# An Advanced Catalytic Solvent for Lower Cost Post-combustion $CO_2$ Capture in a Coal-fired Power Plant

## DE-FE00012926

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http://www.caer.uky.edu/powergen/home.shtml

# Outline

- Project Overview
  - Objective, Team, Funding, Technology and SOW
- Background Review
  - Project Origins
  - Development effort at CAER
- Project Specifics/Details
  - New Solvent: Thermal Stability
  - Mass Transfer and Effects of Rate
  - Catalyst Enhancement
  - Membrane Dewatering
  - Pilot Studies
  - Commercial Deployment

# Goals

Develop a pathway to achieve the NETL Post-combustion CCS Target – 90% $CO_2$ capture with 95% $CO_2$ purity at a cost of $40/tonne of $CO_2$ captured by 2025

# Objectives

Project Scope: Demonstrate the CAER Ad-CCS in the pilot-scale (0.1MWth) -- catalyst, enrichment, and heat integration

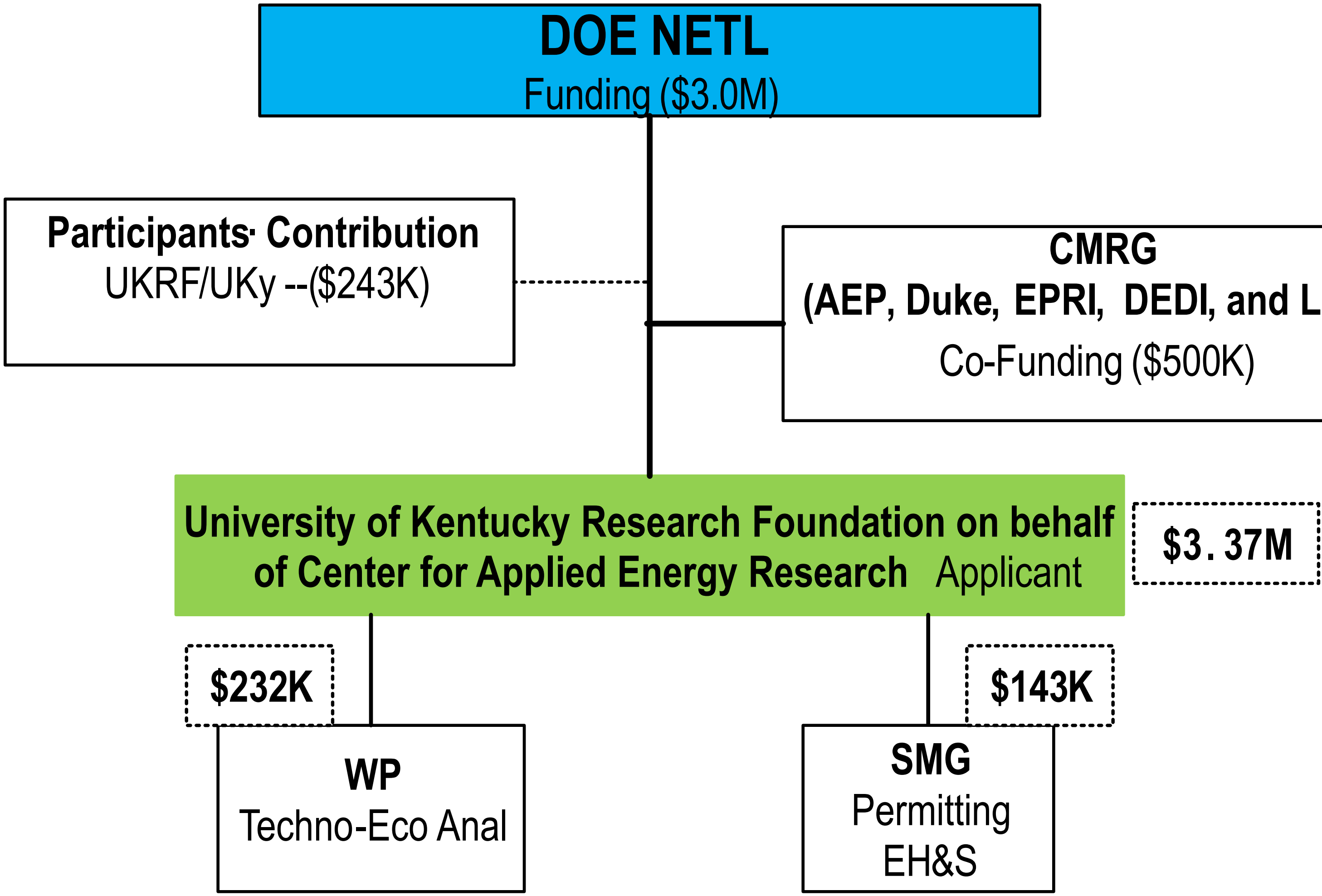
1) Improve the catalyst and membrane performance and reduce the their production cost

2) Gather data on solvent/catalyst/membrane degradation and other information during long-term verification runs (Scale-up process)

3) Mitigate the heavy metal accumulated in the solvent

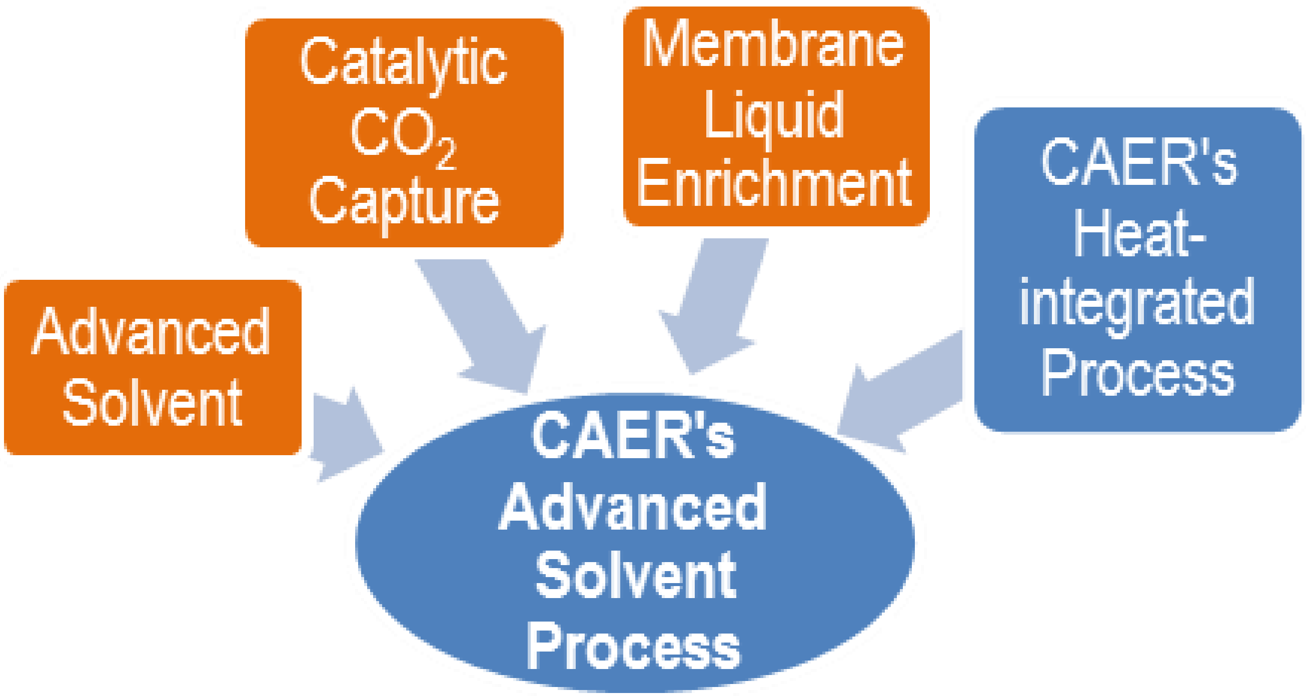
4) Provide data for scaling-up, TEA, and EHS

