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

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DOOSAN

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Center for Applied Energy Research

NETL CO_2 Capture Technology Meeting
July 30, 2014

Notices

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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

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

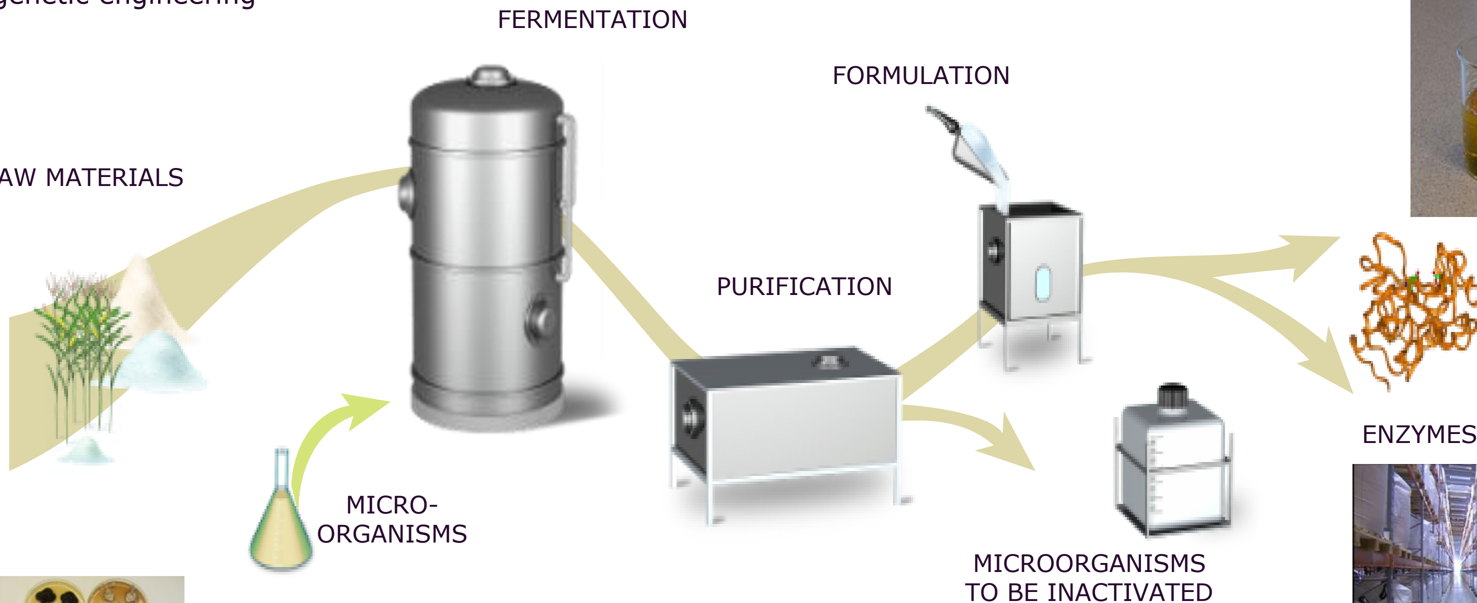
DOE Program Objectives
Develop solvent-based, post-combustion technology that

- Can achieve ≥ 90% CO_2 removal from coal-fired power plants
- Demonstrates progress toward the DOE target of <35% increase in LCOE.

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

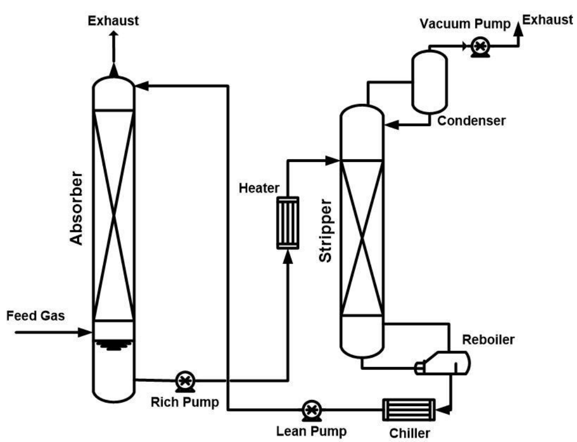


3. Improving the enzyme produced
Improving the efficacy of the enzymes through protein engineering to meet application conditions and process economy requirements

Project 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 (*dissolved*) carbonic anhydrase enzyme catalyst
- and a low temperature vacuum **regenerator**
- in a **re-circulating** absorption-desorption process configuration

