NREL
NATIONAL RENEWABLE ENERGY LABORATORY

DOE Bioenergy Technologies Office (BETO) 2019 Project Peer Review

5.1.3.103 Novel, Biological, Sustainable and Low Energy CO_2 Separation

Session: Carbon Dioxide Utilization

March 7, 2019

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NC STATE UNIVERSITY
Wilson College of Textiles

Center for Applied Energy Research

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Goal Statement

Goal

To develop a novel biological, sustainable, and low energy CO_2 waste gas scrubbing technology using **enzyme-accelerated solvents with low regeneration energy**

Outcome

- Provide advanced CO_2 scrubbing technologies aiming to enable a **20% energy reduction** compared to the monoethanolamine (MEA) reference case (at 90% CO2 capture) using improved carbonic anhydrase (CA) with novel immobilization strategy and solvents with low regeneration energy
- Identify **critical knowledgebase** for industry and research community to further R&D working towards efficient capture of CO_2

Relevance

- Carbon scrubbing of flue gases in current CCS/CCU processes use MEA - a large energetic penalty
- Low energy CO_2 scrubbing technology can not only provide cost savings for fossil fuel production but also lower the production cost for biopower
- Bioenergy with carbon capture and storage (BECCS) combining the use of biopower can produce energy with net-negative emissions

Quad Chart Overview

Timeline

- **Start: FY 2019**
- Merit review cycle: FY2019-2021
- 8 % complete of review cycle

	Total Costs Pre FY17**	FY 17 Costs	FY 18 Costs	Total Planned Funding (FY 19-Project End Date)
DOE Funded				$1.45M
Project Cost Share*				$550K Novozymes (in kind) $75K NCSU $75K UK-CAER

•Partners: If multiple DOE recipients are involved in the project, please list level of involvement, expressed as percentages of project funding from FY 17-18. [(i.e. NREL (70%); INL (30%)]

Barriers addressed:

Ct-D. Advanced Bioprocess Development:

CO_2 mitigation through carbon capture and utilization

- Energy efficiency for CO_2 Capture
- Efficient BECCS

Objectives

- Improve enzyme activity and robustness
- Improve enzyme in-process longevity and post-process sustainability
- Utilize enzyme-accelerated solvents with low regeneration energy

End of Project Goal

Low energy CO_2 waste gas scrubbing technology using enzyme-accelerated solvents with low regeneration energy with aiming to enable a 20% energy reduction compared to the MEA reference case (at 90% CO2 capture)

Project Overview

- The project **directly addresses** the recent BETO Lab call's **Topic Area 5: Novel, Biological Scrubbing Techniques for CO_2 Utilization** and is also applicable to address **Topic Area 3: Biological Biogas Cleanup**

- Our goal is to develop a **low energy CO_2 waste gas scrubbing technology** using improved immobilized thermotolerant carbonic anhydrase (CA) and enzyme-accelerated solvents with low regeneration energy, selectively removing CO_2 from mixed gas streams, with reduced energy consumption and **aim to enable a 20% energy reduction compared to the MEA reference case**

- **Enzyme-based technology offers several advantages for efficient CO_2 capture from various industrial flue gasses for reuse or sequestration:**
  - Current MEA based process requires higher stripping temperature; in addition the solvent is toxic
  - CA-based CO_2 capture allows use of **non-toxic solvents with reduced regeneration energy**
  - However, **enzymes** will need to **withstand harsh process conditions**, high temperature, high pH, high solvent conditions and tolerance of gas and process contaminants

Approach - Management

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Supply pre-commercial thermostable CA to all Tasks for baseline study as well as investigation of novel strategies

NREL integrated — Project Lead
Min Zhang

NREL integrated — Task 1
Min Zhang

Enzyme engineering
Improve enzyme activity and robustness

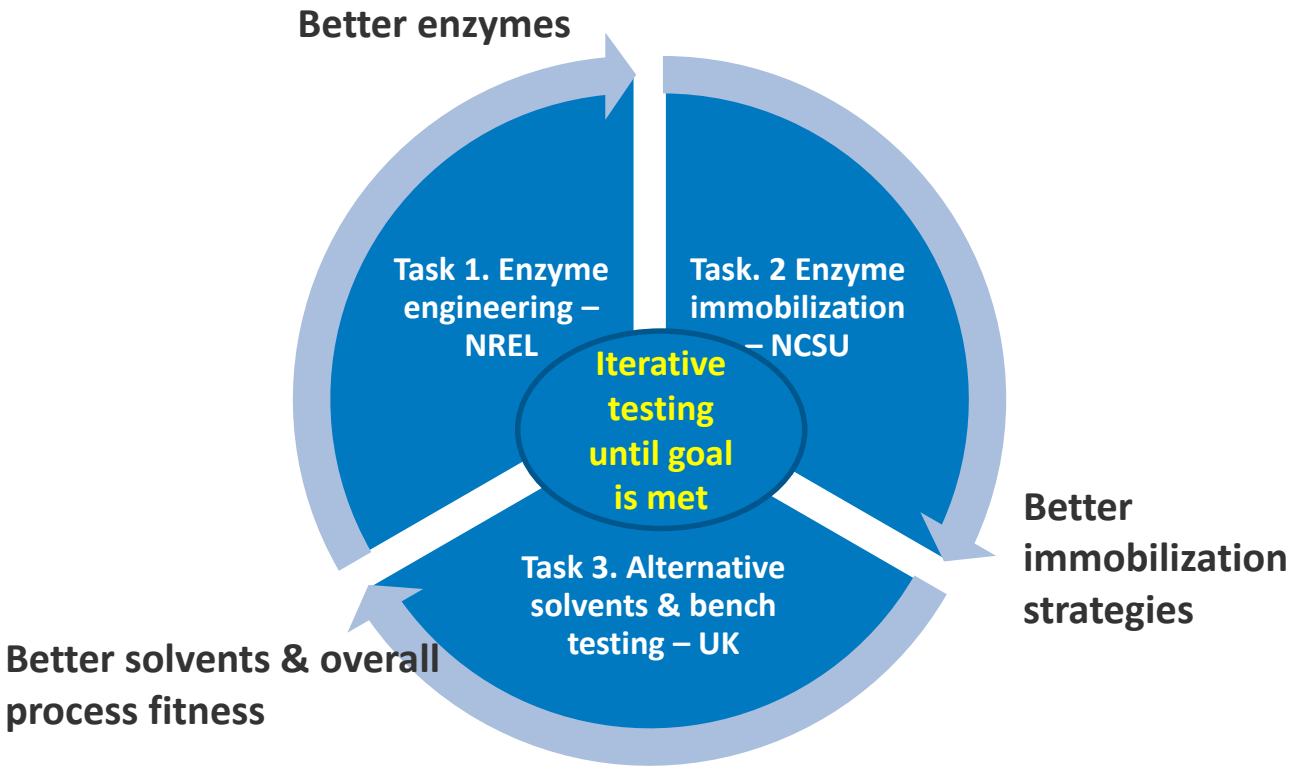
NC STATE UNIVERSITY Wilson College of Textiles — Task 2
Sonja Salmon

