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

Sonja Salmon

DOE/NETL CO2 Capture Technology Meeting
24 June 2015, Pittsburgh

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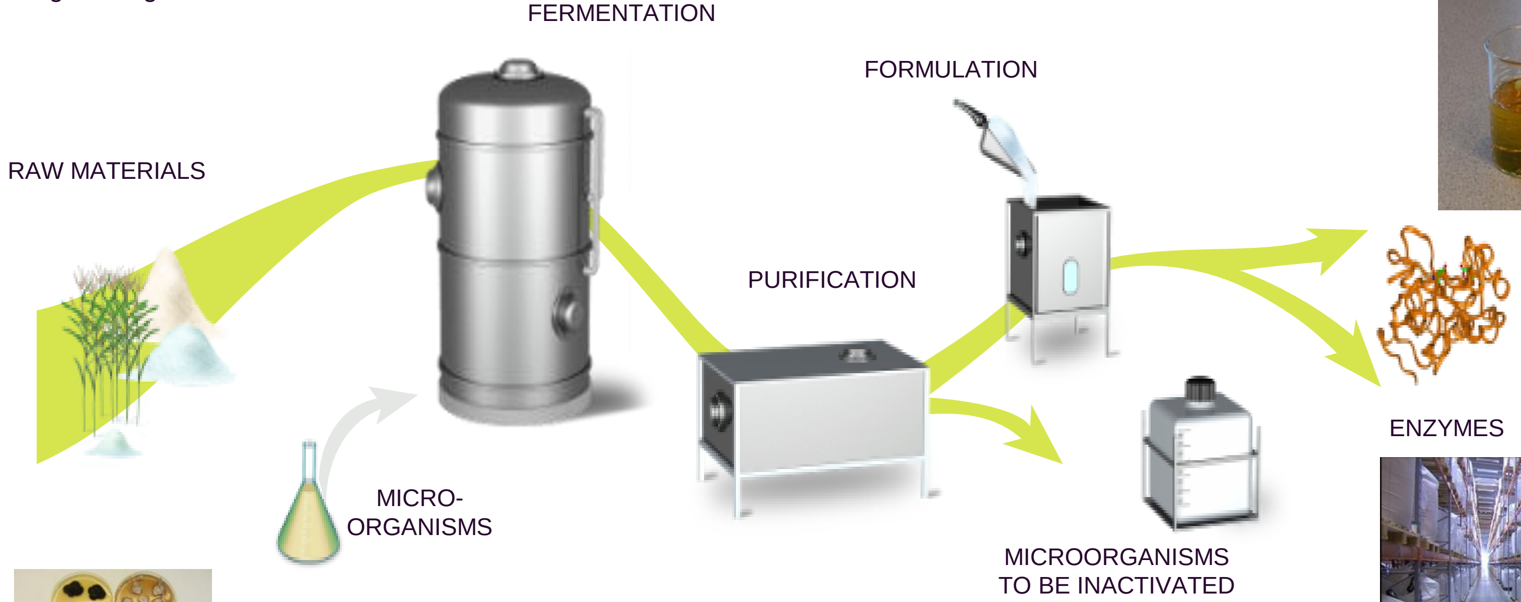
   - Input optimization



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

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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 – June 30, 2015

DOE Program Objectives

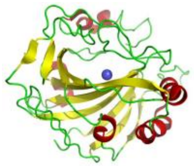
Develop solvent-based, post-combustion technology that

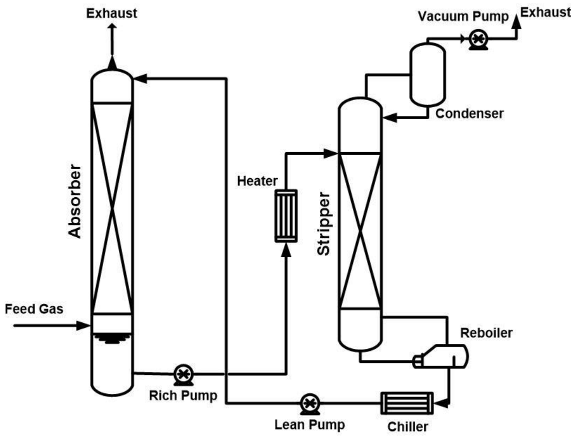
- Can achieve ≥ 90% CO_2 removal from coal-fired power plants
- Shows progress toward DOE target of <35% increase in LCOE