# Team and Funding Structure

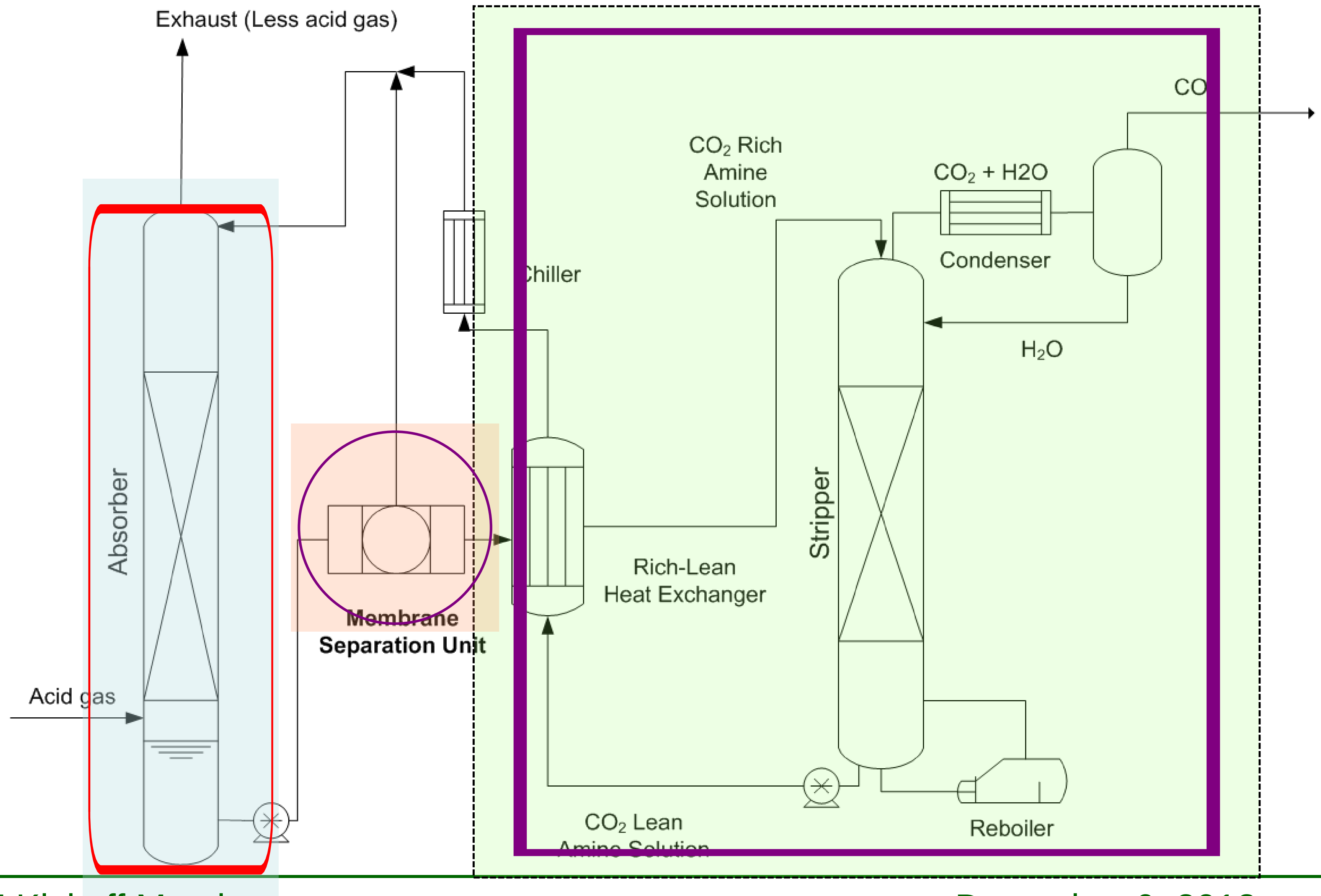



**Subcontractor**

# The CAER Ad-CCS technology



# The Key Focus Points (DE-FE00012926)

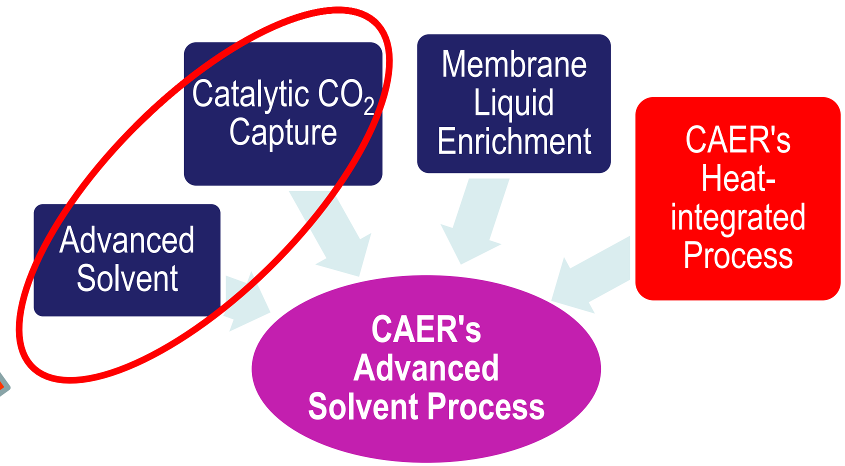


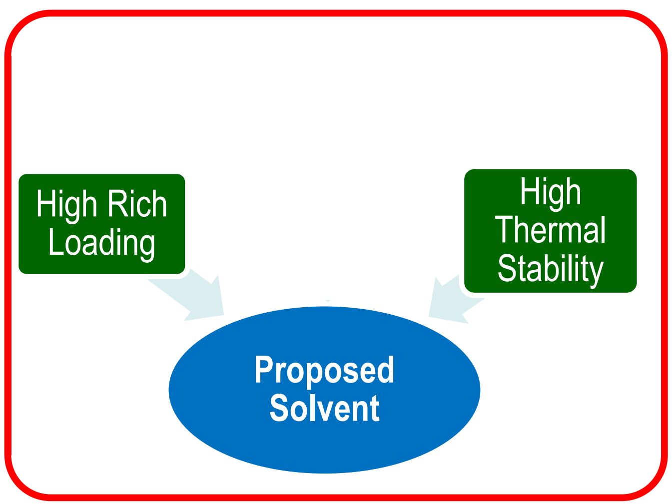
# What will We Do?

- Synthesize and optimize the catalyst in large batch for concentrated amine-based solvent
- Improve the zeolite-based membrane chemical stability and repeatability of membrane produced
- Identify an effective method to mitigate the accumulation of heavy metals in solution
- Parametric investigation and long-term verification;
- Solvent/catalyst degradation (liquid product and gaseous emissions from CCS)

# Background on Catalytic Solvent

- Advanced Solvent
- $CO_2$ Hydration Catalyst
- Membrane Dewatering




*** Lower Capital Cost (Scrubber Kinetics)**

*** Lower Operational Cost (Combined Technologies/Processes)**

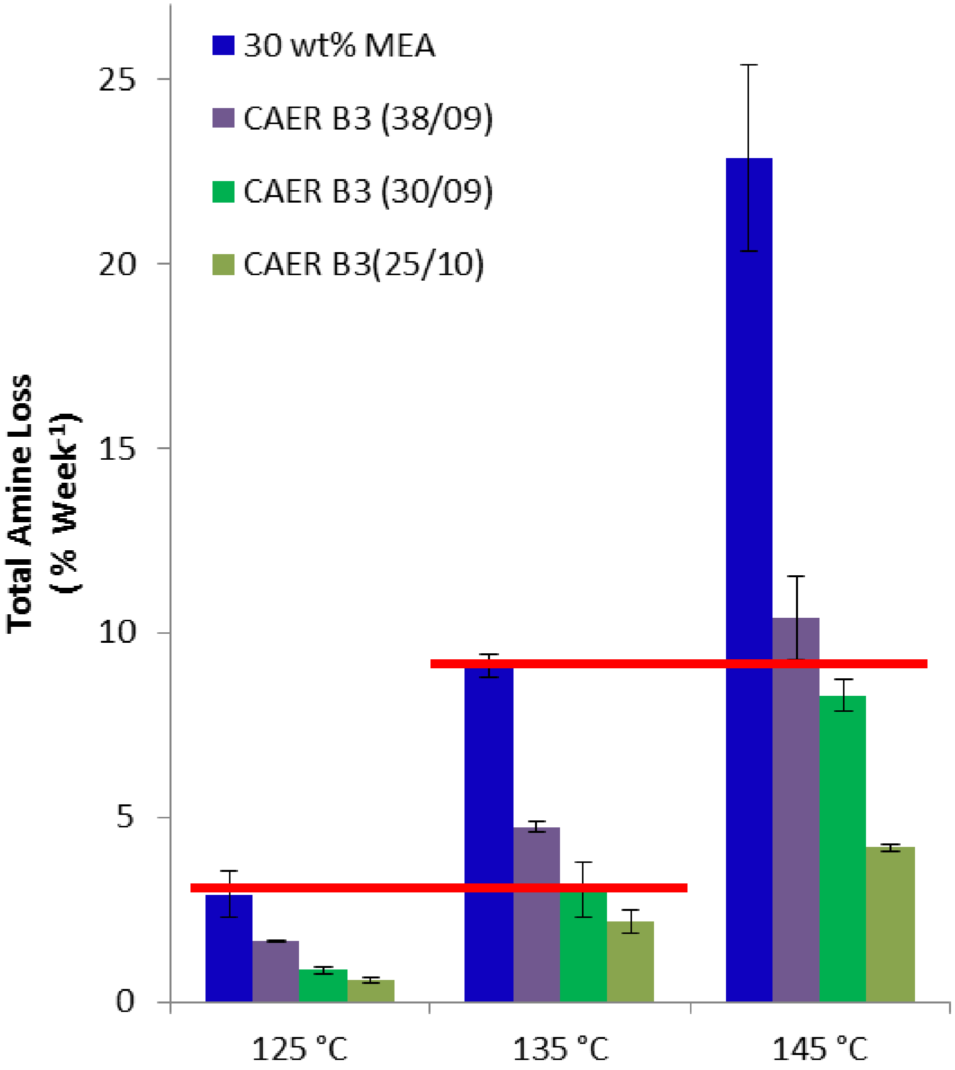
# CAER Advanced Solvent

| | Units | Measured/ Estimated Performance | Projected Performance |
|---|---|---|---|
| **Pure Solvent** | | | |
| Molecular Weight | mol$^{-1}$ | < 90g | < 90g |
| Normal Boiling Point | °C | 160 - 165 | 160 - 165 |
| Normal Freezing Point | °C | -2 C | -2 C |
| Vapor Pressure @ 15 °C | bar | 6.3x10$^{-4}$ [a] | 6.3x10$^{-4}$ [a] |
| **Working Solution** | | | |
| Concentration | kg/kg | 0.39/1.00 | 0.45/1.00 |
| Specific Gravity (15 °C/15 °C) | g/mL | 1.01 [a] | 1.0 [a] |
| Specific Heat Capacity @ STP | kJ/kg·K | 3.4 [b] | 3.3 [b] |
| Viscosity @ STP | cP | 3.04 [c] | 3.3 [c] |
| Surface Tension @ STP | dyn/cm | 36.8 [a] | 36.8 [a] |
| **Absorption** | | | |
| $CO_2$ Partial Pressure | bar | 0.1 | 0.1 |
| Temperature | °C | 40 | 40 |
| Equilibrium $CO_2$ Loading | gmol $CO_2$/kg [/mol amine] | 2.0 [0.42] | 2.1[0.45] |
| Heat of Absorption | kJ/mol $CO_2$ | 74 [d] | 72 [d] |
| Solution Viscosity | cP | 4.88 [c] | 5.9 [c] |
| **Desorption** | | | |
| $CO_2$ Partial Pressure [Total Press.] | bar | 0.25 [3.1] | 0.46 [4.2] |
| Temperature | °C | 125 | 135 |
| Equilibrium $CO_2$ Loading | gmol $CO_2$/kg [/mol amine] | 1.1 [0.23] | 1.1 [0.23] |
| Heat of Desorption | kJ/mol $CO_2$ | 84 [d] | 84 [d] |

