A Novel Molten Salt System for CO_2 Based Oxidative Dehydrogenation with Integrated Carbon Capture

Fanxing Li research group

North Carolina State University

Partners:

West Virginia University

Susteon Inc.

NETL Project Manager: *Naomi Oneil*

Background and Project Overview

Project Funding: DOE - $999,992; Cost share - $254,637

Performance Period: 09/01/2020 – 08/31/2022

Project Participants: North Carolina State University, West Virginal University; Susteon Inc;

Project Objective: To develop a comprehensive proof-of-concept for the sustainable and cost-effective production of propionic acid, and value added C3/C4 olefins, from CO_2 in power plant flue gas and domestic shale gas resources..

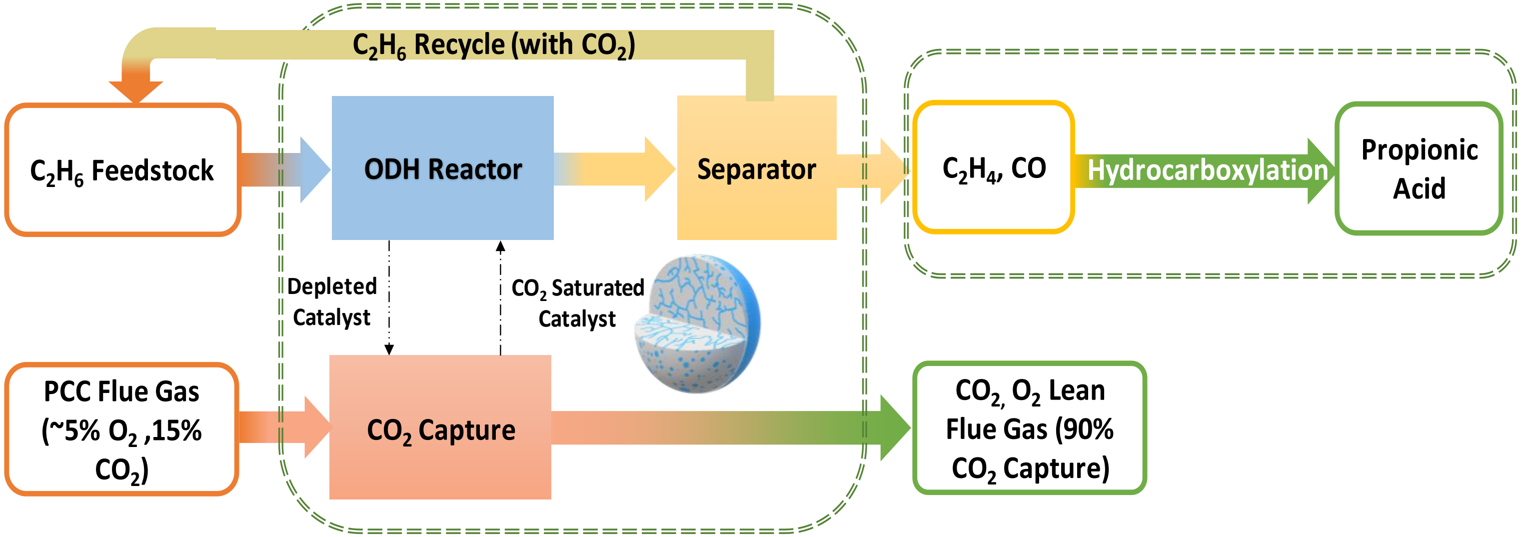
Proposed Strategy: This will be realized via a molten-salt mediated oxidative dehydrogenation (MM-ODH) process that performs reactive CO_2 capture (from power plant flue gas) and CO2 assisted alkane oxidative dehydrogenation in a two-step, thermochemical scheme

Specific Objectives

(1) *Phase I* aims to unveil the optimization strategies for the redox catalysts to further improve their activity and CO_2 capture capacities at low temperatures (≤ 750 C) while maintaining their cyclic stability;

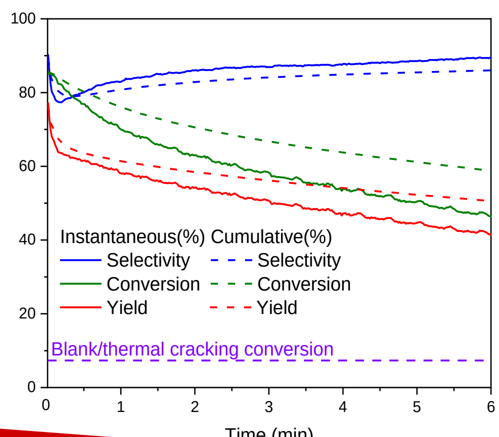
(2) *Phase II* targets to optimize the redox catalysts and comprehensively validate their robustness and long-term performance. High-fidelity kinetic models will also be established for the optimized redox catalysts and used to guide the reactor and process design for scale up and commercialization.

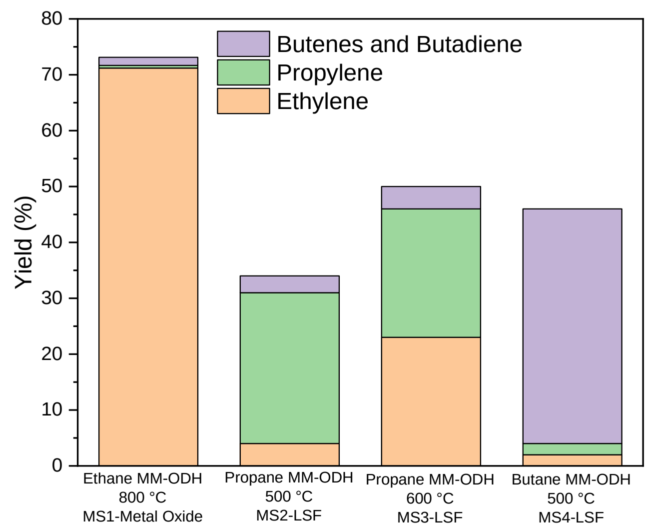
Technology Background

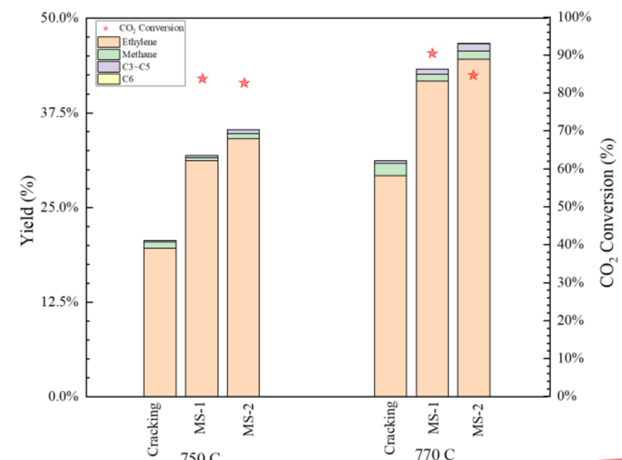


Section I: Upstream MM-ODH System (This Proposal)

Section II: Downstream Hydrocarboxylation Step (Industrially Proven)







Project Scope

Research Plan:

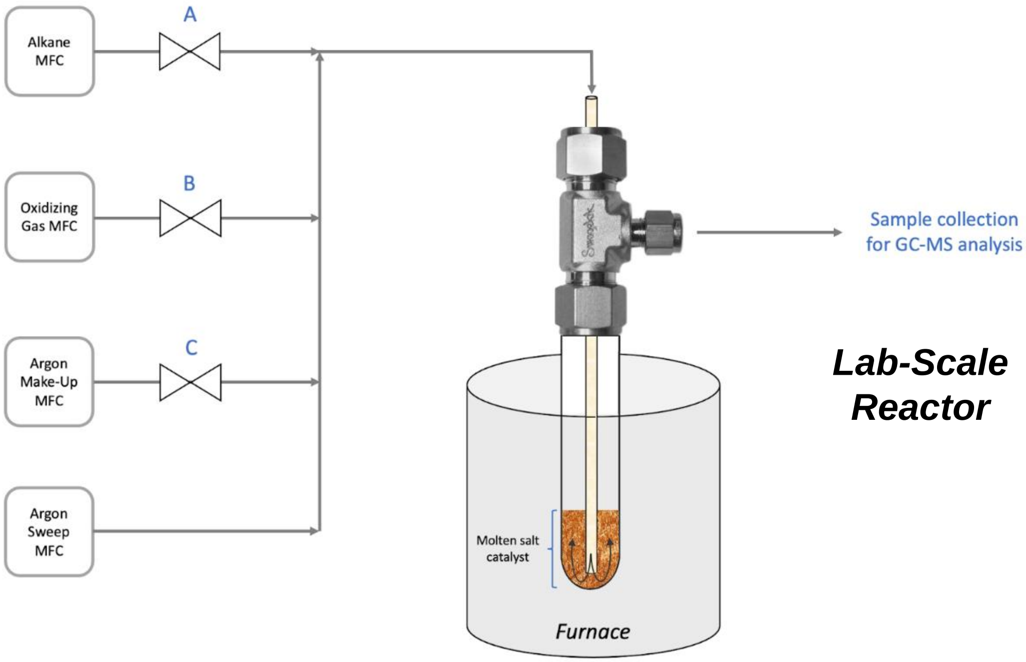
Phase I. Redox catalyst synthesis, screening and characterization; Preliminary TEA and LCA.

