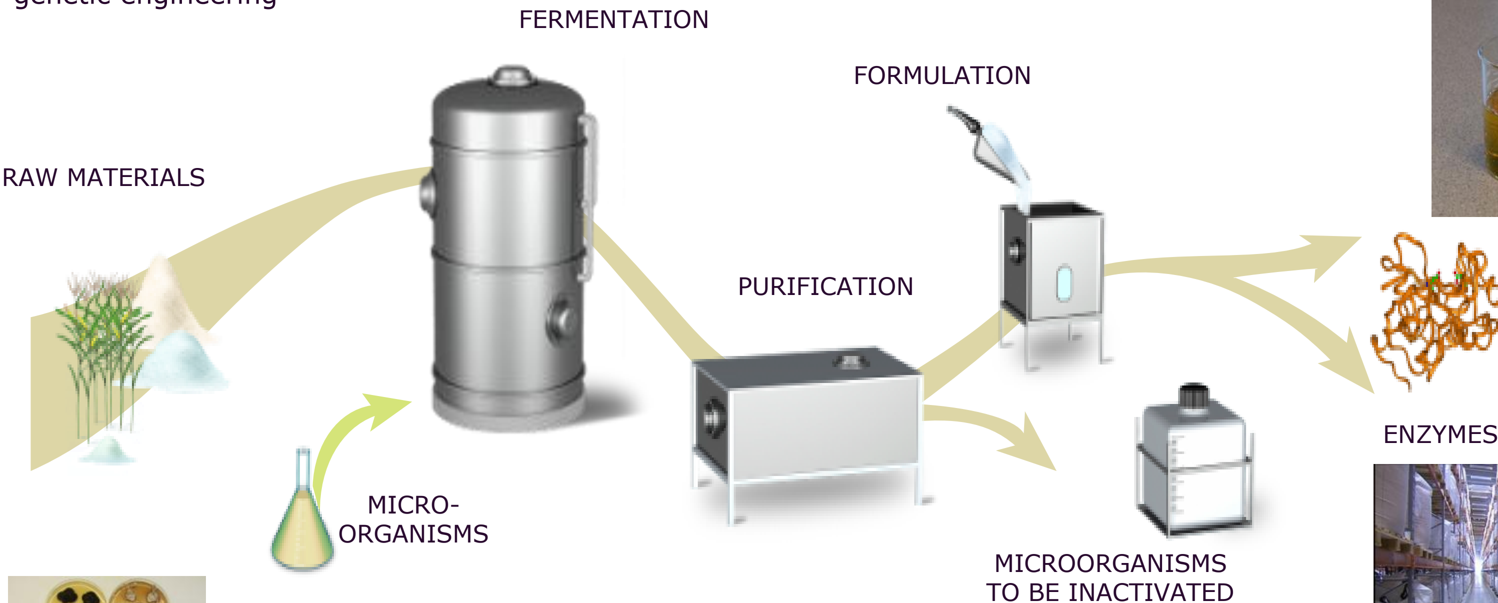
Novozymes in Brief – World Leader in Bioinnovation

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

Project Overview

- Project Participants

Pacific Northwest National Laboratory	Doosan	Novozymes	University of Kentucky Center for Applied Energy Research
Ultrasonics & Aspen®	Full Process Analysis	Enzymes & Solvents	Kinetics & Bench-scale Tests

- 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

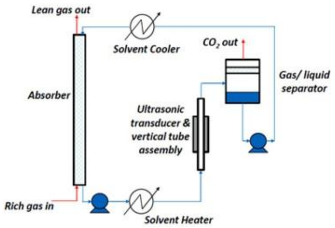
DOE Program Objectives
Develop solvent-based, post-combustion technology that

- Can achieve ≥ 90% CO_2 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 <u>integrates</u>