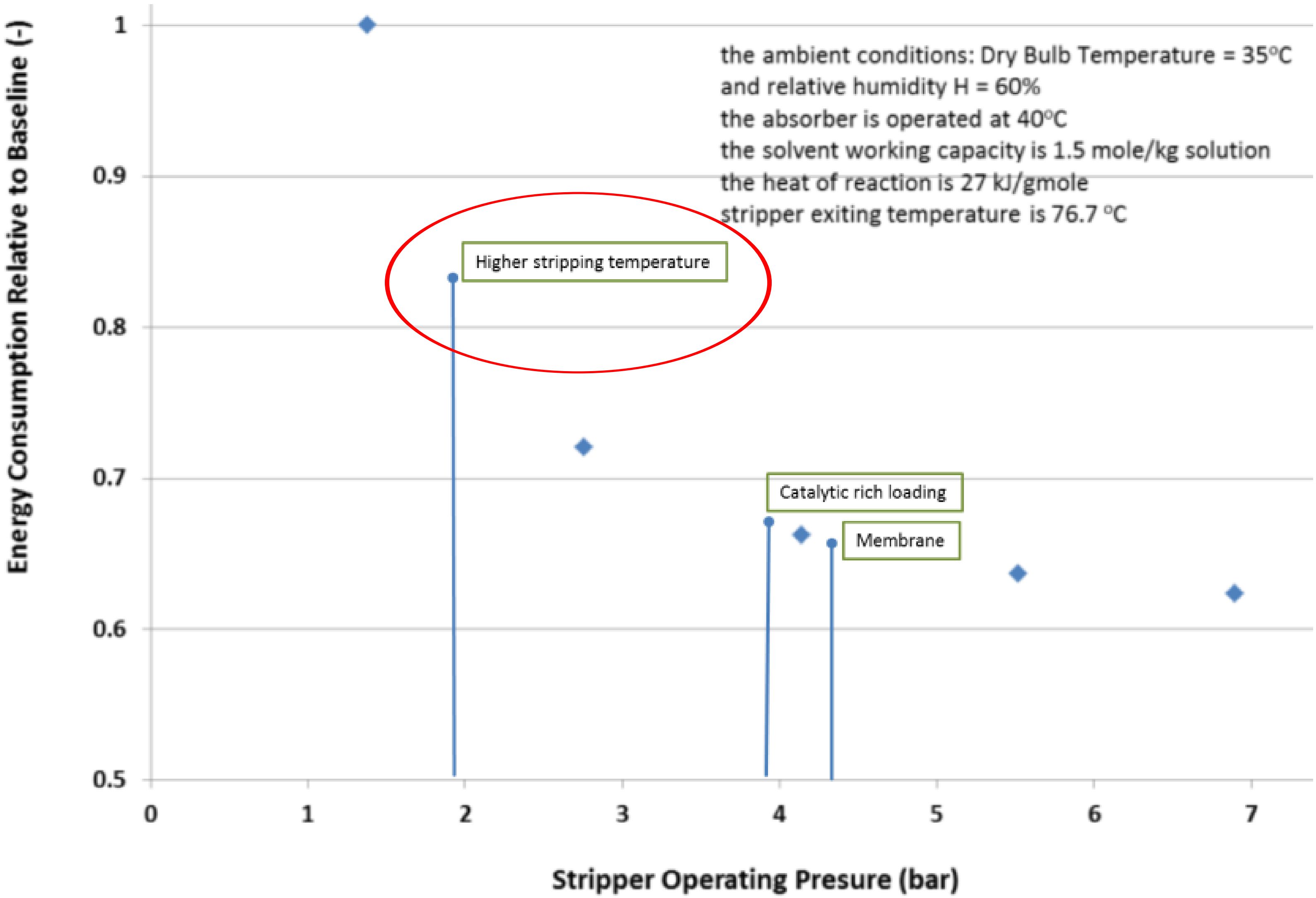
[a] Measured/ estimated at 25 °C
[b] Calculated @ 40 °C
[c] Measured/ calculated @ 40 °C
[d] Determined using Gibbs-Helmoltz method $H_{abs}$ and $H_{des}$ at specified rich and lean loadings respectively

# Advanced Solvent: Thermal Stability

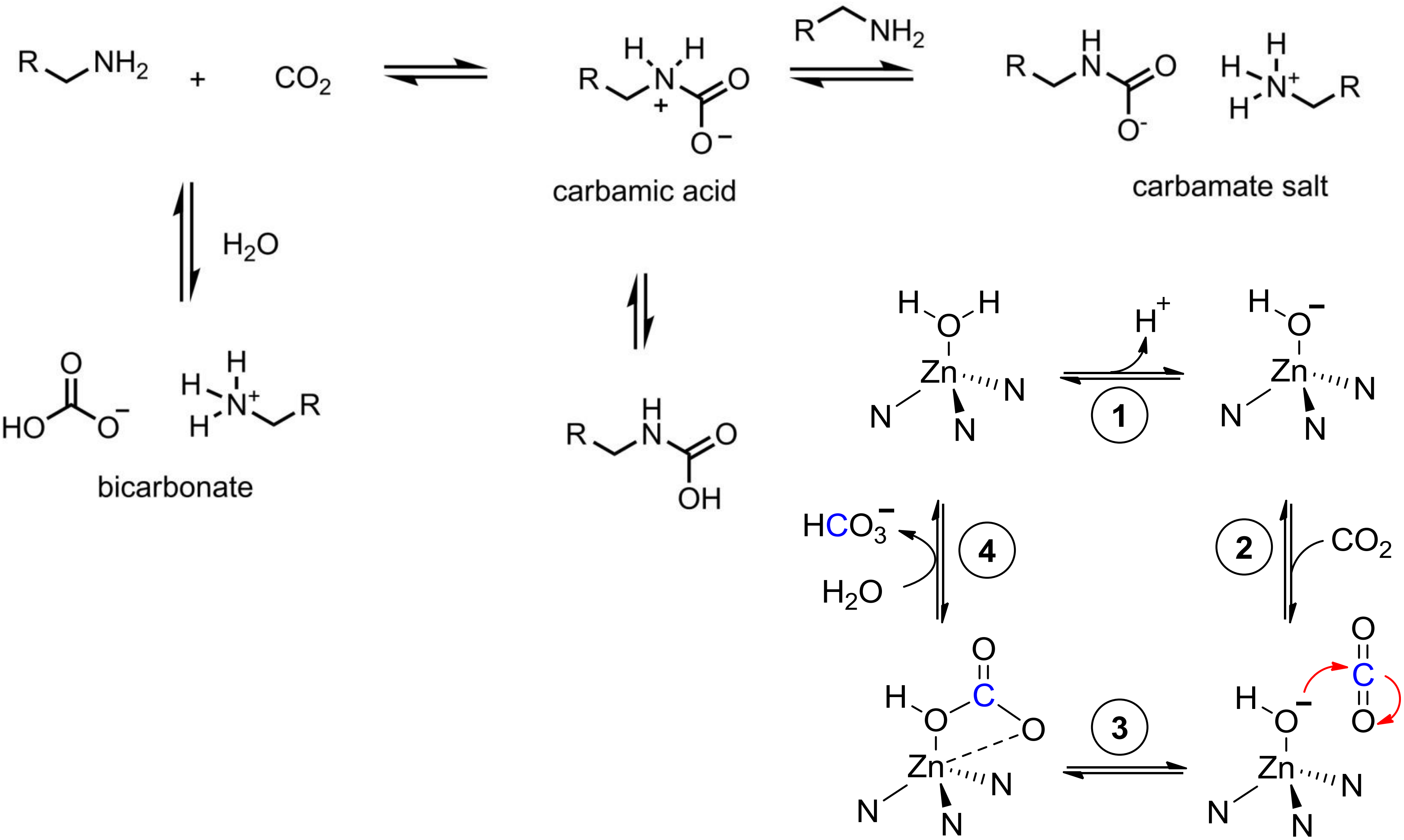
- High Thermal Stability
  - Low Degradation
- Operate at 10 °C higher than reference case (MEA) with same degradation



