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DE-FE0031918

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

Fanxing Li

NC State University

Project Partners: **West Virginia University and Susteon Inc.**

DOE/NETL Project Manager: **Gregory Imler**

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08/14/2023

Outline

- Project Overview and Technology Background
- Technical Approach and Key Results
- Future development plan
- Summary

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Project Overview

Period of Performance: 09/01/2020 - 08/31/2023

	DOE Funds	Cost Share
NC State Univ. *Dr. Fanxing Li*	*$519,993*	*$179,577*
West Virginia Univ. *Drs. John Hu and Xingbo Liu*	*$300,000*	*$75,000*
Susteon Inc. *Dr. Vasudev Haribal*	*$180,000*	*$0*
Total ($)	***$999,993***	***$254,577***

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.

Key Milestones

500 Cycle Test: >85% selectivity and 55% yield for ethylene, 85% CO_2 conversion, and 90% CO_2 capture after 500 cycles.

Refined Reactor Design: based upon 300+ cycle test of at least four temperatures and three cycle durations for an optimized redox catalyst.

TEA/LCA Targets: using optimized experimental results, process model, and pricing of major complements showing profitability at 20% ROI and 25% reduction in energy consumption.

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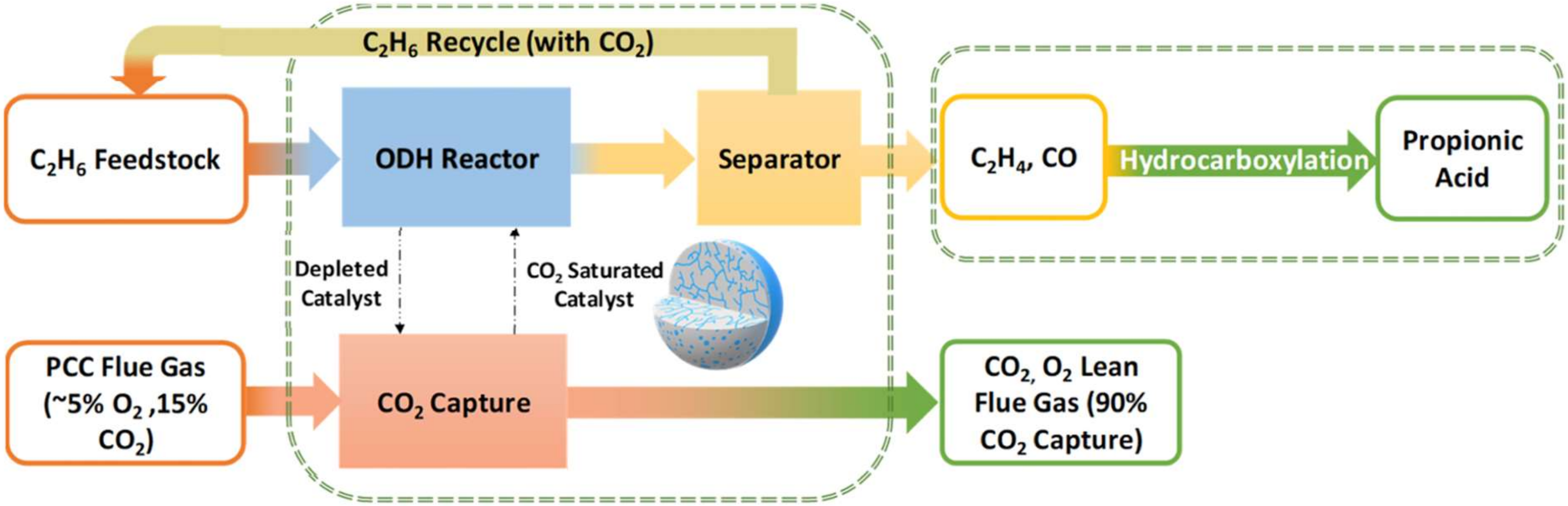
Technology Background: Molten-salt mediated oxidative dehydrogenation (MM-ODH) of ethane



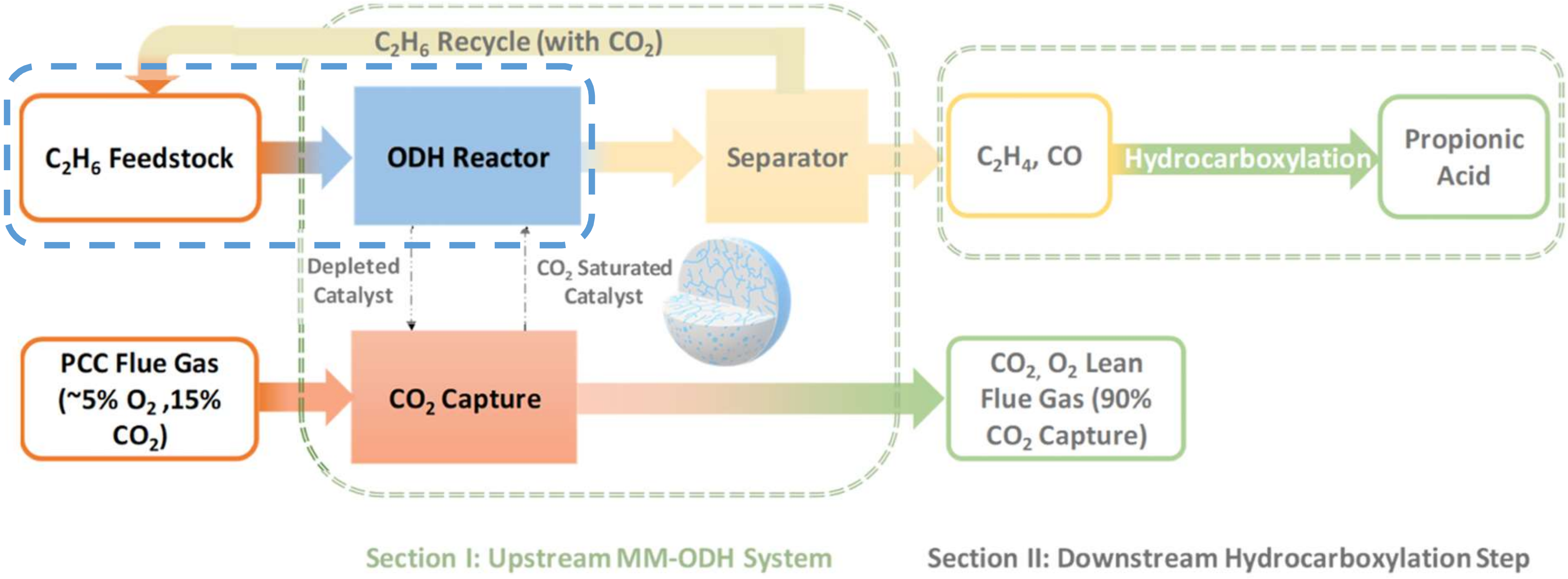
Section I: Upstream MM-ODH System

Section II: Downstream Hydrocarboxylation Step

Technology Background: Molten-salt mediated oxidative dehydrogenation (MM-ODH) of ethane

Molten Salt Mediated CO_2-ODH:

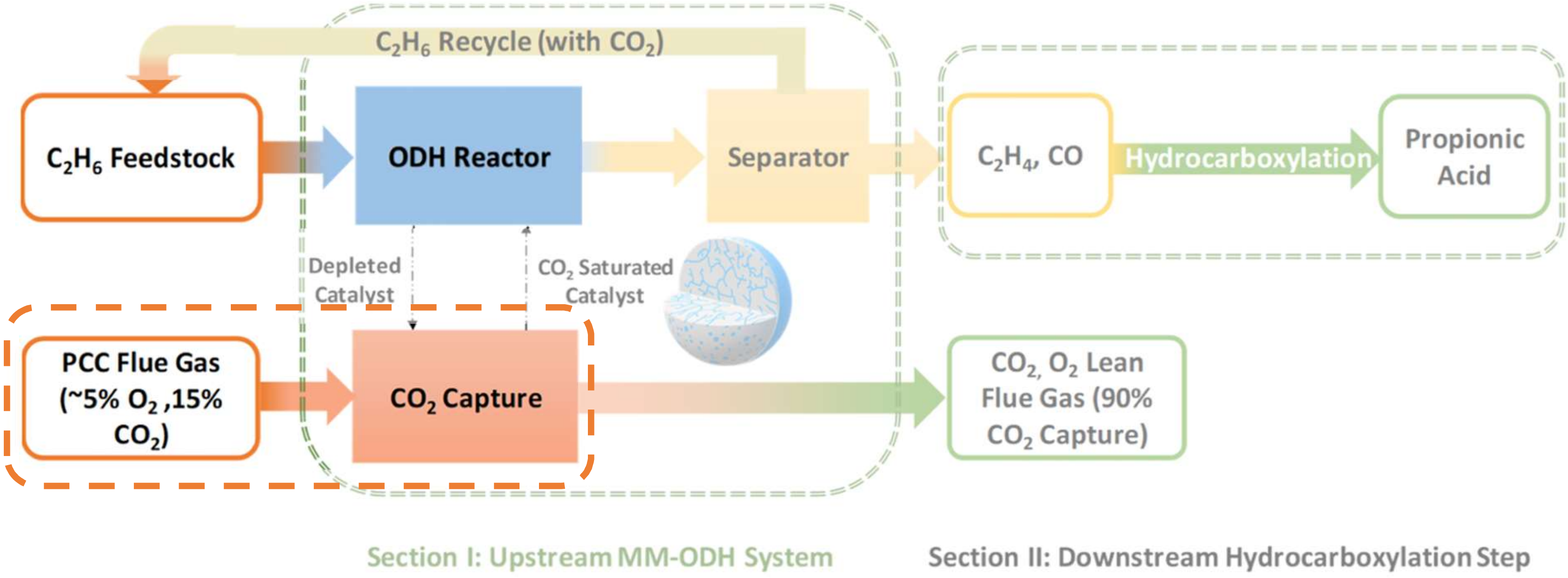
1) $C_2H_6 \rightleftharpoons C_2H_4 + H_2$	*Cracking/Dehydrogenation*
$H_2 + M_2CO_3 \rightleftharpoons 2MOH + H_2O + CO$	*Modified RWGS*
2) $C_2H_6 + MeO_x \rightleftharpoons C_2H_4 + H_2O + MeO_{x-1}$	*ODH*



Technology Background: Molten-salt mediated oxidative dehydrogenation (MM-ODH) of ethane

CO_2-Capture:

1) CO_2 (in flue gas) + 2MOH → $X_2CO_3 + H_2O$
2) MeO_{x-1} + ½O_2 (in flue gas) → MeO_x



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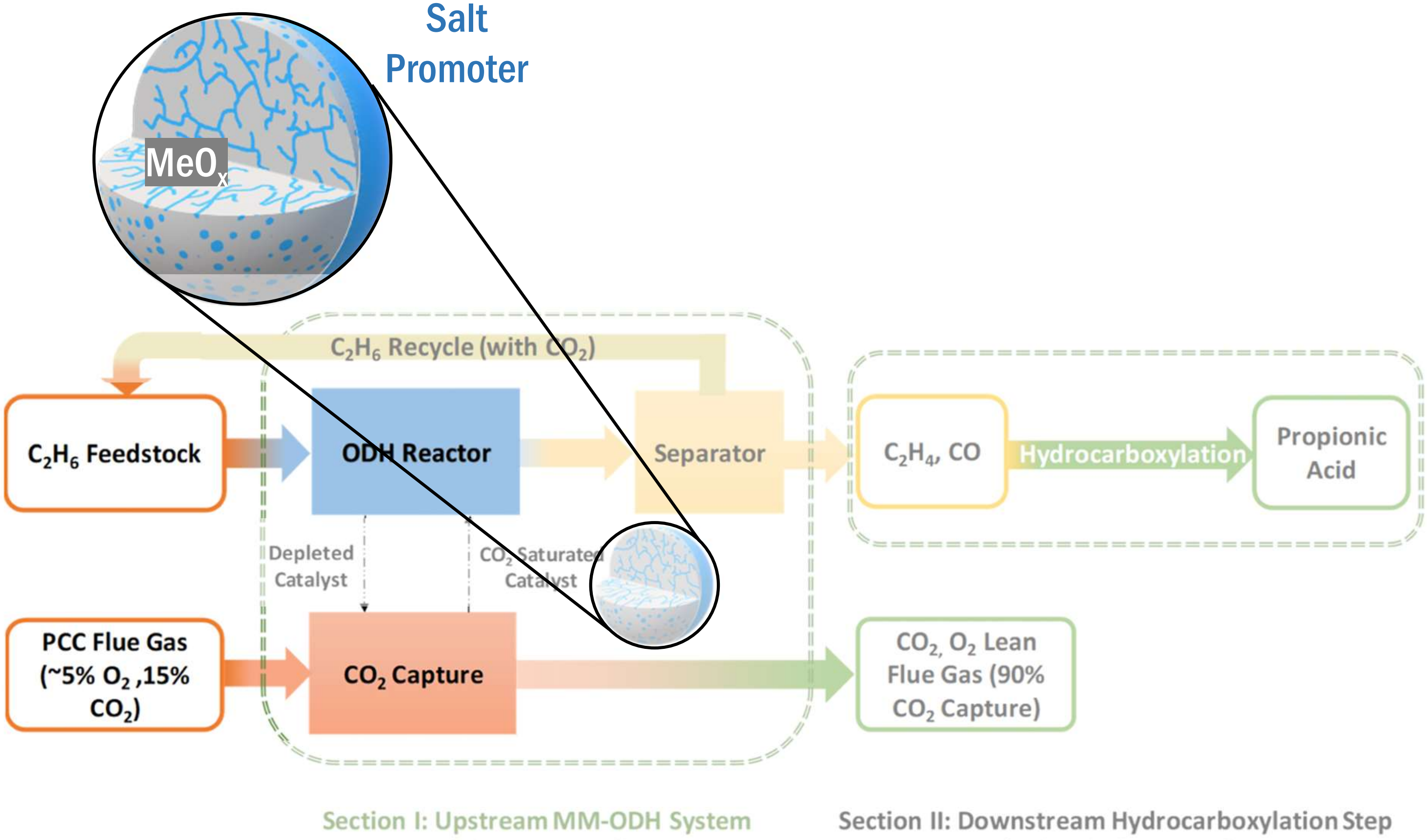

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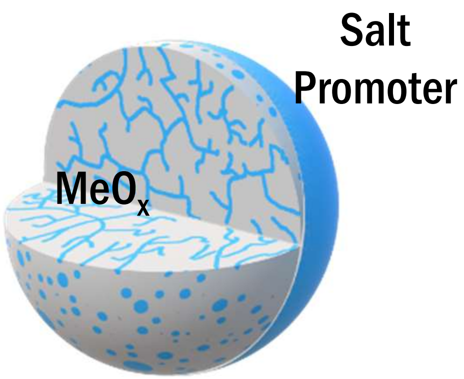
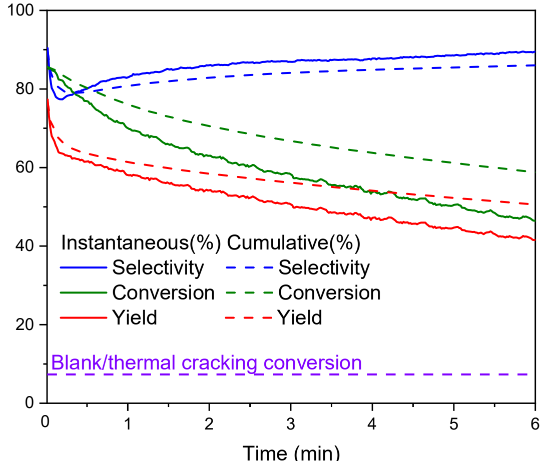
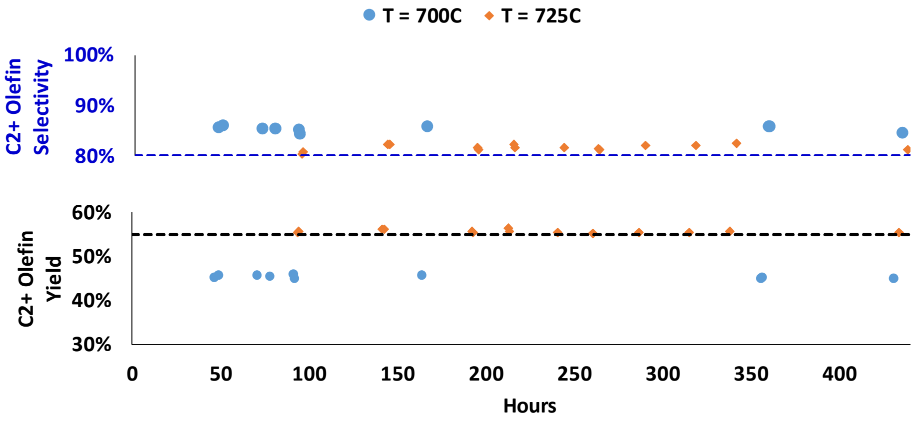
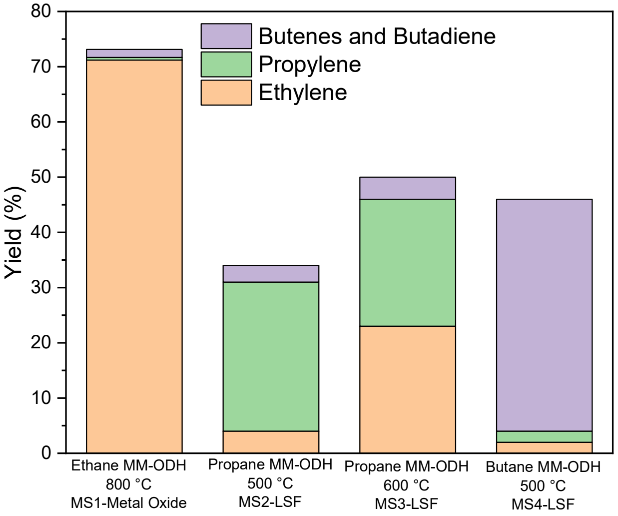
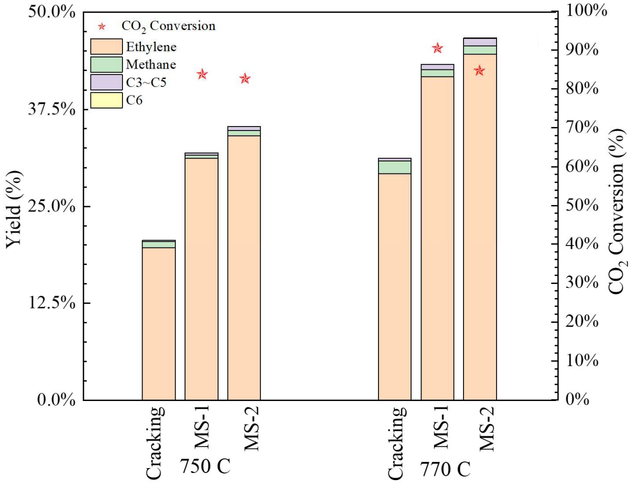
Preliminary Data for MM-ODH