Process Concept, Advantages & Challenges

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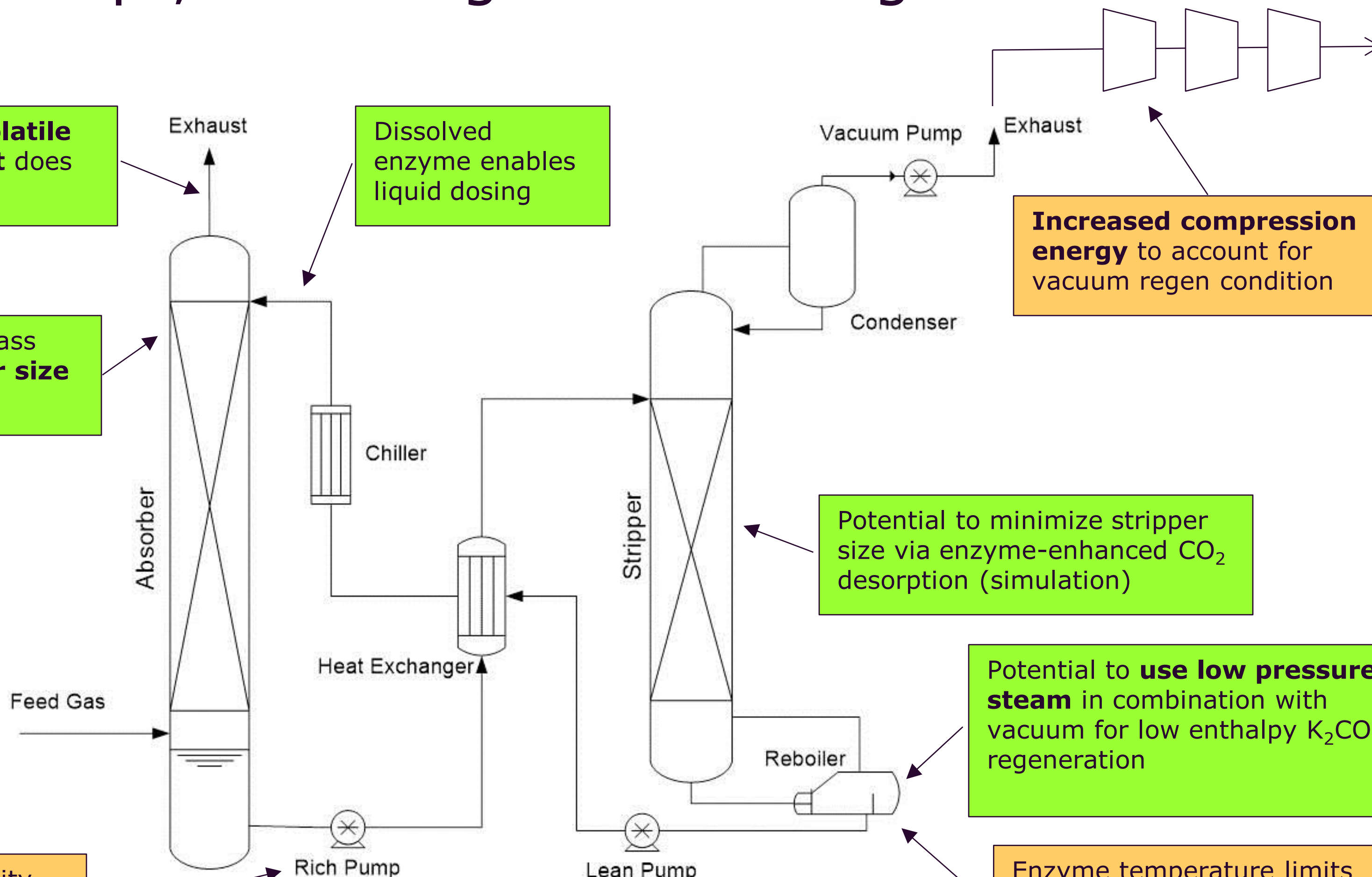


Stable, benign, non-volatile aq. K_2CO_3-based **solvent** does not require water wash

Dissolved enzyme enables liquid dosing

Increased compression energy to account for vacuum regen condition

Enzyme-enhanced CO_2 mass transfer **reduces absorber size** to feasible height

Potential to minimize stripper size via enzyme-enhanced CO_2 desorption (simulation)

Potential to **use low pressure steam** in combination with vacuum for low enthalpy K_2CO_3 regeneration

K_2CO_3 loading capacity limit may increase solvent circulation rate

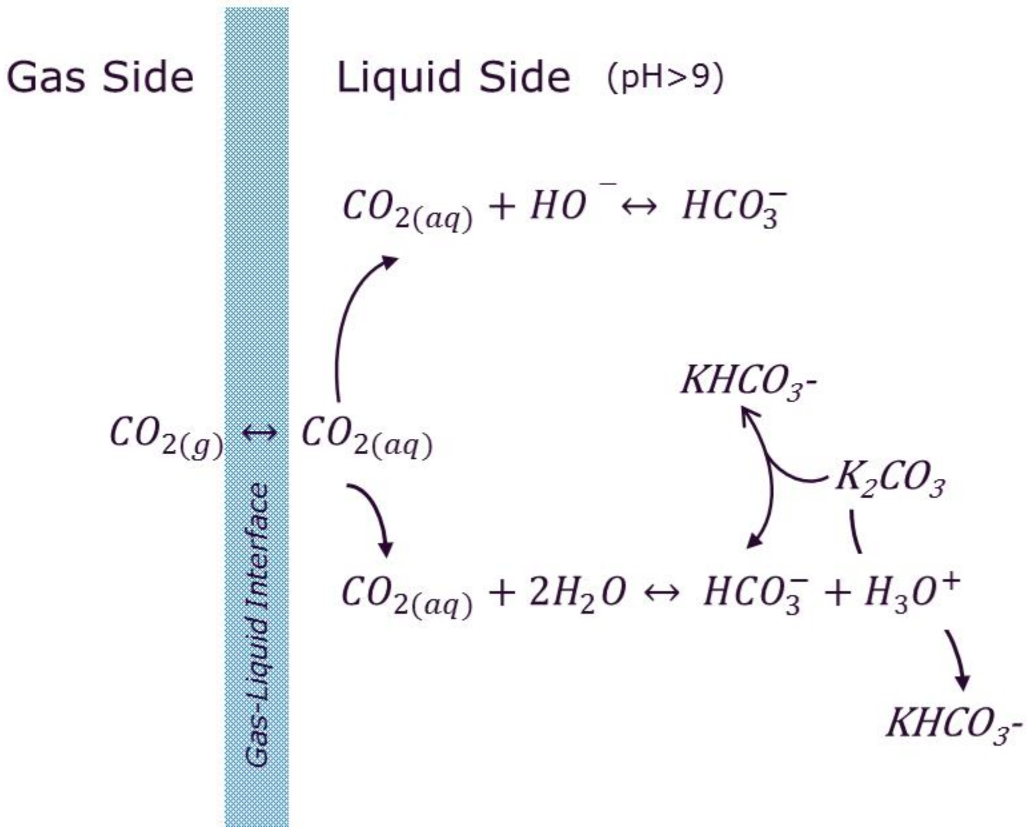
Enzyme temperature limits may result in **high enzyme replenishment** requirement