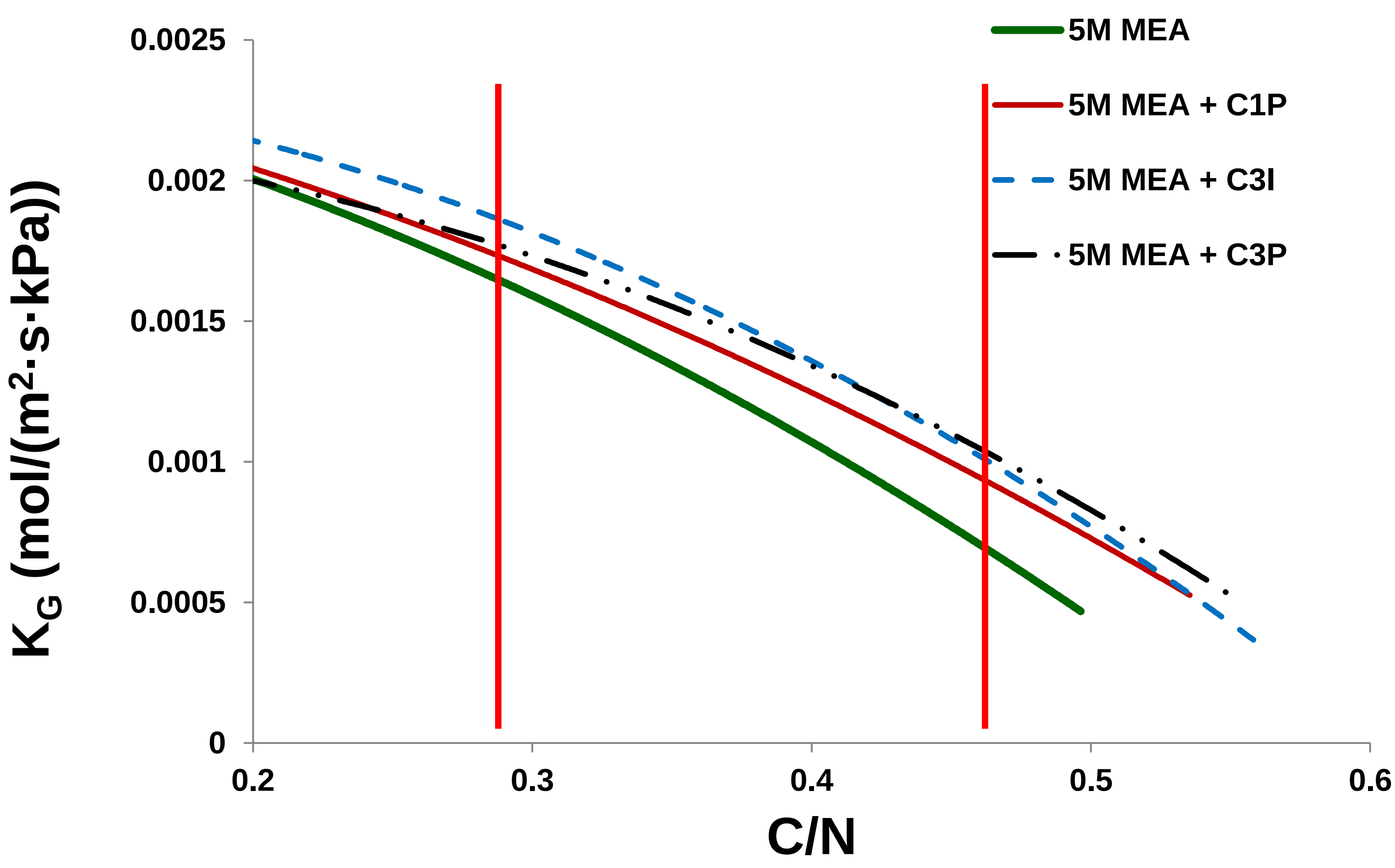
# Thermal Compression Benefits



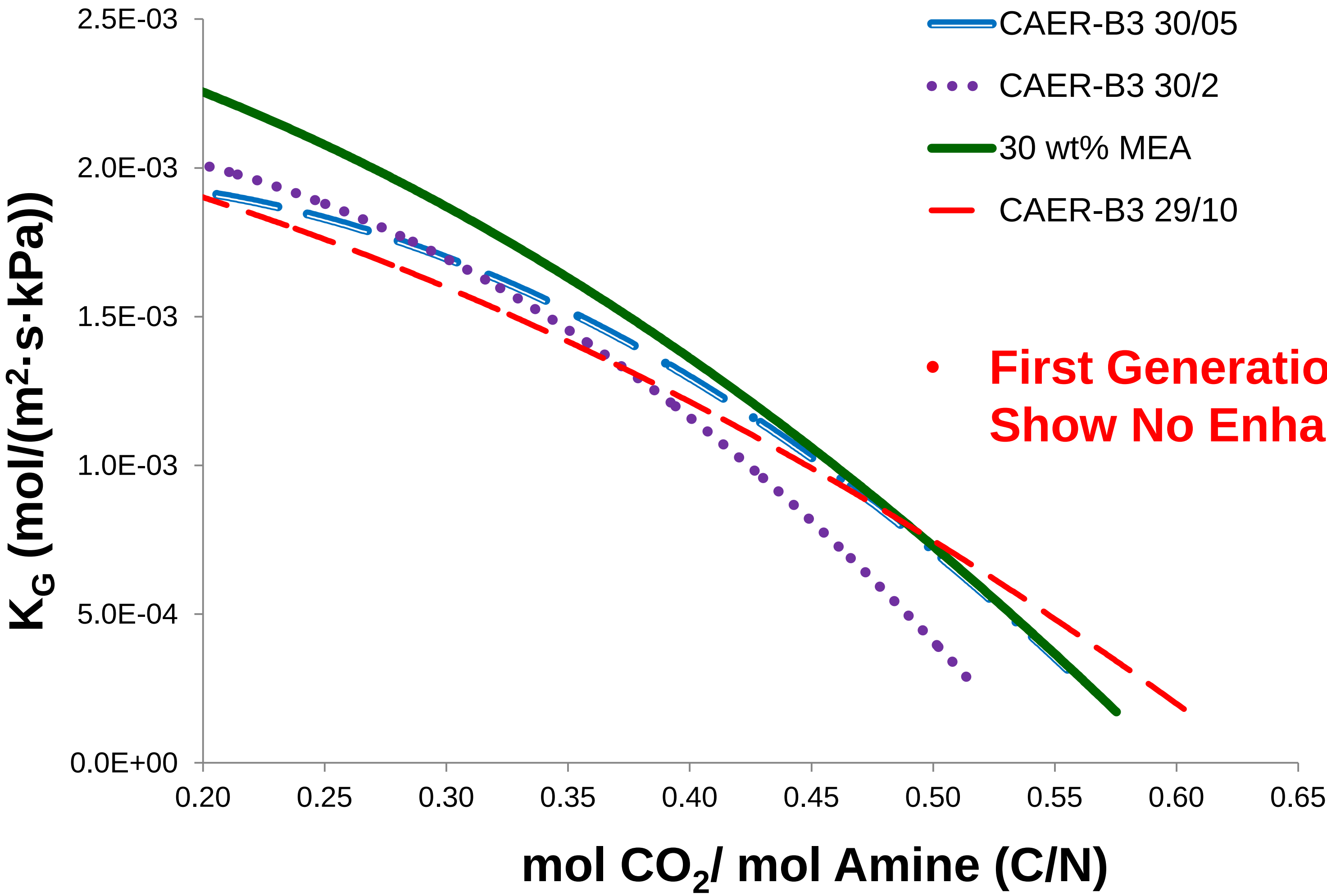
# $CO_2$ Capture Chemistry



# First Generation Catalyst



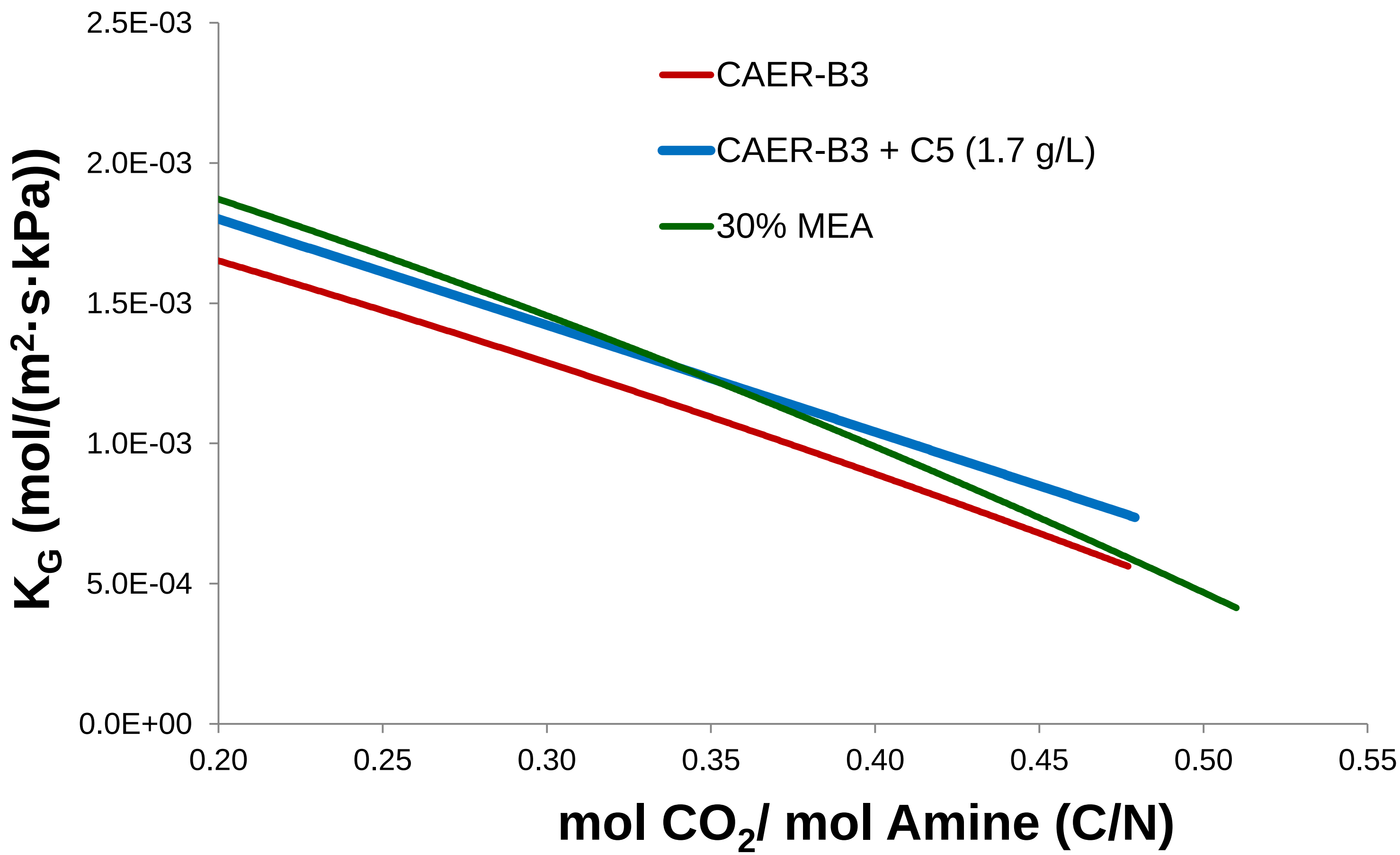
# Advanced Catalytic Solvent?




- **First Generation Catalyst Show No Enhancement**