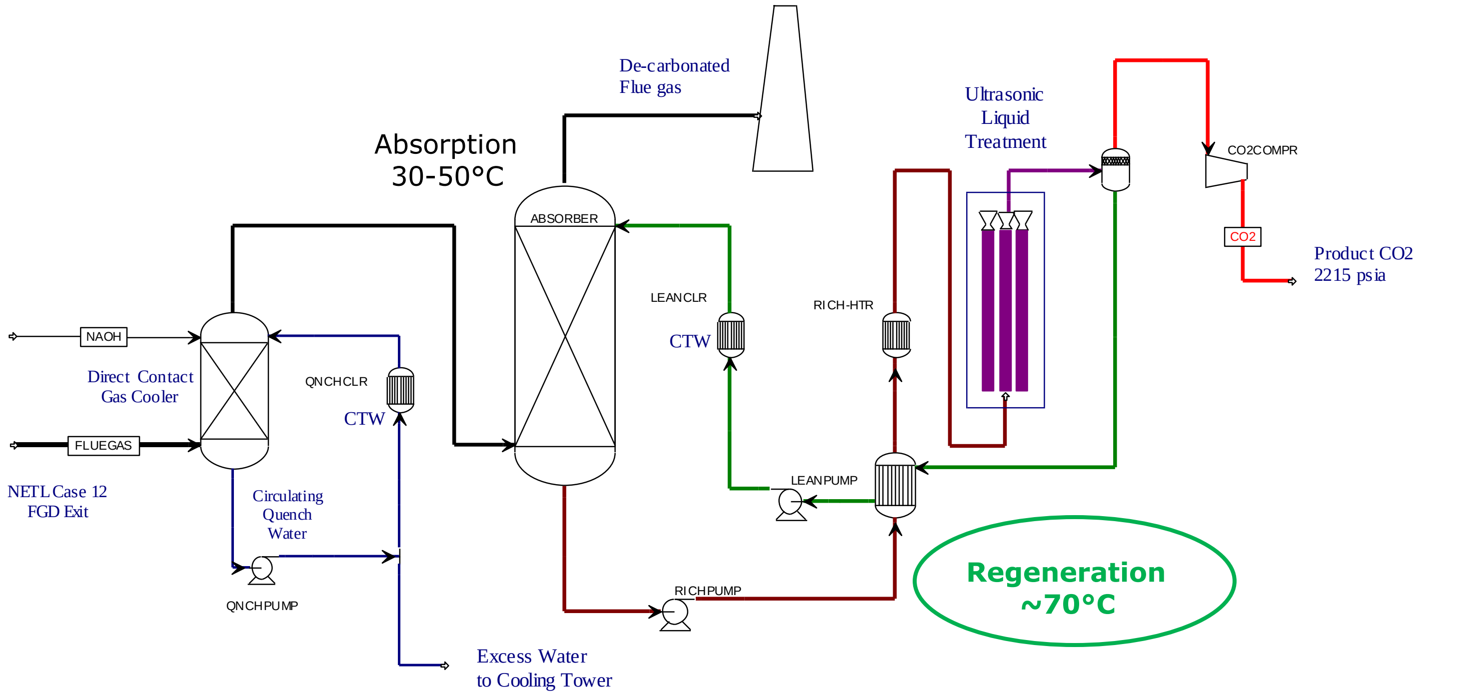
$CO_2 + H_2O + K_2CO_3 \leftrightarrow 2KHCO_3$



- 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

Challenges Encountered

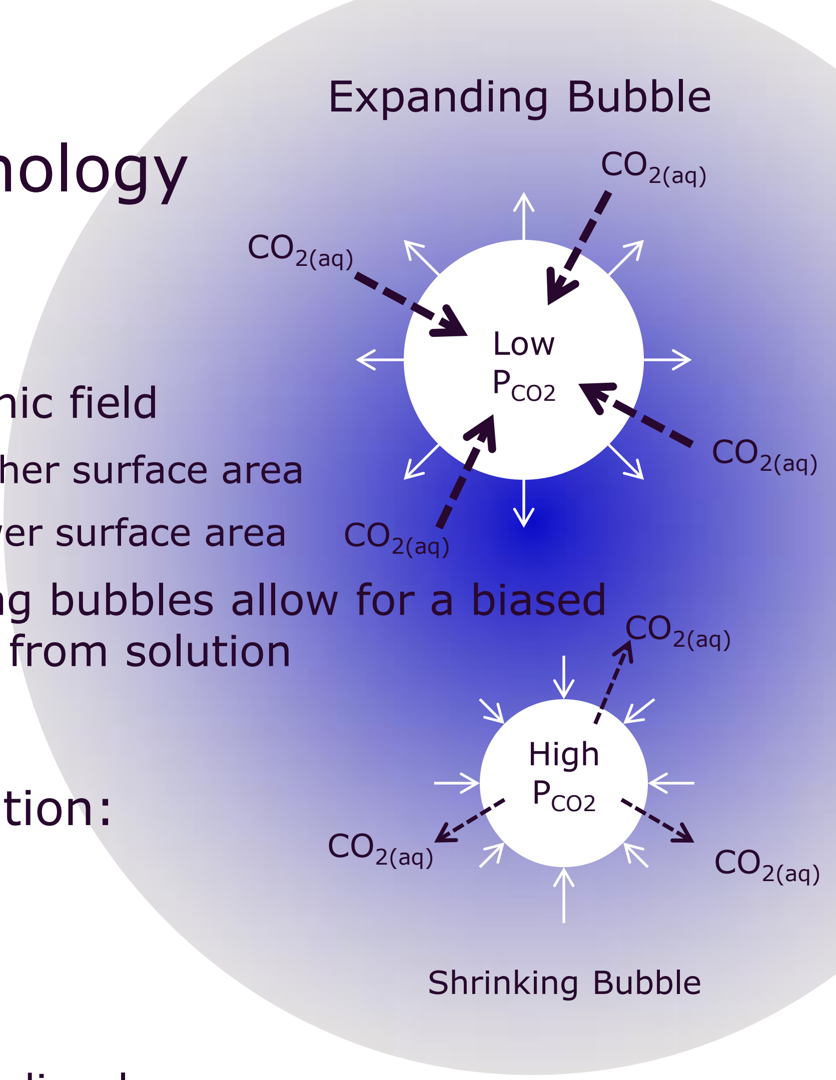
Process Concept



- *Advantages*
  - ➢ Low enthalpy, benign solvent (catalyzed aq. 20% K_2CO_3)
    - K_2CO_3 ΔH_{rxn} 27 kJ/mol CO_2
    - MEA ΔH_{rxn} 83 kJ/mol CO_2
  - ➢ Potential for ~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