Absorption
1 atm/30-40°C

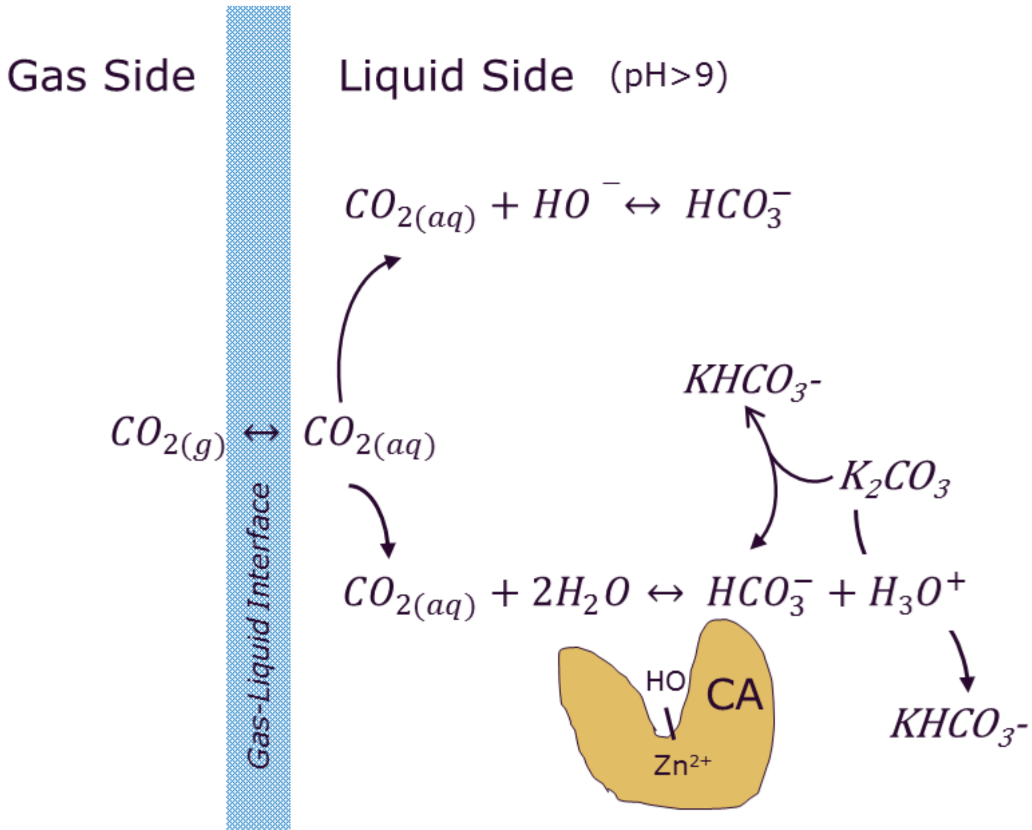
Regeneration
~0.35 atm/76°C

Generating Bench-scale Test Data

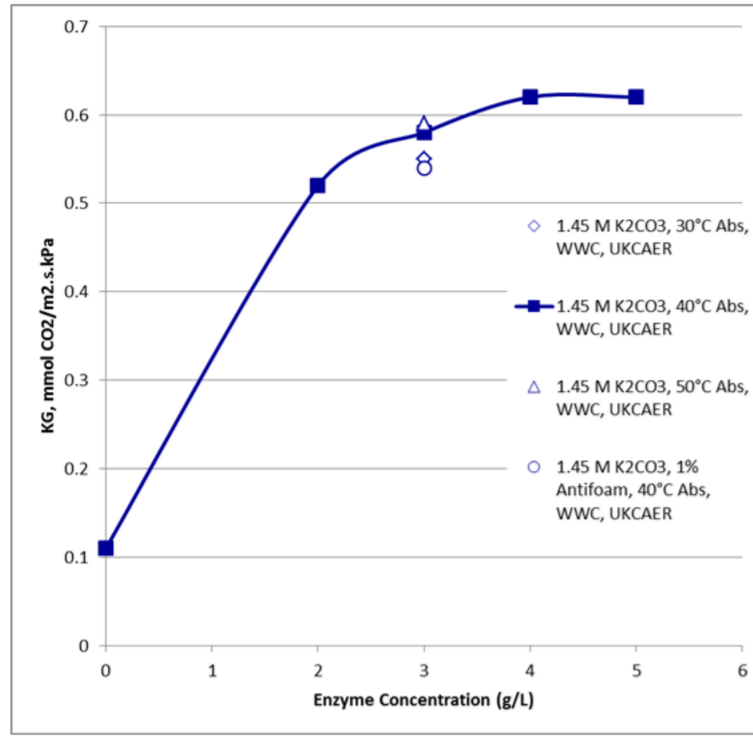
CO_2 Absorption Mechanism



Enzyme Enhanced CO_2 Absorption Mechanism



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

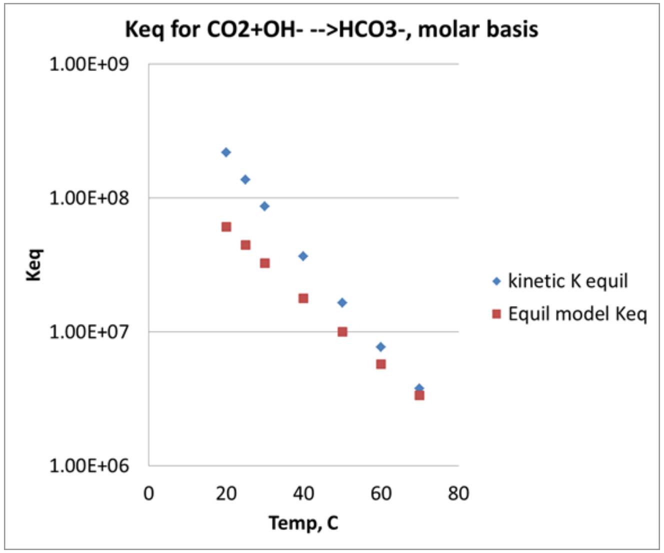


Overall Mass Transfer Coefficient (K_g) Enhanced by Enzyme in WWC

Approach to Kinetic Model

- Improve existing Aspen kinetic model for $CO_2 + OH^- \rightarrow HCO_3^-$
  - 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°C.
- Include a parallel rate expression for $CO_2 + 2H_2O \rightarrow H_3O^+ + HCO_3^-$
  - Model enzyme effect by accelerating this reaction, not hydroxide reaction

Comparison of equilibrium constants predicted by equilibrium model and pre-correction kinetic model.