Enzyme immobilization
Improve enzyme in-process longevity and post-process sustainability

Center for Applied Energy Research — Task 3
Jesse Thompson

Alternative solvents & bench testing
Utilize enzyme-accelerated solvents with low regeneration energy

Approach – Management



- Preliminary TEA analysis help to narrow down the **key cost drivers**
- **Collaborate with key experts** in the field
- Enzyme supply by the enzyme producer Novozymes
- Monthly meeting among the teams and quarterly report/update to BETO
- Following DOE approved Regular (Smart) milestones and GoNoGo decisions
- Publish all findings in peer reviewed journals

Approach - Technical

Background

- **Fast-reacting MEA** CO_2 absorption solvent requires **high regeneration energy** due to high heat of absorption (~84 kJ/mol)
- Alternative, more **benign and sustainable solvents** have lower heat of absorption, but react slower (e.g. 59 kJ/mol MDEA, 27 kJ/mol K_2CO_3)
- Bench-scale and pilot testing has **proven carbonic anhydrase ability to accelerate CO_2 absorption** in alternative solvents in both dissolved-enzyme and immobilized-enzyme forms
- Process improvements are still needed to **achieve energy reduction** versus benchmark MEA

Approach - Technical

Carbonic anhydrase (CA)- one of the fastest known enzymes in nature- can catalyze the CO_2 in low-energy solvent at fast rate:

CO_2

$$CO_2 + H_2O \xleftrightarrow{\text{Carbonic Anhydrase}} HCO_3^- + H^+$$

$$B^- + H^+ \longleftrightarrow BH \quad (\text{B=solvent})$$

- **Improve** CA with thermotolerant, fast CO2 absorption kinetics in selected solvents –Task 1 (NREL)
- **Improve** CA longevity using enzyme-entrapping polymeric structures - Task 2 (NCSU)
- **Utilize** alternative solvents with reduced regeneration energy to improve the process efficiency and sustainability-Task 3 (UK-CAER)

Approach - Technical

- Critical Success factors:
  - Improved thermotolerance with fast CO_2 absorption rate
  - Improved enzyme in-process longevity and post-process sustainability
  - Identified enzyme-accelerated solvents with low regeneration energy

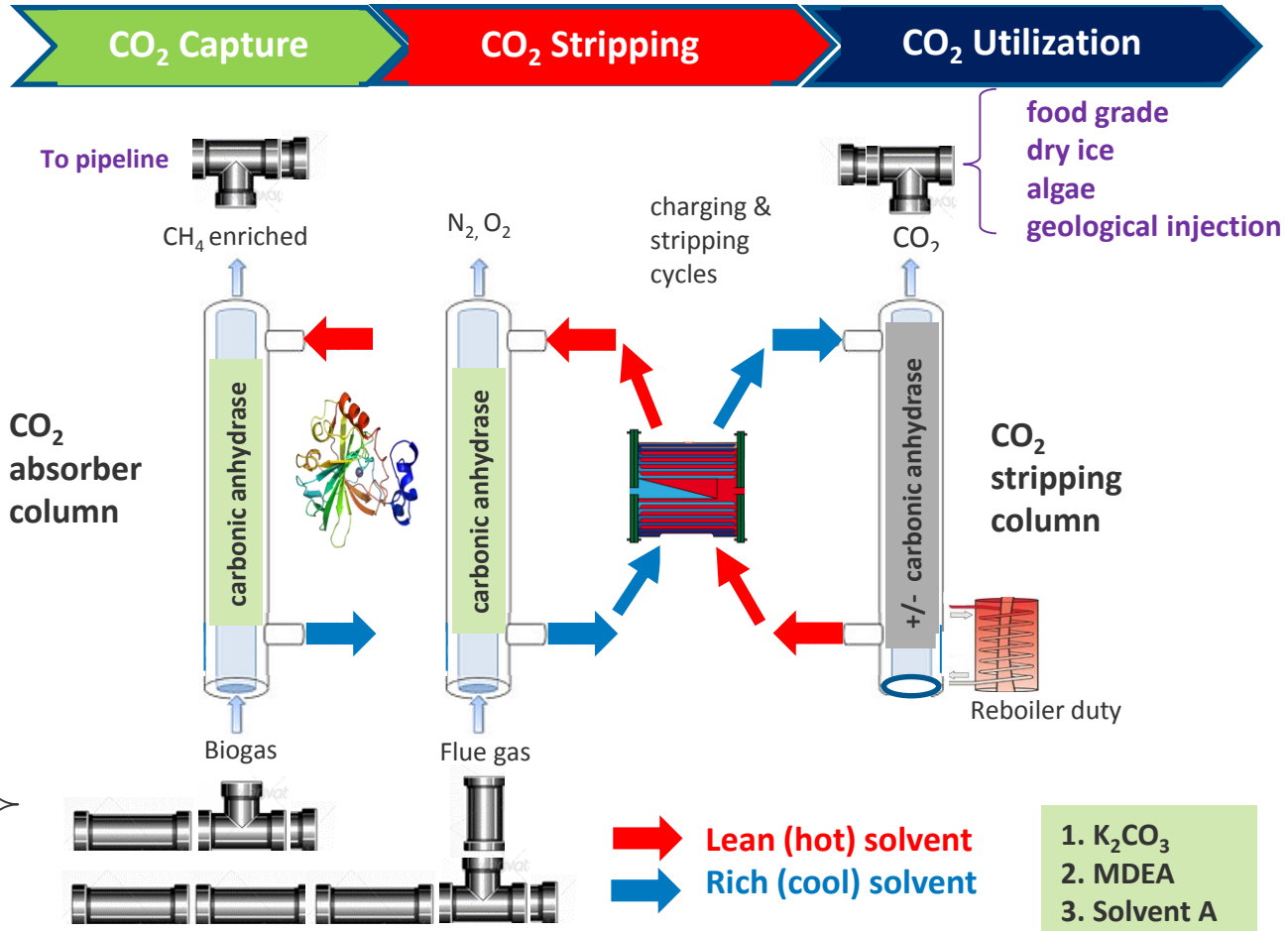
- Challenges:
  - Solvent compatibility with thermotolerant and active enzymes
  - In-process enzyme longevity and post-process sustainability
  - High energy requirement for solvents