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

$CO_2 + H_2O + K_2CO_3 \leftrightarrow 2KHCO_3$

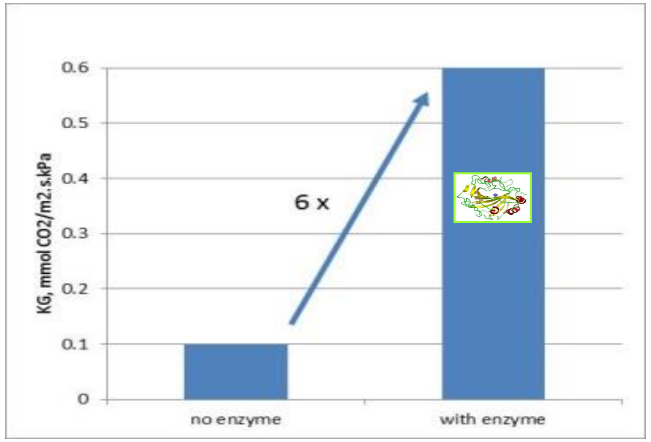


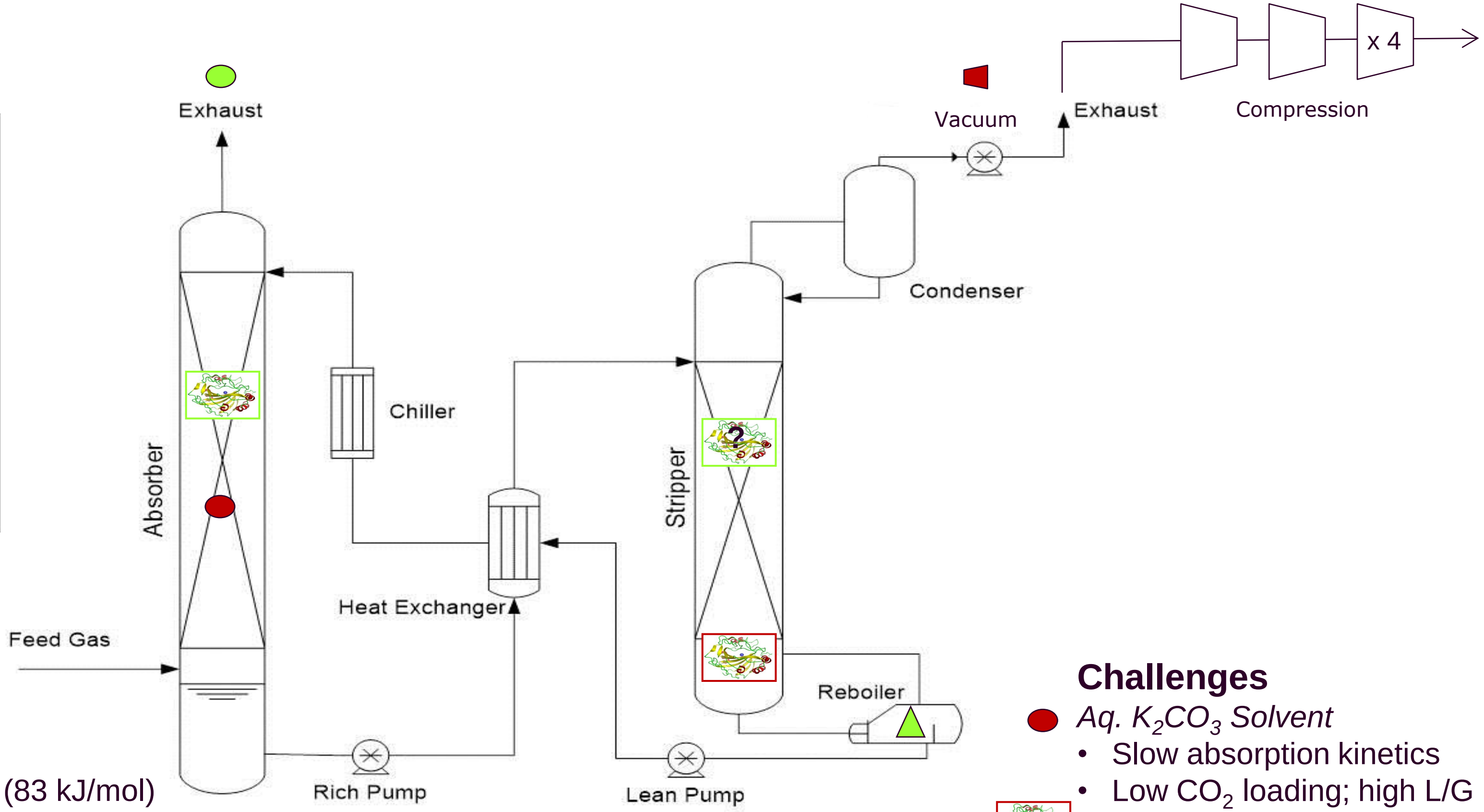


- a **low-enthalpy**, aqueous potassium carbonate-based solvent
- with an **absorption**-enhancing (*dissolved*) carbonic anhydrase enzyme catalyst
- and a low temperature vacuum **regenerator**
- in a **re-circulating** absorption-desorption process configuration

Process Concept, Advantages & Challenges

$$CO_{2(aq)} + 2H_2O \leftrightarrow HCO_3^- + H_3O^+$$





Absorption
1 atm (101 kPa)/40°C

Regeneration
0.35 atm (35 kPa)/77°C

Bench-scale Test Conditions

Advantages

Aq. K_2CO_3 Solvent

- Stable, benign, non-volatile
- Low enthalpy of rxn. (27 kJ/mol) vs. MEA (83 kJ/mol)

Dissolved Enzyme

- Accelerates absorption to reduce column height
- Easy dosing & replenishment
- Potential stripping enhancement (?)

Vacuum Regeneration

- Low reboiler/stripper temp. benefits enzyme longevity
- Potential for use of Very Low Pressure (8 psia) steam

Challenges

Aq. K_2CO_3 Solvent

- Slow absorption kinetics
- Low CO_2 loading; high L/G

Dissolved Enzyme

- Prolonged thermal stress causes activity loss

Vacuum Regeneration

- Increased compression penalty
- Unproven at scale

Project Scope & Technical Accomplishments

Task 2: Process Optimization

Task 3: Initial Technical & Economic Feasibility

Task 4: Bench Unit Procurement & Fabrication

Task 5: Bench-scale Integration & Shakedown Testing

Task 6: Bench-scale Testing

Task 7: Full Technology Assessment

1H12 · 2H12 · 1H13 · 2H13 · 1H14 · 2H14 · 1H15 · June 2015

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- Batch mode ultrasonics tests conducted
- Enzyme-solvent WWC kinetics met target
- Bench-scale system designed, incld. vacuum regeneration
- **CCTM 2012,** 29th IPCC
- Prelim TEA identified opportunities for lower parasitic load vs Case 10

- Prototype flow-through ultrasonic unit built & tested; not pursued
- Integrated bench-scale system with vacuum stripper completed & operational
- **CCTM 2013,** 12th CCUS

- Completed parametric tests incld. enzyme dose-response & alternative solvent tests
- Developed rate-based model for vac stripping
- Completed 500 hour bench-scale testing
- **CCTM 2014,** AIChE 2014

- EH&S: system meets regulatory requirements
- Completed full TEA
- **CCTM 2015**

▼ Provision of Novozymes prototype microbial carbonic anhydrase at no cost to the project