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Project Plan & Accomplishments

Task	Status/Result	Reporting
1 – Management & Administration	Within budget; Project focused on vacuum stripping when flow thru ultrasonics gave < needed results	Current per requirements
2- Process Optimization	Preliminary targets met • Batch-mode ultrasonics tests conducted • Enzyme-solvent absorption kinetics met target in WWC • Bench-scale system designed, incld. vacuum regen	CCTM 2012 29th IPCC
3 - Initial Technical & Economic Feasibility	Versus DOE Base Case 10, identified opportunities for • 55% lower parasitic load with ultrasonics • 43% lower parasitic load with vacuum stripping	BP2 Continuation
4 - Bench Unit Procurement & Fabrication	Prototype flow-through ultrasonic unit built & tested; Constructed bench-scale absorber with vacuum stripper	12th CCUS CCTM 2013
5 - Bench-scale Integration & Shakedown Testing	Shakedown testing w/vacuum stripping completed • Bench-scale system build completed & operational • 90% capture achieved with 30°C absorber; 30 SLPM gas flow; 78°C reboiler; 20 wt% K_2CO_3; 3 g/L Enzyme	BP3 Continuation
6 - Bench-scale Testing	Parametric testing completed • Selected baseline conditions for 500 hr test & obtained data for kinetic model Rate-based simulation for vacuum stripping • Framework for the kinetic model established 500 h testing currently in progress	CCTM 2014 AIChE 2014
7 - Full Technology Assessment	TEA and EH&S in progress • Bench-scale results provide input to the assessment	Completion 1Q15

Bench-scale Unit Description

- Flow Rates
  - Gas: 30 SLPM (15% CO_2, 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
- K_2CO_3 Concentration: 23 wt%
- Enzyme Concentration: 0 – 4 g/L

PFD of Integrated Bench-scale System

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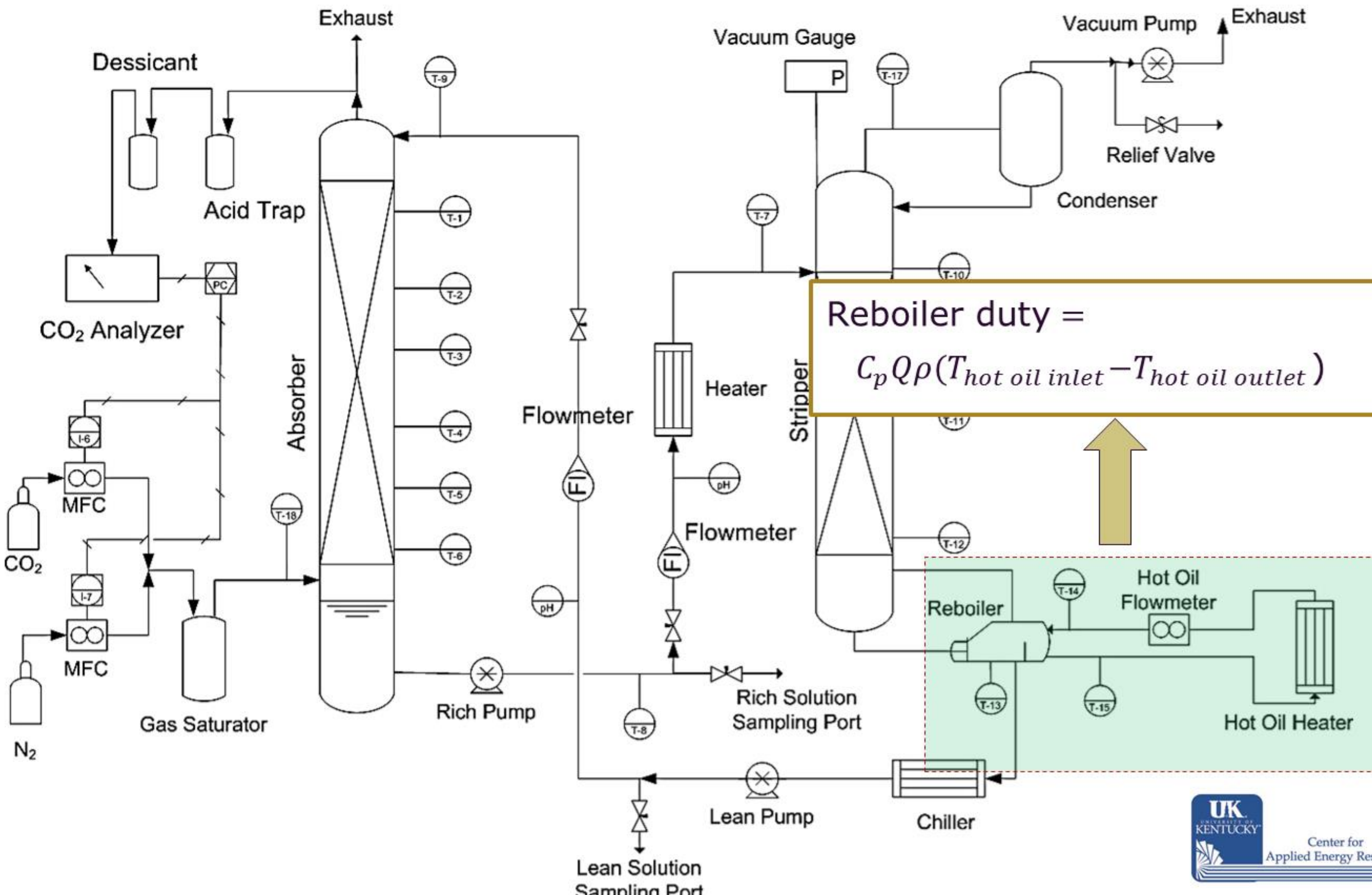