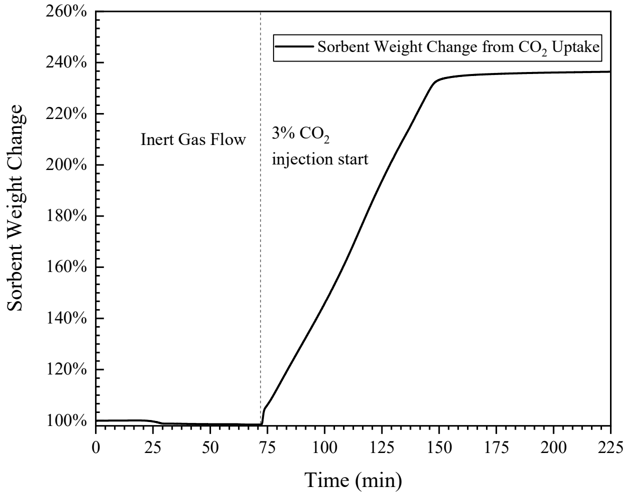












Gao et al, Science Advances 2020, eaaz9339

Gao et al, Science Advances 2022, eabo7343

Outline

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Technical Approach

Task 2 (Q1-Q4). Redox catalyst synthesis and characterizations (NCSU)
Milestone: 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 3 (Q2-Q11). Redox catalyst optimization (NCSU/WVU)
Milestone: two redox catalysts giving at least giving at least 85% selectivity and 55% yield for ethylene, 80% CO_2 conversion, and 90% CO_2 capture

Task 4 (Q1-Q4). Techno-economic and life cycle analysis (Susteon)
Milestone: using preliminary results, process model, and literature review showing profitability at 20% ROI and 25% reduction in energy consumption

Task 5(Q2-Q8). Redox catalyst long-term stability
Milestone: >85% selectivity and 55% yield for ethylene, 85% CO_2 conversion, and 90% CO_2 capture after 500 cycles

Task 6 (Q5-Q12). TEA update

Task 7 (Q6-Q12). TEA driven redox catalyst optimizations
Milestone: Refined reactor design based upon 300+ cycle test of at least four temperatures and three cycle durations for an optimized redox catalyst

Task 8(Q5-Q12). Detailed reactor and process design
Milestone: using optimized experimental results, process model, and pricing of major complements showing profitability at 20% ROI and 25% reduction in energy consumption); compile a commercialization roadmap.

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Success Criteria

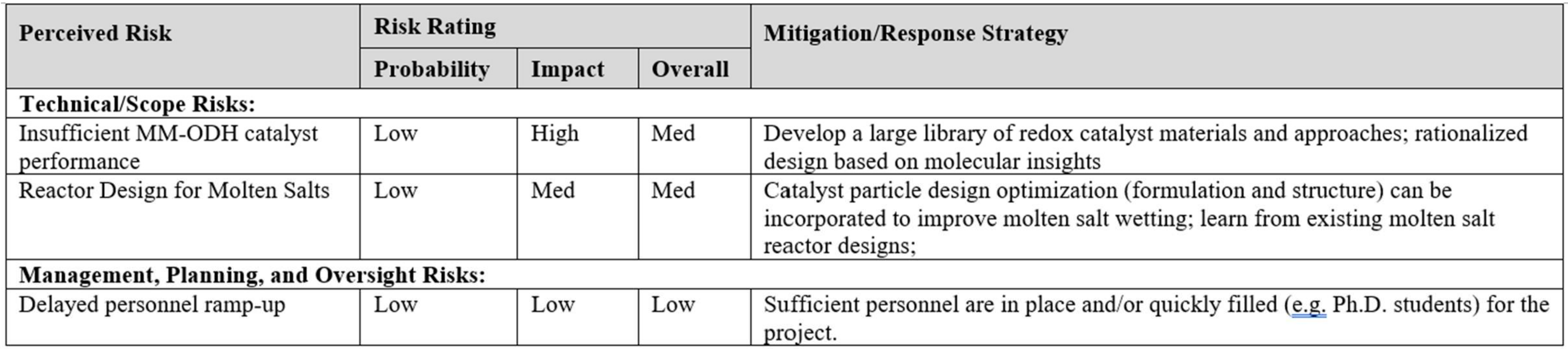
Milestone 3.2 (Q4): Two redox catalysts giving at least giving at least 85% selectivity and 55% yield for ethylene, 80% CO_2 conversion, and 90% CO_2 capture.

Milestone 4.1 (Q4): Initial TEA using preliminary results, process model, and literature review showing profitability at 20% ROI and 25% reduction in energy consumption.

Milestone 5.1 (Q6): 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.

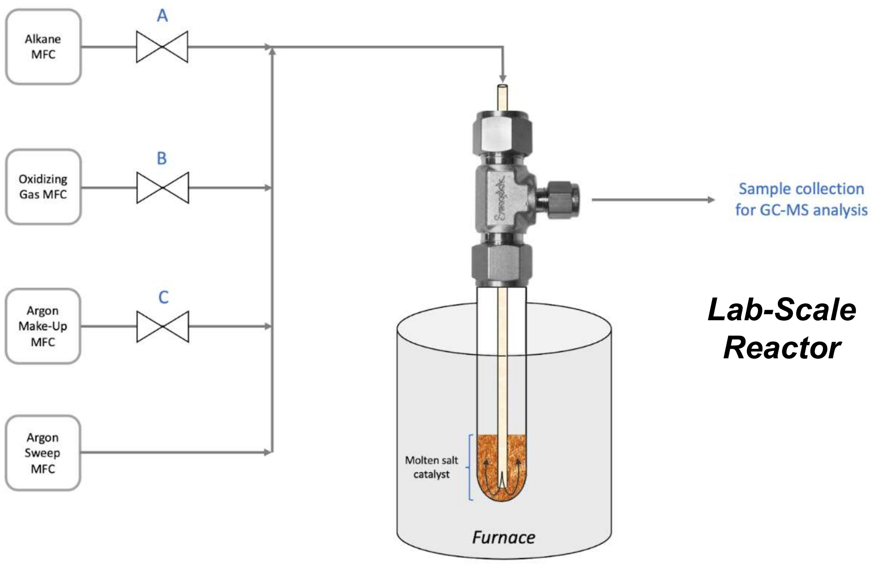
Milestone 8.1 (Q12): Developing a Final TEA/LCA using optimized experimental results, process model, and pricing of major complements showing profitability at 20% ROI and 25% reduction in energy consumption.

Risk Mitigation

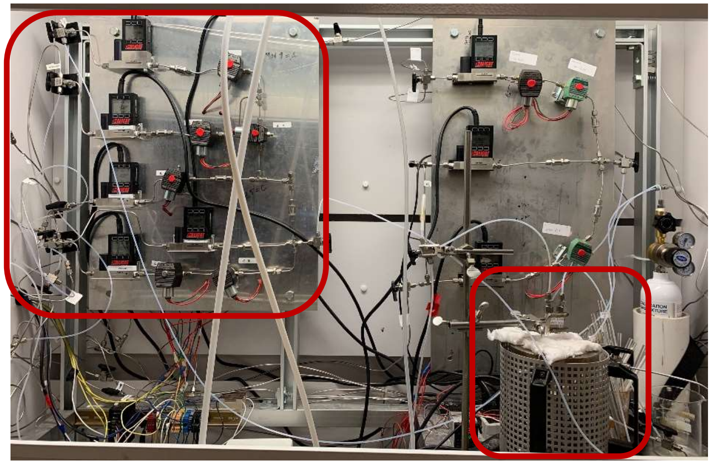


Perceived Risk	Risk Rating			Mitigation/Response Strategy
	Probability	Impact	Overall	
Technical/Scope Risks:				
Insufficient MM-ODH catalyst performance	Low	High	Med	Develop a large library of redox catalyst materials and approaches; rationalized design based on molecular insights
Reactor Design for Molten Salts	Low	Med	Med	Catalyst particle design optimization (formulation and structure) can be incorporated to improve molten salt wetting; learn from existing molten salt reactor designs;
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.

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

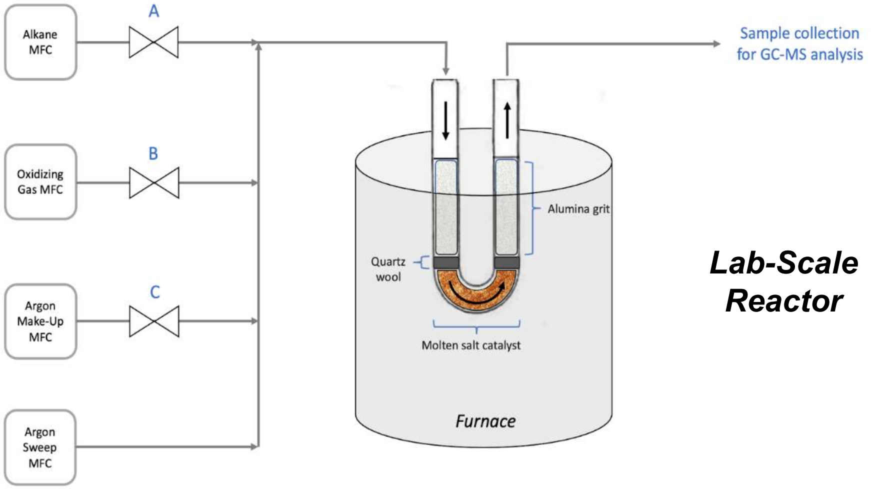
$MeO_{x-1} + 1/2O_2$ (in flue gas) → MeO_x

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 $CH_3\text{-}CH_2$)

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

Project Progress: Experimental Set-up



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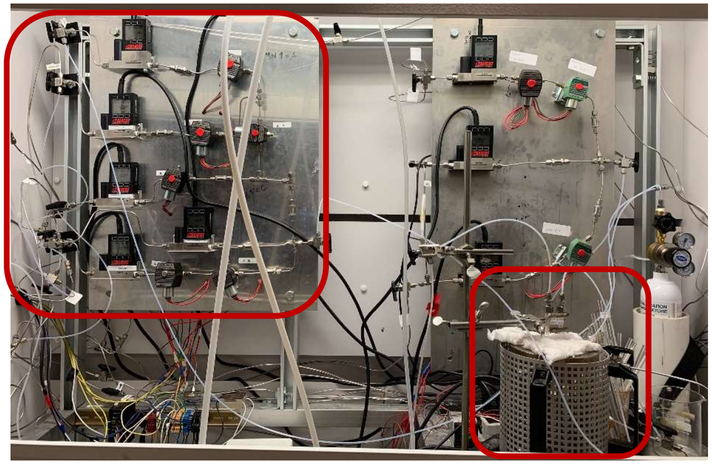

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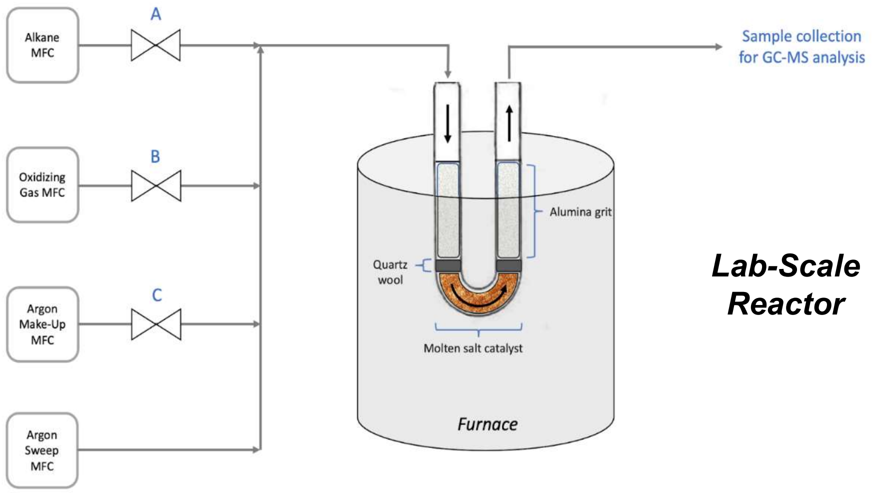

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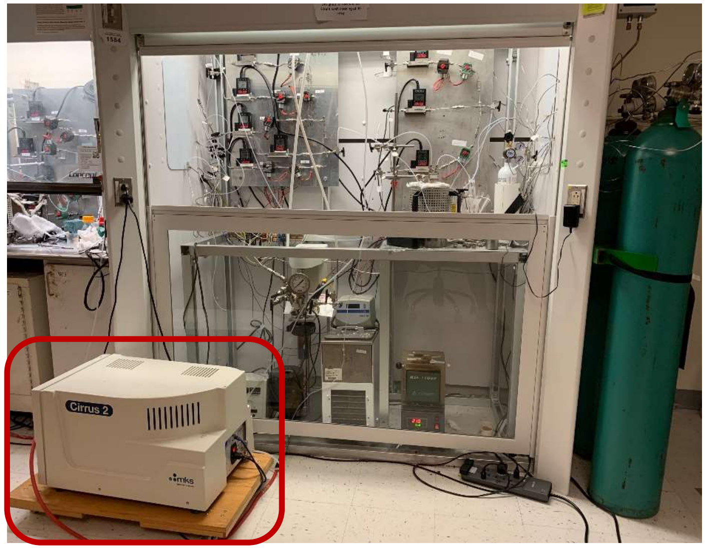

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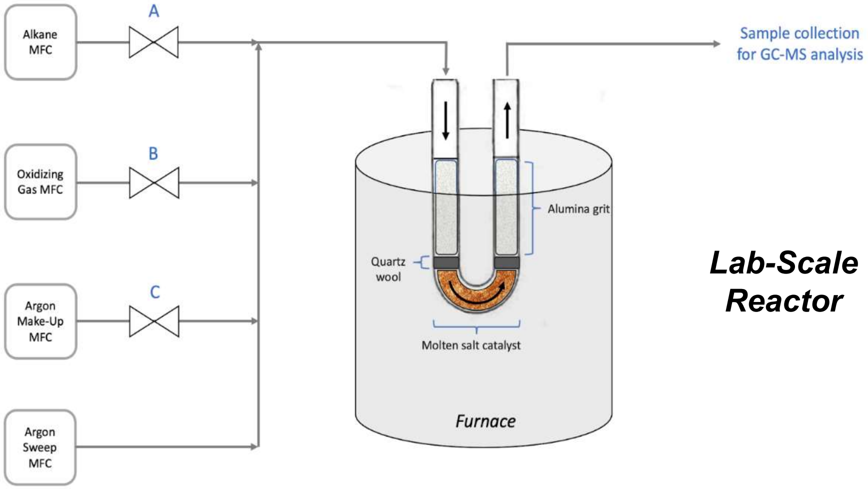