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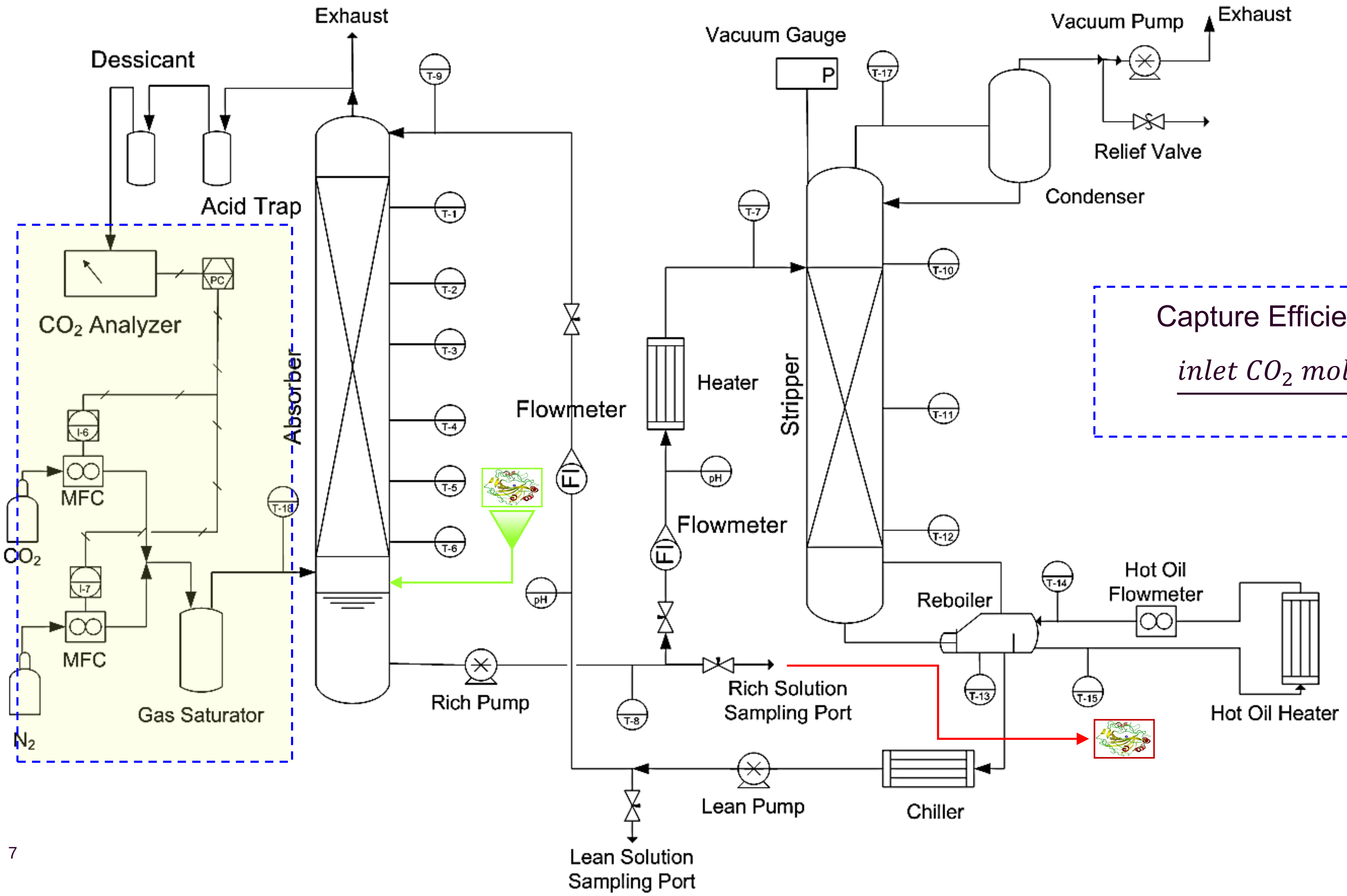
PFD of Integrated Bench-scale System



Icons indicate points of enzyme and aq. K_2CO_3

- addition
- removal

for solvent replenishment

Capture Efficiency=

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

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Bench-scale (Parametric) and 500 Hour Test Conditions

Base Solvent

- Aqueous 23 wt% K_2CO_3 selected for 500 h run
- Solvent pre-testing included tests for higher CO_2 loading capacity
  - Borax or bicine with K_2CO_3 show potential benefits (lab scale)
  - 23 wt% K_2CO_3 with/without 4 wt% borax gave similar result (bench scale)

Operating Parameters

- Column Packing: Rashig ring
- Stripper Pressure: 0.35 atm absolute
- Enzyme Concentration: (1-4) 2.5 g/L

Flow Rates

- Gas: 30 SLPM, 15/85% CO_2/N_2
- Liquid : (300-600) 500 mL/min

Liquid Temperature

- Absorber Inlet: 40°C
- Stripper bulk: ~77°C
- Reboiler Heating Source (Oil Inlet): (90-95) 95°C