Reboiler duty =

$$C_p Q \rho (T_{hot\ oil\ inlet} - T_{hot\ oil\ outlet})$$

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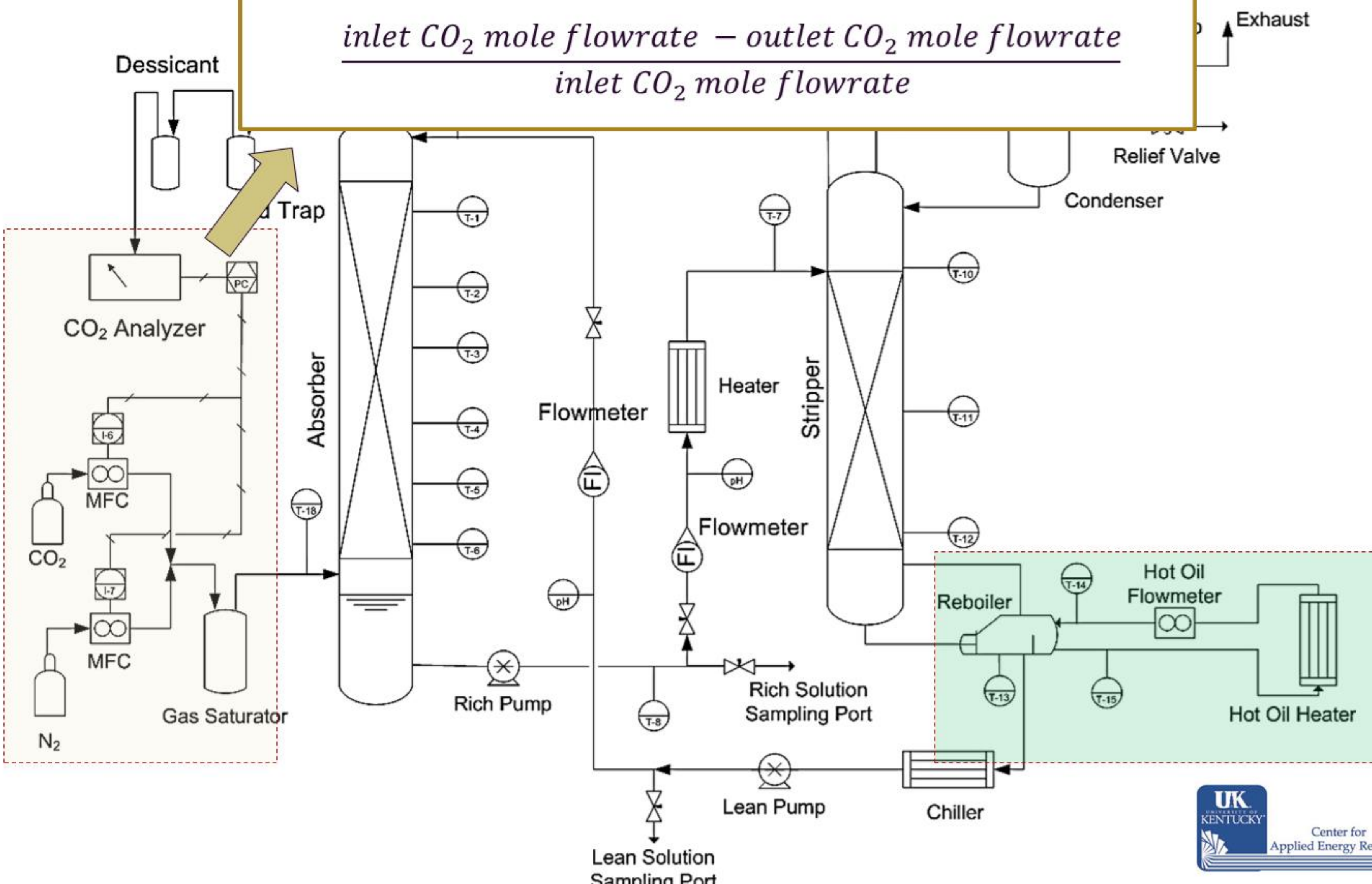
Capture Efficiency=

$$\frac{inlet\ CO_2\ mole\ flowrate\ -outlet\ CO_2\ mole\ flowrate}{inlet\ CO_2\ mole\ flowrate}$$



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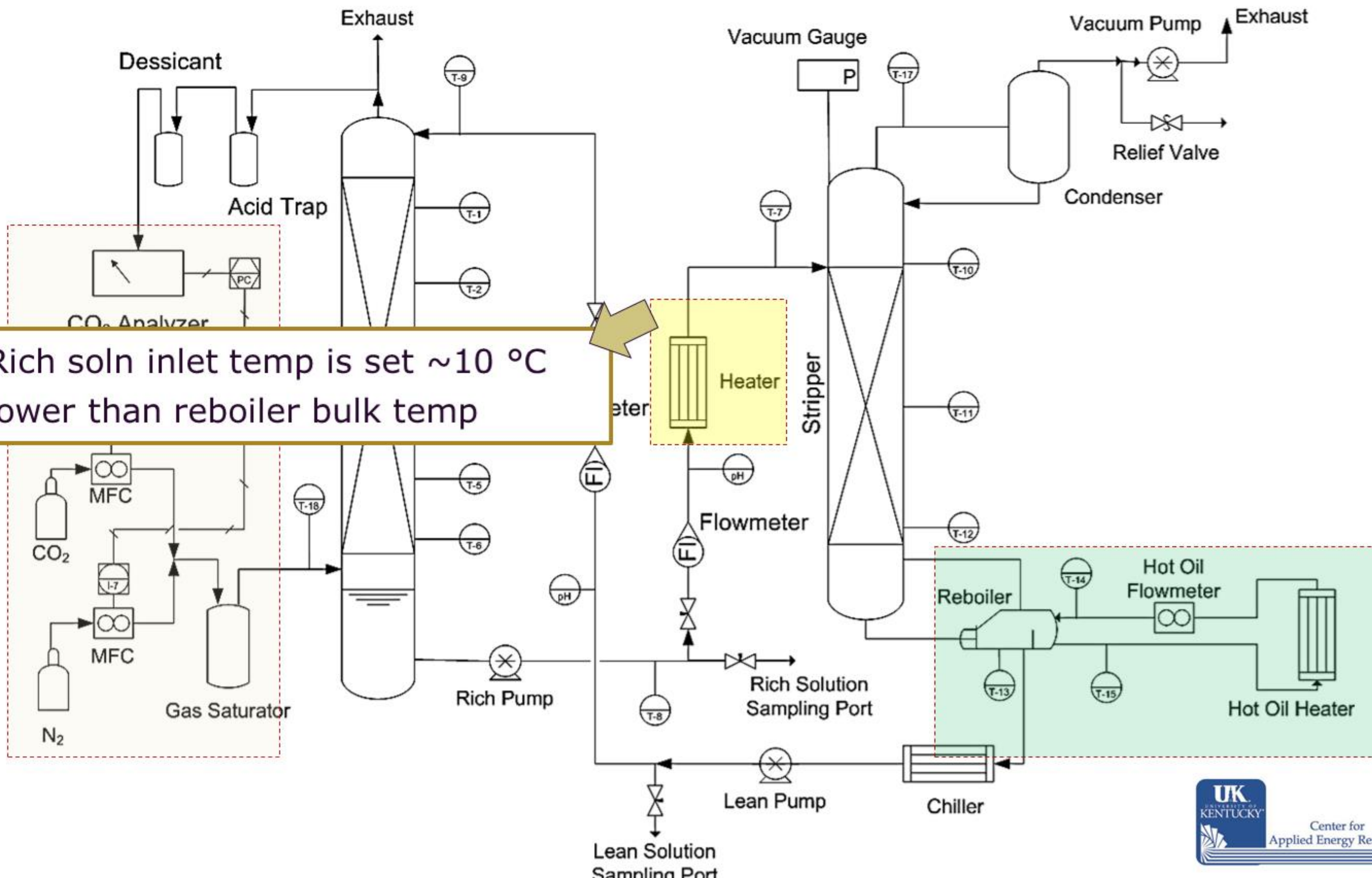