Lab-Scale Reactor

In-line QMS

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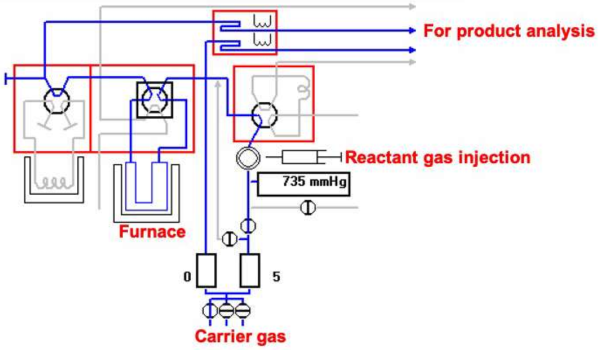
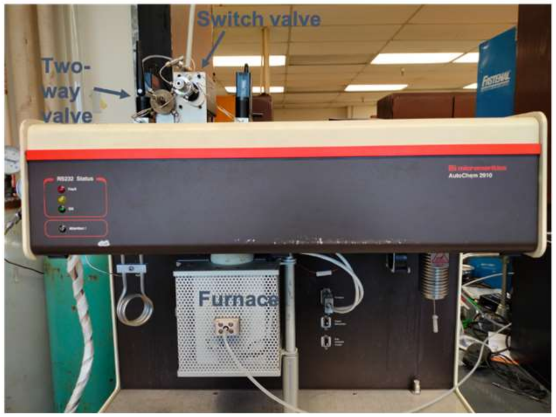
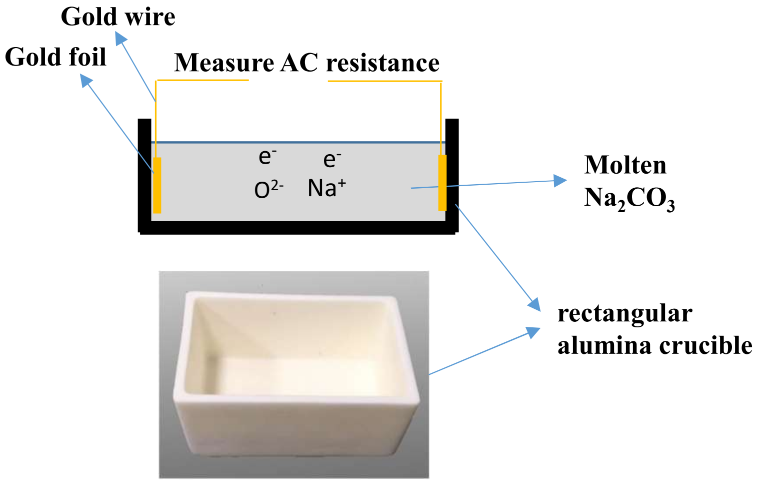
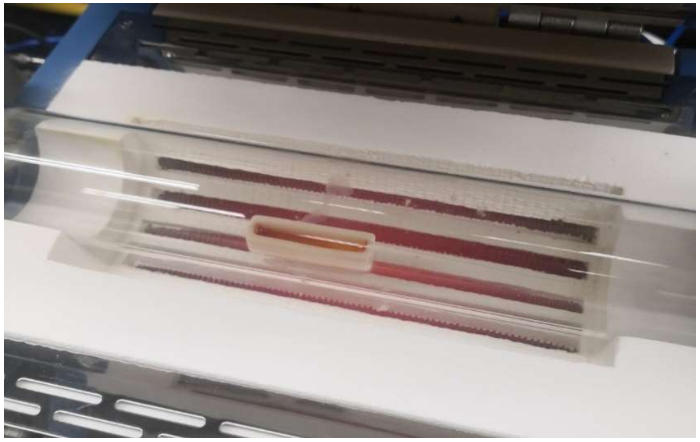
$R\text{-}CH_2\text{-}CH_3 + MeO_x \rightarrow R\text{-}CH{=}CH_2 + H_2O + MeO_{x-1}$

Project Progress: Experimental Set-up at WVU









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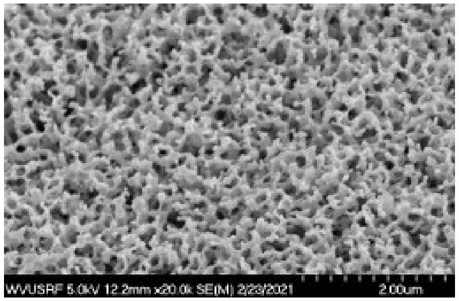
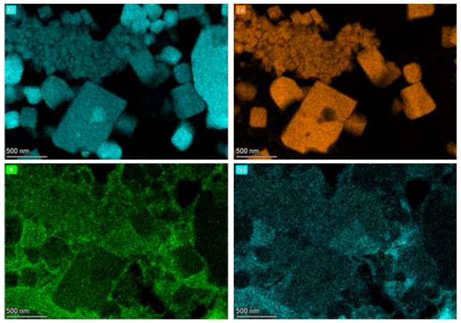
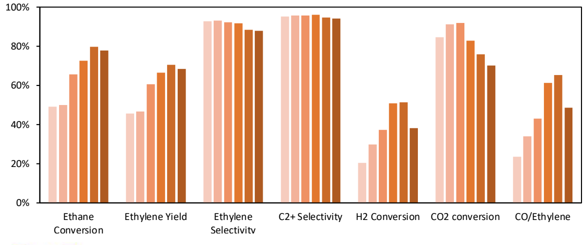
Overview of the Key Results

Material Synthesis, Testing, and Characterizations







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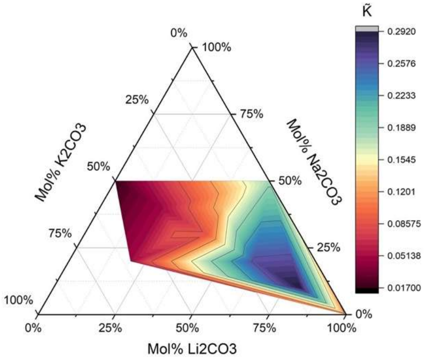
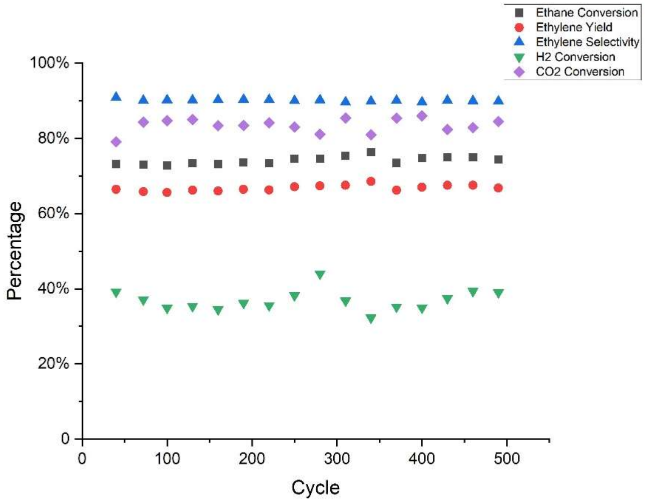
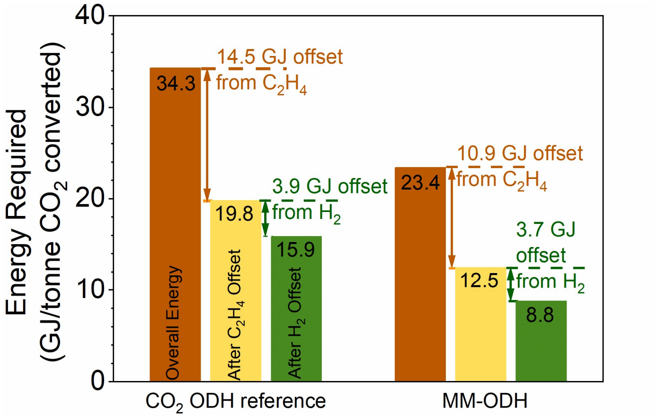
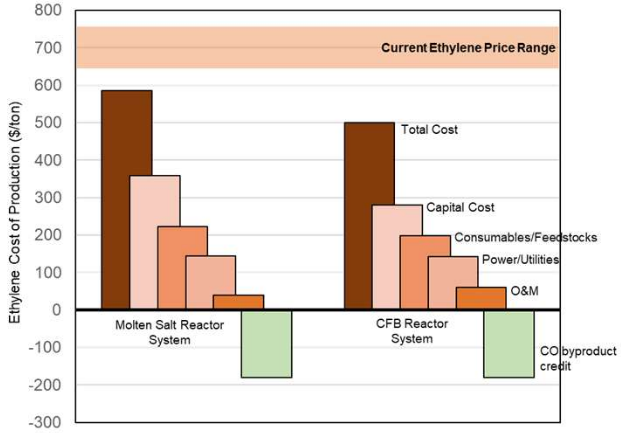
Material Optimizations and Long-Term Stability





Techno-Economics and System Design

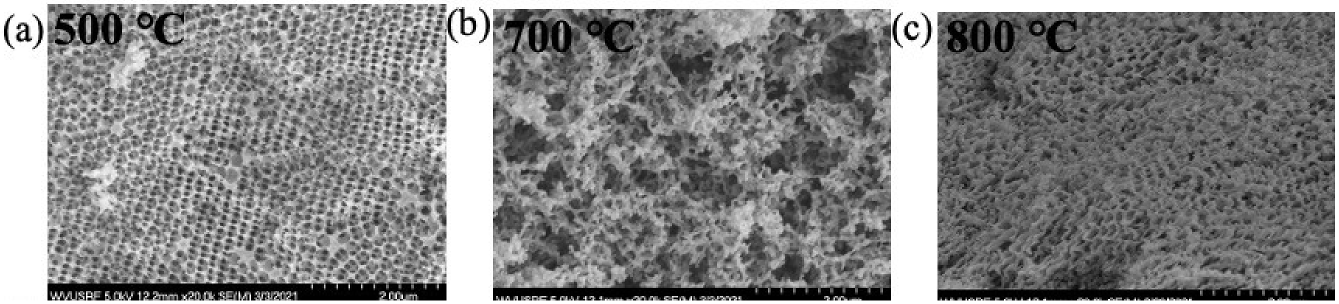




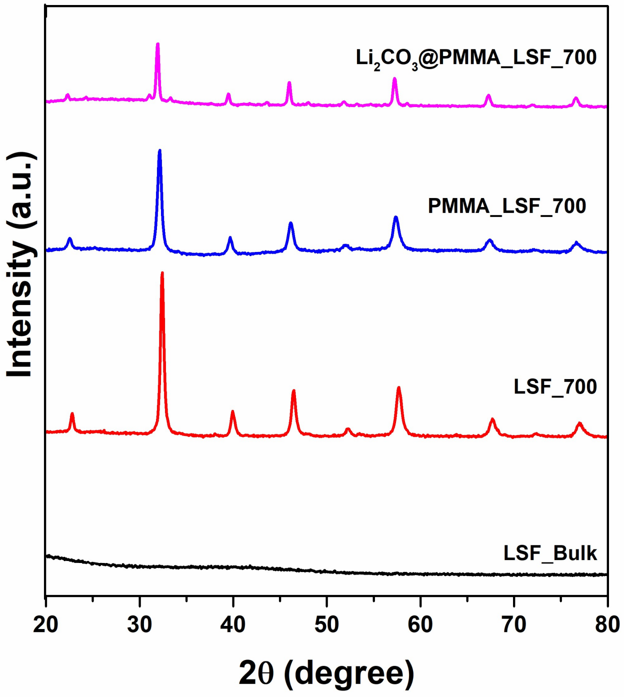
Susteon

Task 2 Redox Catalyst Synthesis and Characterizations

Porous Oxide Synthesis



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%**



XRD analysis of the synthesized catalysts

OBSERVATIONS:

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

Task 2 Redox Catalyst Synthesis and Characterizations

Effect of Ethane Space velocity

Reactive Performance

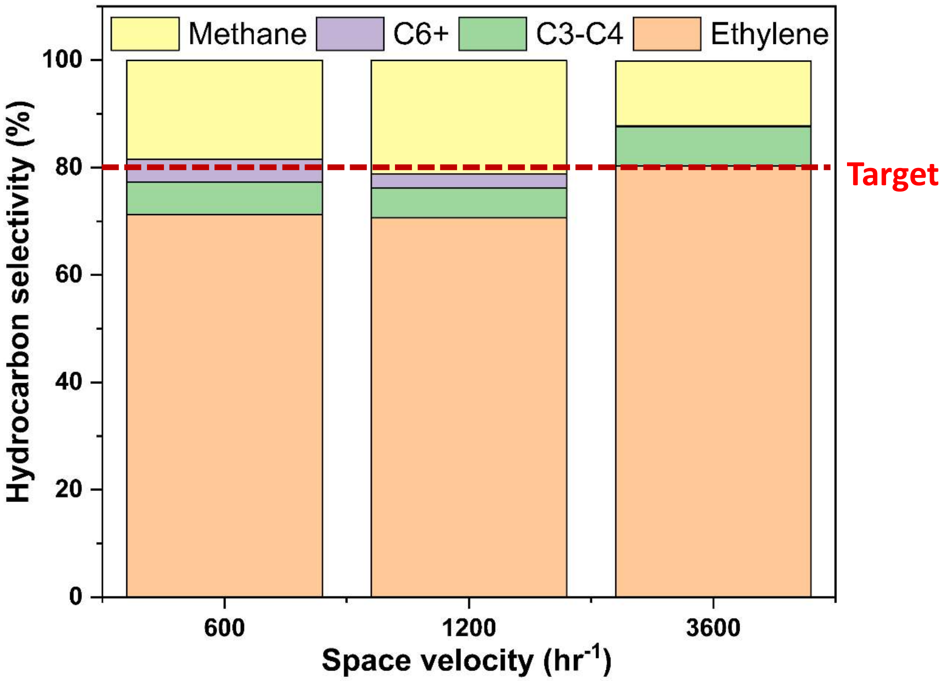


Figure: Hydrocarbon Product distribution during ethane injection (5th injection cycle)

Catalyst: **60%Li_2CO_3@LSF**, Temperature: 750 °C

Injection: Reducing agent: 30 sec, Oxidizing agent: 90 sec

Oxygenate S.V = 600 hr-1

60% Li_2CO_3/ LSF	Ethane Conv. (%)	Ethylene Select. (%)	Methane Select (%)	H_2 Conv. (%)	CO_2 Conv. (%)	CO_2 Capture (%)
600	71.5	71.2	18.4	39	**93.7**	36.4
1200	70.5	70.6	21.3	27	**93.4**	44.5
3600	67.5	**80.3**	12	28	**93.8**	48.1

- Increase in residence time promotes ethylene side reaction which results in decrease of ethylene selectivity
- Increase in space velocity hydrogen produced would have less time to react with CO_2 in the molten salt, resulting in lower H_2 conversion
- Ethylene yield at 3600 hr^{-1} SV is **~55 %**

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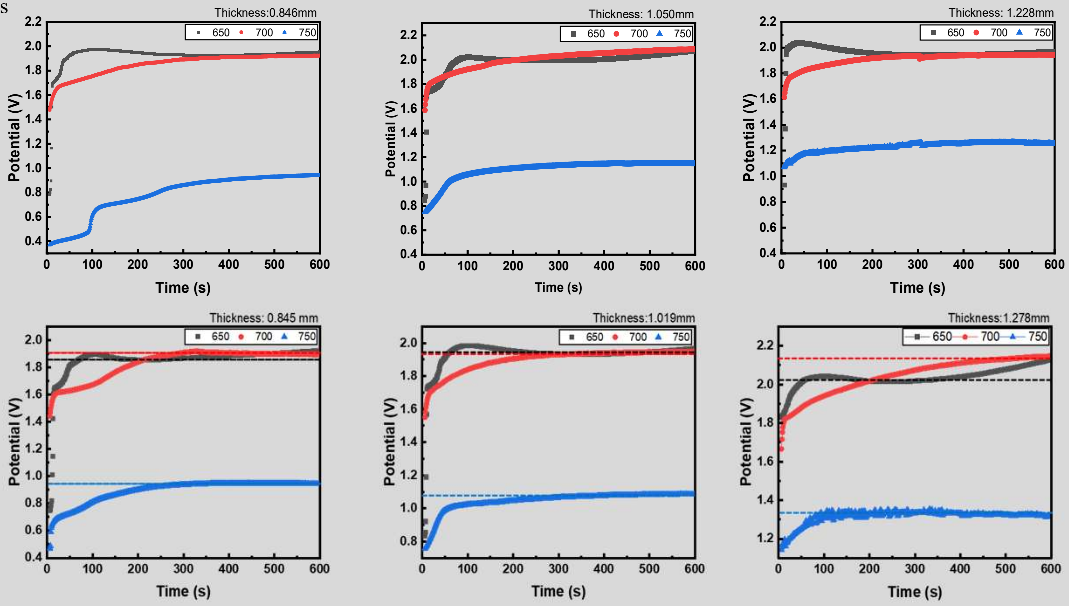
Task 2 Redox Catalyst Synthesis and Characterizations

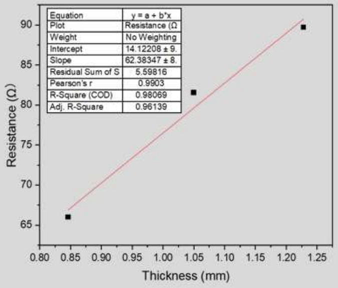
Porous samples

Batch 1

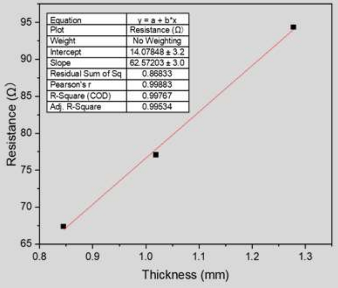
Batch 2



Test Result



Equation	y = a + b*x
Plot	Resistance (Ω
Weight	No Weighting
Intercept	14.12208 ± 9.
Slope	62.38347 ± 8.
Residual Sum of S	5.59816
Pearson's r	0.9903
R-Square (COD)	0.98069
Adj. R-Square	0.96139

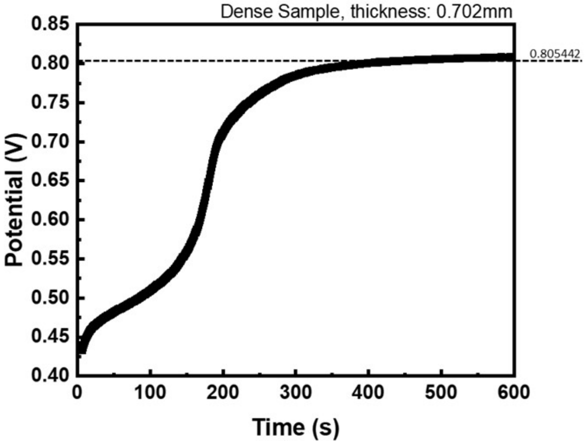


Equation	y = a + b*x
Plot	Resistance (Ω)
Weight	No Weighting
Intercept	14.07848 ± 3.2
Slope	62.57203 ± 3.0
Residual Sum of Sq	0.86833
Pearson's r	0.99883
R-Square (COD)	0.99767
Adj. R-Square	0.99534