# Advanced Catalytic Solvent

- ~16% overall enhancement vs. MEA
- 15% richer solution



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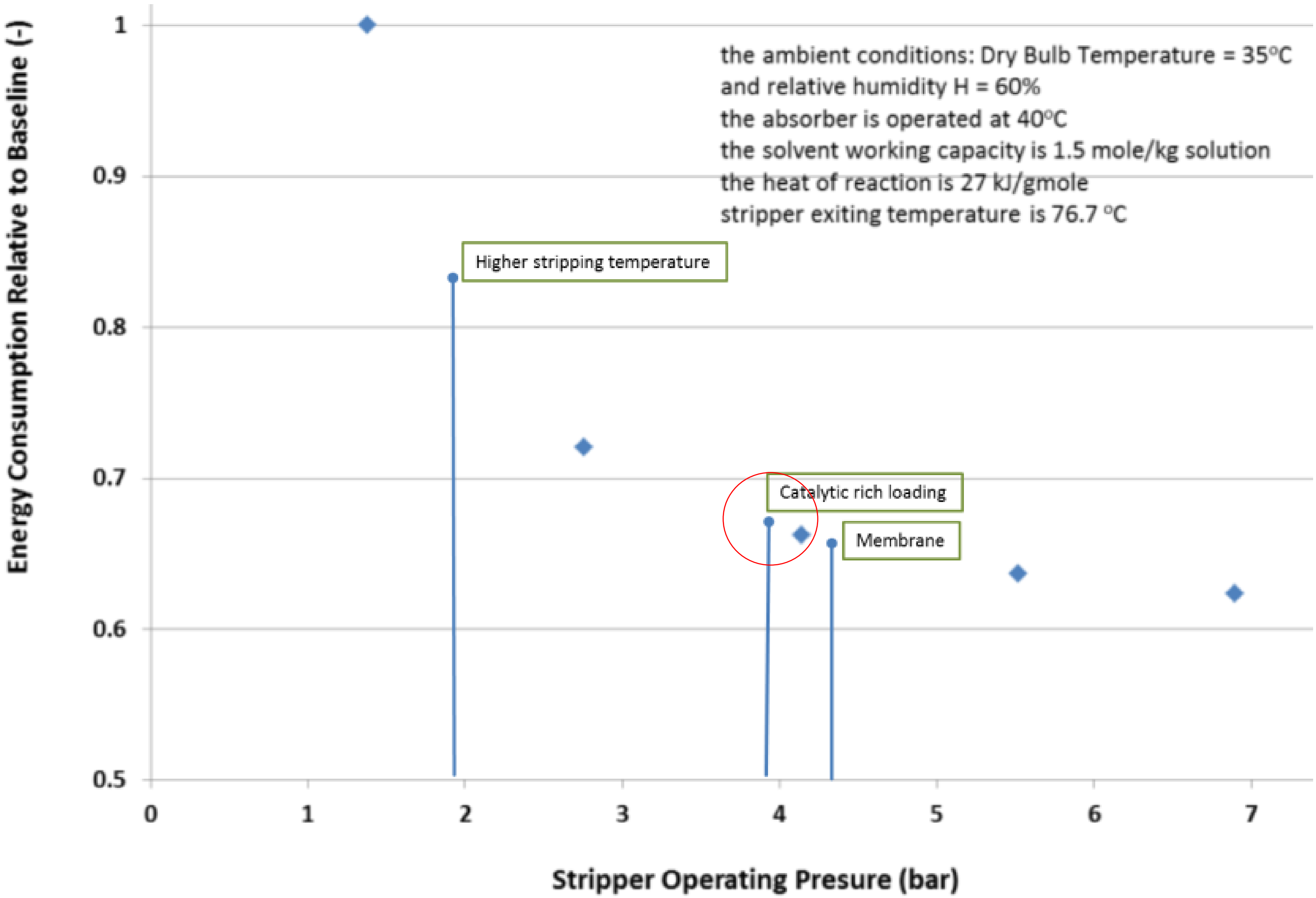
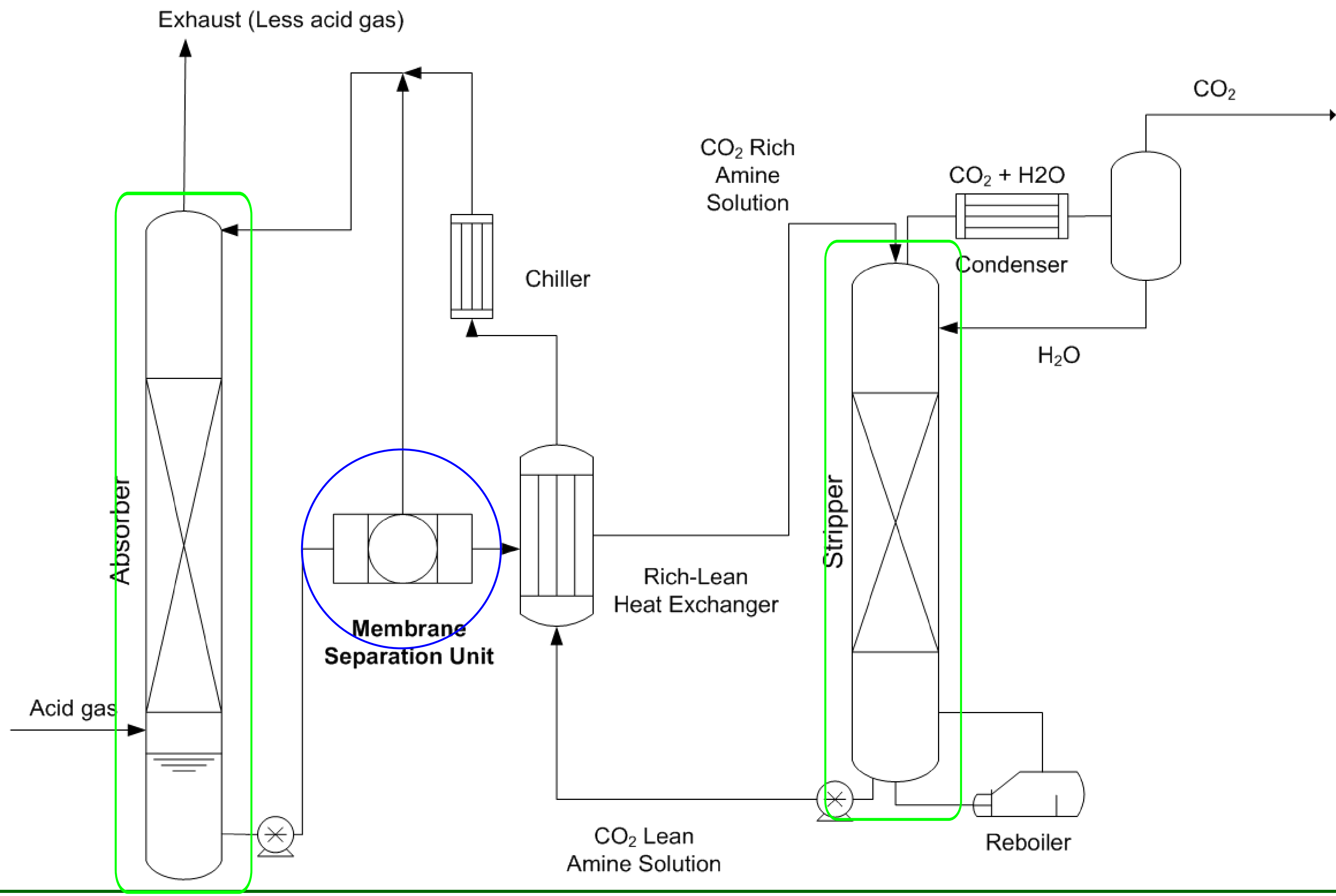
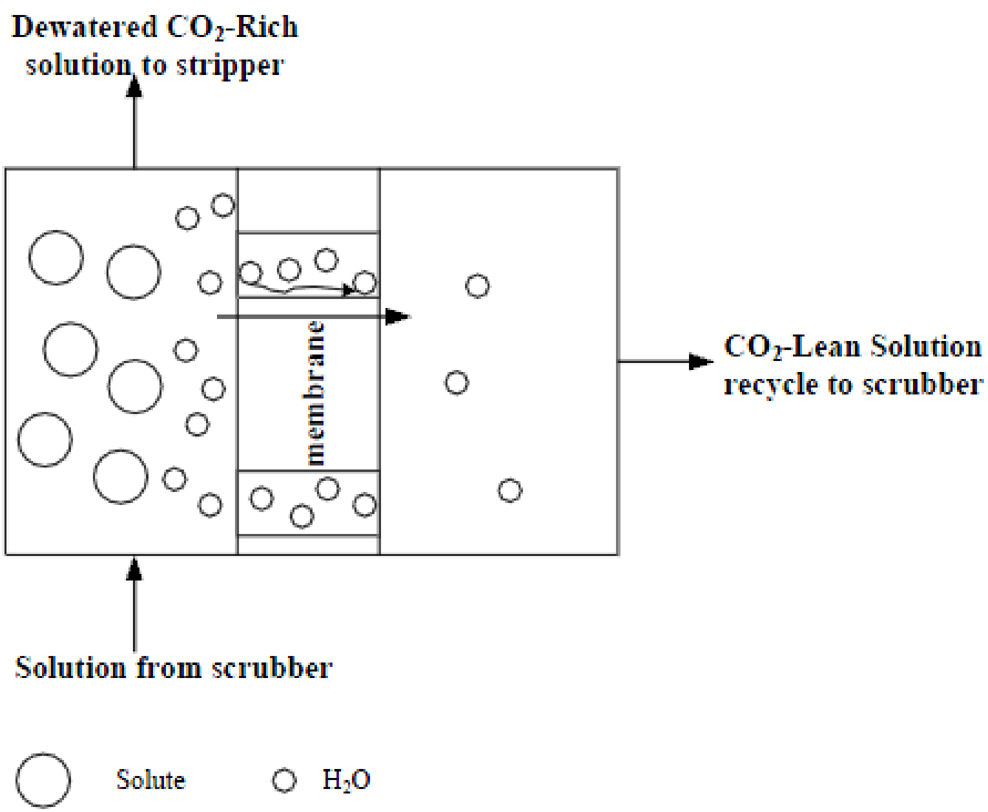