Phase II. Long-term stability validation of redox catalysts; Refined TEA and LCA models.

Key Milestones/Successful Criteria and Timeline:

Q2 Feb. 2021	**Milestone 2.2 *Catalyst Synthesis Screening*:** four redox catalysts giving at least 80% selectivity and 50% yield for ethylene at <750 ºC, and 75% CO_2 conversion with 85% CO_2 capture)
Q4 Aug 2021	**Milestone 4.1 *Initial TEA*:** Initial TEA using preliminary results, process model, and literature review showing profitability at 20% ROI and 25% reduction in energy consumption.
Q6 Feb. 2022	**Milestone 5.1 500 Cycle Test:** 500 cycle tests on two redox catalysts giving at least 85% selectivity and 55% yield for ethylene, 85% CO_2 conversion, and 90% CO_2 capture after cycling.
Q12 Jan.2022	**Milestone 8.1 Final TEA/LCA:** Developing a Final TEA/LCA using optimized experimental results, process model, and pricing of major complements showing profitability at 20% ROI and 25% reduction in energy consumption.

Project Progress: Experimental Set-up



Lab-Scale Reactor

In-line QMS

Gas Chromatography

CO_2-Capture (Step 1):

CO_2 (in flue gas) + X_2O (dissolved alkali metal oxide in the molten salt) → X_2CO_3

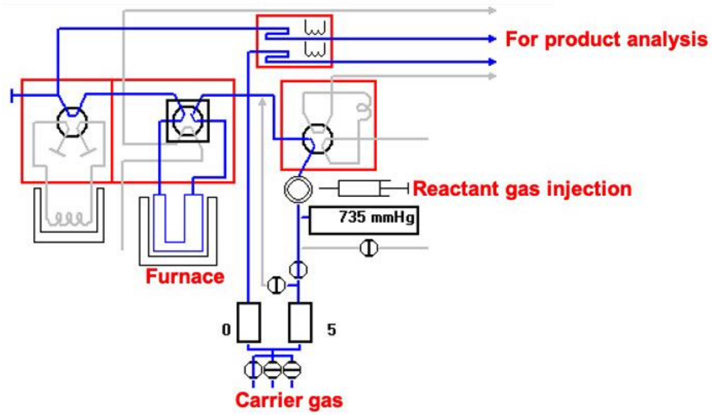
MeO_{x-1} + 1/2O_2 (in flue gas) → MeO_x

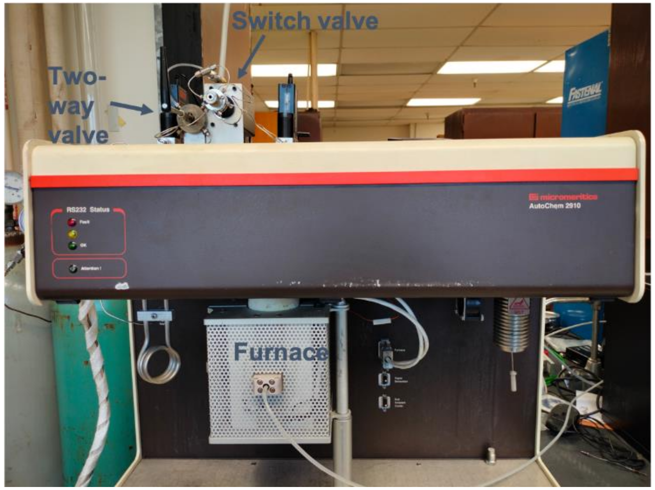
CO_2-ODH (Step 2)

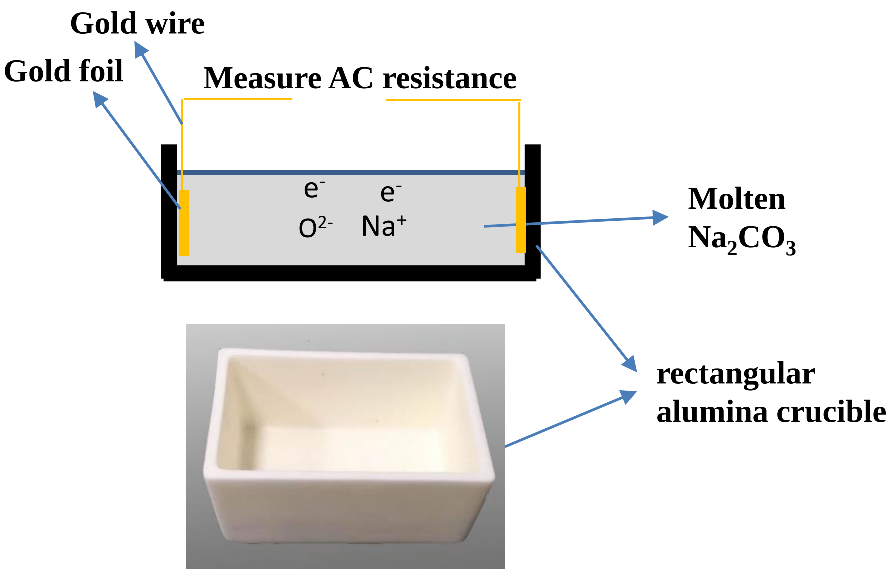
$R\text{-}CH_2\text{-}CH_3 + X_2CO_3 \rightarrow R\text{-}CH{=}CH_2 + CO + H_2O + X_2O$ (R can be H for ethane, CH_3, or CH_3-CH_2)

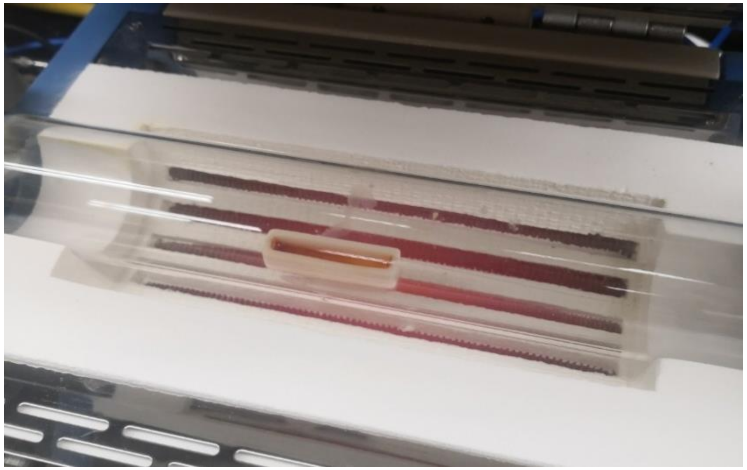
$R\text{-}CH_2\text{-}CH_3 + MeO_x \rightarrow R\text{-}CH{=}CH_2 + H_2O + MeO_{x-1}$

Project Progress: Experimental Set-up at WVU





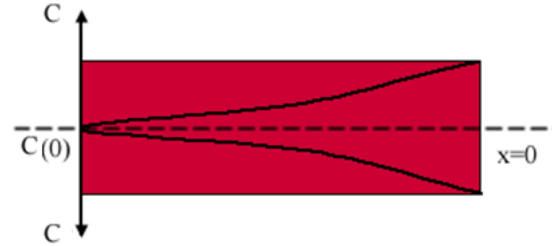




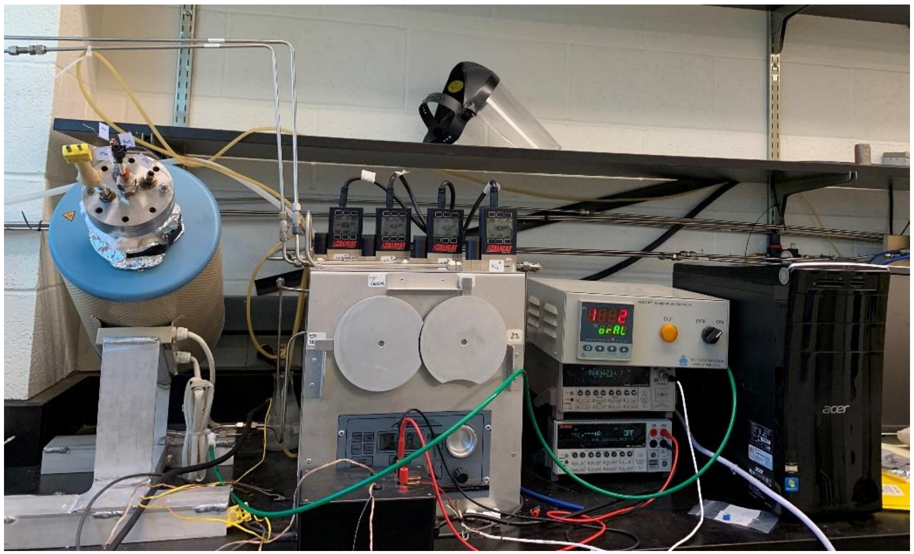
Experimental Set-up

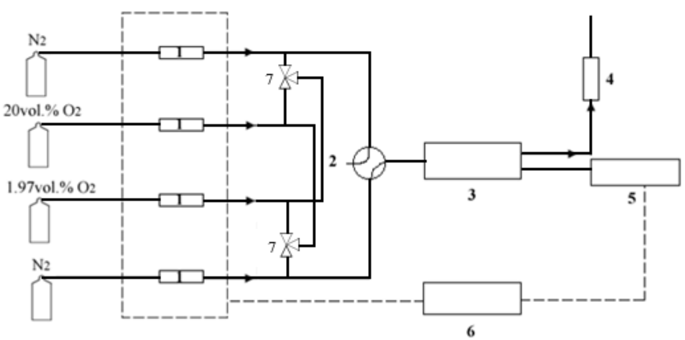
kinetics measurement for diffusion (D) and surface exchange (k) coefficients for MeOx