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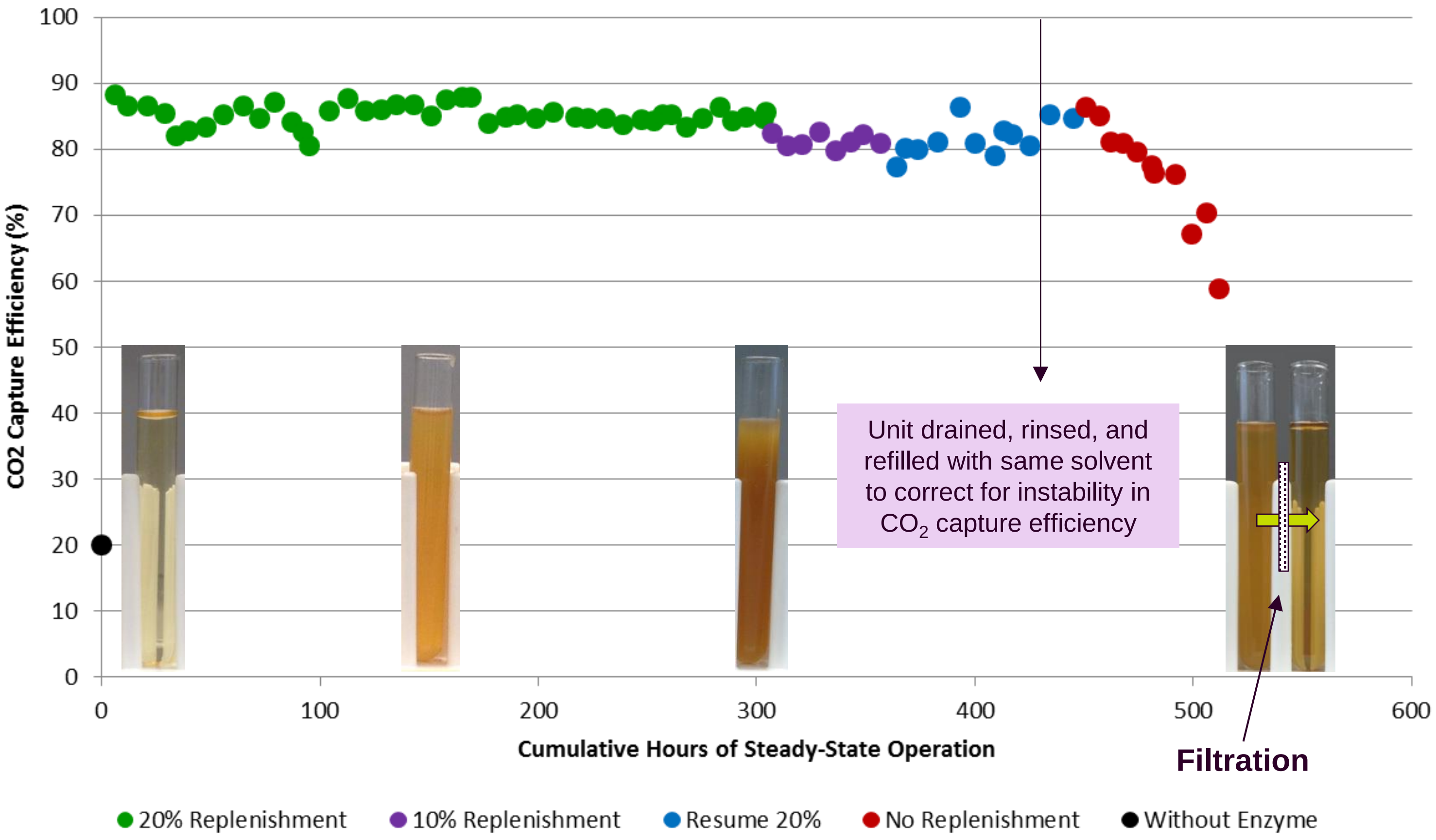
500 Hour Long Term Test Results



- **>80% CO_2 Capture efficiency was maintained**
  - System tolerated daily start-up/shut-down
  - Stabilizing the vacuum condition required frequent manual adjustments
  - Foaming was controllable using antifoam
- **Principle of using dissolved enzyme replenishment to achieve stable operation was demonstrated**
  - Stopping replenishment caused decrease in CO_2 Capture efficiency
- **Solvent darkens and becomes turbid over time**
  - System tolerated turbidity during operation
  - Liquid can be clarified using proper filtration
- **Performance instability occurred and was corrected**
  - Attributed to (protein) solids accumulation on reboiler surfaces
  - Was corrected by rinsing the system

500 Hour Test – Solvent Management

Bench-scale Daily Operation

- System start-up/shut-down daily
- ~7 hour steady-state run day
- Solvent storage at room temperature when not in operation

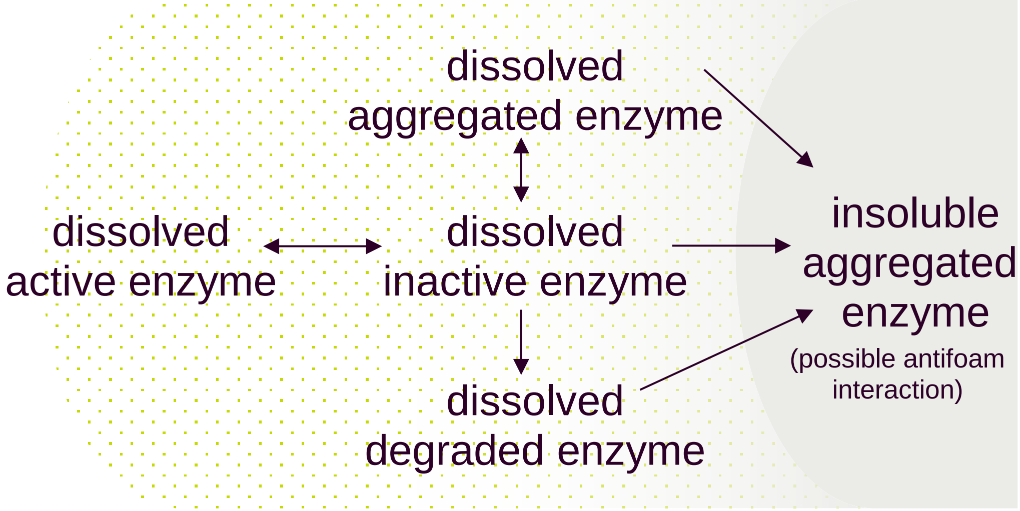
Solvent additions per ~7 h run day

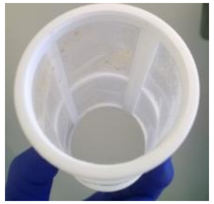
- Antifoam addition: ~0.04%
- Enzyme addition: 0, 10 or 20% of active enzyme inventory (with replacement of equivalent solvent volume)
- Solvent volume and alkalinity were maintained

Observations

- Neither active, nor intact inactive dissolved enzyme accumulated in the system
- Insoluble aggregated enzyme may have accumulated and led to system instability

Enzyme liquid concentrate | K_2CO_3 solution | Working solvent 2.5 g/L CA in K_2CO_3 aq. | Enzyme + K_2CO_3 stock soln. to supply unit during replenishment