Fitting Result

Batch 1

Batch 2

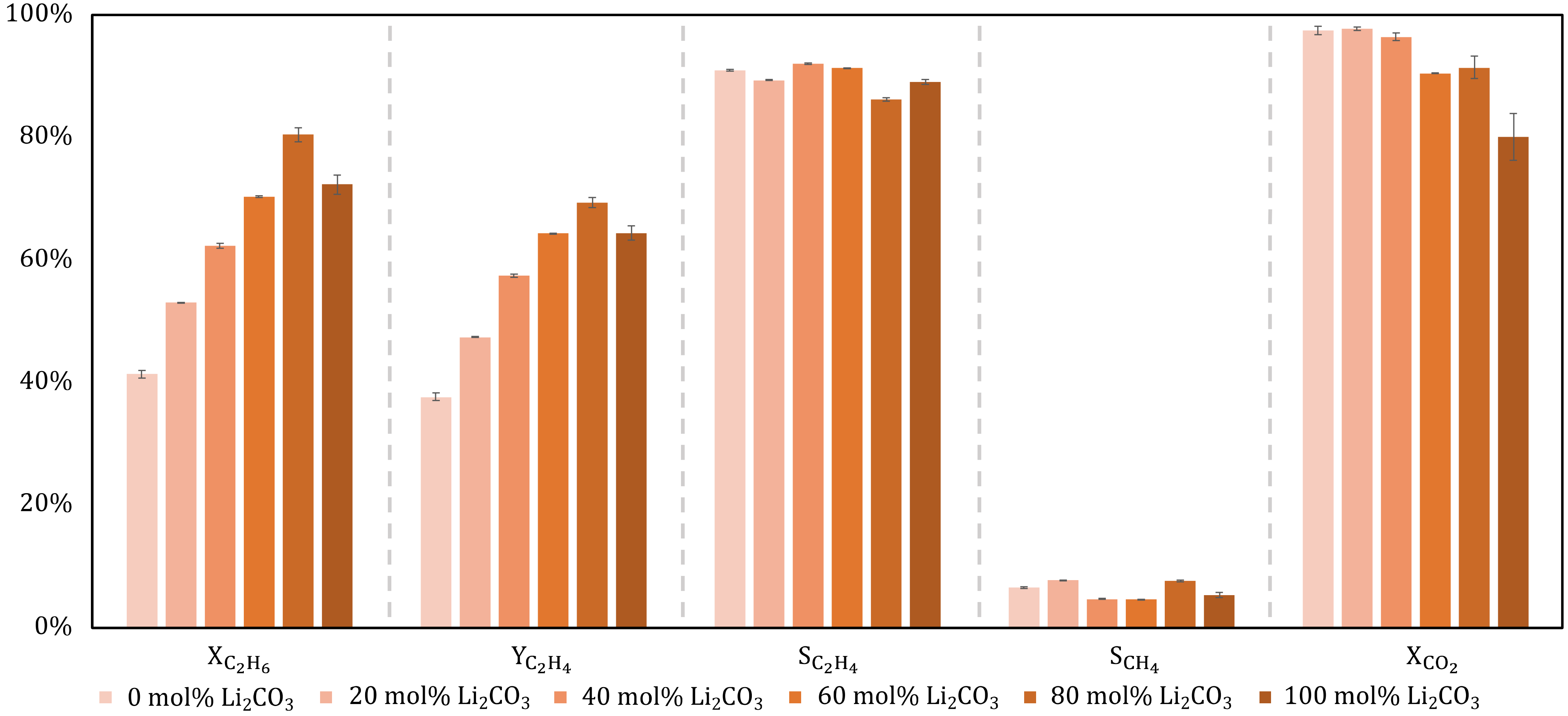


- According to the dense sample, the electronic resistance is 57.43 Ω·cm^2.
- Electronic conductivity =1.22x10^{-3} S/cm
- According to the fitting result: y = 62.48x+14.10, when the thickness is 0.702mm, the mixed resistance is 43.86 Ω·cm^2.
- Electron-oxygen mixed conductivity =1.60x10^{-3} S/cm
- Oxygen conductivity can be calculated as 3.8x10^{-4} S/cm

Small variables such as the fineness of the zirconia powder and the uniformity of the graphite-gold paste mixture can lead to poor repeatability or unstable test data, making experiments challenging.

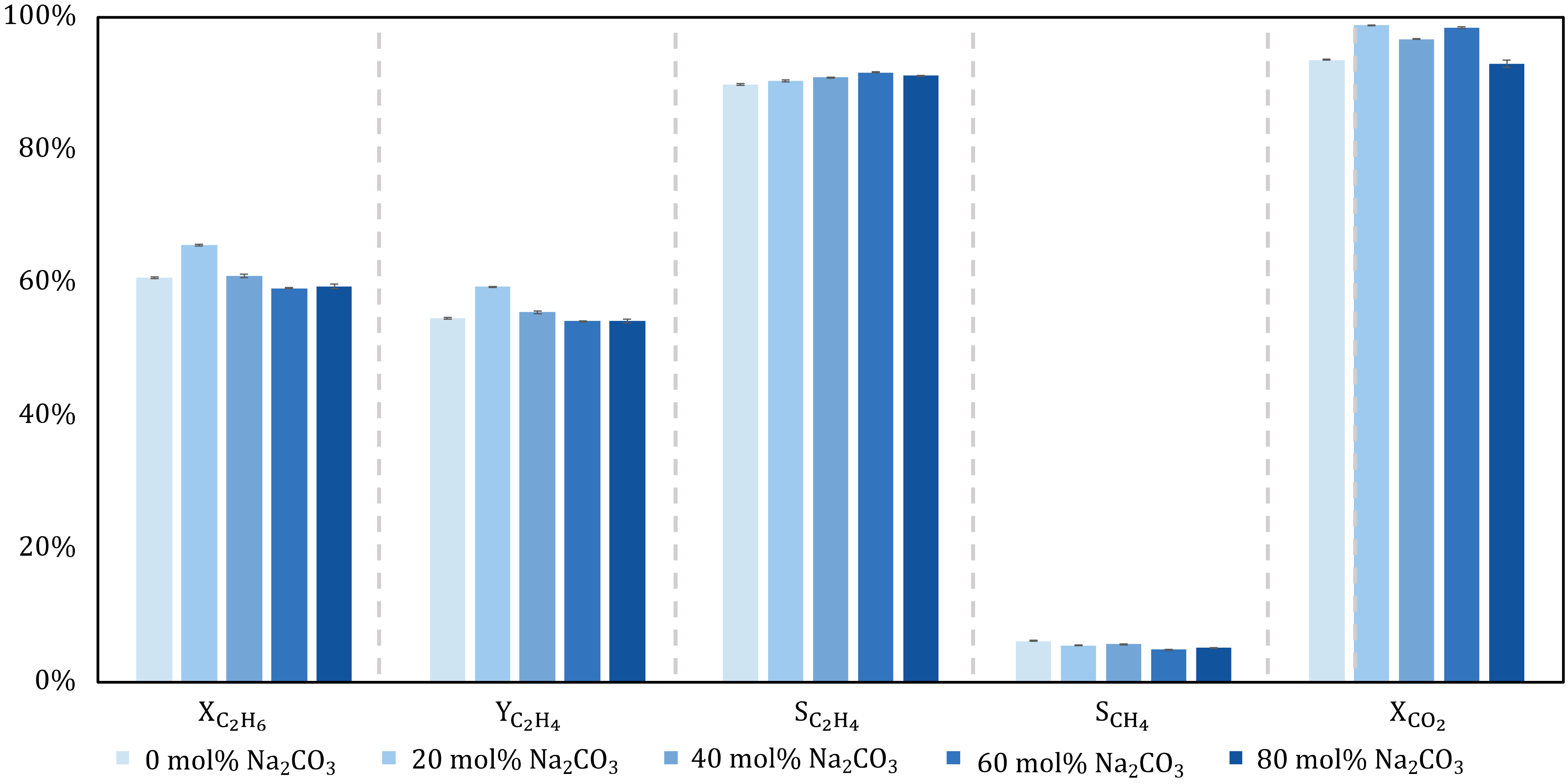
Task 3: Redox Catalyst Optimizations

Increasing the mol% of Li_2CO_3 improves ethane conversion and ethylene yield and decreases CO_2 conversion (except for 100% Li_2CO_3).



Task 3 Redox Catalyst Optimizations

Increasing the mol% of Na_2CO_3 does not significantly impact MM-ODH performance.



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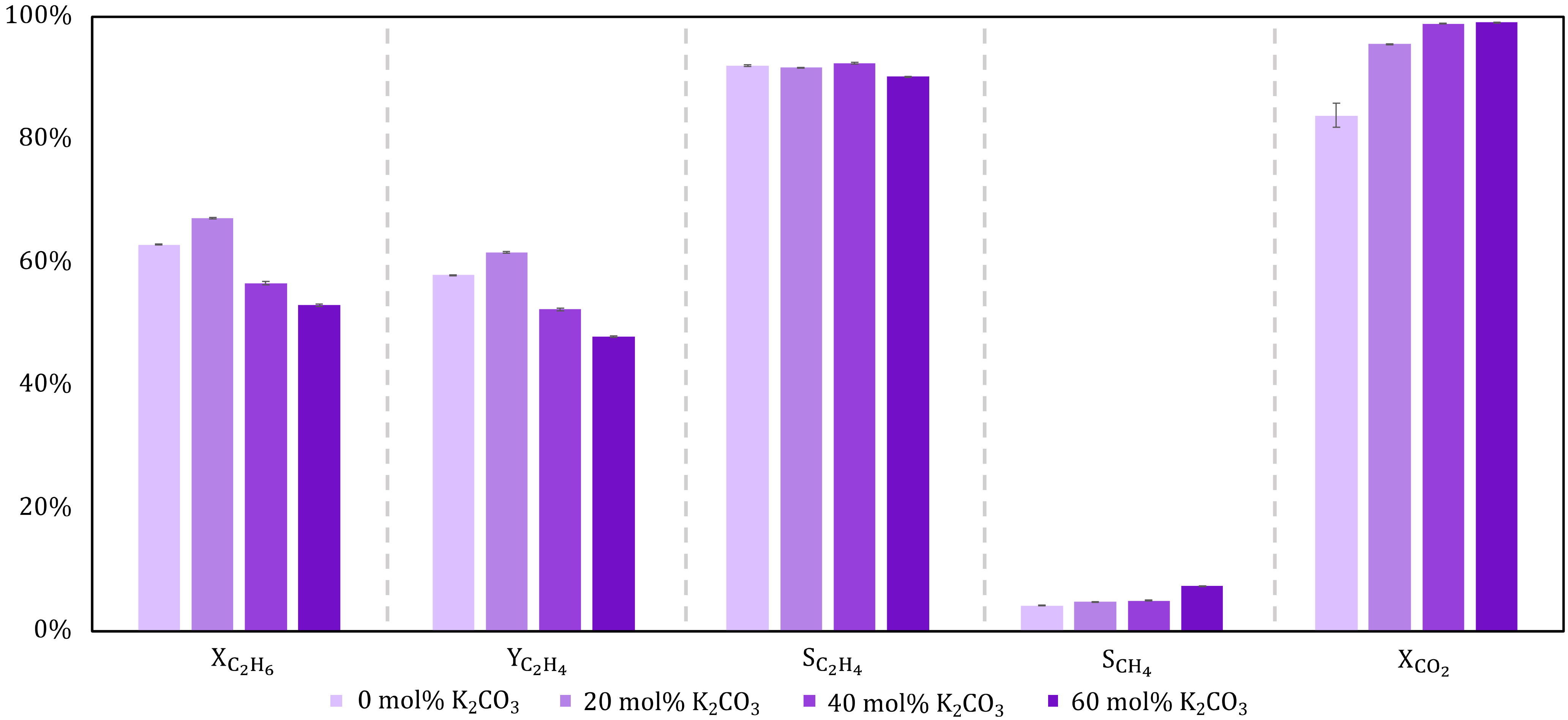
Task 3 Redox Catalyst Optimizations

Increasing the mol% of K_2CO_3 decreases ethane conversion but increases CO_2 conversion



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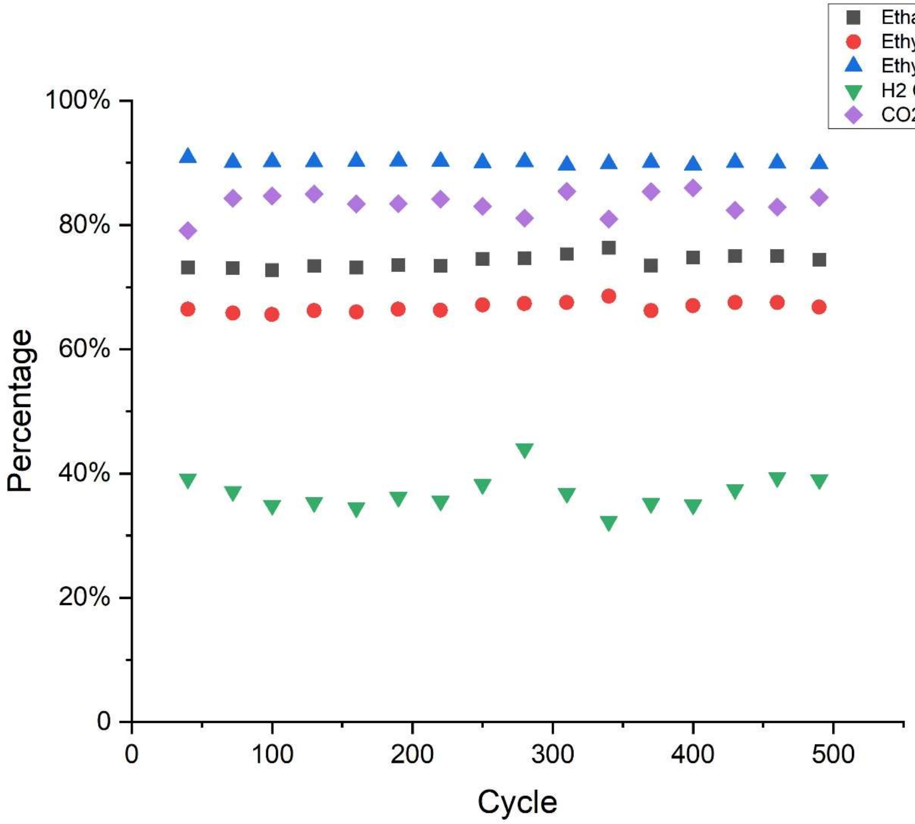
Task 3 Redox Catalyst Optimizations

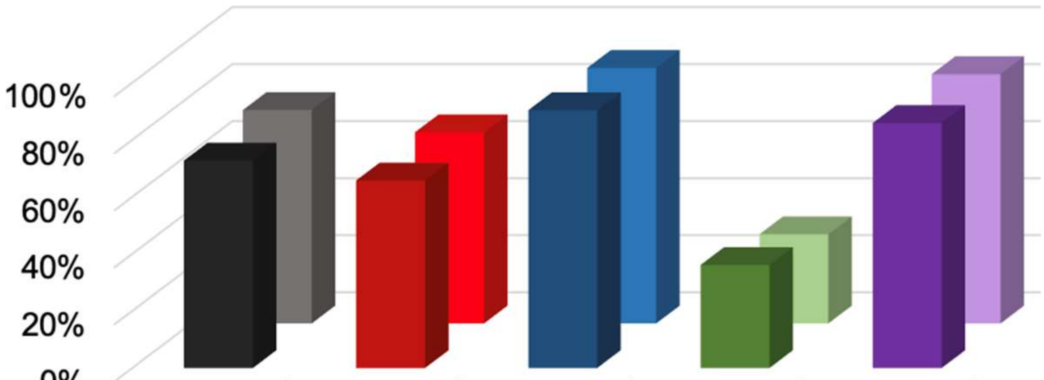
Catalyst	Reaction Metric	Current Performance	DOE Milestone
1) Molten LNK-LSF slurry	Temperature	750^{o}C	$\leq$ 750^{o}C
	Ethylene Yield	~55%	$\geq$ 50%
	Ethylene Selectivity	~81%	$\geq$ 80%
	CO_2 Conversion	~93%	$\geq$ 75%
	CO_2 Capture	~50%	$\geq$ 85%
2) Molten LNK bath with two compositions (80-10-10 and 100-0-0)*	Temperature	800^{o}C	$\leq$ 750^{o}C
	Ethylene Yield	69.5%/64.4%	$\geq$ 50%
	Ethylene Selectivity	86.3%/89.1%	$\geq$ 80%
	CO_2 Conversion	91.4%/80.2%	$\geq$ 75%
	CO_2 Capture	**>85%**	$\geq$ 85%

*x mol% Li_2CO_3 – y mol% Na_2CO_3 – z mol% K_2CO_3

Milestone 2.2 ***Catalyst Synthesis Screening*****:** Report 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 5 Long-Term Stability of the Molten Salt (60 – 20 – 20)





	X_{C2H6}	Y_{C2H4}	S_{C2H4}	X_{H2}	X_{CO2}
Cycle 10	72.7%	65.7%	90.4%	36.1%	85.9%
Cycle 500	74.8%	67.0%	89.6%	31.3%	87.4%