Process Diagram

Biomass Power

Coal Power

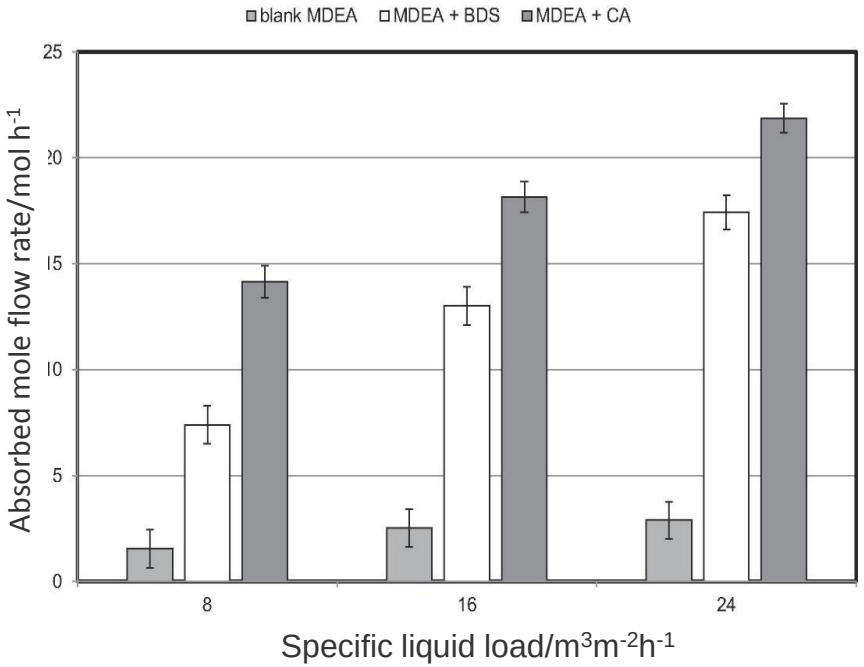
Anaerobic Digestion



Flexible solutions for CO_2 mitigation from waste gas

CO_2 Absorption Enhancement Demos

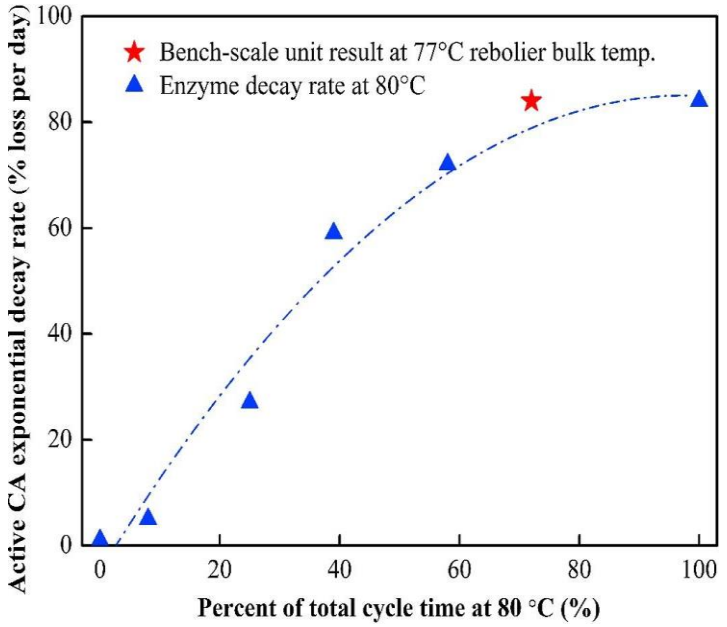
Both dissolved CA and immobilized CA particles (BDS) give significant CO_2 absorption enhancement in MDEA solvent



Leimbrink, Nikoleit, Spitzer, Salmon, Bucholz, Gorak, Skiborowski, *Chem Eng Journal*, 2018, 334, 1195-1205.

EU FP7 funded project

Decreasing cycle time spent at high temperature can extend CA longevity (lab and bench-scale, in aq. K_2CO_3)