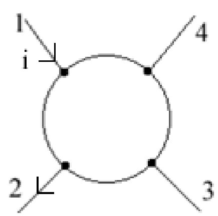
$$MeO_{x-1} + 1/2O_2 \text{ (in flue gas)} \rightarrow MeO_x$$



$$\frac{C(t)-C(0)}{C(\infty)-C(0)} = \frac{\delta(t)-\delta(0)}{\delta(\infty)-\delta(0)} = \frac{\sigma(t)-\sigma(0)}{\sigma(\infty)-\sigma(0)}$$







- Diffusion equation and solution:

$$\frac{\partial \phi}{\partial t} = D\frac{\partial^2 \phi}{\partial x^2}$$

$$-D\partial C/\partial x\big|_{x=\pm a} = k[C(\infty)-C(t)]$$

$$\frac{C(t)-C(0)}{C(\infty)-C(0)} = 1-\sum_{n=1}^{\infty}\frac{2L^2\exp(-\beta_n^2 Dt/a^2)}{\beta_n^2(\beta_n^2+L^2+L)}$$

$$L = \frac{ak}{D} = \frac{a}{l_c} = \beta_n \tan\beta_n$$

Task 2 Redox Catalyst Synthesis and Characterizations

Porous Oxide Synthesis

Objective: Develop a 3-dimensional ordered macro-porous (3DOM) perovskite $La_{0.8}Sr_{0.2}FeO_3$ (LSF) for oxidative dehydrogenation (ODH)

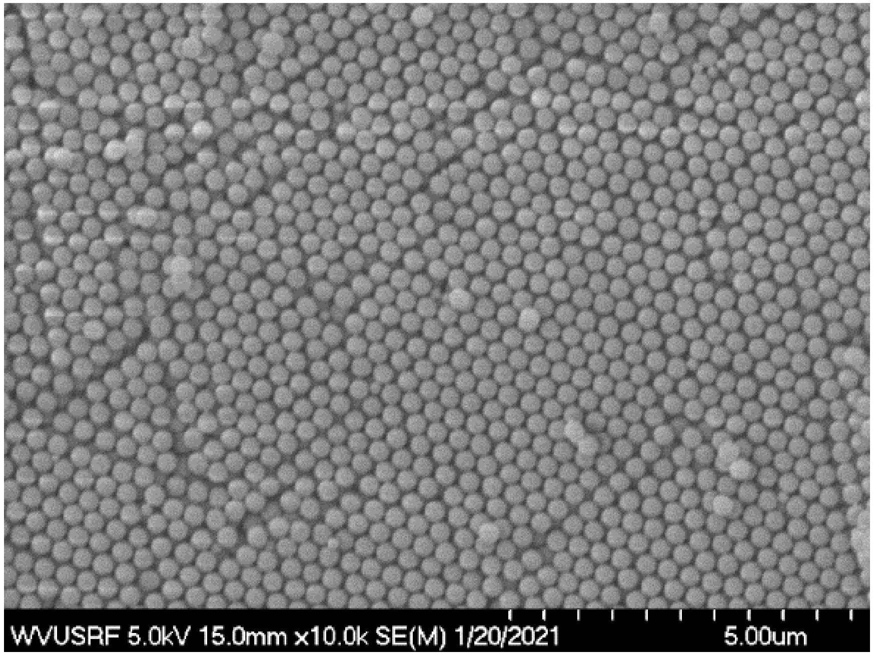


Figure. SEM image of the synthesized PMMA

OBSERVATIONS:

- 3DOM LSF was synthesized by using polymethyl methacrylate (PMMA) as a soft template
- Synthesized PMMA in Figure demonstrated the ordered PMMA microsphere array formed by PMMA microspheres with the uniform diameter (~300 nm).

Task 2 Redox Catalyst Synthesis and Characterizations

Porous Oxide Synthesis

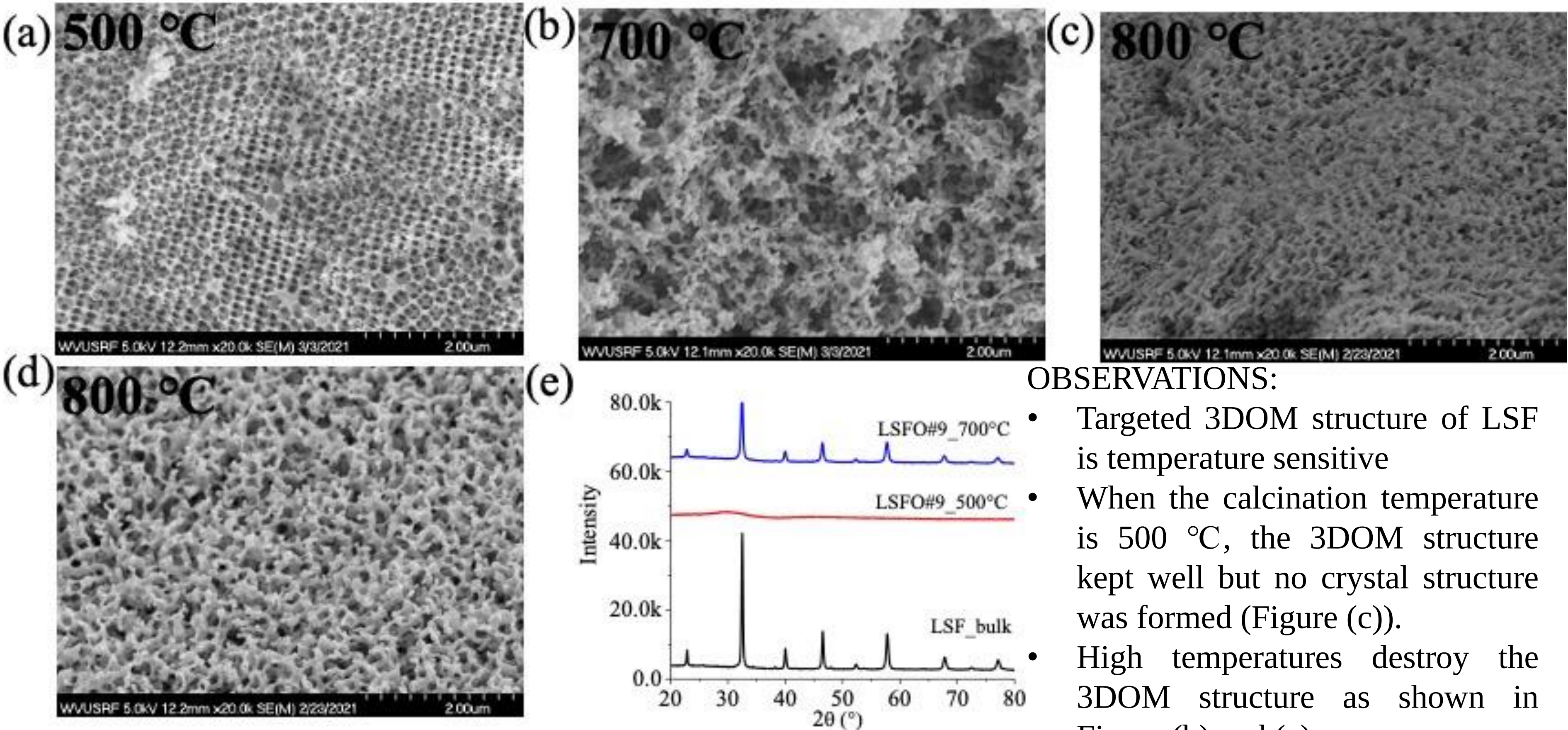


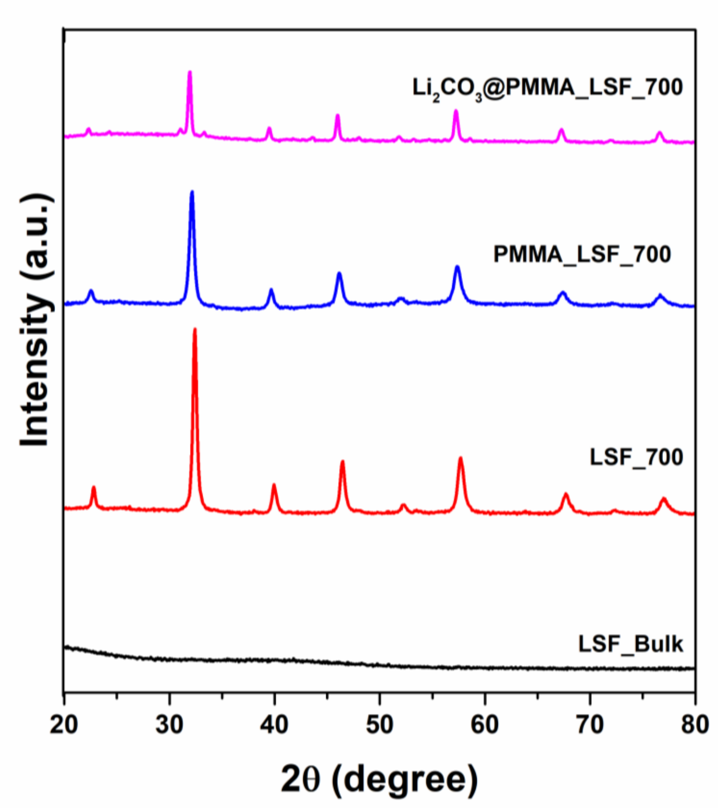
Figure. (a-d) SEM images of LSF prepared at different calcination temperature and e) XRD patterns of LSFO#9 prepared at 500 and 700 °C.