Excellent stability was observed throughout the 500 reaction cycles

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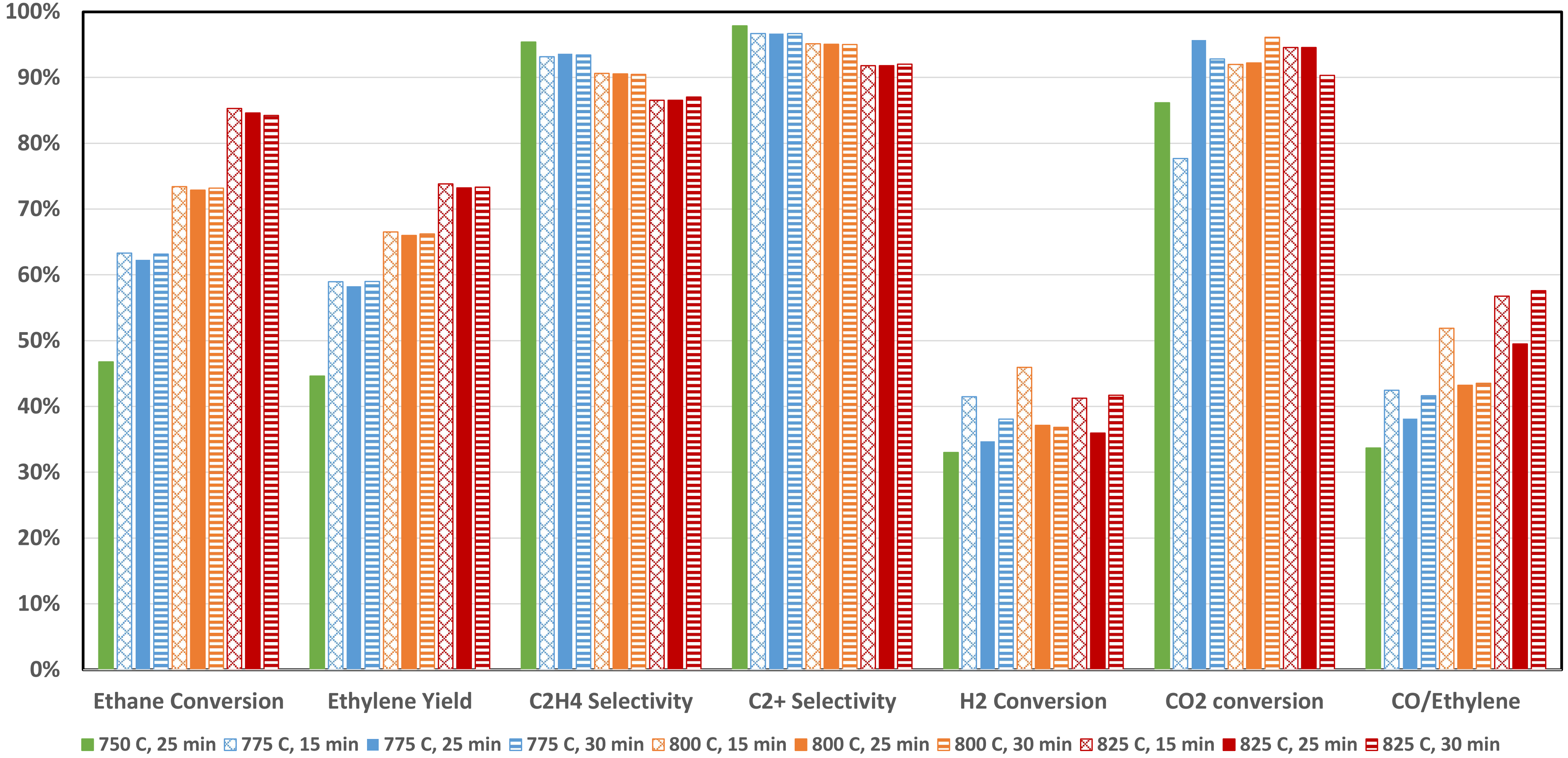
Task 7 TEA-driven redox catalyst optimizations



Ethylene yield improves with temperature and MM-ODH is pretty flexible with cycle time

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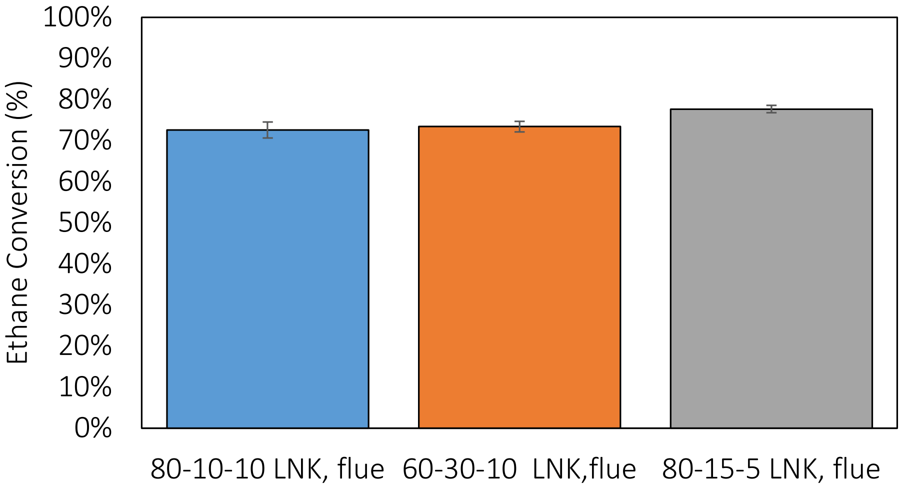
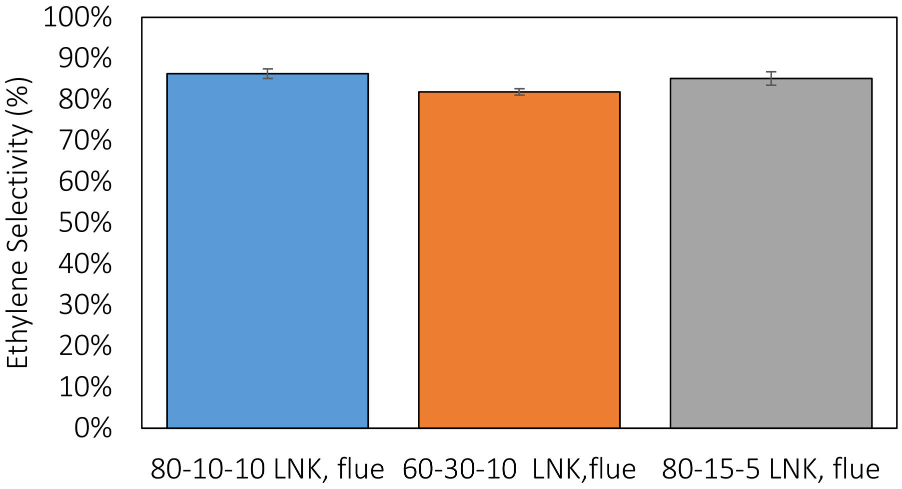
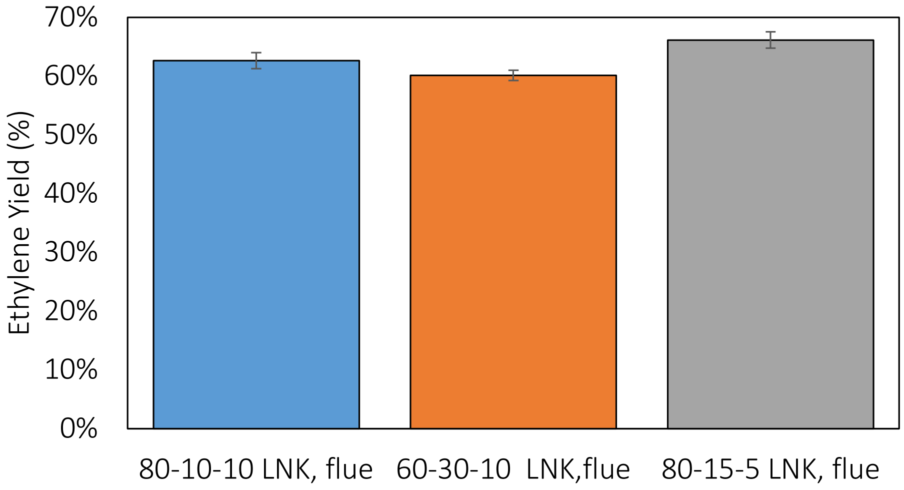
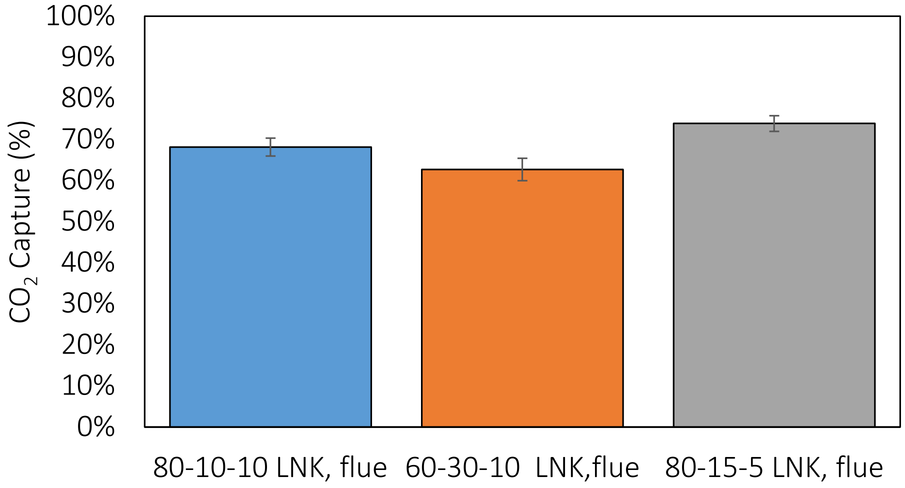
Task 7 Redox Catalyst Optimizations







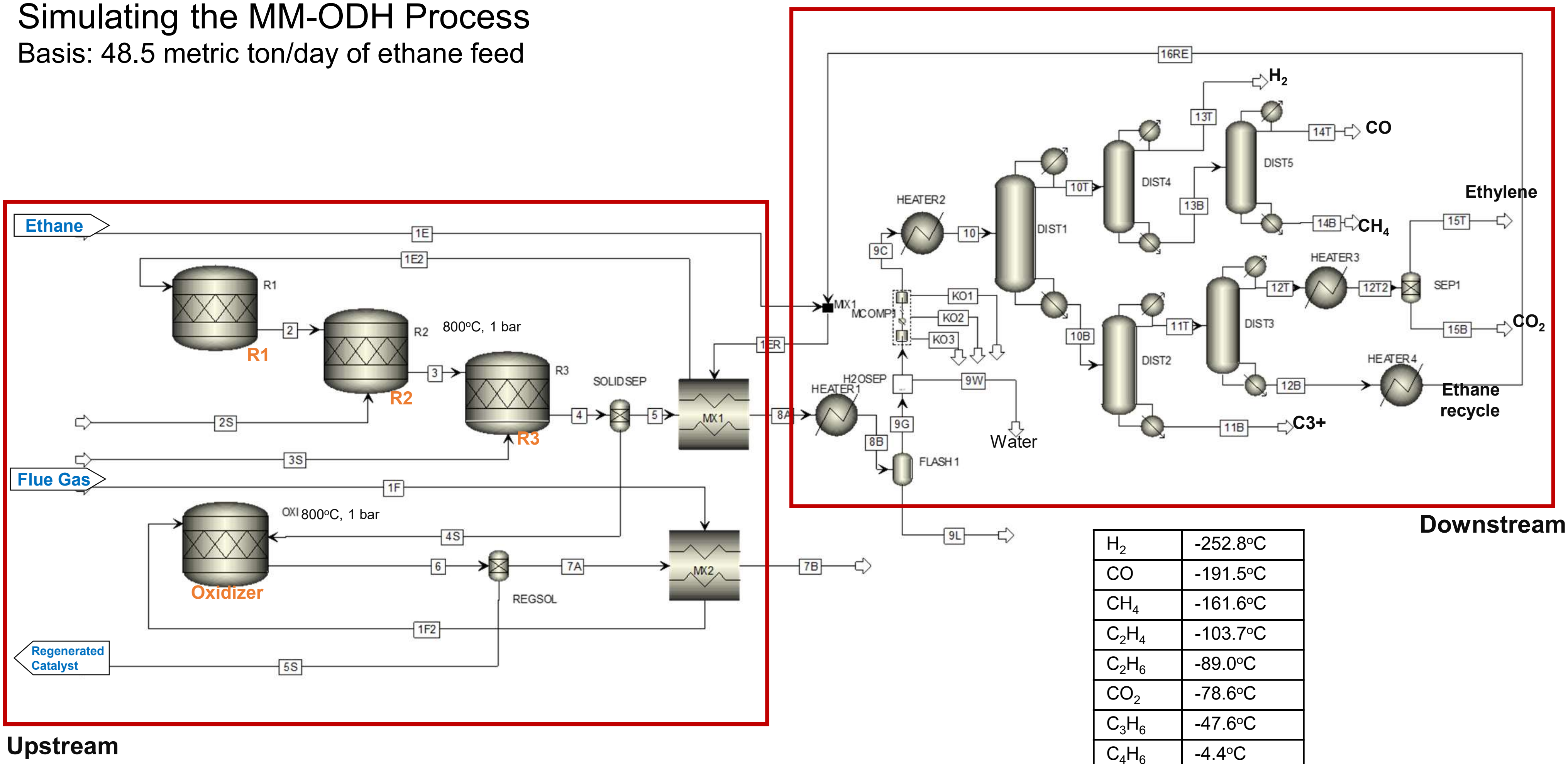


Task 8 Techno-Economic and Lifecycle Analysis

Process Modeling in AspenPlus™

Simulating the MM-ODH Process

Basis: 48.5 metric ton/day of ethane feed



Boiling Points

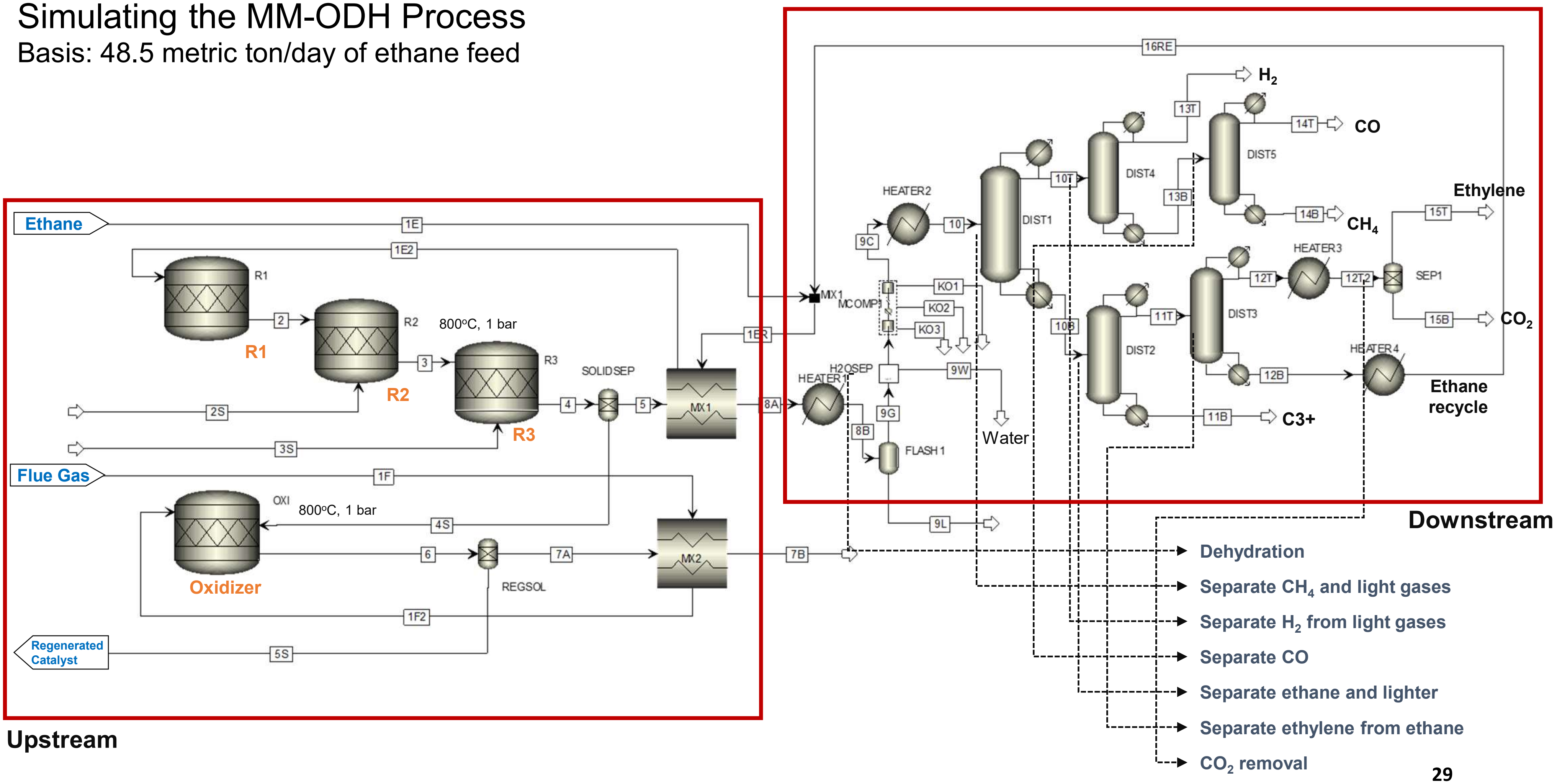
H_2	-252.8°C
CO	-191.5°C
CH_4	-161.6°C
C_2H_4	-103.7°C
C_2H_6	-89.0°C
CO_2	-78.6°C
C_3H_6	-47.6°C
C_4H_6	-4.4°C
C_6H_6	+80.1°C