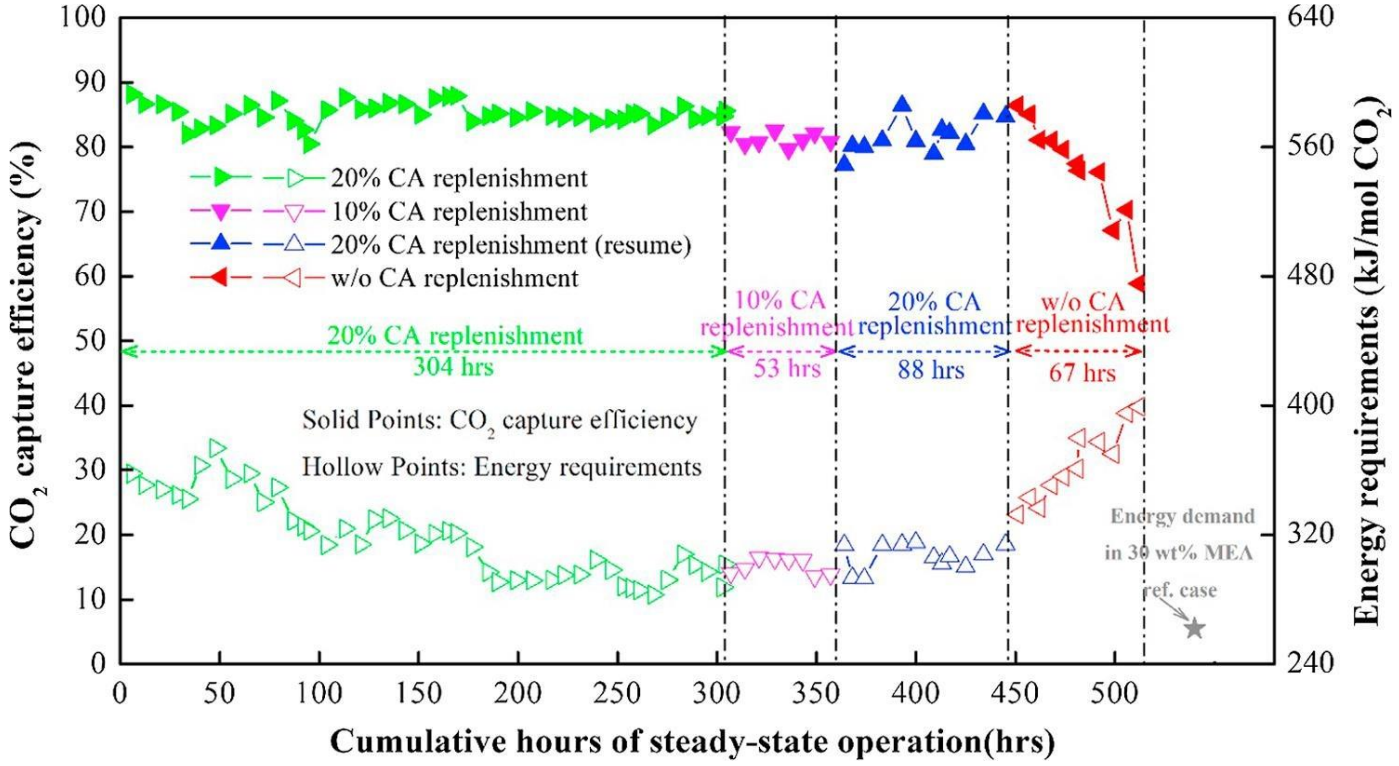


Qi, Liu, House, Salmon, Ambedkar, Frimpong, Remias, Liu, *Applied Energy*, 2018, 209, 180-189.

DOE-NETL funded project (Novozymes)

Prior UK-CAER Bench Scale Demo

- Dissolved CA promoted K_2CO_3 solvent based CO_2 capture system with vacuum stripping
- CA enhanced mass transfer leads to lower energy requirement versus uncatalyzed K_2CO_3
- Improving enzyme stability could reduce replenishment rate



Qi, Liu, House, Salmon, Ambedkar, Frimpong, Remias, Liu, *Applied Energy*, 2018, 209, 180-189.

Relevance

- The goal of the project is to develop a novel biological, sustainable, and low energy CO_2 waste gas scrubbing technology **using enzyme-accelerated solvents with low regeneration energy**
- Provide **energy (and cost) saving technology** for carbon scrubbing of flue gases from power plants with CCS/CCU processes
- Low energy CO_2 scrubbing technology not only provide **cost savings for fossil fuel production** but also **can lower the production cost for biopower**:
  - BECCS combines the use of biopower has the potential to produce energy with net-negative emissions. The National Academy of Science, Engineering, and Medicine recognized that BECCS has the technical potential to provide a portion of the world's energy supply by the end of the century.
  - If commercialized further, BECCS could be a **baseload electricity resource with a net-negative carbon emission profile**
- Impact to **fossil fuel energy industry**, **biopower industry**, **biogas industry** as well as **CO_2 utilization sector**
- Expect to yield new IP and highly cited published work; engage more industrial partners across different sectors, from technology providers to end users, and move towards bringing the technology to commercialization
- Relevant to BETO's new initiative to develop innovations in the use of biomass, municipally-derived biosolids, and sorted municipal solid waste to improve the economic potential of biopower production and use in the United States

Future Work- Task 1 Enzyme Engineering

Objectives:

- Baseline assay top CA candidates including Novozymes CA (NZ-CA)
- Test top candidate CAs for their thermostability and combability with immobilization matrices and in selected solvents (collaboration with Tasks 2 & 3)
- Comparative structure analysis for the best known thermostable and active CAs to identify mutations combine properties for fast CO_2 absorption in relevant process conditions with selected solvents
- Novel design of CAs with best known thermostable enzyme chassis

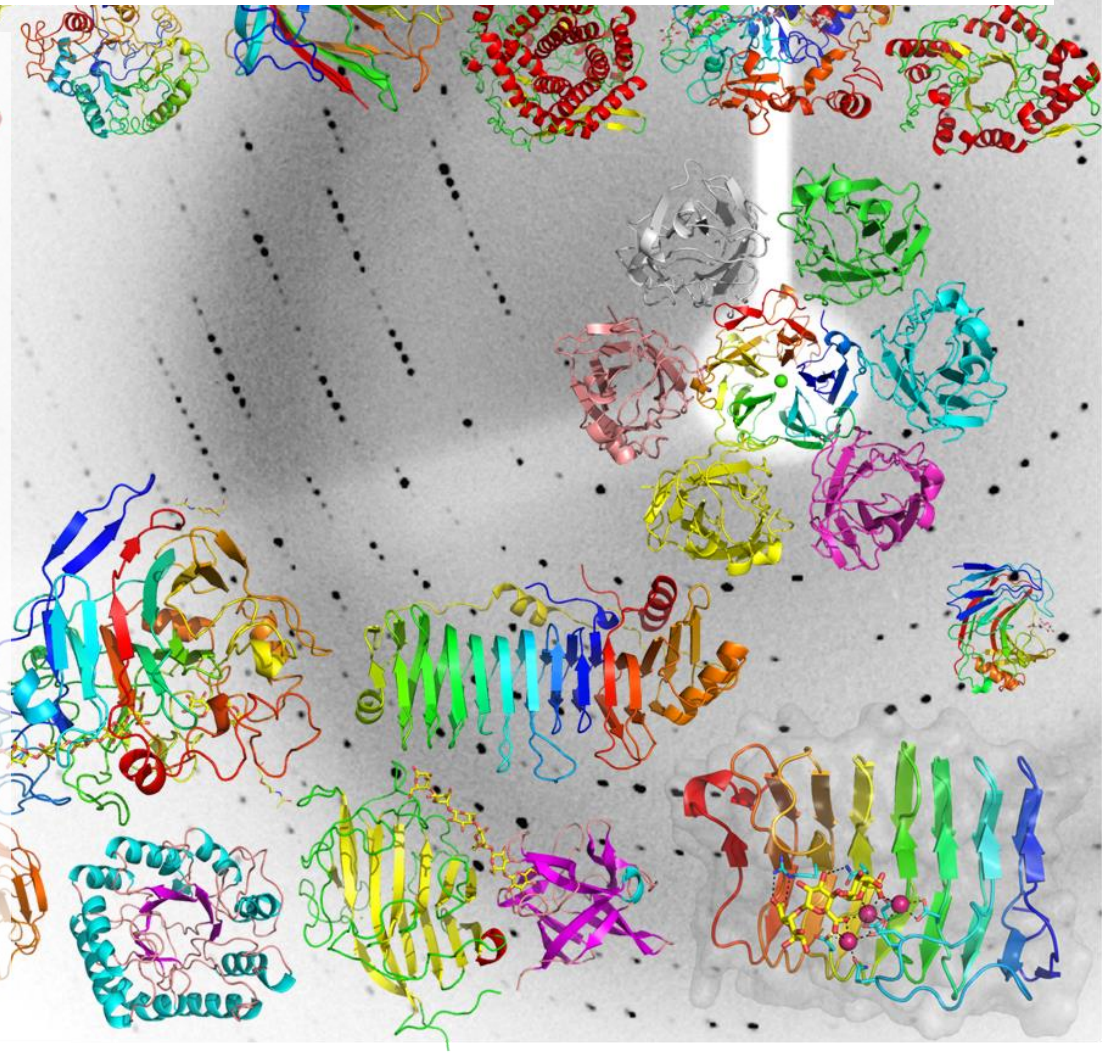
FY19 Annual Smart milestone (9/30/2019):