[1] Louisnard and Gomez (2003): Theoretical predictions of rectified diffusion of air in water (1 bar, 26.5 kHz acoustic field)

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Project Schedule & Status Summary

- Task 1 – Project Management and Planning
- Task 2 – Process optimization
  - Batch-mode ultrasonics provided modest CO_2 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:

		Net efficiency, %	LCOE ($/MWh$_e$)
	Case 10	24.9	119.6
Power Equivalent of 0.0911 kWh/lb of steam	Vacuum Regeneration	24.3	125.2
	Ultrasonic Regeneration	26.6	117.5
Power Equivalent of 0.0665 kWh/lb of steam	Vacuum Regeneration	30.0	112.9
	Ultrasonic Regeneration	31.4	108.9

- Key underlying assumptions were:
  - Acceptable enhancement of CO_2 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

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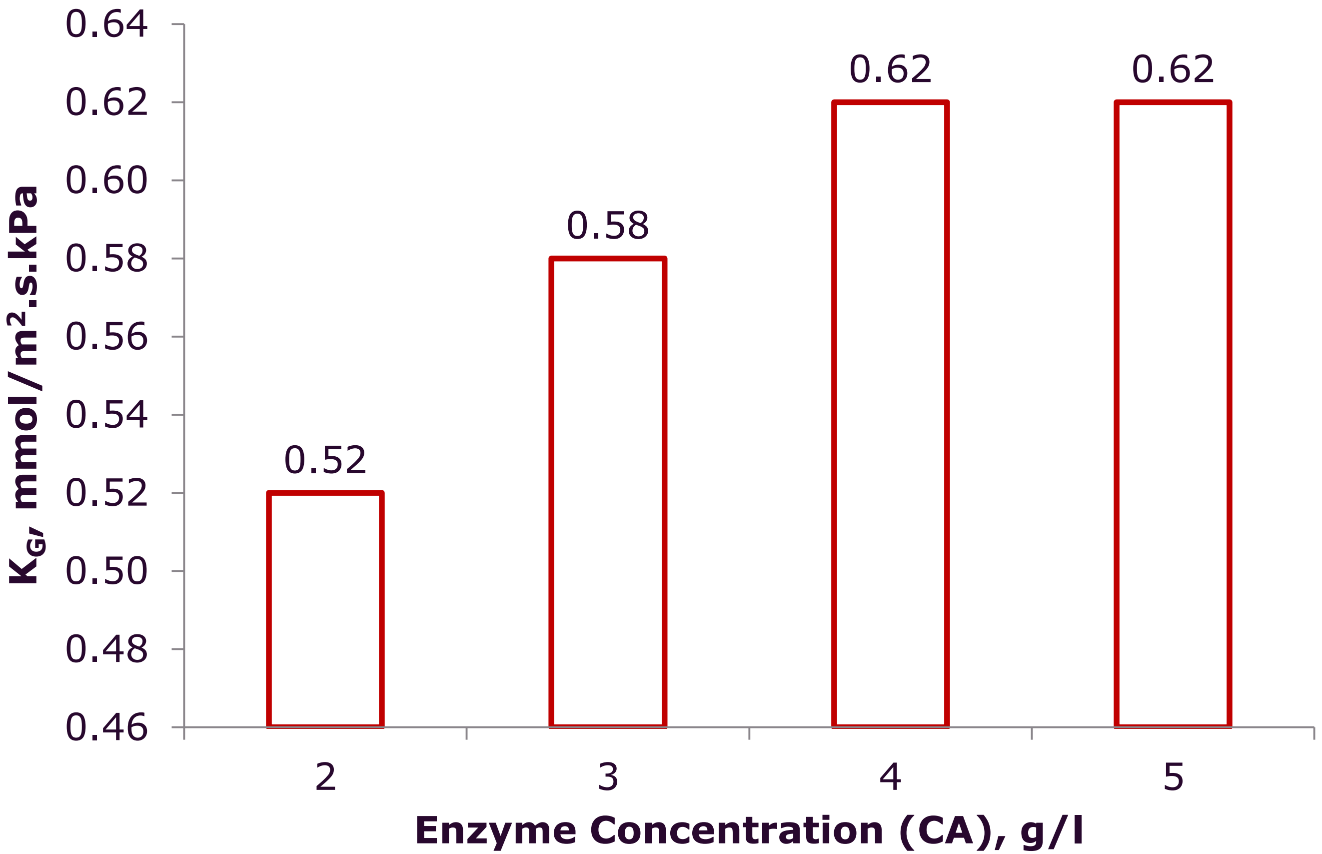
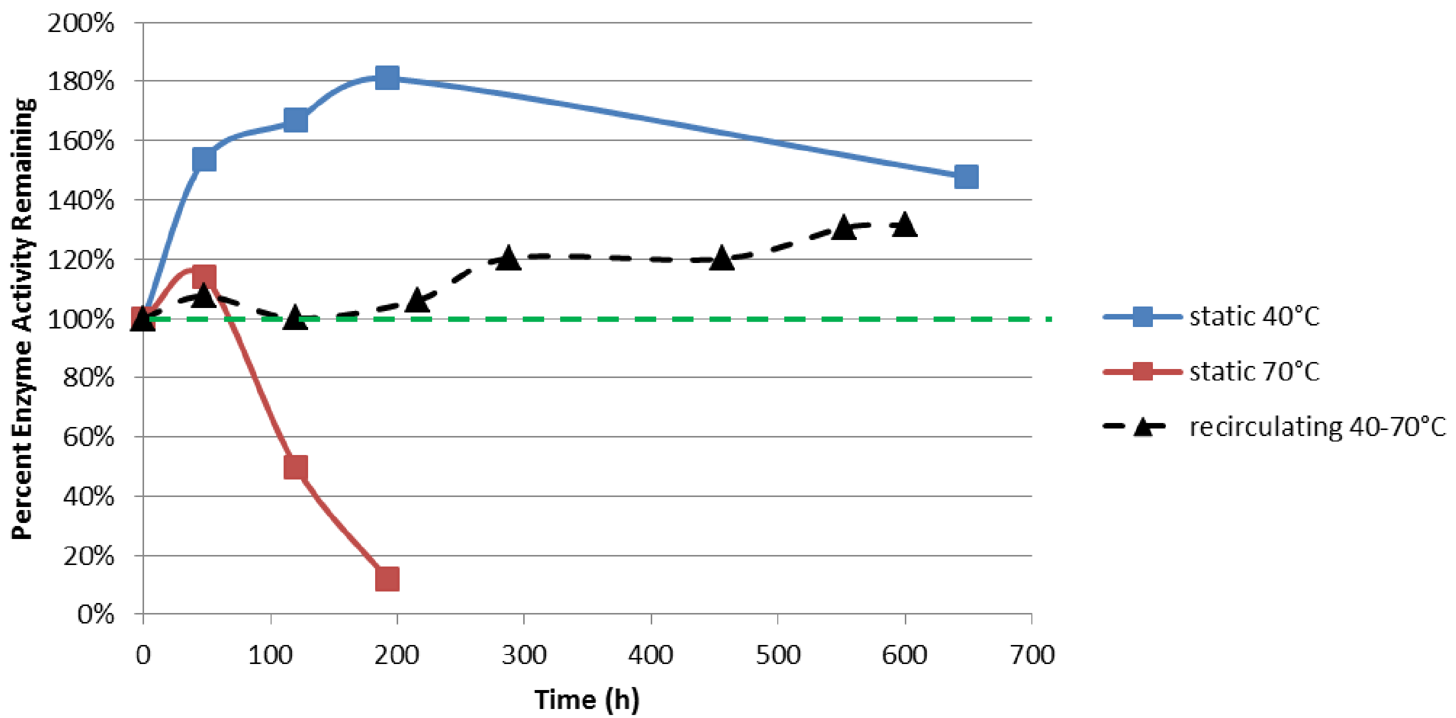
Acceptable CO_2 Absorption Rate