Task 8 Techno-Economic and Lifecycle Analysis

Process Modeling in AspenPlus™

Simulating the MM-ODH Process

Basis: 48.5 metric ton/day of ethane feed



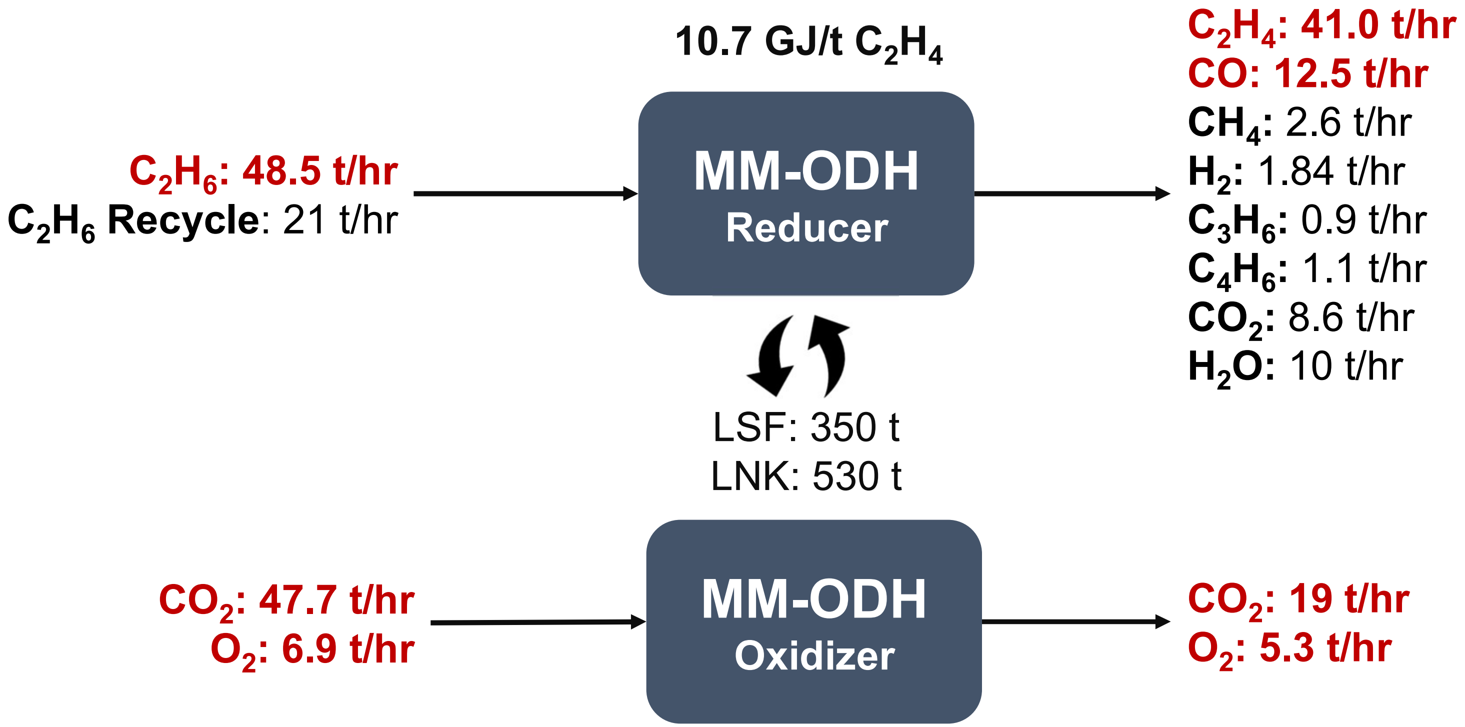
- Dehydration
- Separate CH_4 and light gases
- Separate H_2 from light gases
- Separate CO
- Separate ethane and lighter
- Separate ethylene from ethane
- CO_2 removal

Task 8 Techno-Economic and Lifecycle Analysis

Process Modeling in AspenPlus™

Simulating the MM-ODH Process

Basis: 48.5 metric ton/day of ethane feed



10.7 GJ/t C_2H_4

C_2H_6: 48.5 t/hr
C_2H_6 Recycle: 21 t/hr

MM-ODH
Reducer

C_2H_4: 41.0 t/hr
CO: 12.5 t/hr
CH_4: 2.6 t/hr
H_2: 1.84 t/hr
C_3H_6: 0.9 t/hr
C_4H_6: 1.1 t/hr
CO_2: 8.6 t/hr
H_2O: 10 t/hr

LSF: 350 t
LNK: 530 t

CO_2: 47.7 t/hr
O_2: 6.9 t/hr

MM-ODH
Oxidizer

CO_2: 19 t/hr
O_2: 5.3 t/hr

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Task 8 Techno-Economic and Lifecycle Analysis

Susteon

Estimating Cost of Ethylene Production

Basis: 48.5 metric ton/day of ethane feed

Purchased Equipment Cost (PEC) + **Installation Cost** = **Bare Erected Cost (BEC)**

From scaling factors and quotes

2.47x PEC

+ **Engineering, Procurement and Construction Fees (EPC)** — **15% of BEC**

+ **Process contingency (PC1)** — **X% of BEC**
X = 0 (mature)
= 15 (fairly developed)
= 80 (>40 for novel)

+ **Project contingency (PC2)** — **15% of (BEC + EPC + PC1)**

+ **Owners' Cost** — **20% of (BEC + EPC + PC1 + PC2)**

+ **Land Cost** — **1 acre @ $36,000 per acre**

= **Total Overnight Cost (TOC)**

Capital cost ($/yr)
= TOC ($) * CRF (% per yr.)

i = 10%
n = 20 years
CRF = 12%

$$\mathrm{CRF} = \frac{\mathrm{i}(1+\mathrm{i})^{\mathrm{n}}}{(1+\mathrm{i})^{\mathrm{n}}-1}$$

where i = fixed interest rate, n = fixed number of years

O&M @ % of (BEC + EPC + PC1 +PC2)
Labor: 1%
Maintenance: 2%
Taxes/Insurance: 2%

Power Demand
Electricity @ 7 ¢/kWh

Redox Catalyst
Price @ $30/kg, charged once every 2 years

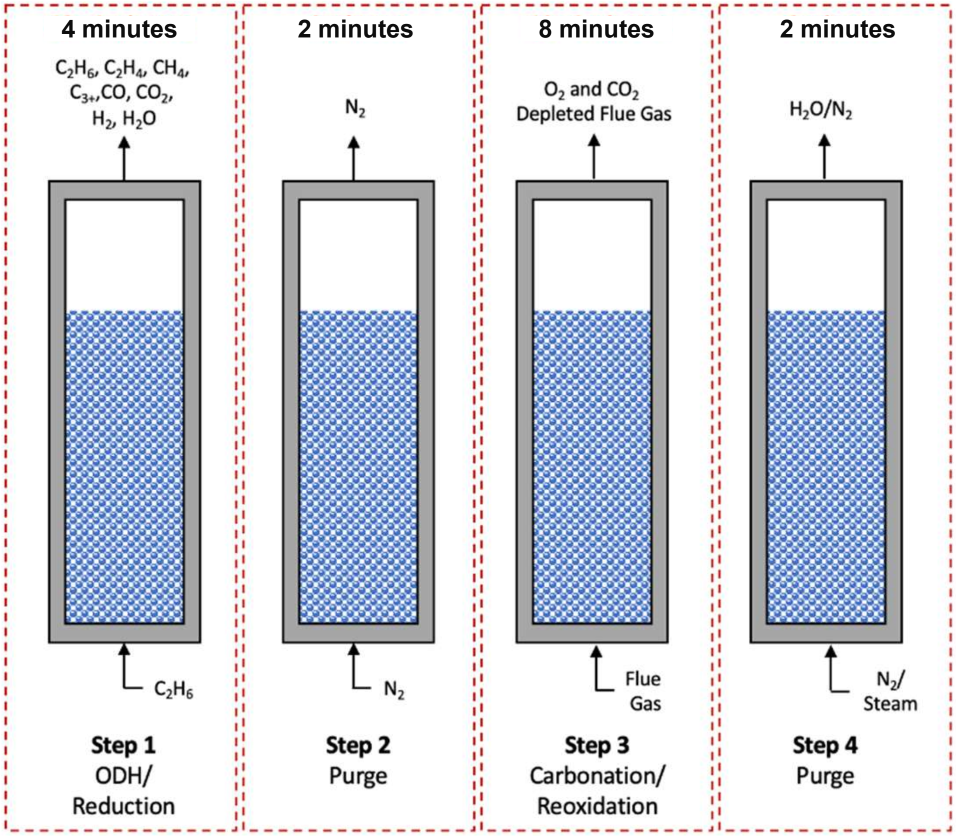
Feedstocks
Ethane @ $0.15/kg, Methane @ $0.145/kg

CO product credit @ $300/metric ton

Task 8 Techno-Economic and Lifecycle Analysis

Estimating Cost of Ethylene Production

Basis: 48.5 metric ton/day of ethane feed



1. **ODH/LSF Reduction**: ethane is converted to ethylene, LSF material released oxygen and the LNK carbonate reduces CO_2 to CO
2. **Purge**: Nitrogen and/or another inert gas is used to purge the reactor of combustible/reducing gases present. Steam can also be considered for this step
3. **LNK Carbonation and LSF Oxidation**: O_2 and CO_2 present in flue gas is used to re-oxidize the LSF particle and carbonate the LNK material, respectively.
4. **Purge:** Steam or an inert gas is used to remove oxidizing gases from the reactor before repeating step 1

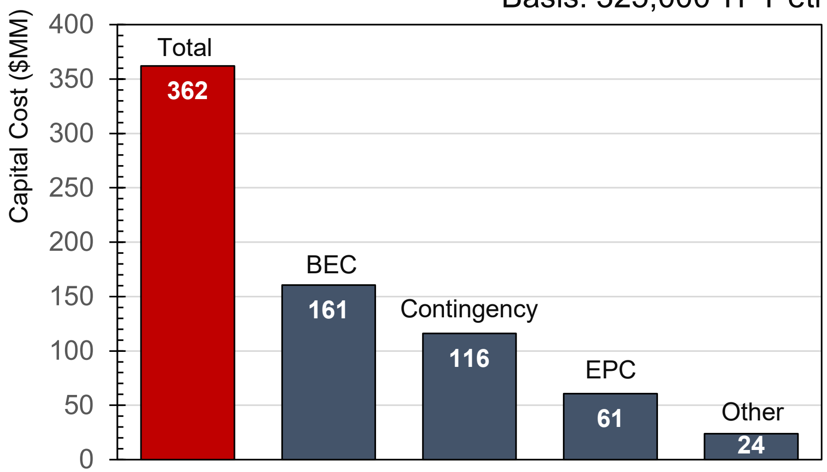
- ☐ Ethane-to-ethylene yield: **63%**
- ☐ CO_2 capture efficiency: **60%**
- ☐ O_2 uptake: **0.35 wt.% LSF**
- ☐ H_2 conversion in SHC: **50%**

Task 8 Techno-Economic and Lifecycle Analysis

Estimating Cost of Ethylene Production

Fabrication cost estimate		
Bed Diameter	m	3.00
Bed height	m	4.21
Packing Height (bottom and top)	m	0.50
Total Height	m	4.71
Refractory Insulation Thickness	m	0.20
Reactor ID	m	3.41
Reactor Volume	m3	42.89
Refractory Volume	m3	13.33
Fabrication Cost (2013 Dollars), per reactor	**USD**	**$1,098,089.30**
Total Fabrication cost (2023)	**USD**	**$24,772,894.52**

Basis: 325,000 TPY ethylene



Highlights

- ☐ Reactor system cost: **$87 million BEC (2023 estimate)**
- ☐ Downstream separation: from AspenPlus™
- ☐ Total overnight cost: **$362 million**
- ☐ Capital intensity of **$1110/TPY ethylene**
- ☐ Large scale (1.5MM TPY) ethane crackers: **$1100/TPY**
- ☐ **~85%** of total cracker capital: fired heaters
- ☐ For MM-ODH: **55% capital upstream**

Reference Ethylene Price: $700-$1000/t (2020-2022)

Cost Component	Annual Charges ($MM/year)	Unit Cost ($/ton ethylene)	Contribution (without credit)
Capital costs	**72.4**	**223**	38%
Power/Utilities	**28.8**	**89**	15%
Consumables/Feedstocks	**79.5**	**245**	41%
O&M	**12.2**	**38**	6%
CO credit		**-77**	
Total	**193.0**	**517**	**100%**

Task 8 Techno-Economic and Lifecycle Analysis

Estimating Net *kg CO_2e emitted per /kg ethylene*

- Main contributing streams: **ethane** feed (0.4 kg CO_2e/kg ethane), production of **redox catalysts**, CO_2 utilized from **flue gas**, **energy** required in the process, **methane**, CO_2 from **construction of units**

- *Scenario I* : reactor endothermicity provided by methane combustion (60% energy transfer efficiency)
- *Scenario II*: renewable electricity is utilized (solar electricity emitting 25 kgCO_2e per MWh)

- An average annual capacity of around 90% (330 operational days).

- Embodied emissions, associated with steel and concrete structures: 1% of total emissions, over an economic life of 20-years

- 500 tCO_2e/yr. from redox catalysts based on the emissions of Li_2CO_3 productions (cradle-to-gate)

- Credit for utilizing CO_2 from flue gas

- Reference case: ethane steam cracking with **1.2 – 1.5 kg CO_2e/kg C_2H_4**

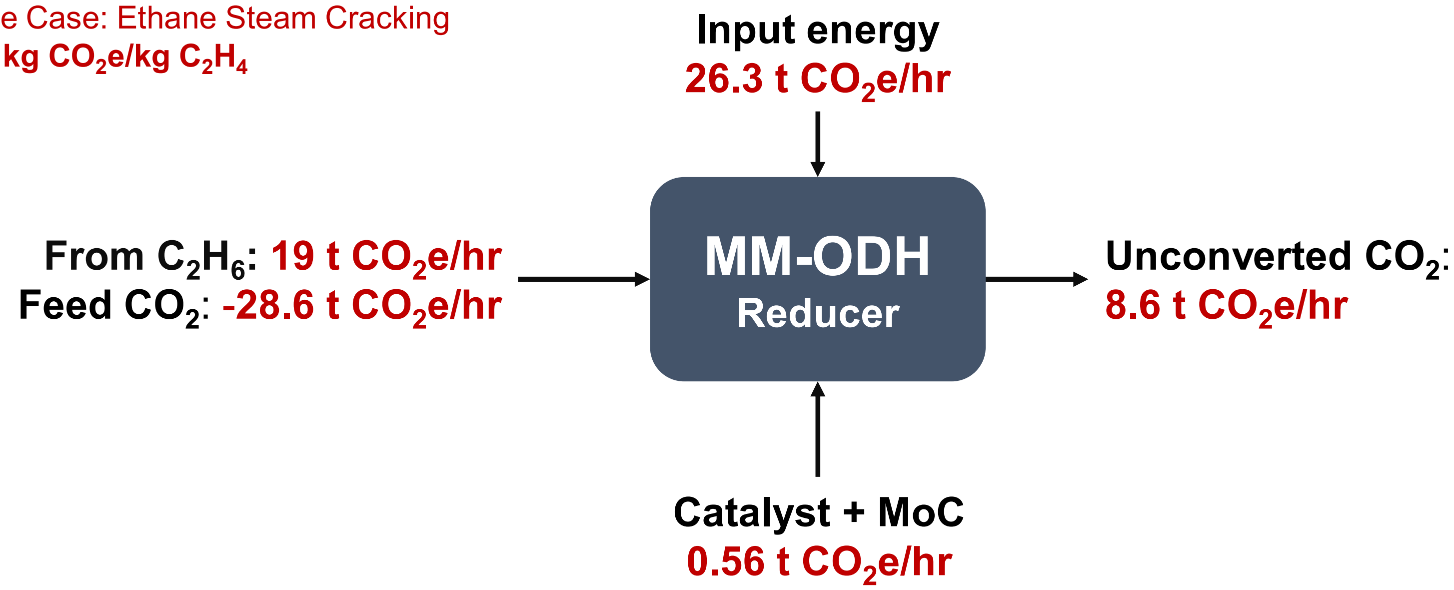
Task 8 Techno-Economic and Lifecycle Analysis

Estimating Net *kg CO_2e emitted per /kg ethylene*

Scenario I

Reactor energy supplied **by methane combustion** at 60% efficiency, other electricity demands supplied by solar energy with negligible energy inefficiencies

Reference Case: Ethane Steam Cracking
1.2 – 1.5 kg CO_2e/kg C_2H_4



Input energy
26.3 t CO_2e/hr

From C_2H_6: 19 t CO_2e/hr
Feed CO_2: -28.6 t CO_2e/hr

MM-ODH
Reducer

Unconverted CO_2:
8.6 t CO_2e/hr

Catalyst + MoC
0.56 t CO_2e/hr

Net CO_2e emissions
25.9 t CO_2e/hr

0.63 kg CO_2e/kg C_2H_4

>50% reduction vs. steam ethane cracking

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Task 8 Techno-Economic and Lifecycle Analysis