Report that the New CA enzyme through diversity screening and targeted mutations with survivability meet/exceed the baseline NZ-CA enzyme under lab benchmarking conditions by 10% (Task 1).

Relevant Enzyme Engineering Experience

Enzyme structure/function studies conducted by team members

- Fucosyl transferase
- Ferridoxins
- Cellobiohydrolases
- Tapirins
- Endoglucanases
- Fusion proteins
- Acetyltransferase
- Transcription regulators
- Chondroitinases
- Cellulose binding domains
- Methyltransferases
- Mg membrane transporter
- Protein-protein complexes
- Aminotransferase
- Kinases

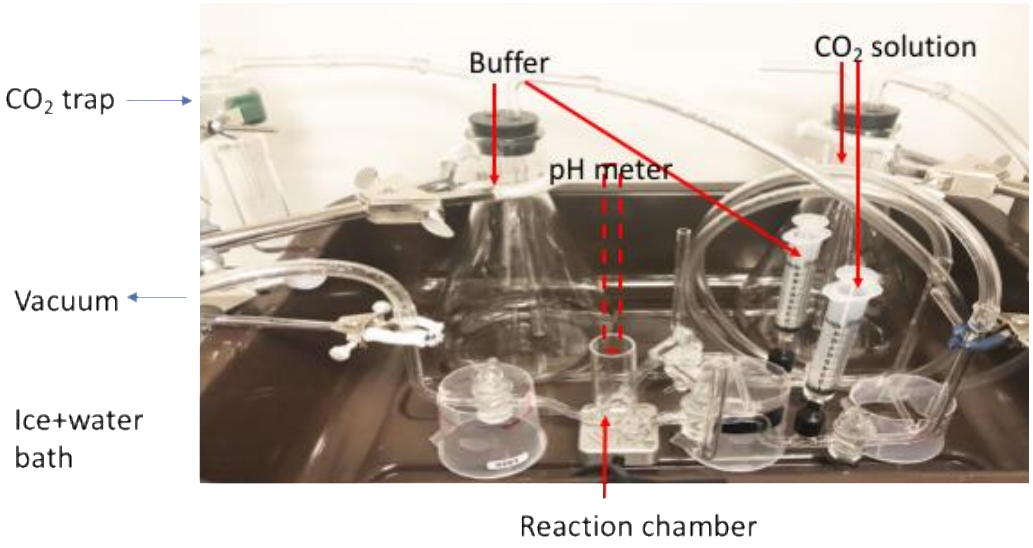


Establish Carbonic Anhydrase Assay

Issue: Thermal tolerance and kinetics data/values in published CA literature come from different international research groups who used different assays.

- Need to achieve data consistency and express, purify and assay the enzymes

1) **Wilbur-Anderson method**. Variations: temperature – 0°C, 4°C, 25°C; Precise pH measurement or color change with dye
2) PNPA esterase activity (spectrophotometric); not all CAs exhibit esterase activity and the levels of such activity are not correlated with CO_2 hydration activity
3) Stopped-flow spectroscopy
4) Analysis of O^{18} isotopes of CO_2



Wilbur-Anderson apparatus - Electrometric method allows fast kinetics measurement

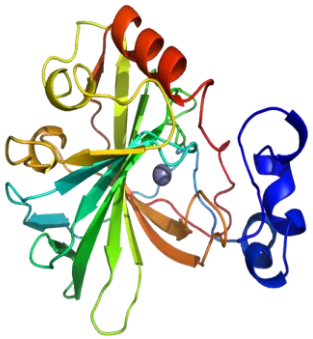
Carbonic Anhydrases

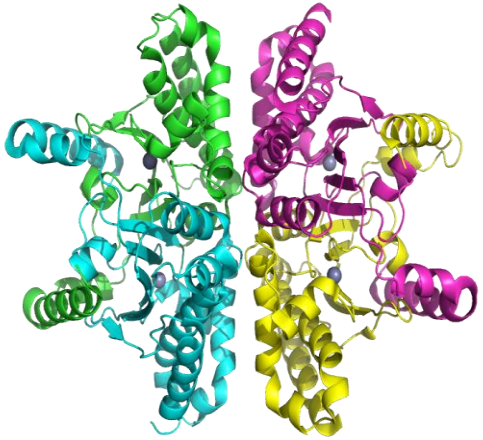
- α-class CA: most studied, thermostable (T_{opt} up to 75^0C) and most active (k_{cat} up to 4400 ms^{-1}), could be monomeric, dimeric and tetrameric
- γ-class CA: most thermostable hosts (T_{opt} above 95^0C)
- Active site formed on the interface between two protein molecules, residues from both molecules are involved