OBSERVATIONS:

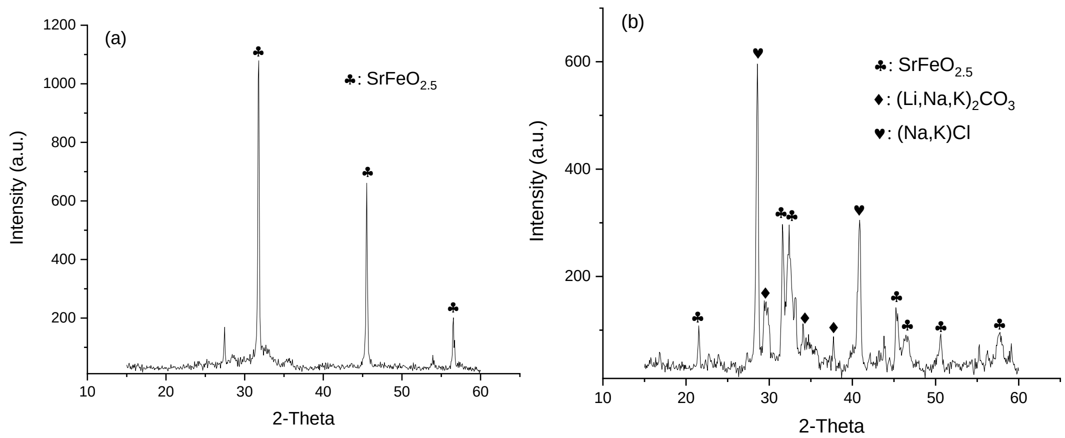
- Targeted 3DOM structure of LSF is temperature sensitive
- When the calcination temperature is 500 °C, the 3DOM structure kept well but no crystal structure was formed (Figure (c)).
- High temperatures destroy the 3DOM structure as shown in Figure (b) and (c)
- Some 3DOM structure was retained at 800 °C, but a large part of these structure was affected (Figure (d)).

Task 2 Redox Catalyst Synthesis and Characterizations

Porous Oxide Synthesis



XRD analysis of the synthesized catalysts



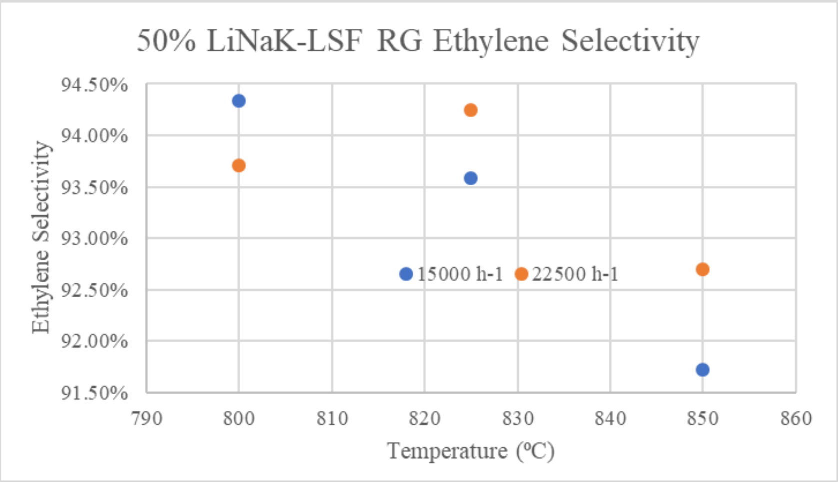
Sample	Pore Volume Estimation ($cm^3\ g^{-1}$)	Estimated Maximum Loading (wt. %)
Nanocast LSF with SBA-15	3.3	88%
Reactive Grinding LSF with NaCl Removed (Batch 1)	0.7	62%
Reactive Grinding LSF with NaCl Removed (Batch 2)	1.4	77%
3DOM LSF	2.2	84%

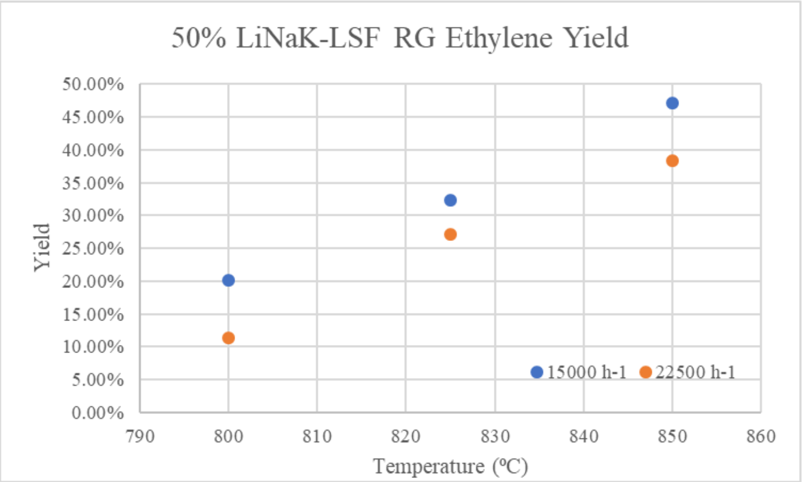
OBSERVATIONS:

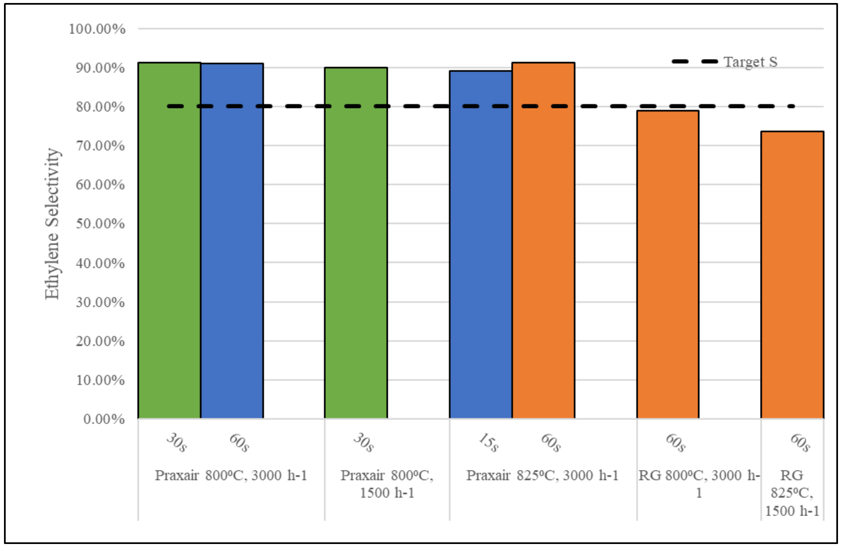
- Carbonate and perovskite phases are compatible;
- Besides 3DOM, **reactive grinding** and **nanocasting** were performed at NCSU, leading to high porosity.

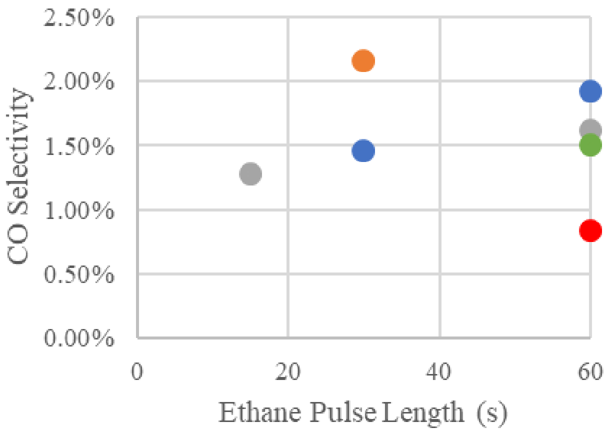
Task 2 Redox Catalyst Synthesis and Characterizations