Susteon

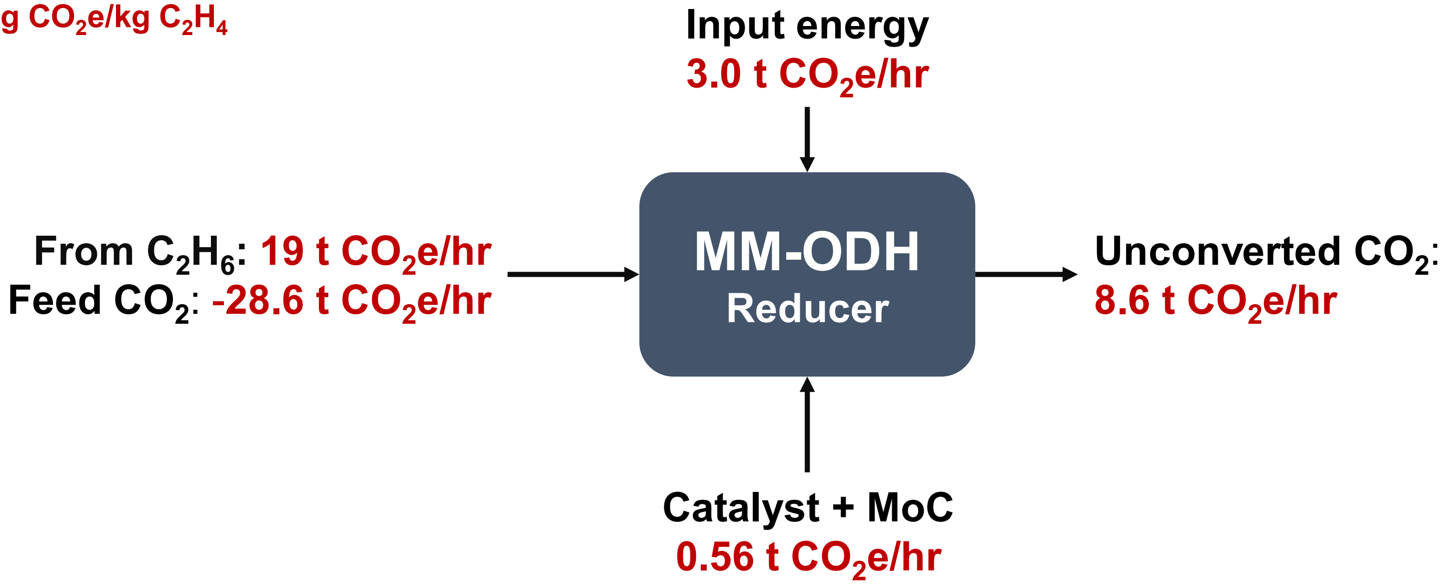
Estimating Net *kg CO_2e emitted per /kg ethylene*

Scenario II

All electricity demands supplied by solar energy with negligible energy inefficiencies

Reference Case: Ethane Steam Cracking

1.2 – 1.5 kg CO_2e/kg C_2H_4



Input energy
3.0 t CO_2e/hr

From C_2H_6: 19 t CO_2e/hr
Feed CO_2: -28.6 t CO_2e/hr

MM-ODH
Reducer

Unconverted CO_2:
8.6 t CO_2e/hr

Catalyst + MoC
0.56 t CO_2e/hr

Net CO_2e emissions
2.6 t CO_2e/hr

0.063 kg CO_2e/kg C_2H_4

requires ~1000 acres of land for solar panels

95% reduction vs. steam ethane cracking

Outline

- Project Overview and Technology Background
- Technical Approach and Key Results
- Future development plan
- Summary

Plans for Future Development

Future work beyond the project:

- Identification of specific application scenarios through discussions with potential industrial partner(s);
- Detailed reaction medium and catalyst cost and scalability study;
- Detailed system design and costing;

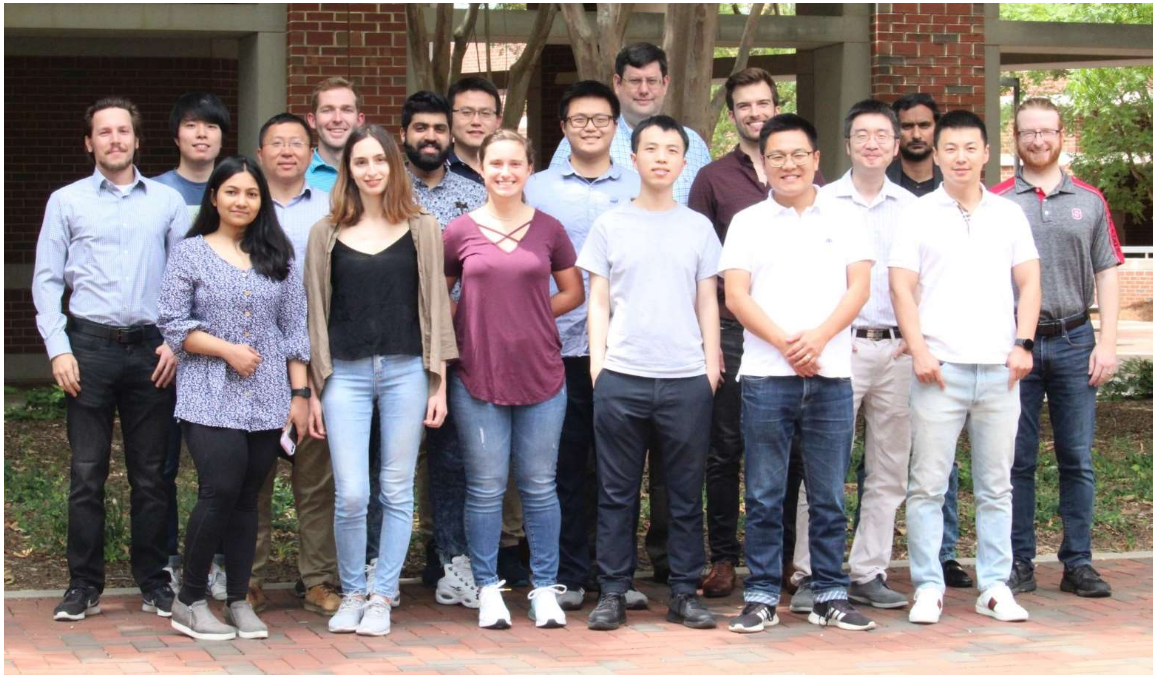
Scale-up potential:

- Further scale up/pilot testing (TRL-5/6, 10 – 100 kg/day);
- Scale out via molten salt based ceramic membrane.

Summary

- Perovskite oxides with high porosity were prepared via various methods;
- Oxide – molten salt compatibility were verified and reactive performance exceeded the CO_2 and ethane conversion targets;
- Molten salt with optimized compositions alone were also shown to be highly effective;
- Various reaction medium compositions were tested, with >85% CO_2 capture, >90% CO_2 conversion, >90% ethylene selectivity, and ~66% ethylene yield. Meeting the proposed milestone;
- 500 cycle confirmed the long-term stability of the system;
- TEA indicates potential for notable energy and CO_2 savings, as well as significant economic benefits;
- All the key milestones have been met.

Acknowledgements



NCSU:

Luke Neal, Kyle Vogt-Lowell, Dennis Chacko

WVU:

John Hu, Sonit Balyan, Xingbo Liu, Wenyuan Li, Shaoshuai Chen

Susteon:

Vasudev Haribal, Raghubir Gupta, Andrew Tong, Emma Li

Naomi O'Neil
Greg Imler

Thanks for the support!
Questions or suggestions?

Project Schedule and Milestones

		Stage I				Stage II								
Task Name	Team Member	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12	Q13
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: Redox Catalyst: Long Term Stability and Flue Gas Contaminant Studies	NCSU/WVU					▨	▨	▨	▨					
Subtask 5.1. Long -Term Testing of Redox Catalysts	NCSU					▨	▨	▨						
Milestone 5.1: 500 Cycle Tests	NCSU						◊							
Subtask 5.2 Empirical Kinetic Parameters Analysis and Validation	WVU					▨	▨	▨	▨					
Task 6.0: Techno-Economic and Life Cycle Analyses Update	Susteon					▨	▨	▨	▨	▨	▨	▨	▨	▨
Task 7.0: Redox Catalyst: Economics Driven Optimizations	NCSU						▨	▨	▨	▨	▨	▨	▨	▨
Subtask 7.1 Techno-Economic Redox Catalyst Optimization	NCSU						▨	▨	▨	▨	▨	▨		
Milestone 7.1: Refined reactor design	NCSU											◊		
Subtask 7.2 Synthesis Optimization for Scale-up	NCSU						▨	▨	▨	▨	▨	▨	▨	▨
Task 8.0: Development of Detailed Reactor and Process Design	Susteon					▨	▨	▨	▨	▨	▨	▨	▨	▨
Milestone 8.1 Final LCA/TEA	Susteon													◊
Milestone 8.2: Commercialization Road Map	Susteon													◊

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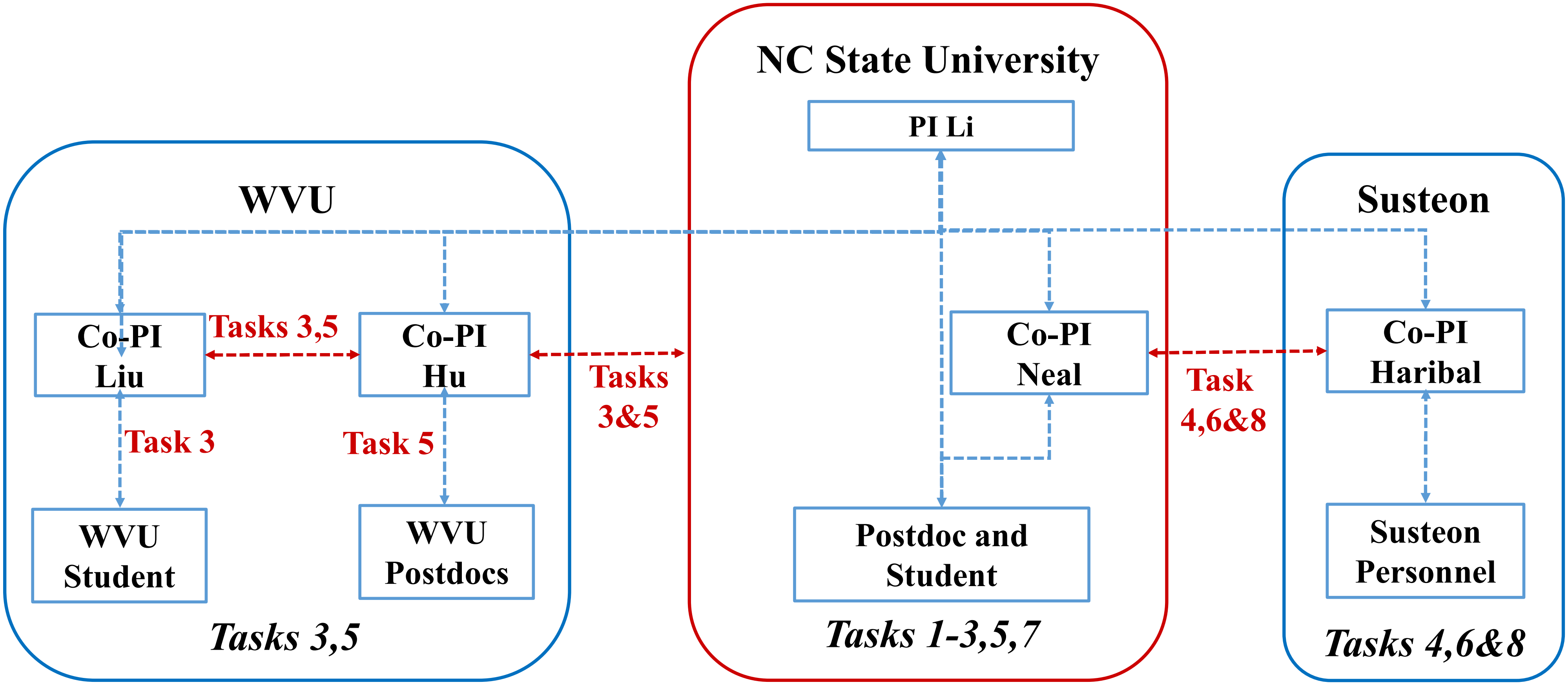
Appendix: Project Organizational Structure



WVU

Co-PI Liu

Co-PI Hu

Tasks 3,5

Task 3

Task 5

WVU Student

WVU Postdocs

Tasks 3,5

Tasks 3&5

NC State University

PI Li

Co-PI Neal

Postdoc and Student

Tasks 1-3,5,7

Task 4,6&8

Susteon

Co-PI Haribal

Susteon Personnel

Tasks 4,6&8

Appendix: Project Schedule

		Stage I				Stage II								
Task Name	Team Member	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12	Q13
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: Redox Catalyst: Long Term Stability and Flue Gas Contaminant Studies	NCSU/WVU					■	■	■	■					
Subtask 5.1. Long -Term Testing of Redox Catalysts	NCSU					■	■	■						
Milestone 5.1: 500 Cycle Tests	NCSU						◊							
Subtask 5.2 Empirical Kinetic Parameters Analysis and Validation	WVU					■	■	■	■					
Task 6.0: Techno-Economic and Life Cycle Analyses Update	Susteon					■	■	■	■	■	■	■	■	■
Task 7.0: Redox Catalyst: Economics Driven Optimizations	NCSU						■	■	■	■	■	■	■	■
Subtask 7.1 Techno-Economic Redox Catalyst Optimization	NCSU						■	■	■	■	■	■		
Milestone 7.1: Refined reactor design	NCSU											◊		
Subtask 7.2 Synthesis Optimization for Scale-up	NCSU						■	■	■	■	■	■	■	■
Task 8.0: Development of Detailed Reactor and Process Design	Susteon					■	■	■	■	■	■	■	■	■
Milestone 8.1 Final LCA/TEA	Susteon													◊
Milestone 8.2: Commercialization Road Map	Susteon													◊

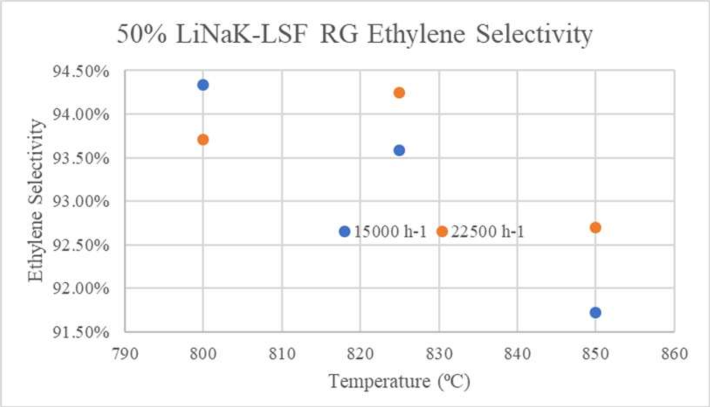
Task 7 TEA driven redox catalyst optimizations

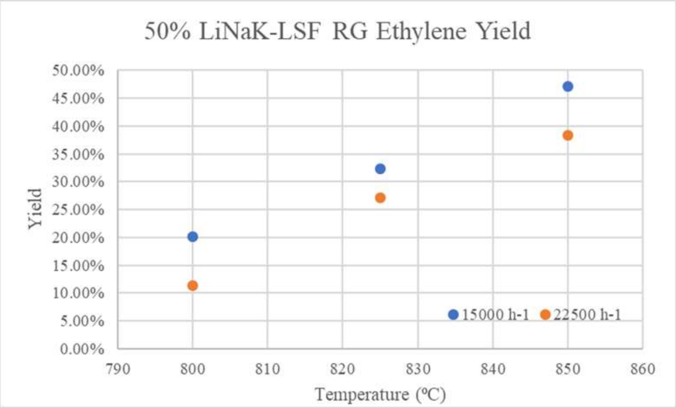
Temperature (°C)	Cycle Time (min)	Ethane Conversion	Ethylene Yield	C_2H_4 Selectivity	C_{2+} Selectivity	H_2 Conversion	CO_2 conversion
750	15	-	-	-	-	-	-
	25	46.80%	44.60%	95.40%	97.80%	33.00%	86.20%
	30	-	-	-	-	-	-
775	15	63.30%	59.00%	93.20%	96.70%	41.50%	77.70%
	25	62.30%	58.30%	93.60%	96.70%	34.70%	95.70%
	30	63.20%	59.00%	93.40%	96.70%	38.10%	92.80%
800	15	73.40%	66.50%	90.60%	95.10%	45.90%	92.00%
	25	72.90%	66.00%	90.60%	95.00%	37.10%	92.20%
	30	73.20%	66.20%	90.50%	95.00%	36.80%	96.10%
825	15	85.30%	73.80%	86.50%	91.80%	41.30%	94.50%
	25	84.60%	73.20%	86.50%	91.80%	36.00%	94.50%
	30	84.20%	73.30%	87.00%	92.00%	41.70%	90.30%

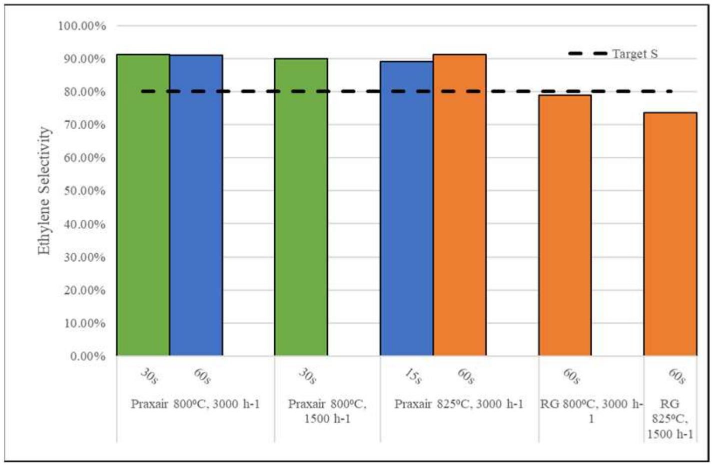
Ethylene yield improves with temperature and MM-ODH is pretty flexible with cycle time

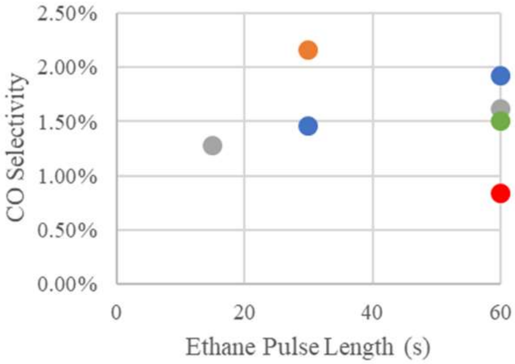
Task 2 Redox Catalyst Synthesis and Characterizations

Reactive Performance









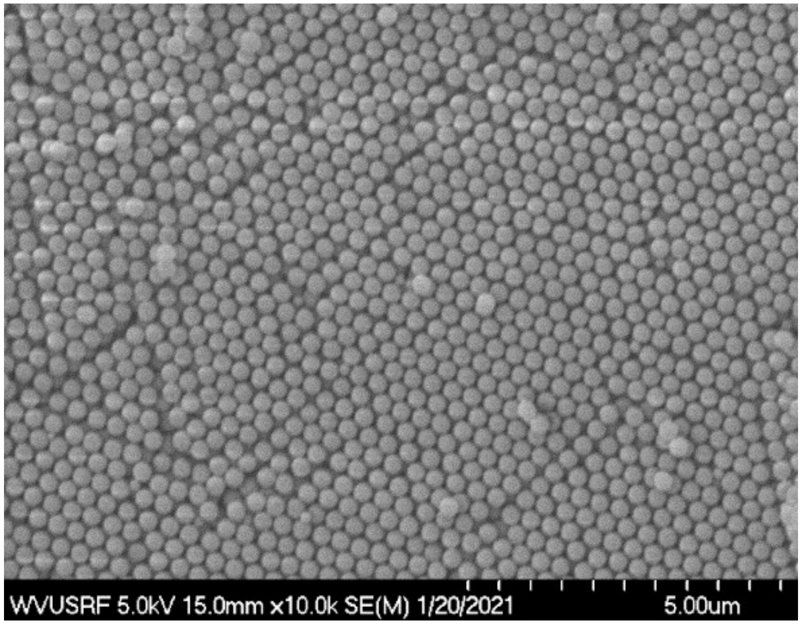
CO yields were unsatisfactory!