Rich soln inlet temp is set ~10 °C lower than reboiler bulk temp

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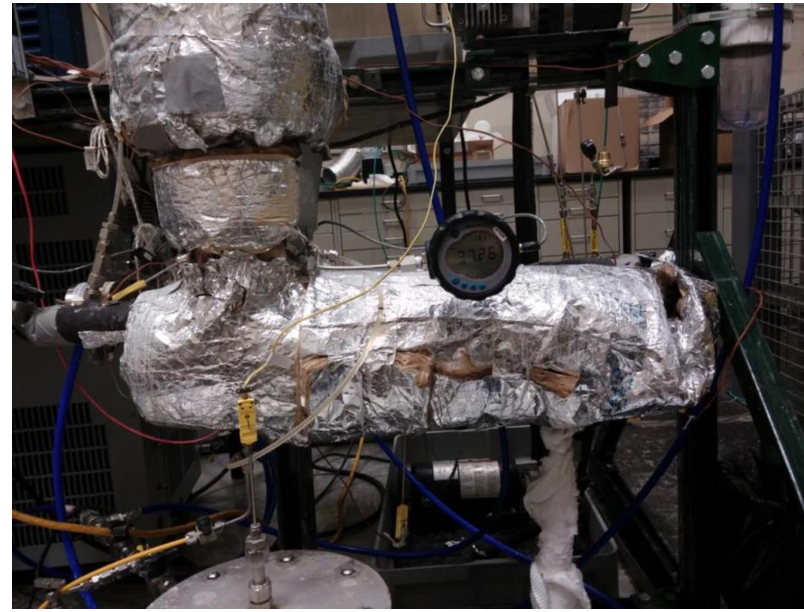
Bench-scale Operational Observations

Absorber bottom

Stripper top



Stripper bottom

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)

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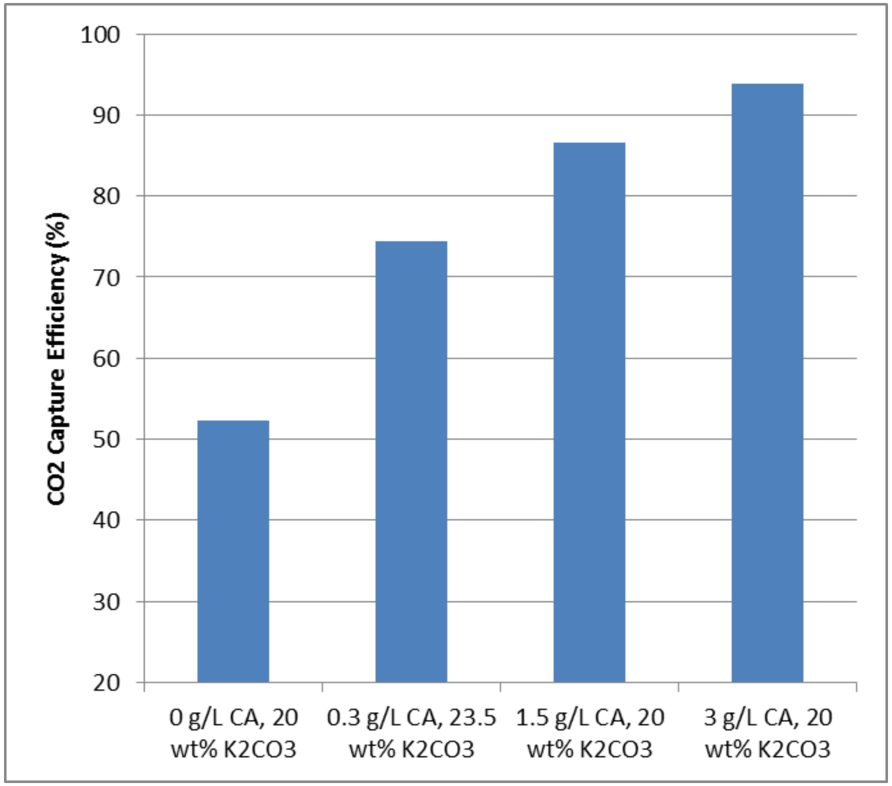
Shakedown: Enzyme Dose Impacts CO_2 Capture



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.