Solids trapped by bench-unit filter

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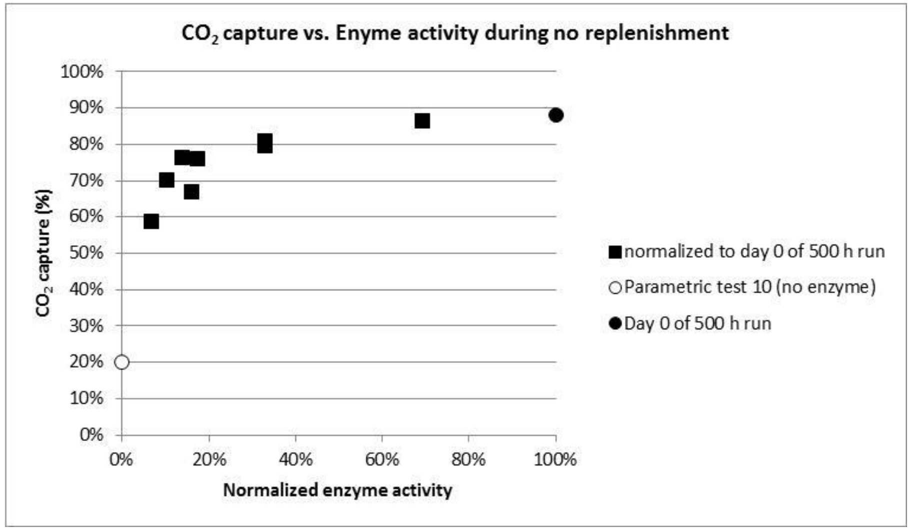
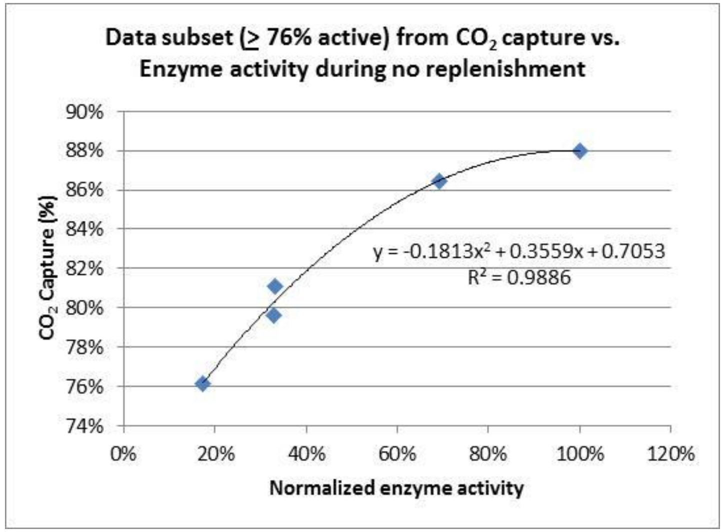
Non-linear Relationship Observed Between Enzyme Activity % CO_2 Capture





- **A nonlinear relationship correlates loss of active enzyme and loss of CO_2 capture efficiency**
  - Approximate 75% loss in active enzyme corresponded to a 10% loss in CO_2 capture efficiency
  - > 50% CO_2 capture was obtained with < 20% enzyme activity remaining; illustrates partial capture potential
  - One explanation could be overdosing of enzyme, suggesting further dose optimization could be possible
- **No accumulation of intact, inactive enzyme was detected**
  - Analysis confirmed that lower activity samples showed higher level of degraded CA by protein analysis (SDS-PAGE)