- Solvent: aq. 20% K_2CO_3 + carbonic anhydrase
- Demonstrated acceptable kinetics (mass transfer) with enzyme
- Temperature (30-50°C) had minimal impact

UK University of Kentucky Center for Applied Energy Research

Acceptable (Lab Scale) Enzyme-solvent Longevity



Solvent: aq. 22% $K_2CO_3/KHCO_3$ with 3 g/L enzyme and adjusted to lean pH.

- 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.

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 CO_2 regeneration = 4.9 kJe/ kg of solvent
  - Laboratory horn used. Poor CO_2 removal (significant re-dissolution)
  - Demonstrated value = 10.3 kJe /mol of CO_2, 0.021 kg of CO_2 removal per kg of recirculated solvent recirculation assumed.
- Full-scale CO_2 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)

[2] "Ballast water treatment technology, Current status," February 2010 (http://www.lr.org/Images/BWT0210_tcm155-175072.pdf)

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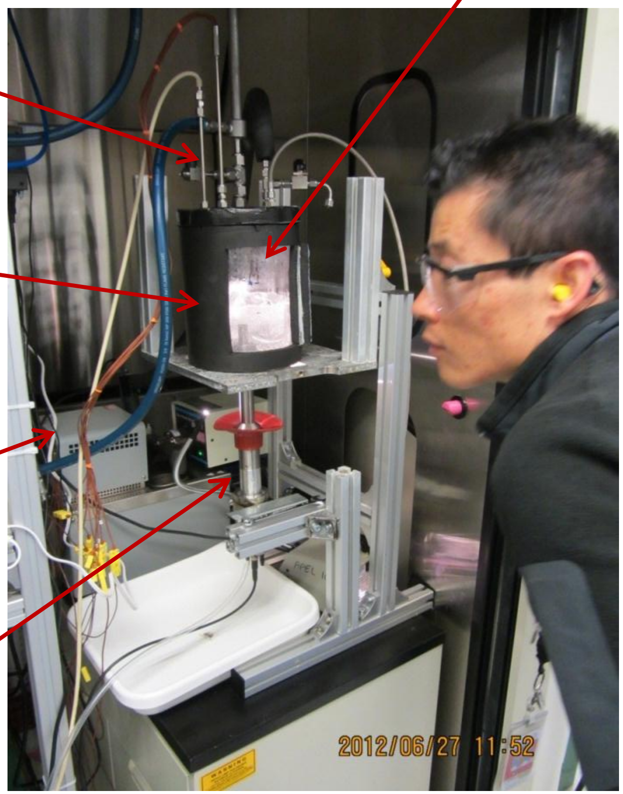
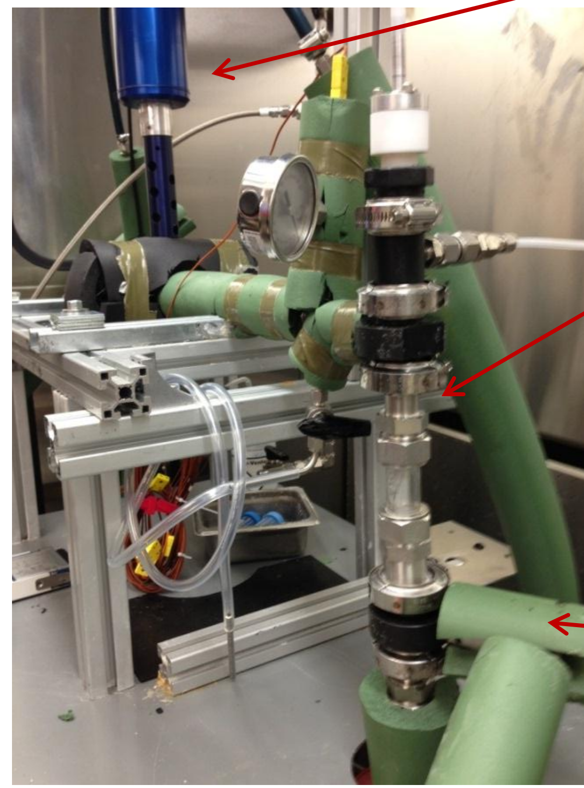
Ultrasonic Testing Platforms





Batch System

Can introduce ultrasonic power while maintaining temperature to within 2^{o}C.

Semi-Continuous System

Large reservoir of solvent recirculated. Gas separated after sonication via hydroclone

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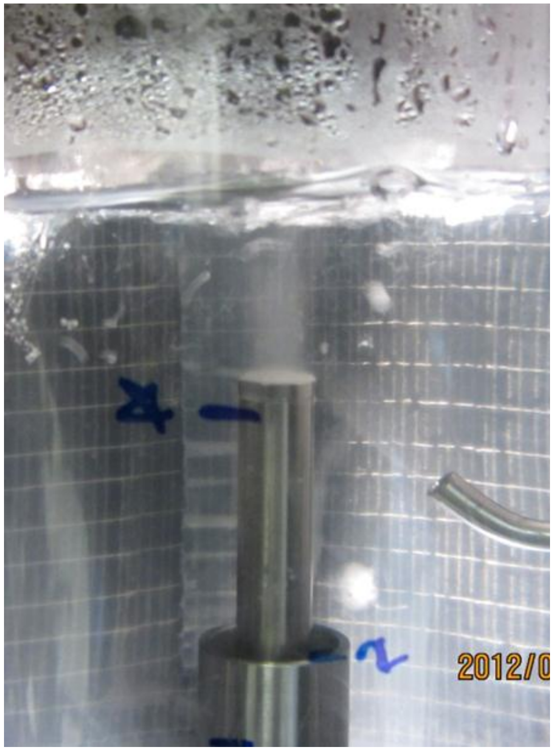
Initial Batch Ultrasonic Experiments