# Process Towards Goals



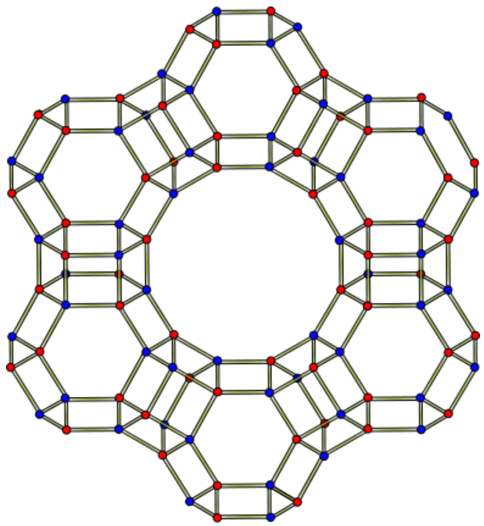
# Membrane Dewatering

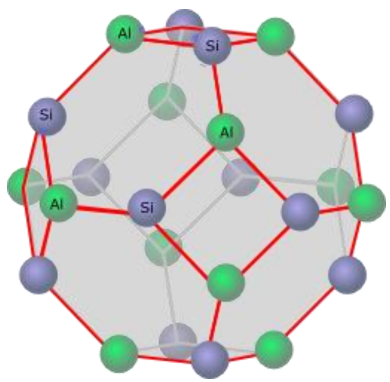


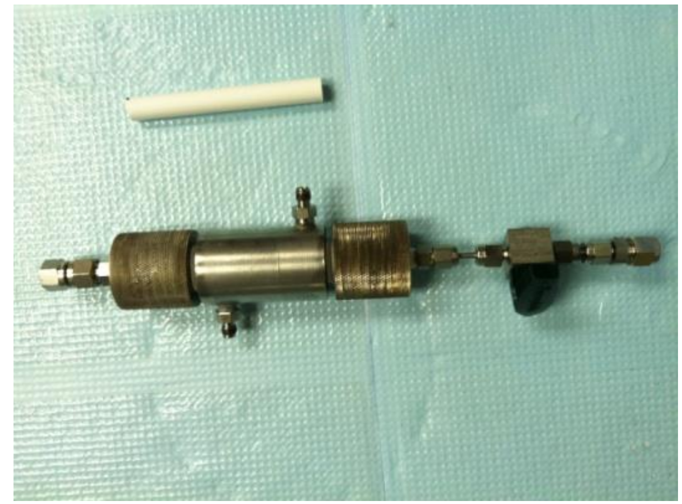

| Membrane | Solute (Solvent) | Flux ($kg/m^2h$) | Rejection Rate (%) |
|---|---|---|---|
| FAU-28-1 | $(NH_4)_2CO_3$ (water) | 2.18 | 84.76 |
| CAER-FAU | $(NH_4)_2CO_3$ (water) | 32 | 14 |