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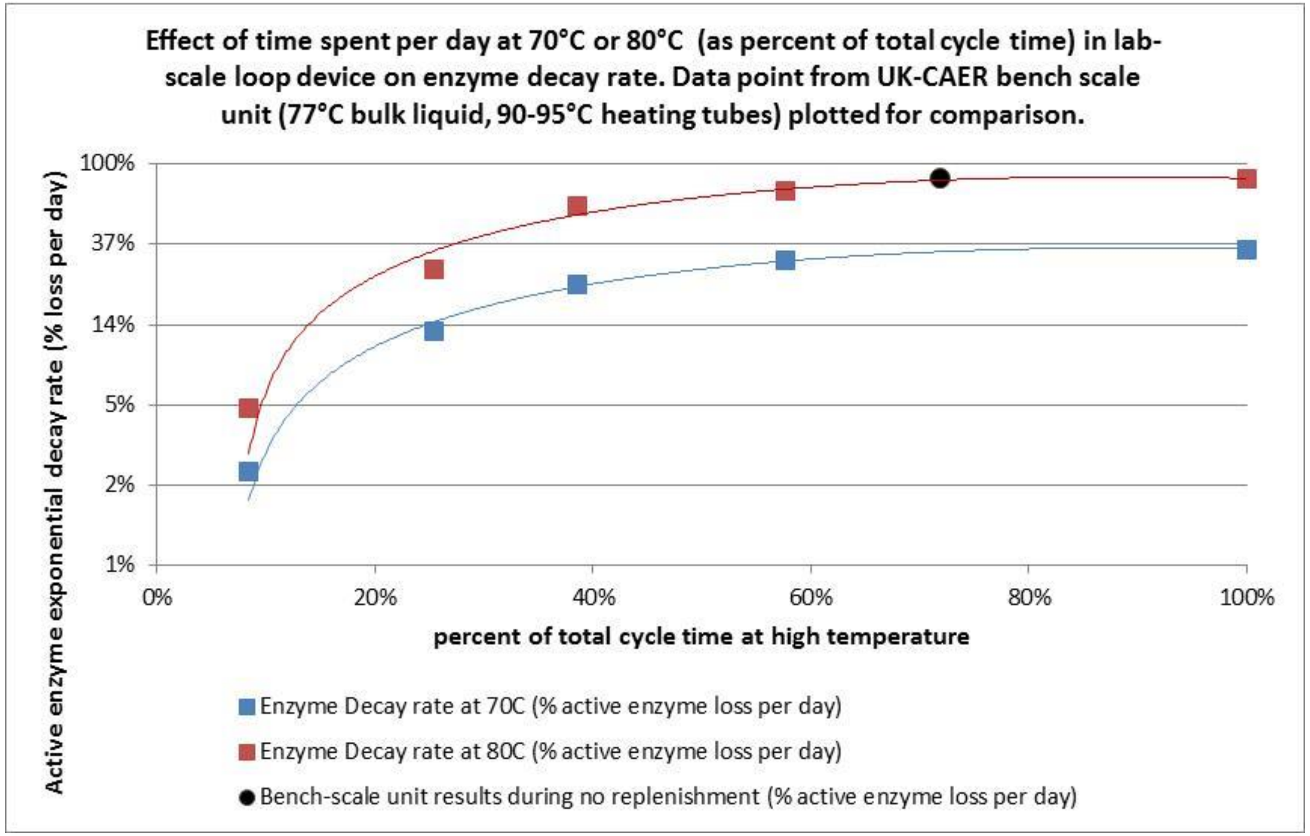
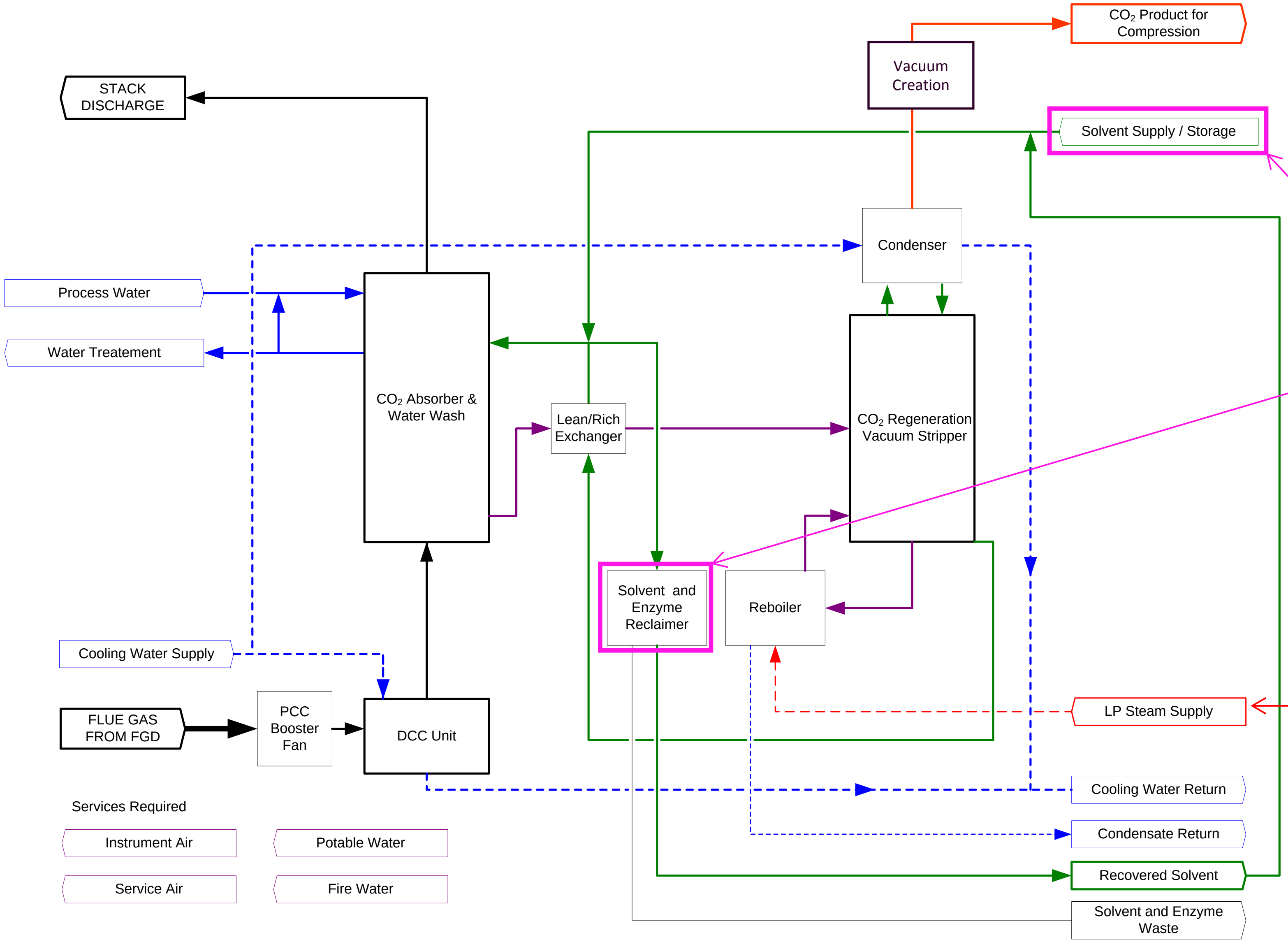
Lab Study Confirms Bench-scale Decay Rate



- Lab scale study shows that longer residence time and higher temp → faster decay rate
- In the bench scale unit, the solvent spent 72% of total cycle time in the reboiler
- Reducing the percent of total cycle time at high temperature and/or reducing the temperature can yield substantial improvements in enzyme longevity in the system

Simplified PFD of Full Plant PCC System



Enzyme Replenishment

- Addition of fresh enzyme using liquid dosing
- Separation of deactivated enzyme solids and solvent recovery

Reboiler Heating

- LP steam from existing IP/LP crossover
- VLP steam from new LP/VLP crossover; requires new turbine

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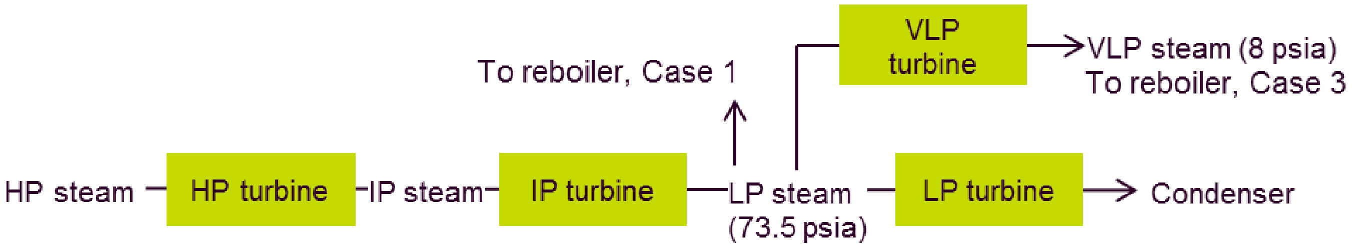
Techno-Economic Analysis Cases

Case	Enzyme Location	Stripper Pressure	Bulk Stripper Temperature	Pros	Cons
DB1	Travels with solvent	6 psia	70°C; Uses LP steam	Enzyme-enhanced kinetics throughout; Uses currently available technologies	Commercially available, reasonably-sized vacuum equipment operating at its limits; Requires strengthened equipment for vacuum
DB2	Travels with solvent	3 psia	53°C; Uses LP steam	Enzyme-enhanced kinetics throughout; Extended enzyme longevity	Further equipment strengthening needed; Vacuum creation possibly beyond practical limits with existing equipment
DB3	Travels with solvent	6 psia	70°C; Uses VLP steam	Enzyme-enhanced kinetics throughout; Additional turbine generates electricity	Same as DB1; VLP process has higher risk/ uncertainty; Turbine size requirements and costs would have to be confirmed through detailed design; Not off the shelf
DB4	Excluded from stripper	6 psia	70°C; Uses VLP steam	Enzyme-enhanced absorber kinetics; Conventional stripper; Additional turbine generates electricity	Same as DB3
DB5	None	6 psia	70°C; Uses VLP steam	Additional turbine generates electricity	Same as DB3, however without kinetic enhancement; < 20% CO_2 Capture

Inputs from bench-scale system operation, laboratory-based observations, AspenPlus® process simulation and modelling, Aspentech's "Capital Cost Evaluator" (CCE®) Parametric Software, current vendor quotations, and project partners' know-how of unit operations, were combined to develop four techno-economic cases with enzyme (DB1-DB4), a case without enzyme (DB5), and a set of sensitivity studies based on enzyme longevity improvements (based on DB1-DB3).