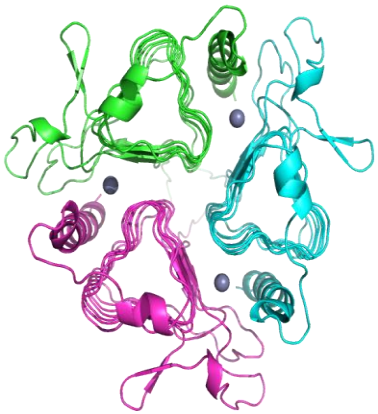
α-class CA

β-class CA

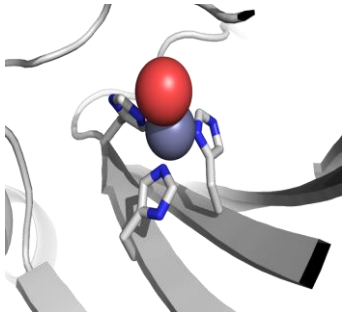
γ-class CA

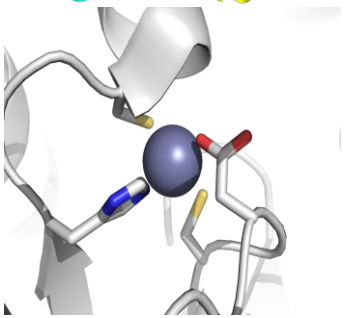


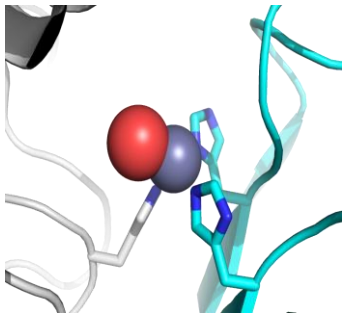




Active site geometry







Carbonic Anhydrase Candidates Identified

Top carbonic anhydrase performers:

- *Thermovibrio ammonificans* (TaCA)
- *Persephonella marina* (PmaCA)
- *Sulfurihydrogenibium yellowstonense* (SspCA)
- *Sulfurihydrogenibium azorense* (SazCA)
- LOGACA (from thermal vent metagenome)
- *Pyrococcus abyssi* (PabCA)
- *Pyrococcus horikoshii* (PhoCA)
- Codexis DvCA-mutant

α-class

γ-class

β-class

- Express, purify and assay top performers
- Comparative analysis on differences in enzymatic activity - a critical step allowing us to obtain firsthand information to conduct comparative enzymatic kinetic studies with the prototype CA from Novozymes and further improve them via protein engineering

Go/No-Go Decisions

Name	Description	Criteria	Date
Report that the New CA exceeds NZ-CA performance (25-30% longer survivability (hours) at process temperature while maintaining kinetic turnover).	A GO decision indicates continuing improving New CA. A NOGO decision, discontinue work on New CA and conduct further protein engineering efforts to improve NZ-CA (Task 1).	Enzyme performance exceeds NZ-CA (25-30% longer survivability (hours) at process temperature while maintaining kinetic turnover).	3/30/2020

Project Status

- NREL's research started in FY19 Q1
  - Conducted extensive literature review
  - Identified 8 top CA candidates and the genes are synthesized to express in *E. coli*, purify and assay for a comparative study with Novozymes CA
  - Assay apparatus (Wilbur) custom-built
  - Novozymes CA received
- NDAs and MTAs in place
- Working on placing the subcontracts with NCSU and UK-CAER

Future Work
- Task 2 Enzyme Immobilization

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Objectives:

- Proof of concept for biodegradable enzyme-entrapping polymeric structures (BEEPS) fabrication using NZ-CA
- Verify NZ-CA-BEEPS longevity and compatibility with selected solvents at lab benchmarking conditions
- Demonstrate NZ-CA-BEEPS scale-up feasibility and test accordingly in lab-scale or bench-scale CO_2 capture systems
- Proof of concept for BEEPS fabrication and performance using NREL-NewCA.
- Proof of concept for spent BEEPS-solvent biodegradability

Annual Smart milestone (12 months):

Report that BEEPS provide ≥ 50% enzyme activity versus equivalent amount of non-immobilized enzyme in short-term test lab benchmarking conditions. (Task 2)

Enzyme Immobilization Approach

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- Enzyme immobilization can improve enzyme efficiency, longevity and process control
  - Restrains enzyme to critical reaction zone(s) in the CO_2 scrubber
- Novel BEEPS will provide immobilization advantages while also addressing end-of-use sustainability
- Polymers to be evaluated include polysaccharides (e.g. chitosan), protein (e.g. fibroin) and potentially others