Reactive Performance







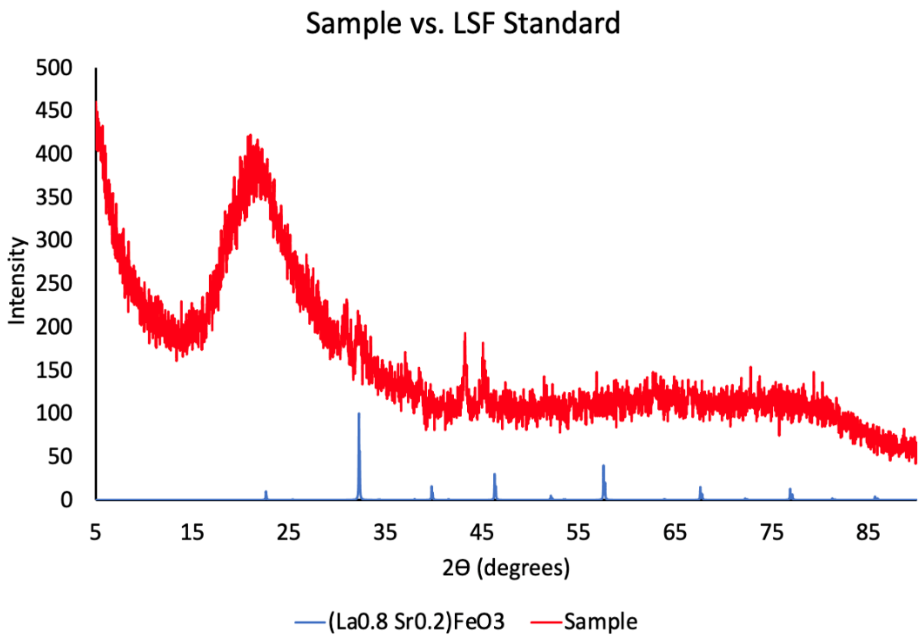


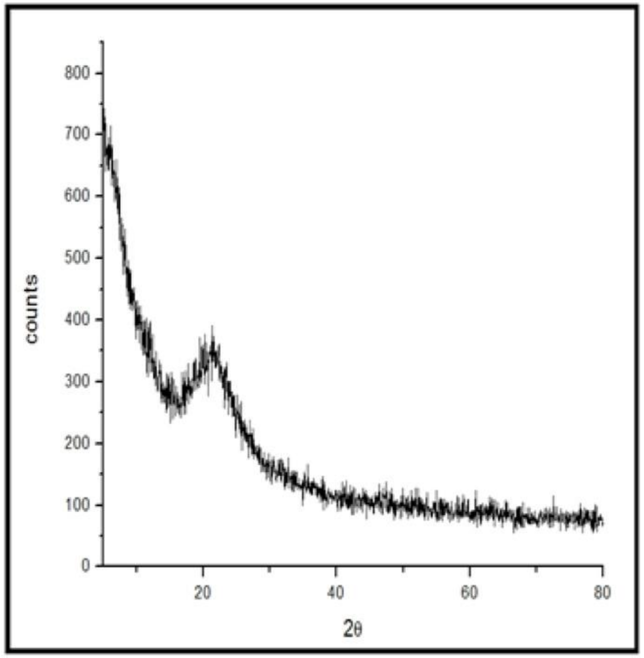
CO yields were unsatisfactory!

Milestone 2.2 ***Catalyst Synthesis Screening*****:** four redox catalysts giving at least 80% selectivity and 50% yield for ethylene at <750 ºC, and 75% CO_2 conversion with 85% CO_2 capture)

Task 2 Redox Catalyst Synthesis and Characterizations

Reactive Performance





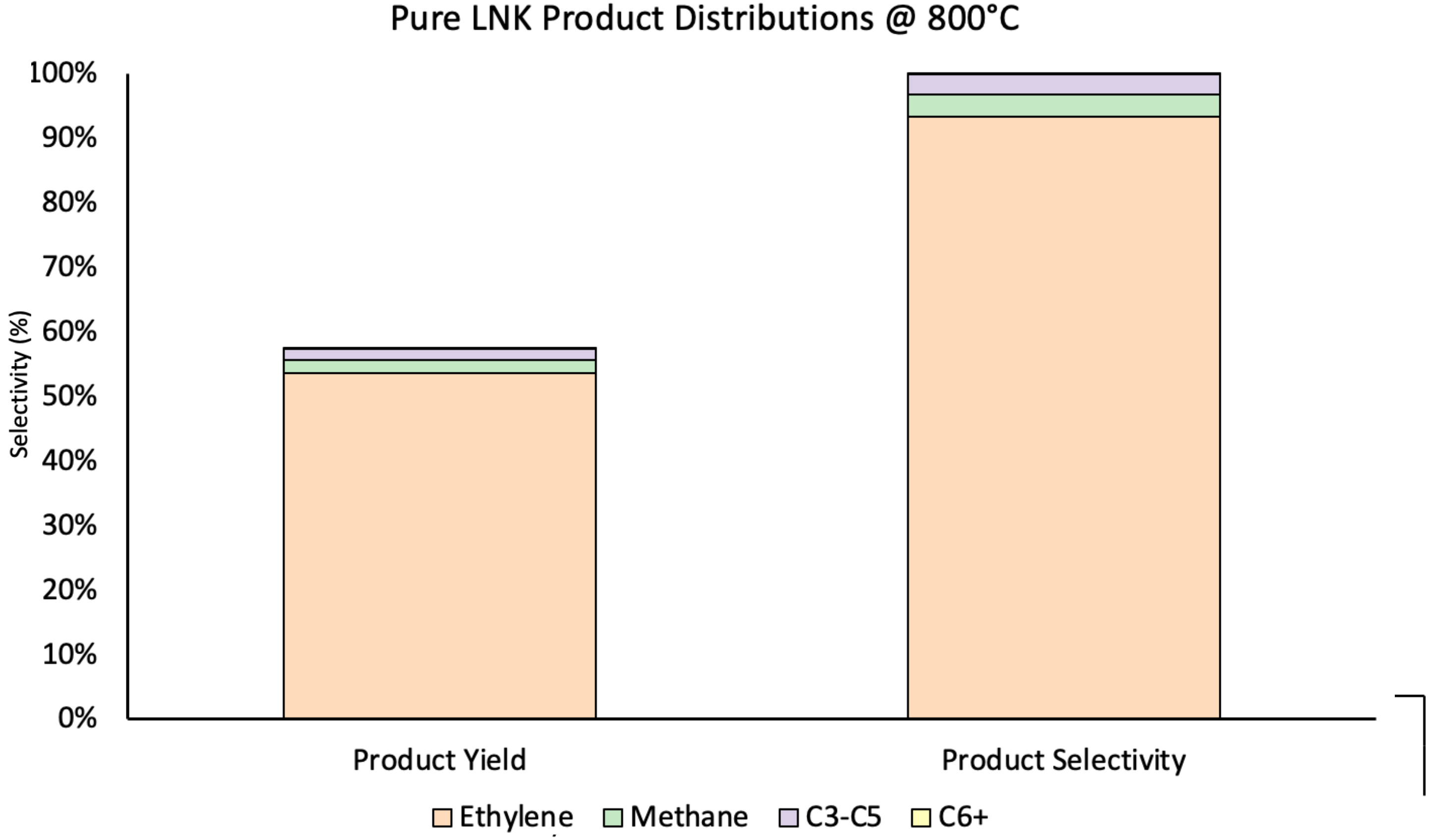
XRD pattern of amorphous silica from literature.[1]

Milestone 2.2 *Catalyst Synthesis Screening*: four redox catalysts giving at least 80% selectivity and 50% yield for ethylene at <750 ºC, and 75% CO_2 conversion with 85% CO_2 capture)

[1]Biswas, R. K. *et al.* Study of short range structure of amorphous Silica from PDF using Ag radiation in laboratory XRD system, RAMAN and NEXAFS. *Journal of Non-Crystalline Solids* **488**, 1–9 (2018).