Full TEA Results (550 MW net power output, subcritical PC plant)

Performance/Cost[1]	Case 9[2]	Case 10[2]	Case DB1	Case DB2	Case DB3	Case DB4	Case DB5
CO_2 Capture Performance (%)	0	90	90	90	90	90	18
Total Plant Cost (2007$/kW)	1,622	2,942	2,964	3,141	3,006	3,006	NA
Total Overnight Cost (2007$/kW)	1,996	3,610	3,658	3,863	3,699	3,699	
COE (mills/kWh, 2007$)	59.4	109.6	119.6	119.0	116.3	116.2	
• *CO_2 TS&M Costs*	0	5.8	5.9	5.9	5.9	5.9	
• *Fuel Costs*	15.2	21.3	18.5 [3]	19.4	16.6	16.5	
• *Variable Costs*	5.1	9.2	21.2	15.7	19.0	18.9 [4]	
• *Fixed Costs*	7.8	13.1	13.1	13.6	13.2	13.2	
• *Capital Costs*	31.2	60.2	60.9	64.3	61.6	61.6	
LCOE (mills/kWh, 2007$)	75.3	139.0	151.7	150.9	147.5	147.3	
Cost of CO_2 Captured (2007$/tonne)	NA	48.1	68.0	63.5	70.7	70.8	
Cost of CO_2 Avoided (2007$/tonne)	NA	68.2	80.0	79.8	74.6	74.4	

*[1] All costs were adjusted to **2007 US dollars**; tonne = one metric ton (1000 kg); [2] "Cost and Performance Baseline for Fossil Energy Plants – Volume 1: Bituminous Coal and Natural Gas to Electricity," DOE/NETL-2010/1397 Study, Final Report, Rev. 2a, (September 2013); [3] Note that the bench-scale experiment required higher energy demand than predicted by the model; [4] Enzyme cost was held equivalent to Case DB3*

TEA Sensitivity Study

Performance/Case	Case 10	DB1a[1]	DB1b[2]	DB2a	DB2b	DB3a	DB3b
COE (mills/kWh, 2007$)	109.6	111.2	108.4	114.7	113.3	109.0	106.5
LCOE (mills/kWh, 2007$)	139.0	140.9	137.4	145.4	143.6	138.2	135.1
Stripper Temperature, average/peak (°C)		70/77	70/77	53/60	53/60	70/77	70/77
Cost of CO_2 Captured (2007$/tonne)	48.1	57.4	53.9	58.4	56.7	60.5	57.2
Cost of CO_2 Avoided (2007$/tonne)	68.2	68.8	65.1	74.1	72.2	65.0	61.7

[1] Stage 1 development of enzyme; [2] Stage 2 development of enzyme

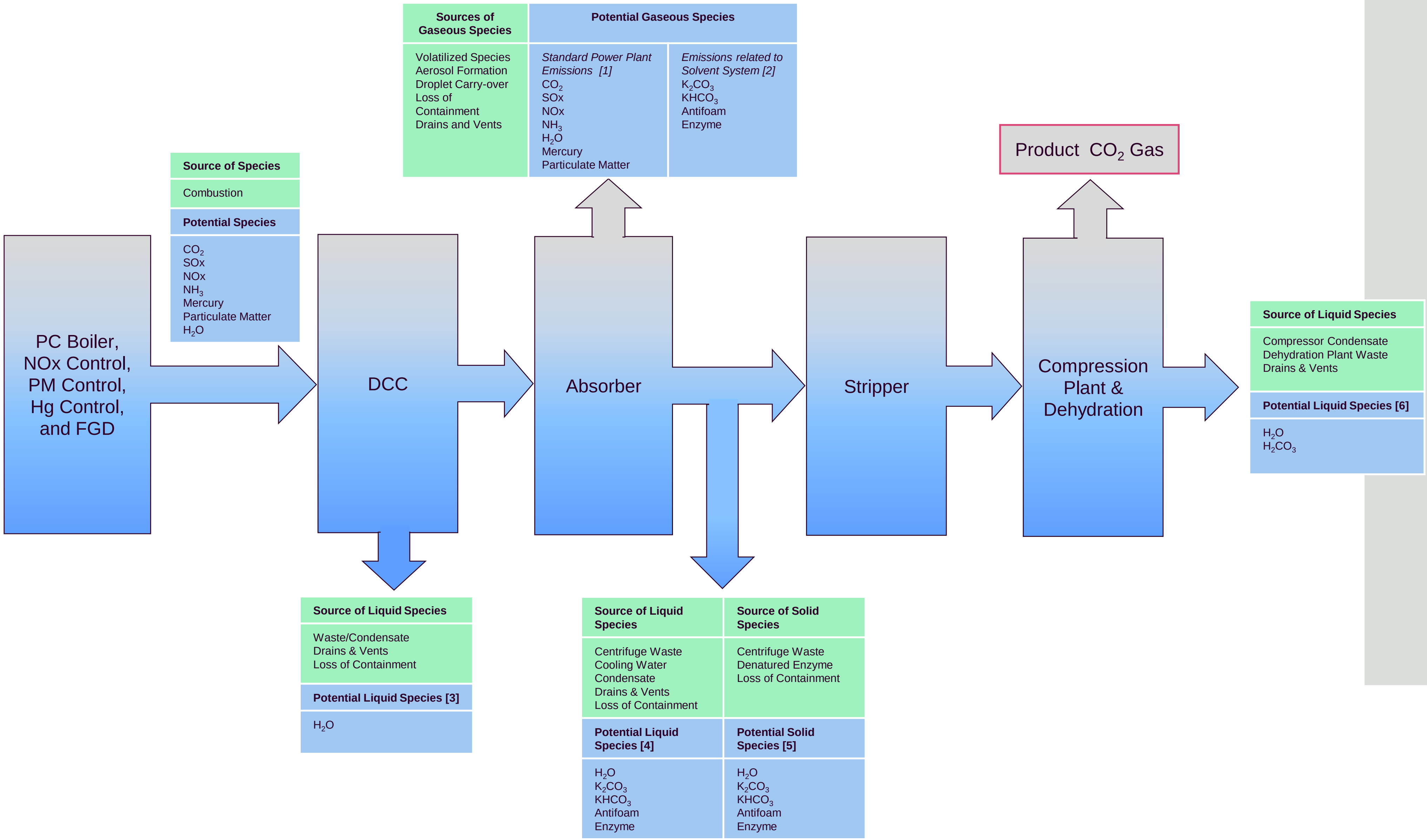
Findings with respect to DOE performance targets