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Parametric Test Matrix

Each condition was evaluated over 2-3 run days

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

Condition for long term test (Run 1)

No-enzyme reference condition (Run 10)

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Selected Parametric Test Results

	#1	#10
Enzyme Dosing, g/L	2.5	0
Liquid Flow Rate, mL/min	500	500
Feed Gas Temp, ^{o}C	40	40
Reboiler Solution Temp, ^{o}C	77	76
Lean Solvent Temp, ^{o}C	40	40
Outlet CO_2 Conc, %	1.9	12.4
Total Gas Flow, LPM	30	30
Hot Oil Inlet Temp, ^{o}C	95	95
Q, Reboiler, KW	1.1	1.1
Capture Efficiency (%)	89%	19%
Energy Demand (kJ/mol CO_2 captured)	382	1611
Stripper Top Pressure, kPaa	35	35
Rich Conversion	54%	43%
Lean Conversion	35%	39%

Results shown are average values from duplicate runs for each test.

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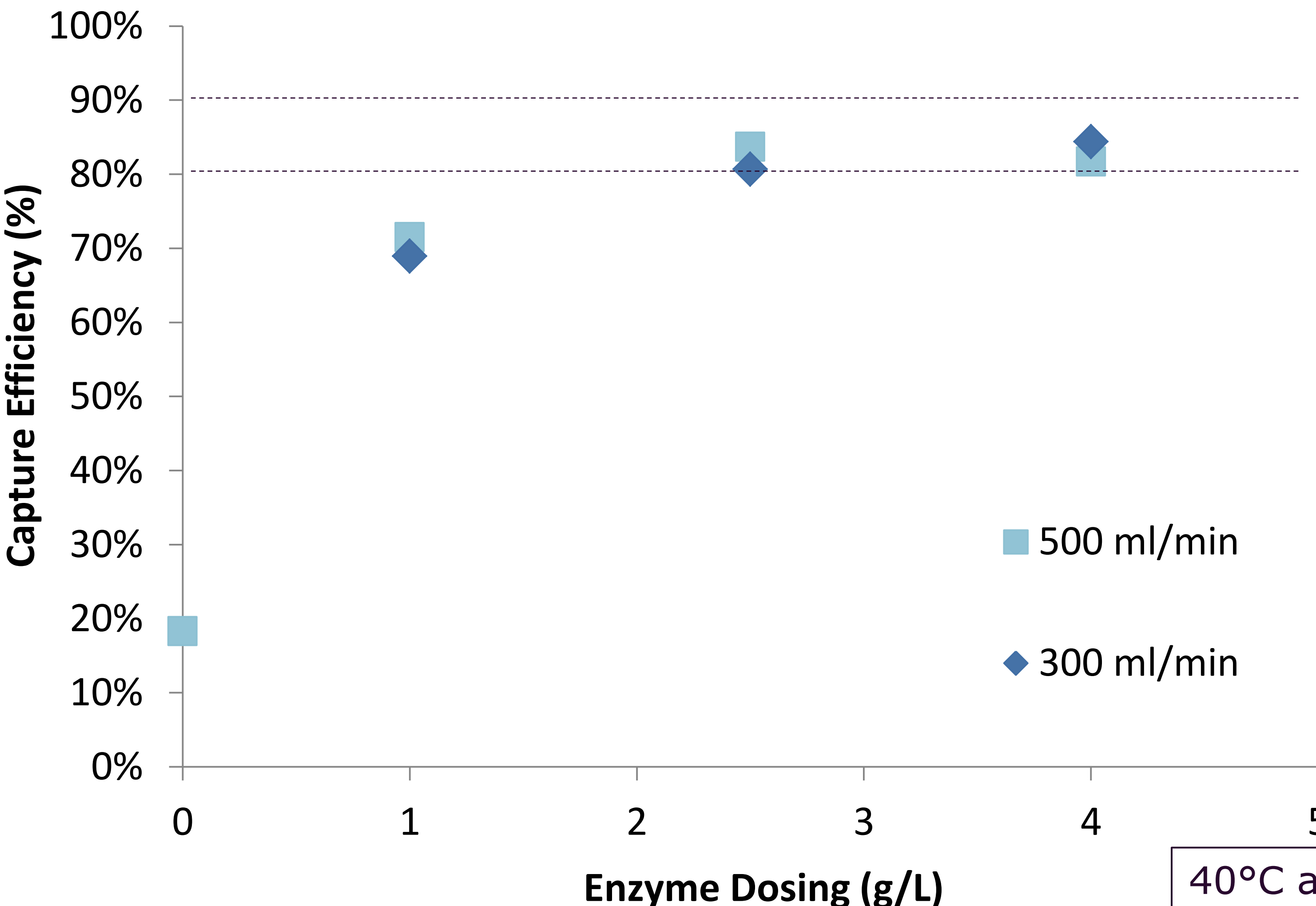
Impact of Enzyme Conc. and Liquid Flow Rate