Task 2 Redox Catalyst Synthesis and Characterizations

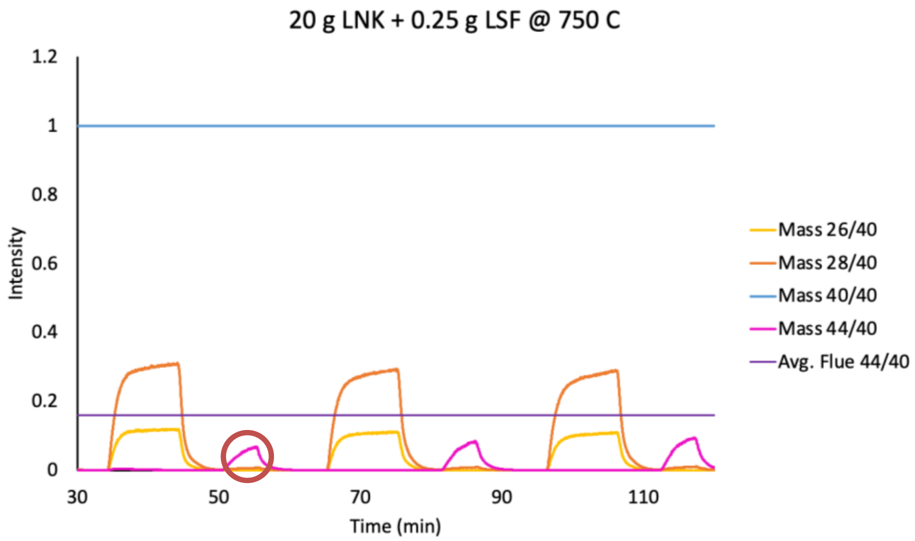
Reactive Performance

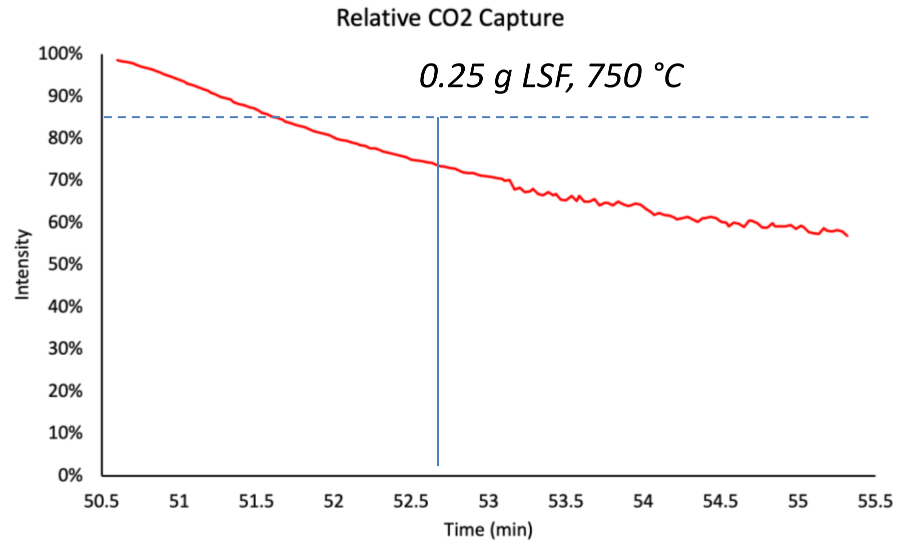


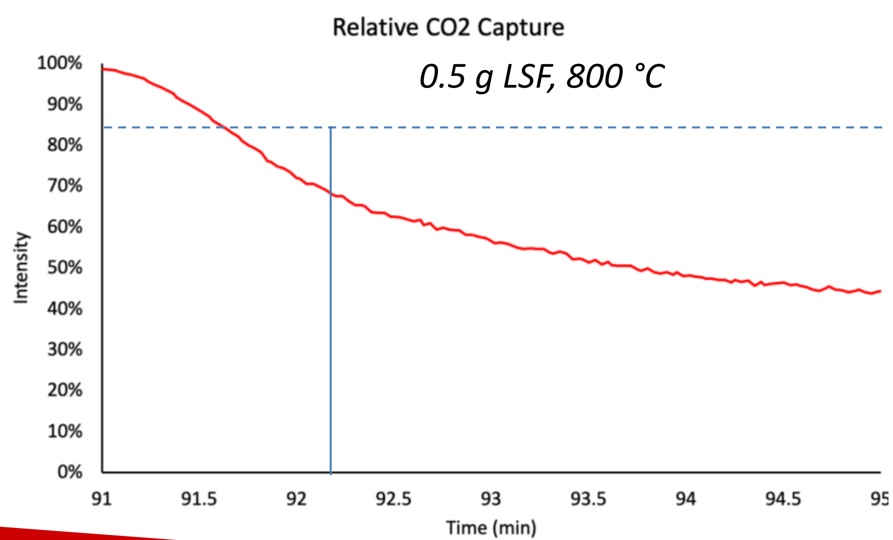
Milestone 2.2 *Catalyst Synthesis Screening*: four redox catalysts giving at least 80% selectivity and 50% yield for ethylene at <750 ºC, and 75% CO_2 conversion with 85% CO_2 capture)

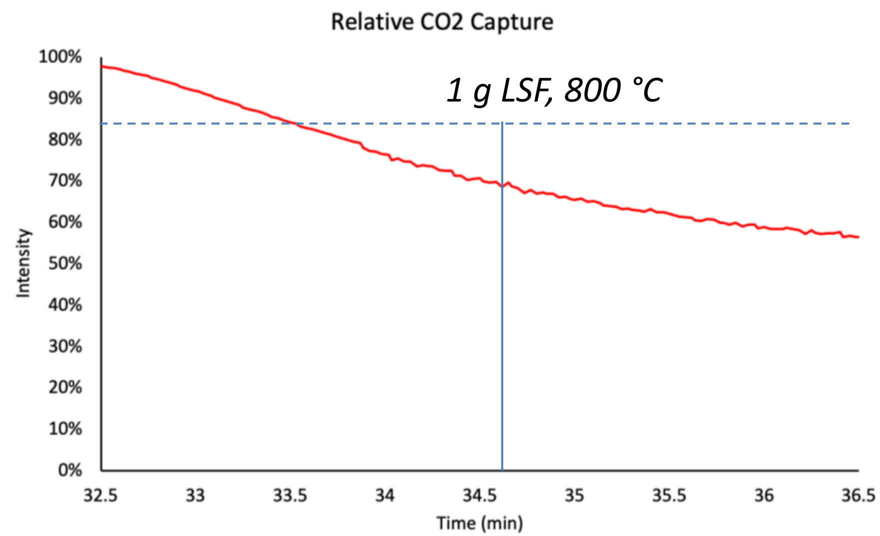
Task 2 Redox Catalyst Synthesis and Characterizations

Reactive Performance









Task 3 Redox Catalyst Optimization

Catalyst	Reaction Metric	Current Performance	DOE Milestone
1) Molten LNK-LSF slurry	Temperature	800ºC	≤ 750ºC
	Ethylene Yield	~65%	≥ 50%
	Ethylene Selectivity	> 90%	≥ 80%
	CO_2 Conversion	~90%	≥ 75%
	CO_2 Capture	~80% (>85% with shortened duration)	≥ 85%
2) Molten LNK bath	Temperature	800ºC	≤ 750ºC
	Ethylene Yield	53.62%	≥ 50%
	Ethylene Selectivity	93.40%	≥ 80%
	CO_2 Conversion	94.63%	≥ 75%
	CO_2 Capture	~80% (>85% with shortened duration)	≥ 85%

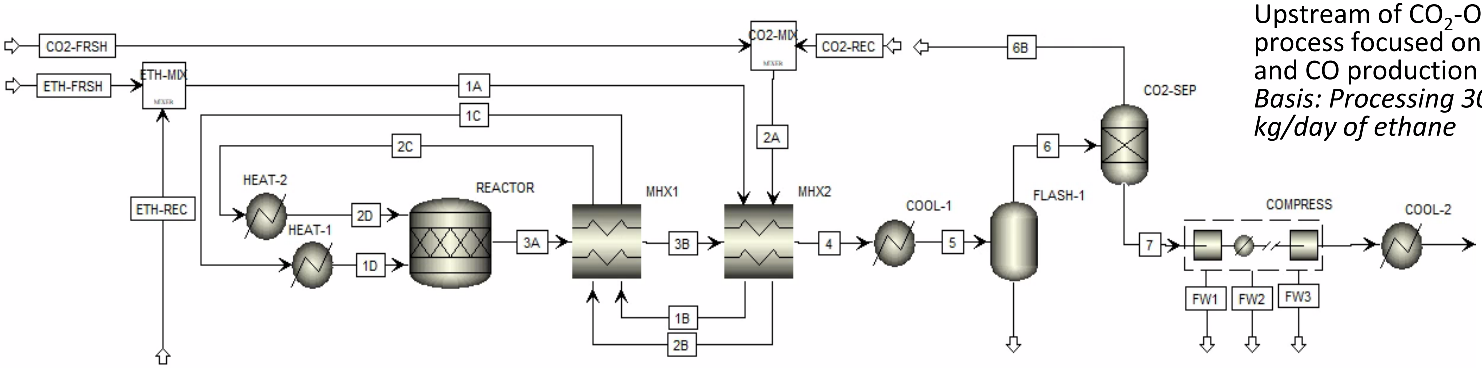
Milestone 2.2 *Catalyst Synthesis Screening*: four redox catalysts giving at least 80% selectivity and 50% yield for ethylene at <750 ºC, and 75% CO_2 conversion with 85% CO_2 capture)

Task 4 Techno-Economic and Lifecycle Analysis

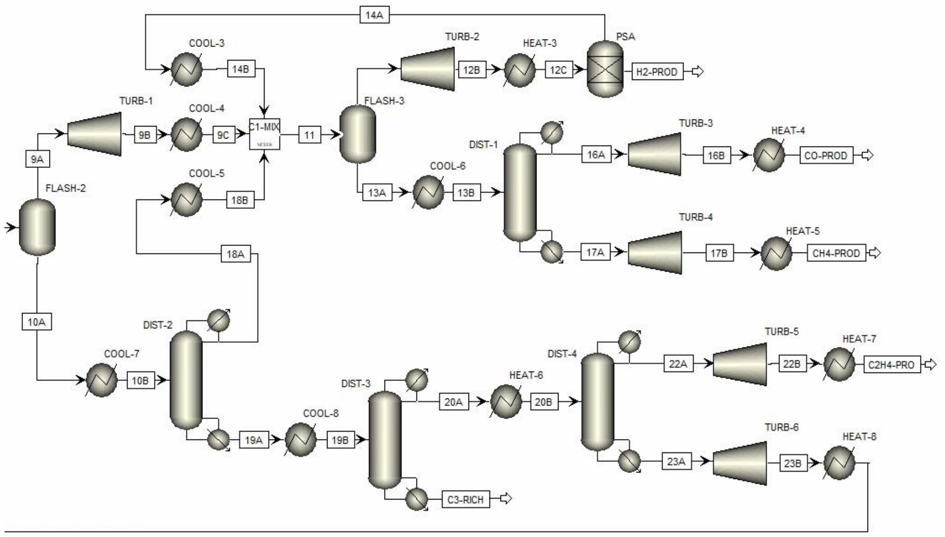
Susteon

Preliminary Process Models in AspenPlus™

Comparing ethane CO_2-ODH with MM-ODH



Upstream of CO_2-ODH process focused on olefin and CO production
Basis: Processing 3000 kg/day of ethane