BEEPS Concept

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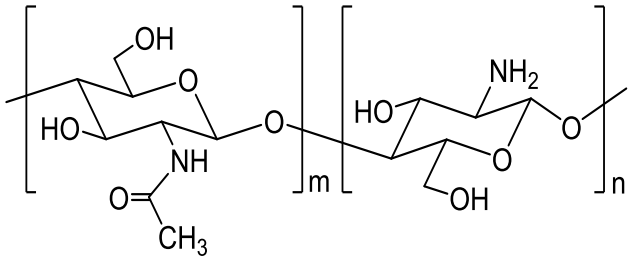
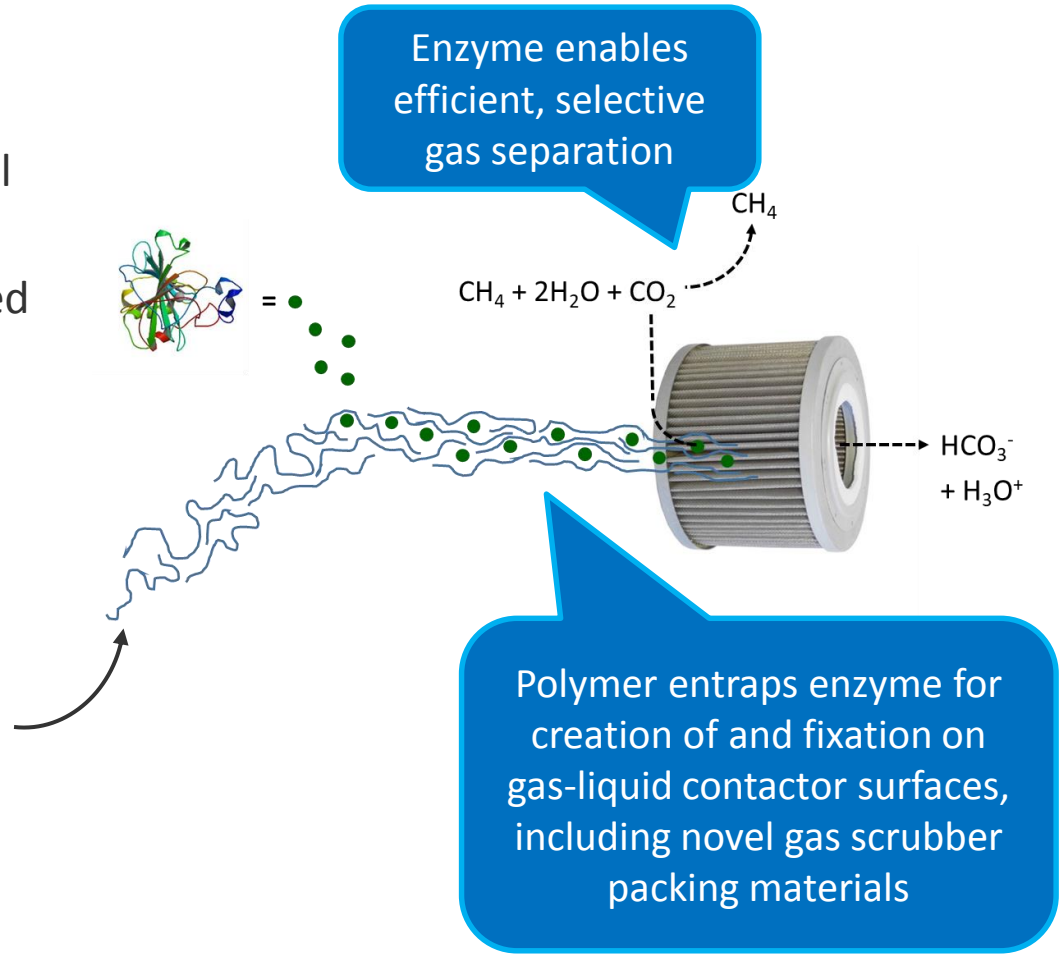
Chitosan polymer

- Naturally derived, commercially available and biodegradable
- Desirable processing and technical performance characteristics
- Versatile fabrication of immobilized enzyme for gas-liquid contact





Colorimetric Method for CA Activity

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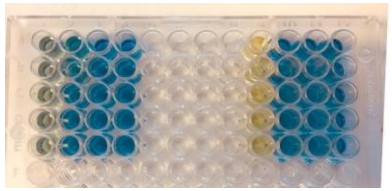
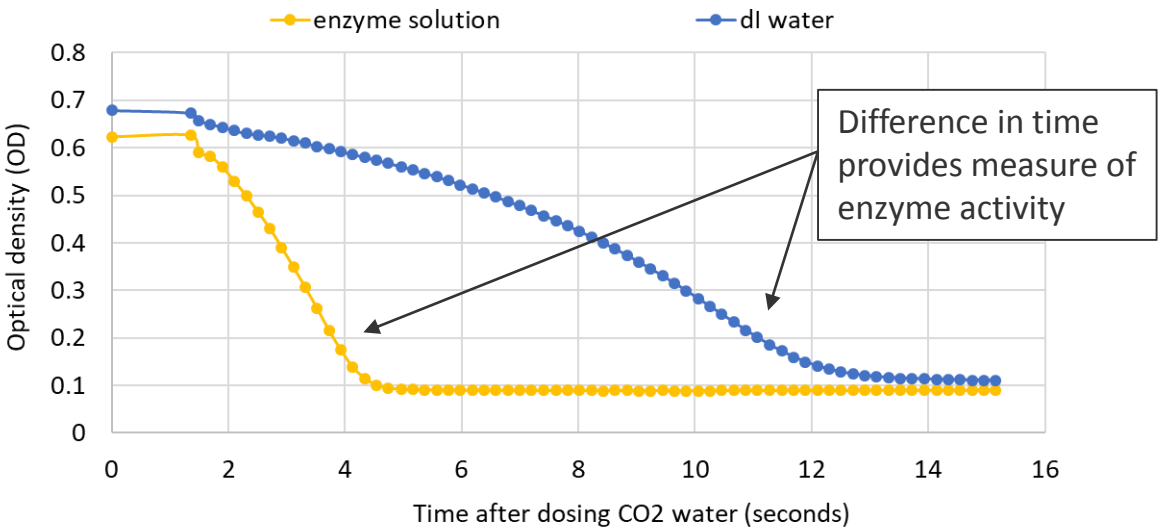
Allows increase sample throughput and decrease the use of reagents



Spectophotometer



CO_2 hydration → **pH change** → **Color change of indicator**
(Bromothymol blue)

Future Work-
Task 3 Alternative Solvents Selection and Bench Scale Testing and Integration

Center for Applied Energy Research

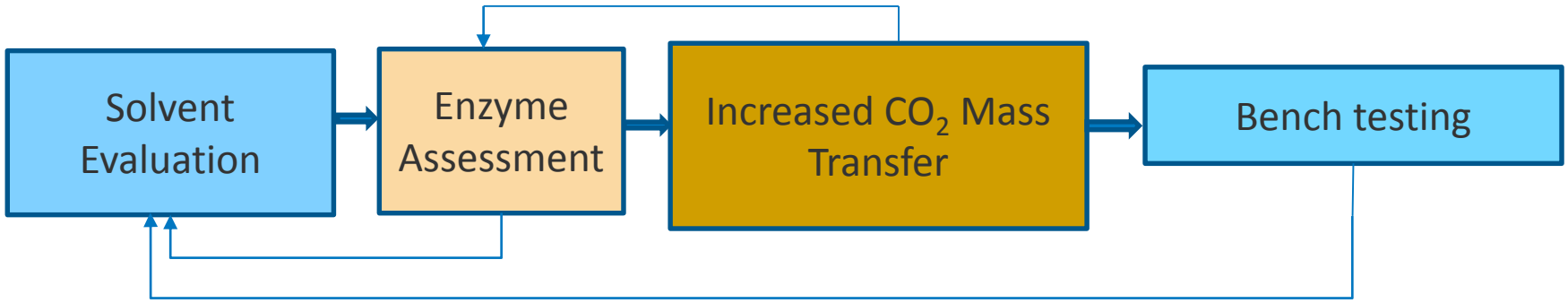
Objectives:

- Select solvent for CO_2 mass transfer enhancement and baseline bench-scale testing
- Verify compatibility of solvent and enzyme and baseline solvent/enzyme testing
- Bench-scale testing and optimization of solvent/enzyme with 20% reduction in regeneration energy

Annual Smart milestone (12 months):

Report on process energy consumption metric for solvent-NZCA baseline testing in bench-scale system. (Task 3).