- 90% CO_2 Capture performance was achieved
- Equivalent LCOE to Case 10 was predicted by sensitivity study, assuming realistic enzyme longevity improvements

Additional observations

- Increase in LCOE for the best modelled cases was ~80% versus ~85% for Case 10
- Cases based on DB1 give highest confidence in immediate technical feasibility using currently available technologies
- After Stage 2 enzyme development, other factors, e.g. CAP costs, dominate further system optimization
- Scale-up testing of the system would be needed to validate assumptions and verify performance

EH&S Assessment



Emissions Handling

[1] As is – no concerns

[2] Very small quantities expected during normal operation – Single Stage Water Wash and demister proposed to ensure no emissions during transient cases

[3] Recycled to maintain PCC plant water balance

[4] Solvent to be recovered following treatment in centrifuge and returned to plant solvent make-up

[5] Enzyme to be separated following treatment in centrifuge; solids exported as biomass product

[6] Water to undergo treatment at PC Plant water treatment facility prior to discharge

Potential emissions were found to pose no significant environmental, health or safety EH&S concerns and were compliant with the Federal legislation reviewed; assessment should be revisited in the event of scale-up.

Findings from Adjacent Funded Projects

- Codexis (DE-AR0000071)
  - Developed a protein engineered, dissolved carbonic anhydrase (CA) for 4.2 M MDEA and >85°C
  - Stable performance, 60 h test at the National Carbon Capture Center (NCCC)
  - Demonstrated that significant enzyme longevity (solvent & temperature tolerance) improvements are possible
- Akermin (DE-FE0004228)
  - Developed immobilized CA as a coating for packing in the absorber
  - Stable performance, 5 months at NCCC
  - Demonstrated immobilized enzyme tolerance to actual post-FGD flue gas conditions
  - Demonstrated that proper integration of enzyme in the capture process leads to commercially-relevant performance longevity
- Illinois State Geological Survey, Yongqi Lu Laboratory (DE-FC26-08NT0005498, and others)
  - Evaluated process concepts, immobilization options, temp. stability, kinetics, etc.
  - Laboratory results showed dissolved enzyme tolerance to simulated flue gas contaminants (e.g. SOx, NOx)
  - Filled important gaps in fundamental data for K_2CO_3-based solvents in ambient/moderate temp/pressure regimes
  - Evaluation of low temperature stripping options, e.g. direct injection of (low temperature) exhaust steam

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Conclusions

- Integrated bench-scale system operated successfully with an average 86 % CO_2 capture for an accumulated 500 hours of steady-state operation under vacuum conditions
  - On- and off-line operational measurements provided a full process data set, with recirculating enzyme, that allowed for kinetic parameter and enzyme replenishment calculations
  - Dissolved enzyme replenishment and conventional process controls (e.g. antifoam addition) were demonstrated as a straightforward approach to maintain system performance
- Four techno-economic cases for enzyme-enhanced benign aq. K_2CO_3 solvent and a corresponding set of sensitivity studies were developed and evaluated
  - LP steam Case DB1b is considered to be the optimal case due to commercial availability of equipment and realistic expectations for enzyme longevity improvements
  - VLP steam Case DB3b suggests the benefit of using a VLP steam turbine for generating the necessary steam and additional electrical power
  - Best cases were similar to NETL Case 10 with respect to LCOE; however validation in larger scale would be needed to eliminate uncertainties
- EH&S profile of the system is favorable
- Bottom Line: Met DOE target of 90% capture and demonstrated a benign enzyme-enhanced aq. K_2CO_3-based alternative to Case 10 with similar LCOE
- Scale-up evaluations would be beneficial for validation and analyze identified opportunities for improvement

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Recommendations for Future Developments

Evaluations

- Process and cost performance with
  - Enzyme retained in absorber stage & vac. regen. to minimize steam requirement
  - Enzyme retained in the absorber stage & utilizing a conventional reboiler
  - Thermal integration of reboiler to utilize heat source outside the steam cycle & determine optimal regeneration pressure
  - Direct (low temp) steam injection
- Demonstrate integrated continuous “cook & filter” enzyme replenishment
- Validate the probable EH&S benefits
- Utilize alternative solvents or mixed solvents that could provide higher CO_2 loading capacity and lower L/G
- Utilize less costly construction materials compatible with aq. salt-based solvents

Improvements

- Integrate improved vacuum/pressure swing creation options
  - Validate enzyme-enhanced desorption
- Alternative low temperature stripper designs, incorporating
  - Reduced residence time at high temperature
  - Membranes, sweep gas, secondary air stripping, hybrid processes
- Develop enzymes with improved longevity and reduced dosage to minimize initial fill and replenishment costs
  - Improved longevity at stripper conditions
  - Develop robust modified enzymes, e.g. in combination with physical matrices, such as particles, or chemical modifications, or solvent formulation adaptations
  - Minimize initial fill and replenishment costs.
  - Increase enzyme activity per unit amount or localize enzyme to the gas-liquid interface

Next Steps

Determine level of interest in scaling up the technology and/or evaluating alternative process configurations

Notices

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

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