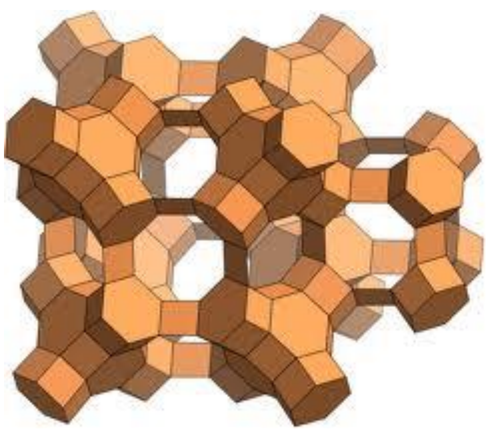
# Zeolites

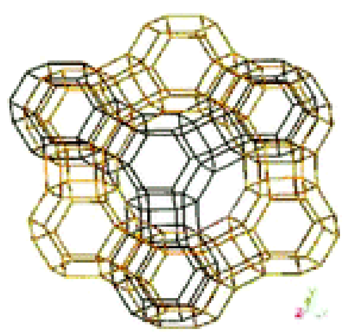




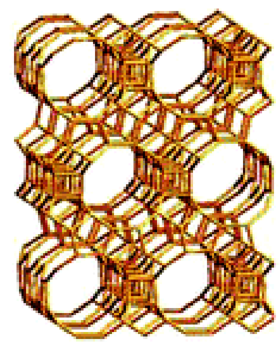


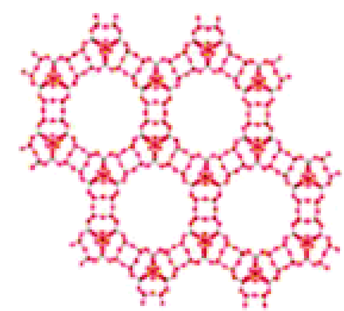




Faujasite



Zeolite beta



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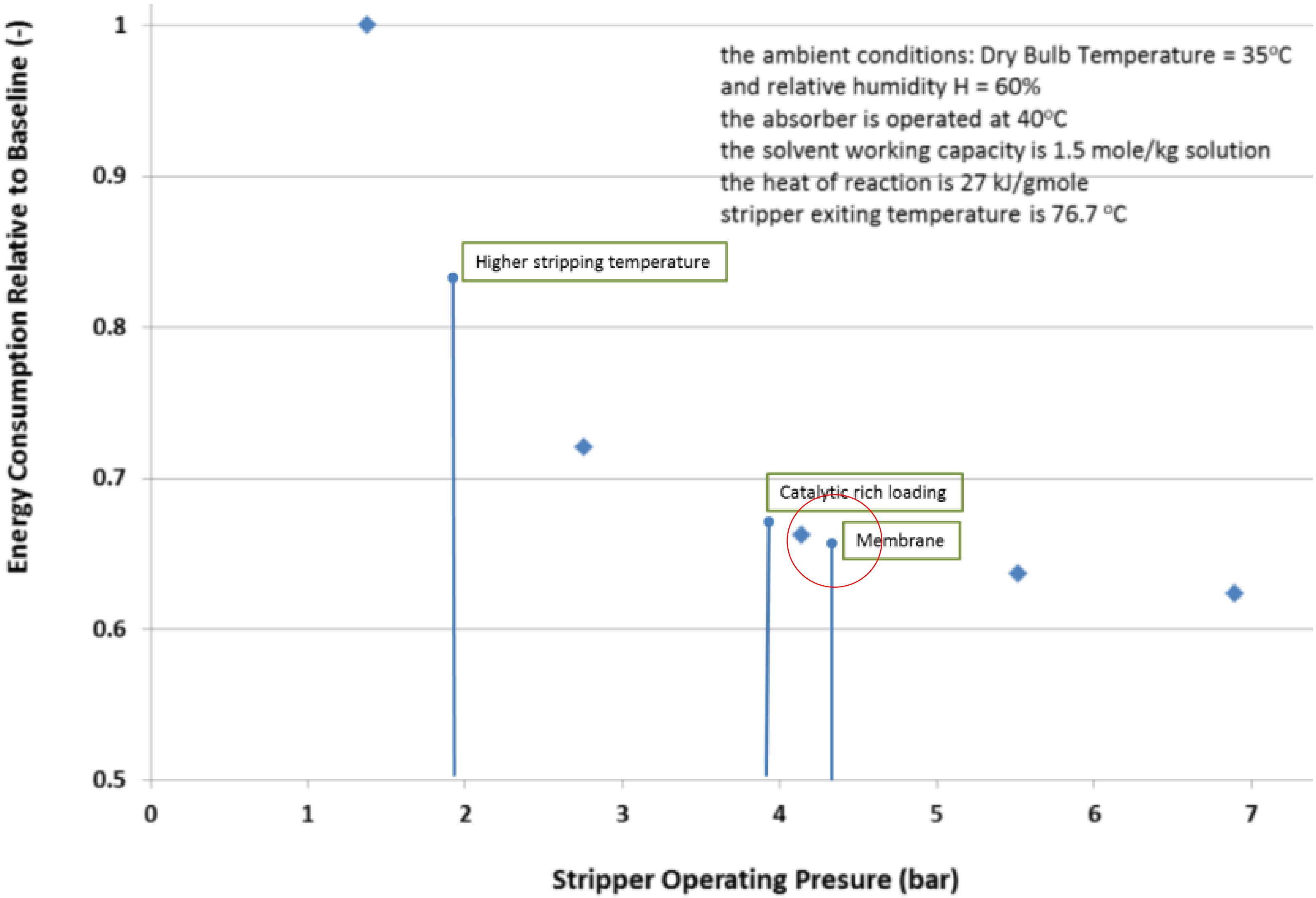
# Preliminary FAU Type Zeolite Performance

- Operating pressure: 60 psi
- Operating temperature: 21 $^oC$

| Membrane | Solvent | Time (hr) | Flux (kg/hr*m$^2$) | Permeate alkalinity (mol/kg) | Feed alkalinity (mol/kg) | Rejection rate |
|---|---|---|---|---|---|---|
| 1 | B3 | 1 | 0.93 | 1.96 | 4.14 | 52.7% |
| 1 | B3 | 2 | 0.66 | 3.83 | 4.14 | 7.49% |
| 2 | B3 | 1 | 3.96 | 3.81 | 4.58 | 16.7% |
| 2 | B3 | 2 | 2.71 | 4.47 | 4.58 | 2.42% |
| 3 | B3 | 1 | 7.02 | 4.15 | 4.39 | 5.42% |
| 3 | B3 | 2 | 1.69 | 3.99 | 4.45 | 10.1% |

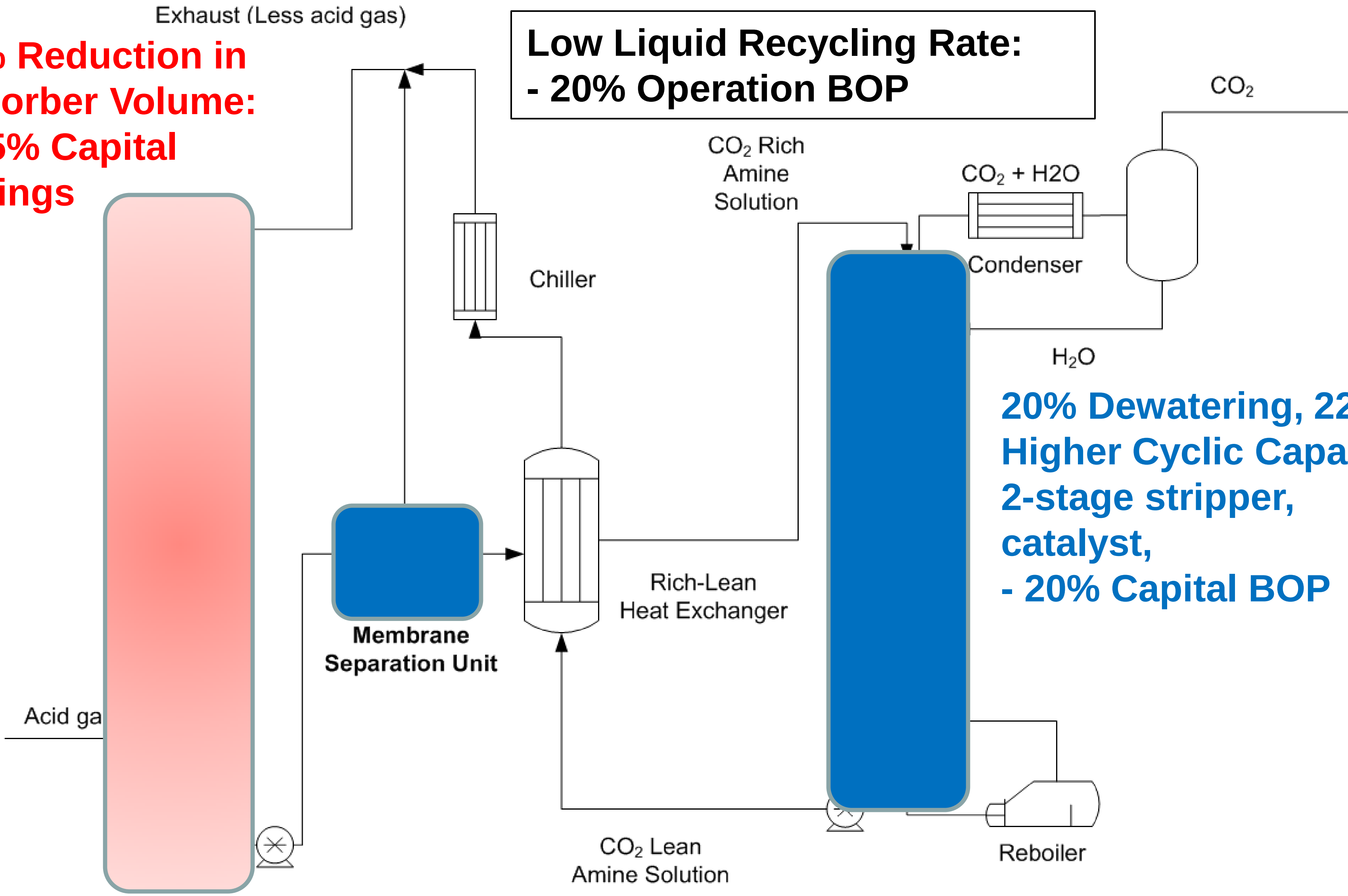
# Thermal Compression Benefits



# Anticipated Benefits!

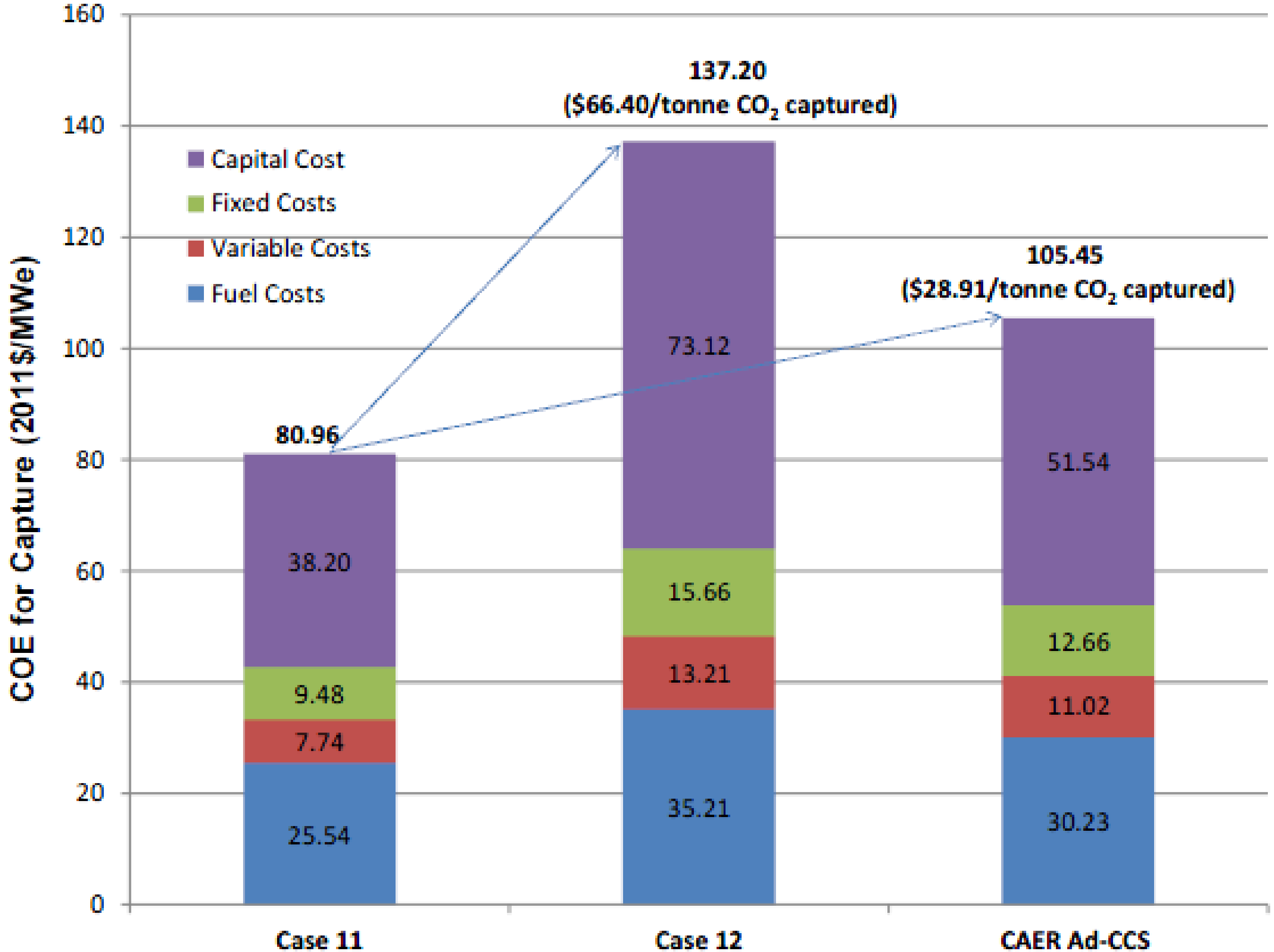
**20% Reduction in Absorber Volume:**
**- 9.5% Capital Savings**