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 K_2CO_3 solution at 70°C

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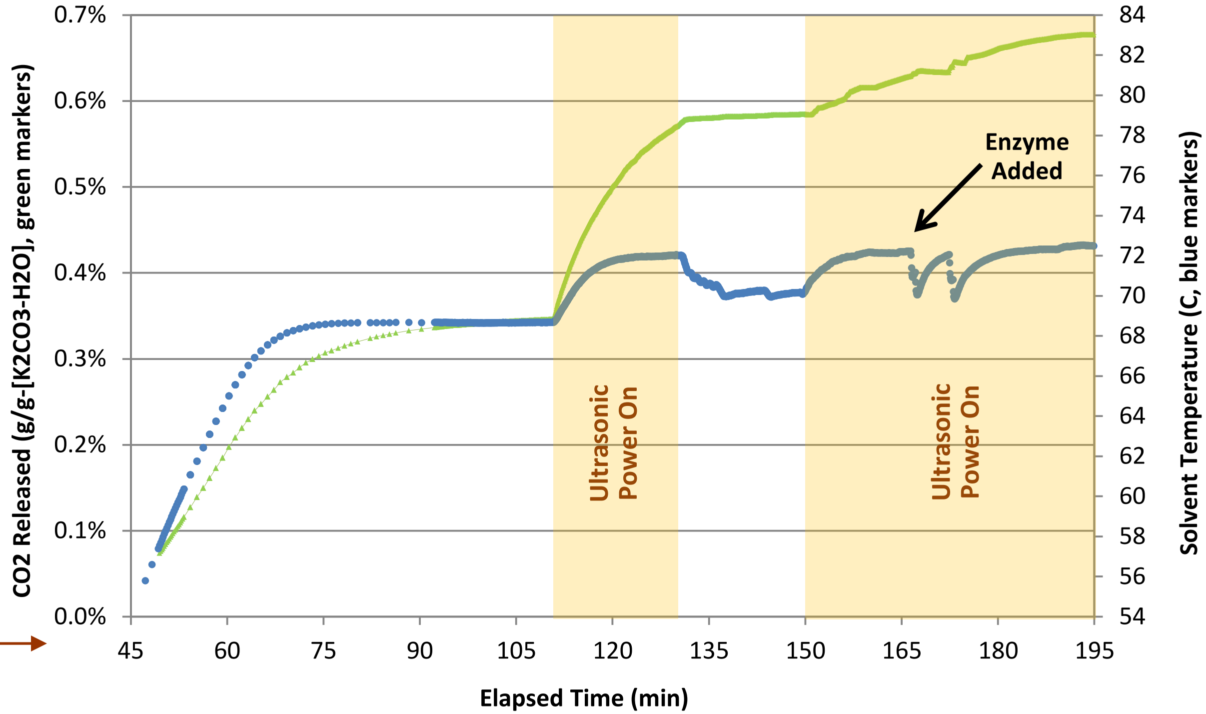
Batch Test Results for Ultrasonic Regeneration



Initially purged the gas-tight headspace with humidified CO_2

- Testing with 20 wt% K_2CO_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

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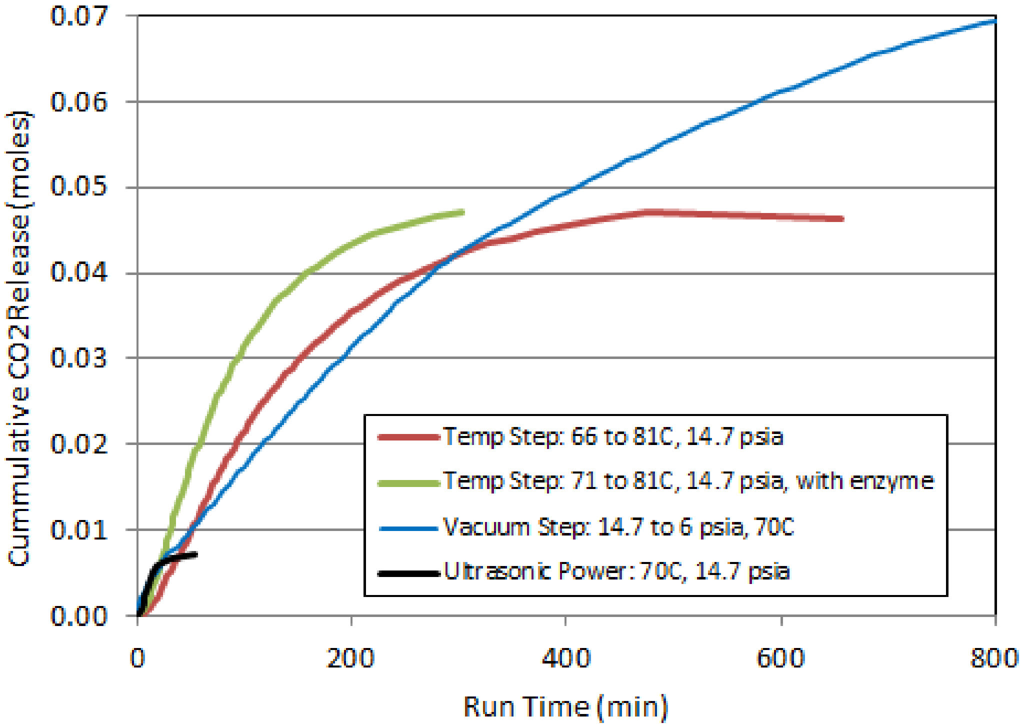
Comparison of Batch-mode Regeneration



- All tests with 20 wt% K_2CO_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