Task 3 – Solvent/Catalyst Bench Testing



Measure physical properties of aqueous amine solvent and assess physical property changes from enzyme addition

Unique Facility - 30 L/min Small Bench Unit

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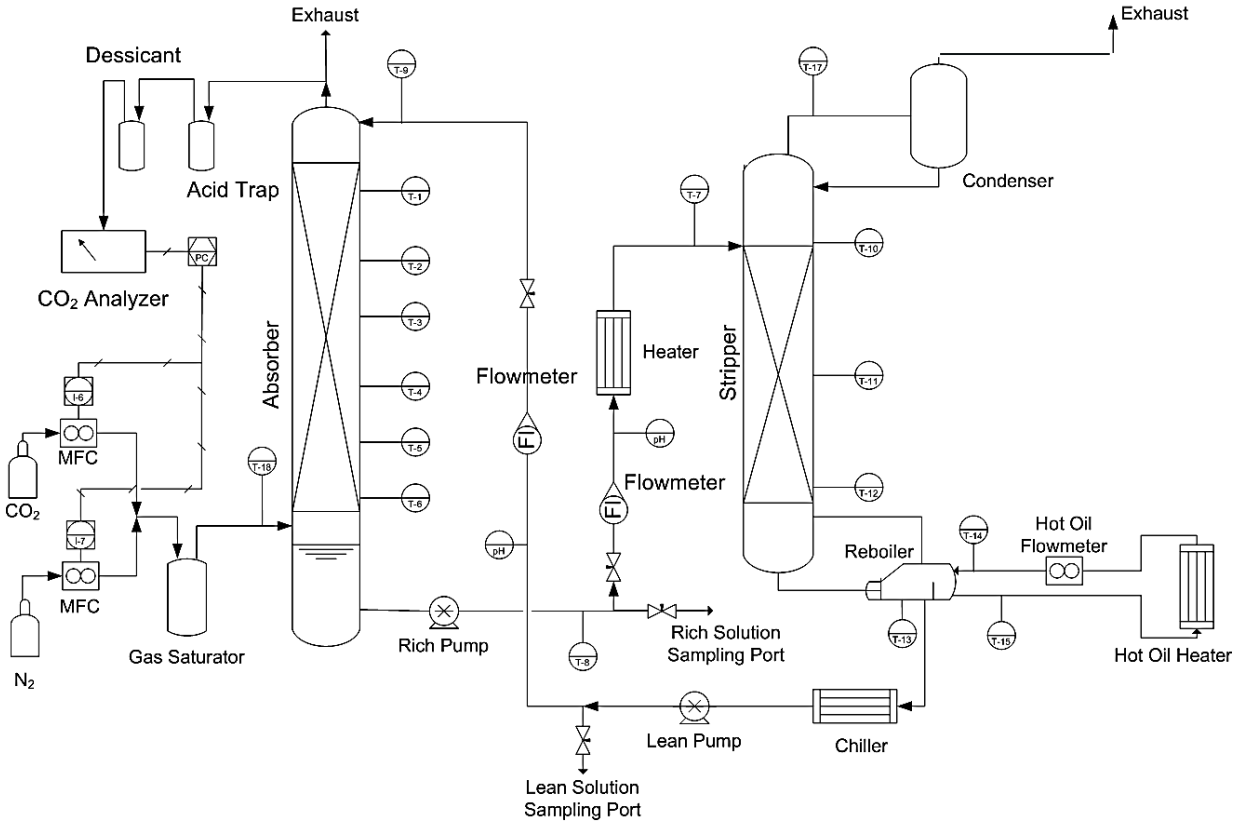
- A bench-scale integrated carbon capture unit built for testing enzyme enhanced solvents
- Allow comprehensive data gathering on temperature profile along the absorber and stripper column and calculate mass transfer flux and regeneration energy consumption



Summary

- **Goal**: To develop a novel biological, sustainable, and low energy CO_2 waste gas scrubbing technology using **enzyme-accelerated solvents with low regeneration energy.**

- **Technical Approaches**: Identify and engineer **better CAs** for improved enzyme activity and process robustness; Investigate **novel immobilization method** with **effective compatibility with solvents** for improved enzyme in-process longevity and post-process sustainability; Utilize enzyme-accelerated **solvents with low regeneration energy** and integrated process with **low energy consumption**.

- **Relevance**: Provide **energy (and cost) saving technology** for carbon scrubbing of flue gases from power plants with CCS/CCU processes, BECCS, enable cheap electricity from biomass.

- **Future Work**: Established detailed three year research plan with milestones and research targets within the project team, NREL, NCSU and UK-CAER **in enzyme engineering, enzyme immobilization, compatible solvents selection and bench scale testing and integration** as well as TEA analysis with the support from Novozymes.

Acknowledgements

- ***Funding***
  - **U.S. DOE EERE Bioenergy Technology Office (BETO)**
    - HQ: Jonathan Male, Kevin Craig, Ian Rowe
    - NREL LPM and Platform Lead: Zia Abdullah, Rick Elander
  - **Novozymes provided in kind cost share**

Project Members

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  Vladimir Lunin
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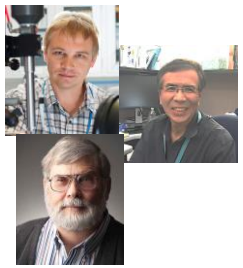
  Michael Himmel



- NCSU
  Sonja Salmon and team
- UK-CAER
  Jesse Thompson and team
- Novozymes
  - Mike Elder
  - Alan House

Thank You

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NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.

Response to Reviewers' Comments 2017

Publications

Presentations