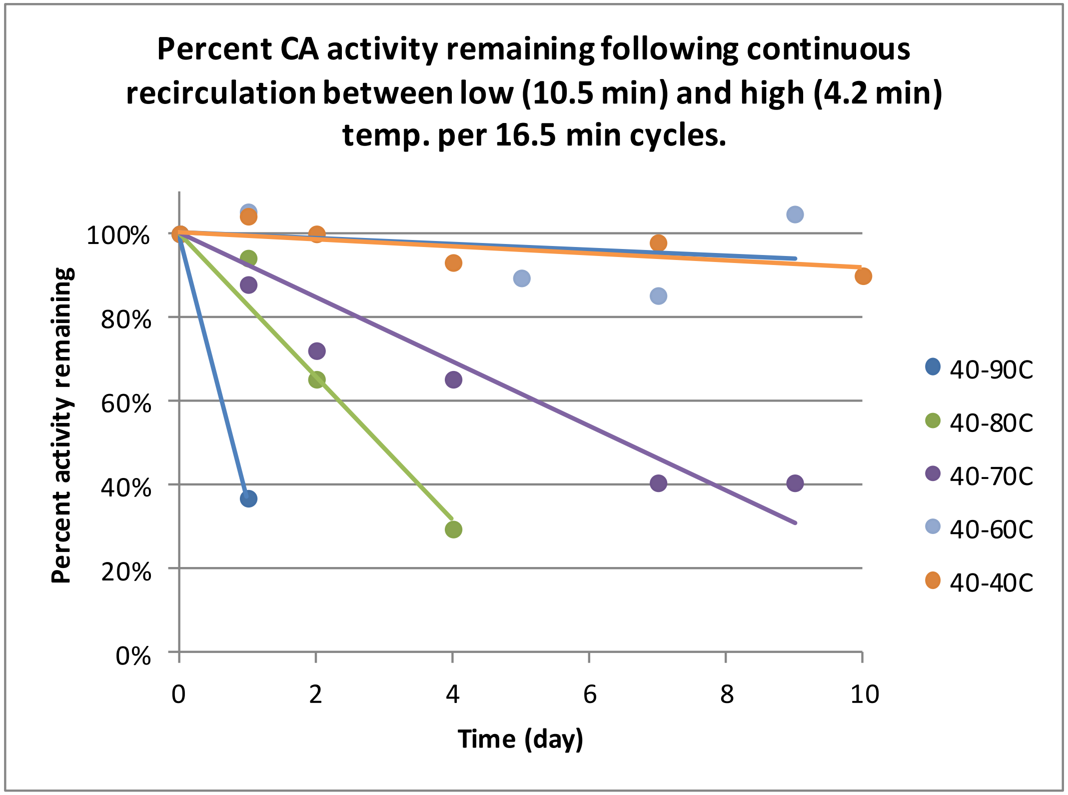


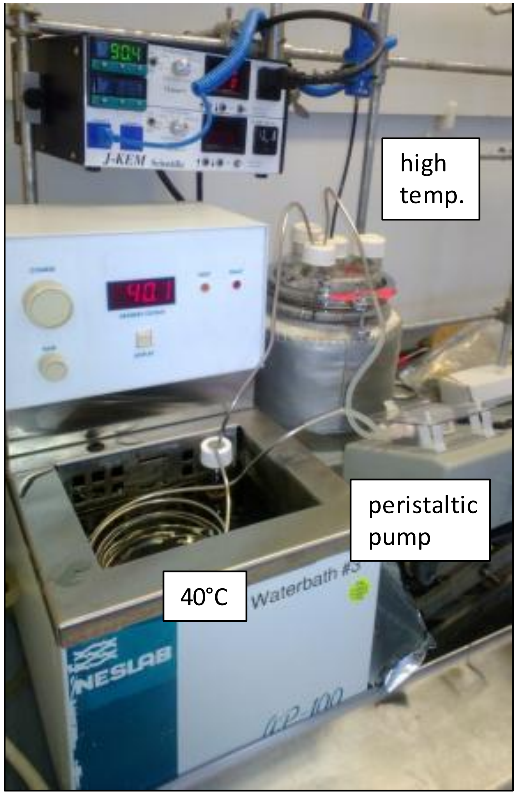
40°C absorber
90°C hot oil inlet

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

Current Enzyme Temperature Stability





- 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.

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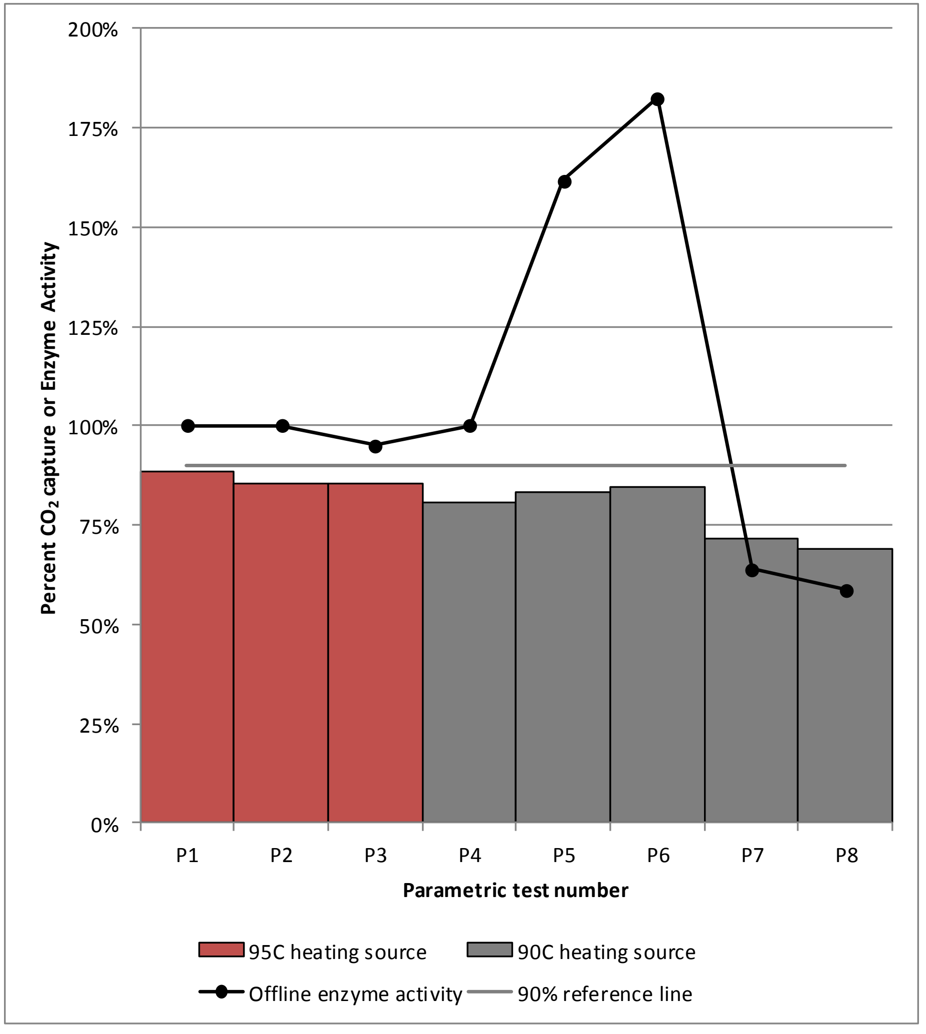
Enzyme Replenishment for Parametric Tests



- 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.

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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% CO_2 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

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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_2CO_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

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