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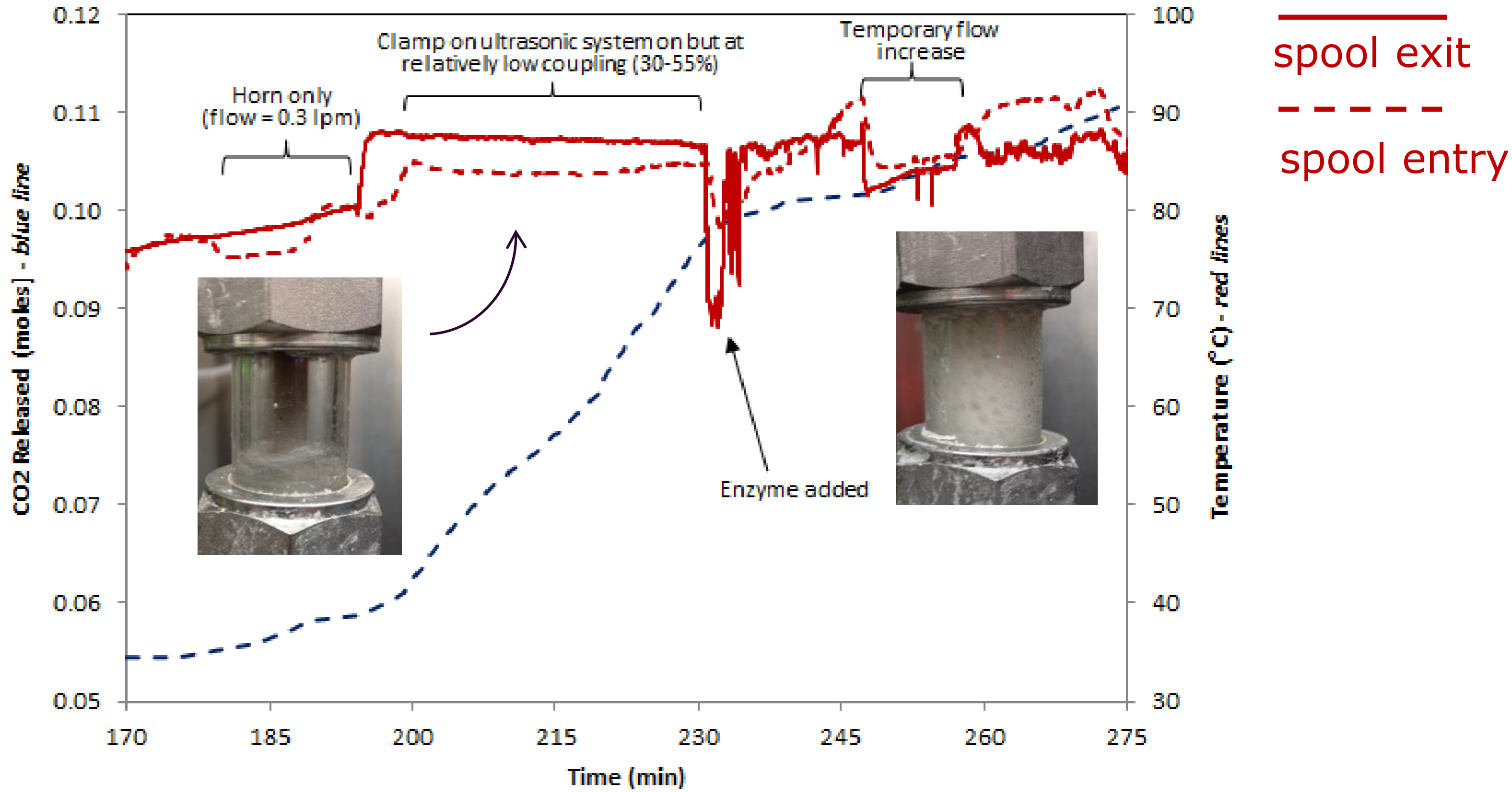
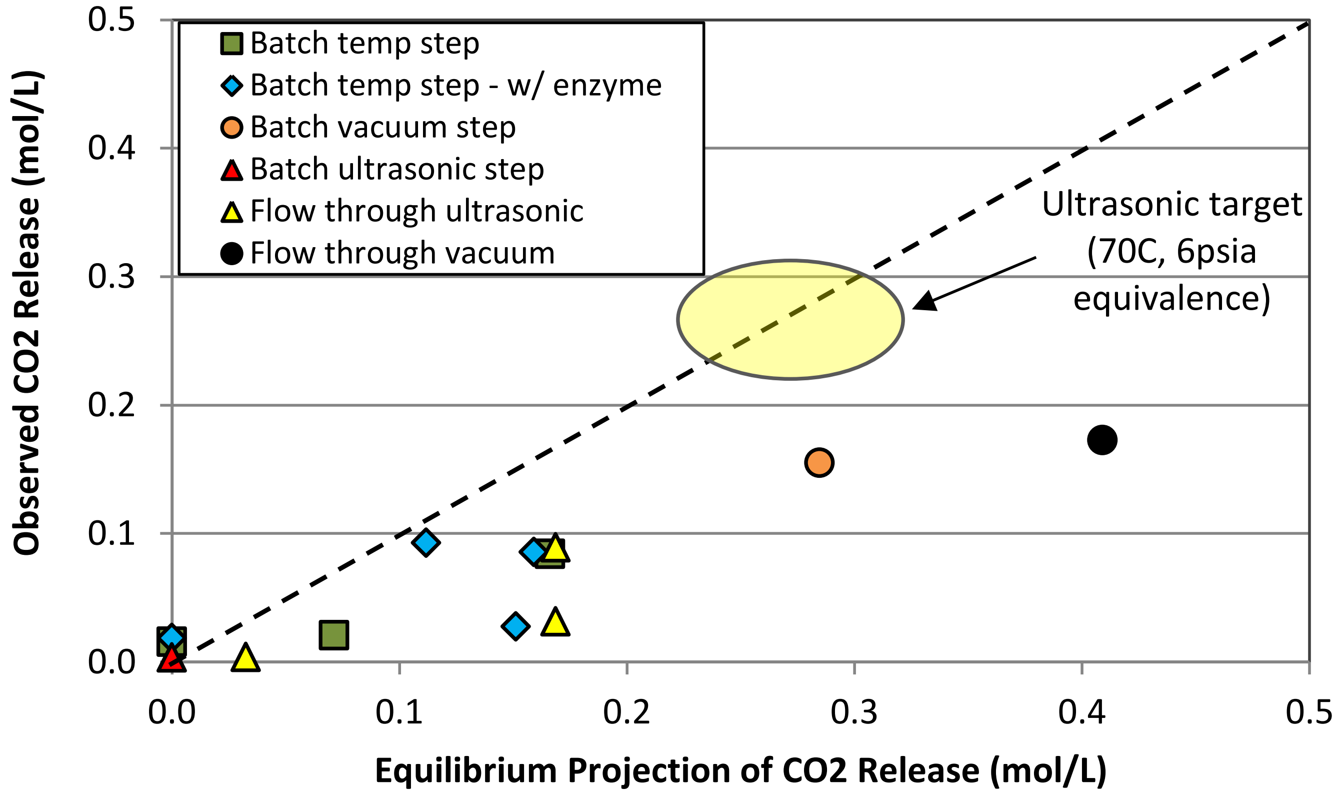
Ultrasonic Flow-Through Results