**Low Liquid Recycling Rate:**
**- 20% Operation BOP**




**20% Dewatering, 22% Higher Cyclic Capacity: 2-stage stripper, catalyst,**
**- 20% Capital BOP**

# Preliminary Cost Analysis




**No CCS** **MEA reference case**

# BP's and Tasks

| BP | Task | Name |
|---|---|---|
| | 1.0, 7.0, 12.0 | Project Management and Planning |
| 1 | 2 | Collection of Physical Properties and Solvent Optimization |
| | 3 | Membrane Performance Evaluation |
| | 4 | Catalyst Scale Up |
| | 5 | Initial Techno-Economic Analysis |
| | 6 | Initial EH&S Assessment |
| 2 | 8 | Catalyst Production |
| | 9 | Parametric Testing of Baseline Solvent |
| | 10 | Parametric Testing of Catalytic Solvent |
| | 11 | Membrane and Fixed-bed Column Design |
| 3 | 13 | Long Term Verification Study of Catalytic Solvent |
| | 14 | Large-Scale Membrane Fabrication |
| | 15 | Membrane Integration, Commissioning, and Evaluation |
| | 16 | Final Techno-Economic Analysis |
| | 17 | Final EH&S Assessment |

# Platform for Pilot Experiment

# Catalyst Scale-up

- Currently: 0.5g – 2g synthetic scale
  - Need ~ 250g per pilot plant test
    - Requires synthesis scale up to 50g-100g
    - New equipment for large scale synthesis
      - Overhead stirring reactor
      - Large glassware/reactors

**0.05L - 1L**

**10L - 20L**

# Membrane Scale-up

- Shell tube type membrane module
  - Currently: 6 inch [length] single tube
  - Need 1 ft, 100 tube array

# Pilot Investigations

| Factors for evaluation using the bench-scale test | | |
|---|---|---|
| **Factor** | **Units** | **Range** |
| Liquid Load to Achieve Different L/G Ratios | gpm/1000 acfm | 35 to 50 |
| Temperature of Liquid Stream Entering Absorber | °C | 35 to 45 |
| Stripper Pressure | bar | 1.5 to 5 |
| Flue Gas CO2 Concentration | vol % | 14 to 17 |

Summary of long term solvent degradation analysis methods

| Analysis | Analytical Method | Sampling location | Sample Type |
|---|---|---|---|
| Alkalinity | CAER Alkalinity | Absorber/ Stripper | Liquid |
| Carbon loading | CAER Carbon loading | Absorber/ Stripper | Liquid |
| Density | CAER Density | Absorber/ Stripper | Liquid |
| pH | CAER pH | Absorber/ Stripper | Liquid |
| Viscosity | CAER Viscosity | Absorber/ Stripper | Liquid |
| Heat stable salt | CAER IC-Anion | Absorber | Liquid |
| Total amine degradation | CAER IC-Cation | Absorber | Liquid |
| Heavy metals | UKy ICP-MS | Absorber | Liquid |
| Oxidative degradation | CAER IC and LC/MS | Absorber | Liquid |
| Amine thermal degradation | CAER IC and CAER LC/MS | Absorber | Liquid |
| Nitrosation | CAER GC/MS, LC/MS, Chemiluminescence | Absorber | Liquid |
| Volatiles (amine loss and $NH_3$) | CTM-027 + CAER IC w/ Isokinetic | Absorber/ Stripper | Gas emissions |
| Aldehydes | Method 0011 w/ LC/MS | Absorber/ Stripper | Gas emissions |
| Nitrosation | CAER LC/MS w/ Isokinetic, Chemiluminescence | Absorber/ Stripper | Gas emissions |
| Alkylamines | CAER LC/MS w/ Isokinetic | Absorber/ Stripper | Gas emissions |

# BP1 Tasks

| BP | Task | Name |
|---|---|---|
| | 1.0, 7.0, 12.0 | Project Management and Planning |
| 1 | 2 | Collection of Physical Properties and Solvent Optimization |
| | 3 | Membrane Performance Evaluation |
| | 4 | Catalyst Scale Up |
| | 5 | Initial Techno-Economic Analysis |
| | 6 | Initial EH&S Assessment |

| Task | Milestone Description | Date |
|---|---|---|
| 2.2 | Model regression for VLE data completed and delivered to WP for process simulation | 6/30/14 |
| 2.3-4 | Mass transfer and kinetic values provide to WP for final catalyst and concentration in CAER-B3 solvent | 9/30/14 |
| 3 | Membrane made and shown to effectively dewater catalyzed CAER-B3 solvent | 4/9/14 |
| 4 | Methodology developed for synthesis of > 50 g/batch of catalyst. | 1/31/14 |
| 5 | Initial Techno-Economic Analysis for the CAER's completed | 7/31/14 |
| 6 | Completion of Initial EH&S Assessment | 4/30/14 |

| Success Criteria | Date |
|---|---|
| Initial TEA completed showing at least a 20% cost reduction compared to MEA case | 9/30/14 |
| Initial EHS assessment showing no risk/hurdles in moving forwards | 9/30/14 |
| Synthesis of a 50g batch of catalyst with >90% purity | 9/30/14 |

# BP2 Tasks

| | | |
|---|---|---|
| 2 | 8 | Catalyst Production |
| | 9 | Parametric Testing of Baseline Solvent |
| | 10 | Parametric Testing of Catalytic Solvent |
| | 11 | Membrane and Fixed-bed Column Design |

| Task | Milestone Description | Date |
|---|---|---|
| 7.1 | Updated Project Management Plan for budget period 2. | 10/30/14 |
| 8 | Production of at least 500 g of CAER catalyst | 12/31/14 |
| 9.1 | Parametric study without catalyst at bench-scale completed | 1/30/15 |
| 10 | Parametric study with catalyst at bench-scale completed | 1/30/15 |
| 11 | Membrane test module design competed | 6/30/15 |

| Success Criteria | Date |
|---|---|
| A minimum process energy operating condition established based on parametric testing for the CAER catalyzed advanced amine solvent showing at least a 20% reduction in stripping energy. | 6/30/15 |
| Demonstration of the CAER membrane dewatering process yields a 20% reduction in rich solution water content | 6/30/15 |
| Membrane performance at the lab-scale maintains stability for 50 hour run demonstrated. | |
| The completed final technical and economic analysis of the proposed process concept for a 550 MW power plant that shows that the CAER process using the catalyzed advanced amine solvent can achieve carbon capture up to 90% with a less than $30/tonne $CO_2$ captured. | 6/30/15 |

# BP3 Tasks

| | | |
|---|---|---|
| 3 | 13 | Long Term Verification Study of Catalytic Solvent |
| | 14 | Large-Scale Membrane Fabrication |
| | 15 | Membrane Integration, Commissioning, and Evaluation |
| | 16 | Final Techno-Economic Analysis |
| | 17 | Final EH&S Assessment |

| Success Criteria | Date |
|---|---|
| A 500 h long-term verification study with coal derived flue gas completed using the 0.1 MWth bench-scale test facility using the CAER catalyzed, advanced amine solvent demonstrates the long term stability of CAER amine and catalyst to thermal compression (> 3 bar) conditions and to flue gas contaminants from coal combustion. | 9/30/16 |
| A comparative case shown for the advantages of the CAER catalyzed amine to the uncatalyzed CAER advanced amine solvent demonstrating at least a 10% increase in overall mass transfer or 5% more rich solution at the bench-scale evaluation. | 9/30/16 |
| Membrane test module in 0.1 MWth bench-scale test unit shows 20% dewatering achievable | 9/30/16 |

| | |
|---|---|
| 12.3 Final Technical Report | 9/30/16 |

# Our Goal is to Prevent This!


***Keep fossil fuel-based power generation as a viable option***