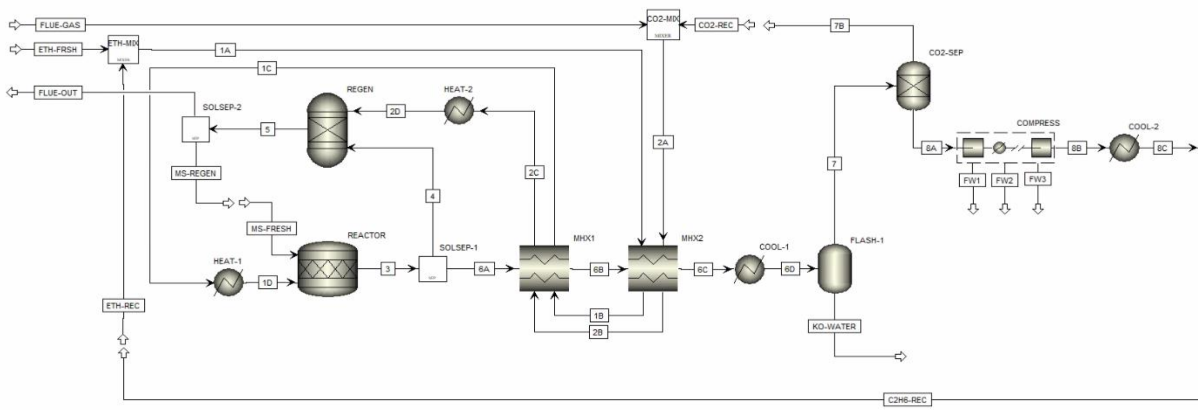
Downstream of CO_2-ODH process focused on olefin and CO purification

Working towards Milestone 4.1 *Initial TEA*: Initial TEA using preliminary results, process model, and literature review showing profitability at 20% ROI and 25% reduction in energy consumption.

Susteon

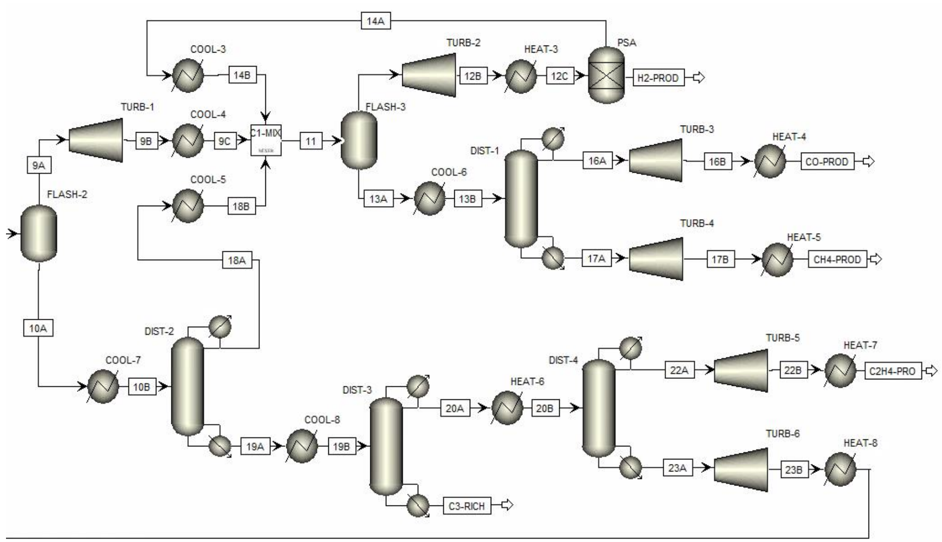
Preliminary Process Models in AspenPlus™

Comparing ethane CO_2-ODH with MM-ODH



Upstream of MM-ODH process focused on olefin and CO production

Basis: Processing 3000 kg/day of ethane



Downstream of MM-ODH process focused on olefin and CO purification (similar to CO_2-ODH)

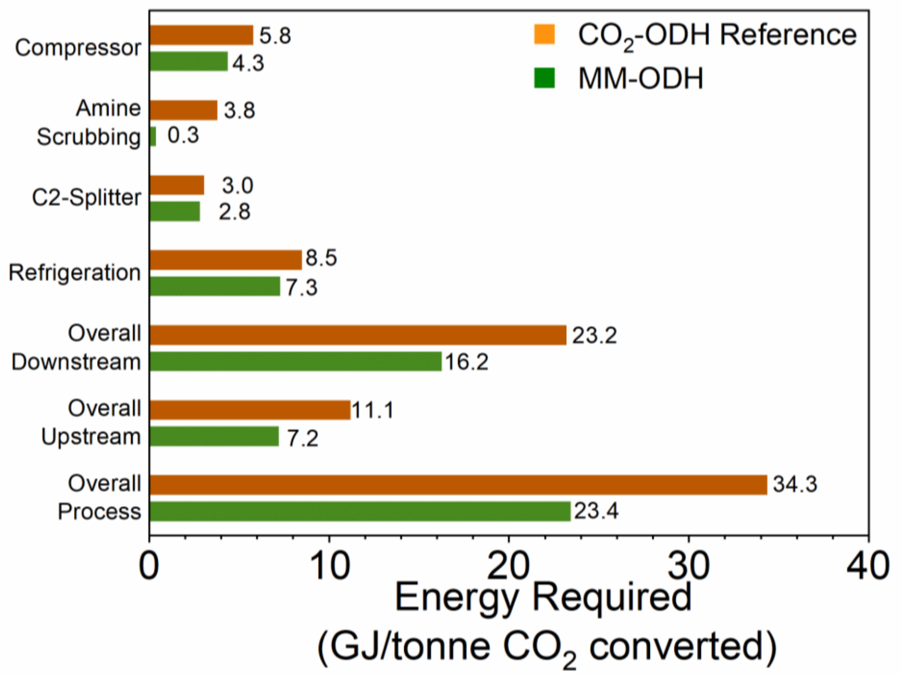
Working towards Milestone 4.1 *Initial TEA*: Initial TEA using preliminary results, process model, and literature review showing profitability at 20% ROI and 25% reduction in energy consumption.

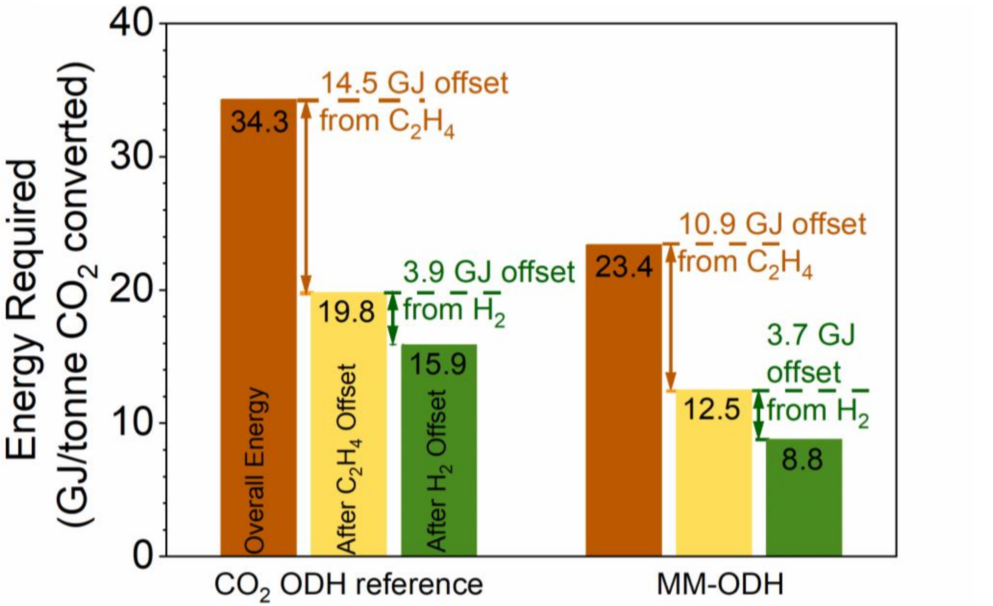
Task 4 Techno-Economic and Lifecycle Analysis

Susteon

Preliminary Process Models in AspenPlus™

Comparing ethane CO_2-ODH with MM-ODH





Working towards Milestone 4.1 *Initial TEA*: Initial TEA using preliminary results, process model, and literature review showing profitability at 20% ROI and 25% reduction in energy consumption.

Plans for Future Development

Future work within this project:

- Catalyst and reaction medium optimization;
- Long-term stability validation;
- Detailed reactor and system design for optimal performance;
- Scale-up and commercialization roadmap.

Future work beyond the project:

- Further scale up testing;
- Detailed reaction material cost and scalability study;
- Identification of commercialization partners;
- Demonstration and commercialization.