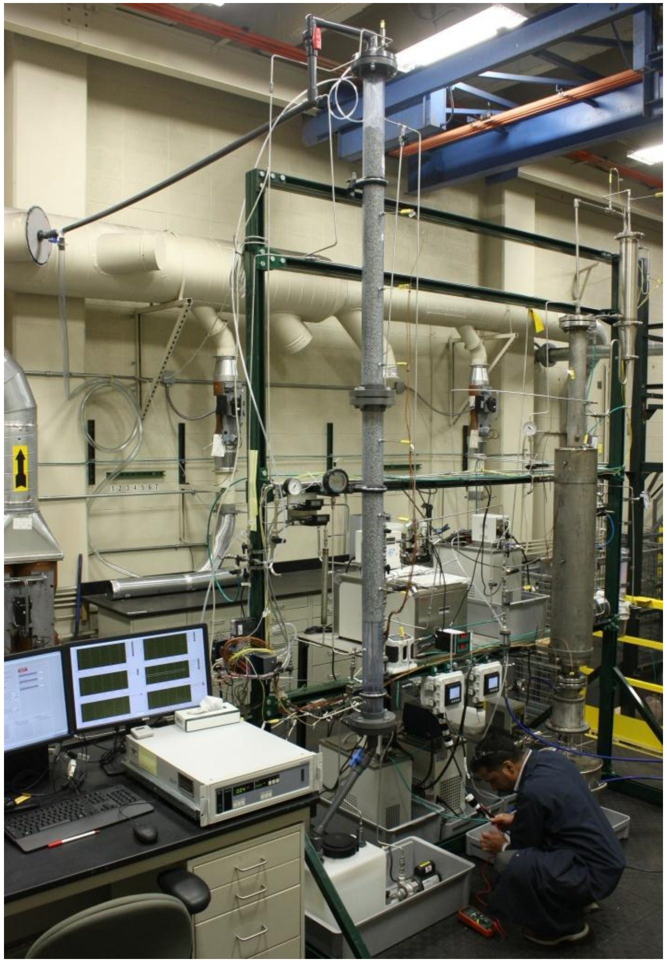
- CO_2 release rate similar to batch studies – can be explained by temperature increase alone
- Enzyme additions unexpectedly decreased release rate – likely due to foaming

Summary of Regeneration Testing Results



- Multiple passes (5+) required for significant CO_2 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 CO_2 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

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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
    - CO_2 release rates below single-pass stripping target for the project
    - Low CO_2 release rates may point toward a kinetic limitation in stripping; enzyme catalyst could help overcome this limitation
    - Ultrasonics in current configuration delivers insufficient CO_2 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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