Summary Slide

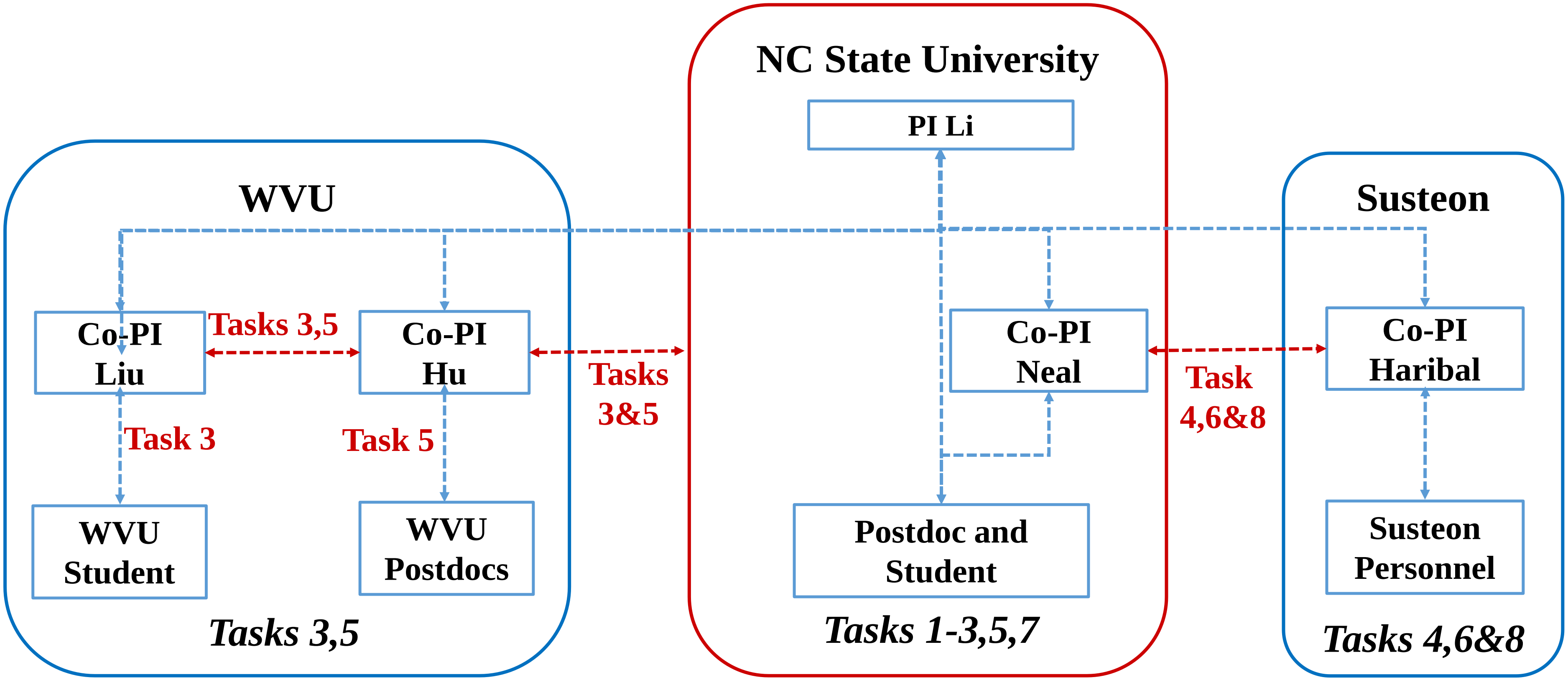
- Perovskite oxides with high porosity were prepared via reactive grinding, nanocasting and 3DOM methods;
- Oxide – molten salt compatibility were verified and reactive performance exceeded the targets in terms of ethane conversion/selectivity;
- Reactor material interaction with the salt caused delays, which was timely resolved;
- >4 reaction medium compositions were tested, with 80% average and >85% maximum CO2 capture, 90% CO_2 conversion, >90% ethylene selectivity, 65% ethylene yield. Meeting the proposed milestone;
- Preliminary TEA indicates potential for notable energy savings.

NC STATE UNIVERSITY

Appendix: Project Schedule and Milestones

Task Name	Team Member	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8
Task 1 Project Management and Planning	NCSU/Susteon								
Milestone 1.1: PMP modification	NCSU	◊							
Milestone 1.2: TMP	NCSU/Susteon	◊							
Task 2.0: Redox Catalyst Synthesis and Characterizations	NCSU								
Subtask 2.1 Redox Catalyst Synthesis	NCSU								
Subtask 2.2 Characterization of the Redox Catalysts	NCSU								
Milestone 2.2: Catalyst Synthesis Screening	NCSU		◊						
Task 3.0: Redox Catalyst Optimization	WVU/NCSU								
Subtask 3.1. Determination of Rate Limiting Step	WVU								
Subtask 3.2. Redox Catalyst Optimization	NCSU								
Milestone 3.2: Optimized Catalyst	NCSU				◊				
Task 4.0: Techno-Economic and Lifecycle Analysis	Susteon								
Subtask 4.1 Process Model Refinement and Analysis	Susteon								
Milestone 4.1: Initial TEA	Susteon				◊				
Subtask 4.2 Analysis of Alternative Commercial Products	Susteon								
Task 5.0: Long Term Stability, Flue Gas Contaminants and Kinetic Studies	NCSU/WVU								
Subtask 5.1. Long -Term Testing of Redox Catalysts	NCSU								
Milestone 5.1: 500 Cycle Tests	NCSU						◊		
Subtask 5.2 Kinetic Parameter Analysis and Reactor Sizing/Design	WVU								
Task 6.0: Techno-Economic and Life Cycle Analyses Update	Susteon								
Task 7.0: TEA-Driven Redox Catalyst Optimizations	NCSU								
Subtask 7.1 Redox Catalyst Optimization Based on TEA Feedback	NCSU								
Milestone 7.1: Refined reactor design	NCSU							◊	
Subtask 7.2 Synthesis Optimization of the Redox Catalysts	NCSU								
Task 8.0: Development of Detailed Reactor and Process Design	Susteon								
Milestone 8.1: Final TEA/LCA	Susteon								◊
Milestone 8.2: Commercialization Road Map	Susteon								◊

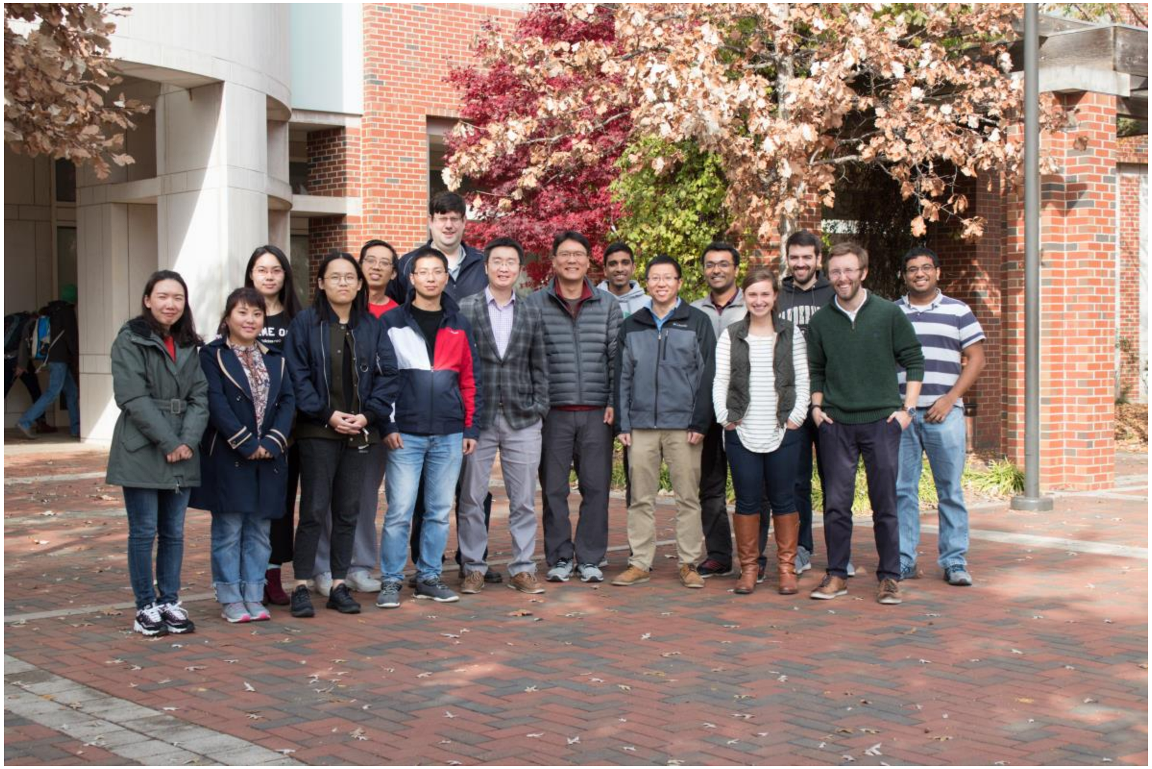
Appendix: Organization Chart



Appendix: Risk Management

Perceived Risk	Risk Rating Probability (Low, Med, High)	Impact	Overall	Mitigation/Response Strategy
Financial Risks:				
N/A	N/A	N/A	N/A	Project not dependent upon outside financing
Cost/Schedule Risks:				
Delayed/Extended negotiations	Med	Low	Low	Facilities are in place for rapid ramp up
Technical/Scope Risks:				
Insufficient MM-ODH catalyst performance	Low	High	Med	Develop a large library of redox catalyst materials and approaches; rationalized catalyst design based on molecular insights
Reactor Design for Molten Salts	Low	Med	Med	Catalyst particle design optimization (formulation and structure) can be incorporated to improve molten salt wetting and limit runoff
Management, Planning, and Oversight Risks:				
Delayed personnel ramp-up	Low	Low	Low	Sufficient personnel are in place and/or quickly filled (e.g. Ph.D. students) for the project.
ES&H Risks:				
N/A	N/A	N/A	N/A	Use of existing laboratory facilities and procedures
External Factor Risks:				
None/NA				

Acknowledgement



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Susteon:

Raghubir Gupta, Vasudev Haribal, Ryan Dudek

WVU:

John Hu, Sonit Balyan, Xingbo Liu, Wenyuan Li