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

Porous Oxide Synthesis

Objective: Develop a 3-dimensional ordered macro-porous (3DOM) perovskite $La_{0.8}Sr_{0.2}FeO_3$ (LSF) to enhance pore volume



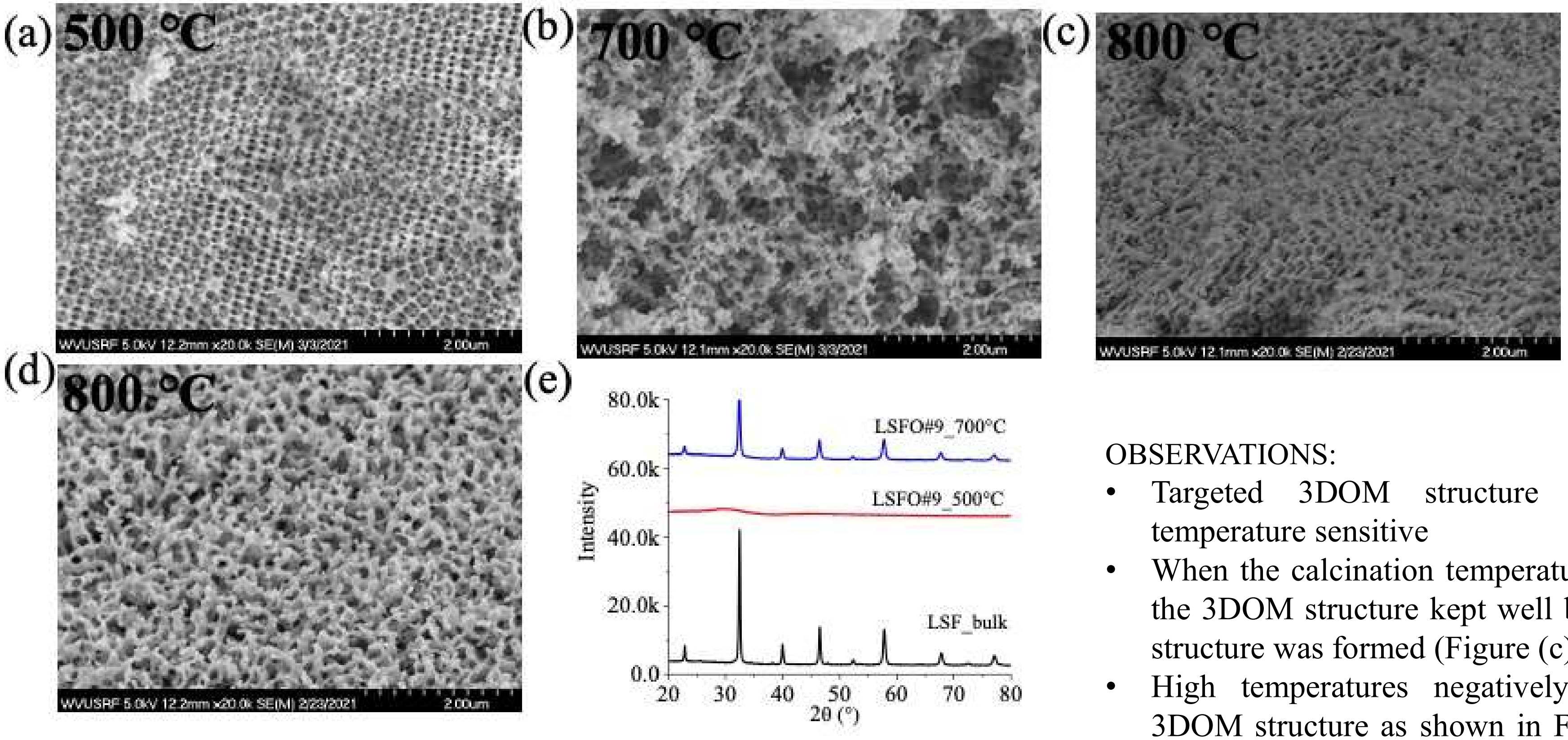
SEM image of the as-synthesized PMMA

OBSERVATIONS:

- 3DOM LSF was synthesized 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

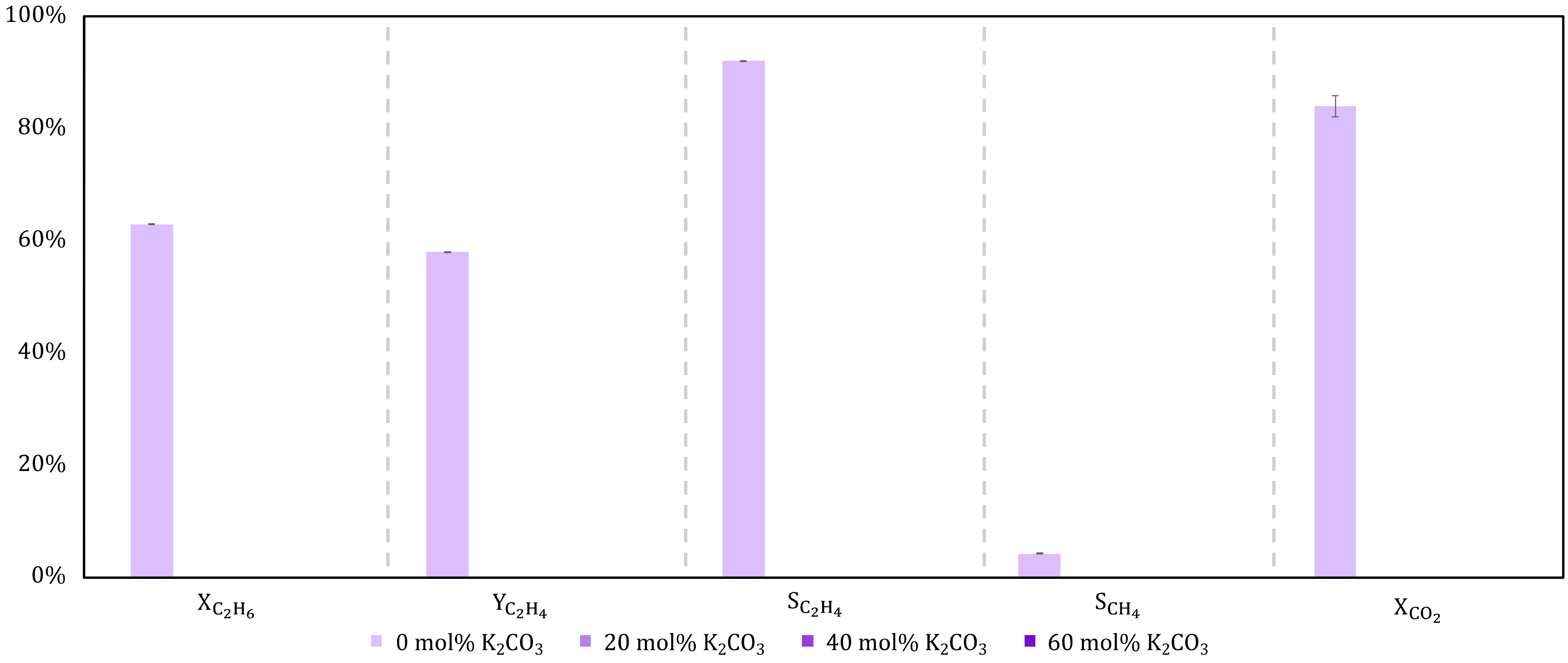


(a-d) SEM images of LSF prepared at different calcination temperature and e) XRD patterns of LSFO#9 prepared at 500 and 700 °C.

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 negatively impact 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)).

Increasing the mol% of K_2CO_3 decreases ethane conversion and ethylene yield and improves CO_2 conversion.



Task 2 Redox Catalyst Synthesis and Characterizations

Effect of CO_2 Space velocity

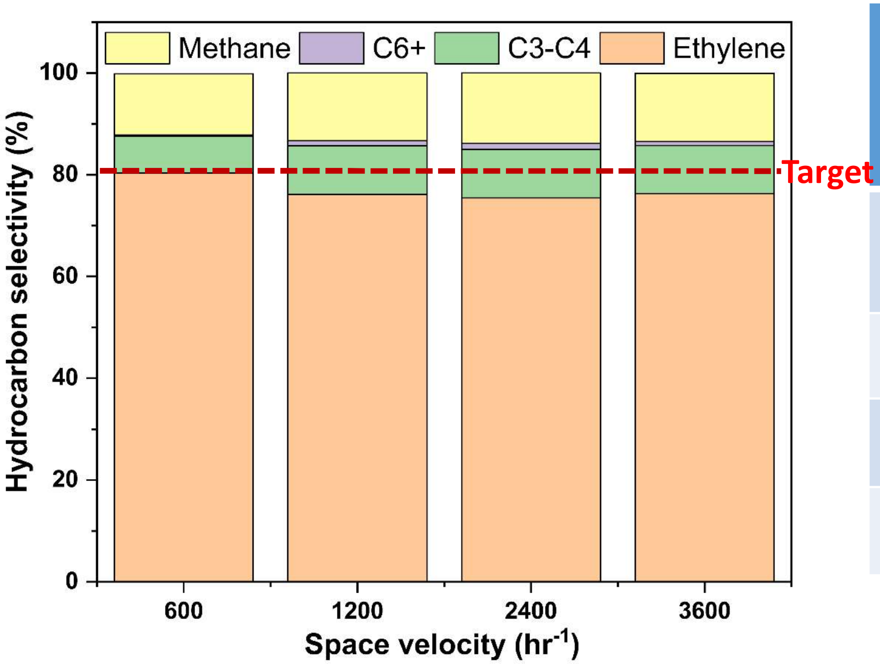


Figure: Hydrocarbon Product distribution during ethane injection (5th injection cycle)

Catalyst: **$60\%Li_2CO_3$@LSF**, Temperature: 750 °C
Injection: Reducing agent: 30 sec, Oxidizing agent: 90 sec
Ethane S.V = 3600 hr-1

Reactive Performance

60% Li_2CO_3/ LSF	Ethane Conv. (%)	Ethylene Select. (%)	Methane Select (%)	H_2 Conv. (%)	CO_2 Conv. (%)	CO_2 Capture (%)
600	67.5	80.3	12	28	93.8	48.1
1200	56.1	76.3	13.3	17.5	89.4	28
2400	53.2	75.6	13.8	17.8	89.4	22.4
3600	48.1	76.4	13.4	17.4	89.4	22.1

- An increase in CO_2 space velocity leads to less residence time to replenish molten carbonate salt which results in decrease in CO_2 capture of the molten salt

Task 2 Redox Catalyst Synthesis and Characterizations

Reactive Performance

Effect of oxygenate molecule

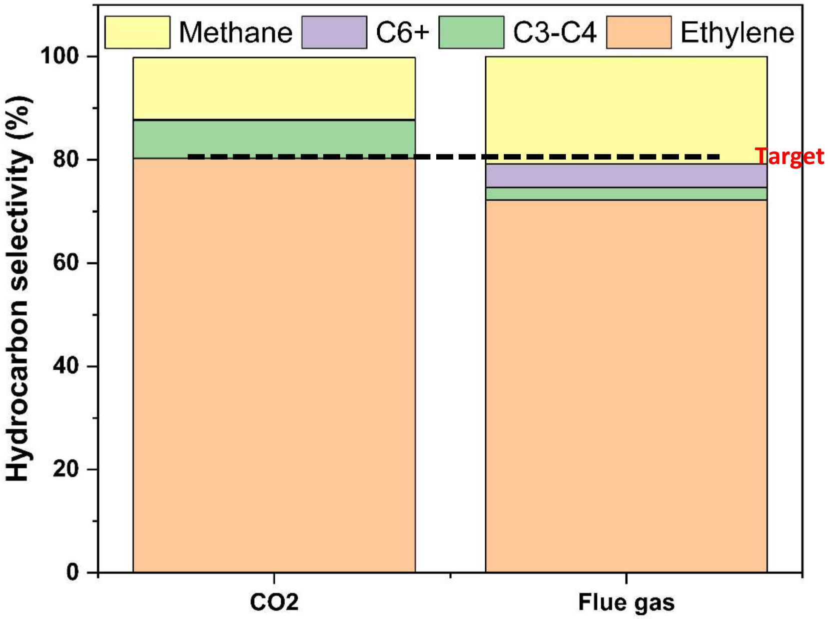


Figure: Hydrocarbon Product distribution during ethane injection (5th injection cycle)

Catalyst: **60%Li_2CO_3@LSF**, Temperature: 750 °C
Injection: Reducing agent: 30 sec, Oxidizing agent: 90 sec
Oxygenate S.V = 600 hr-1, Reducing agent S.V = 3600 hr^{-1}

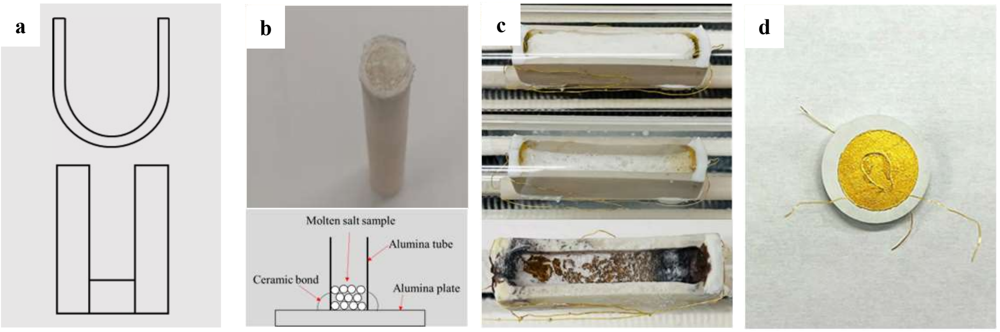
60% Li_2CO_3/ LSF	Ethane Conv. (%)	Ethylene Select. (%)	Methane Select (%)	H_2 Conv. (%)	CO_2 Conv. (%)	CO_2 Capture (%)
CO_2	68	80	12	29	**93.8**	48
Flue gas	85	72	20	32	**93.7**	39

- Decrease in CO_2 capture is observed for the catalyst system oxidized with flue gas because the content of CO_2 is low in flue gas

- Increase in ethane conversion is observed when catalyst is oxidized with flue gas

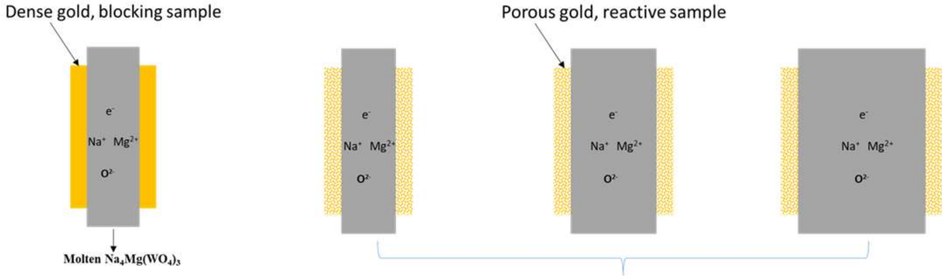
Task 2 Redox Catalyst Synthesis and Characterizations

Three sample assembly schemes investigated



- **a) U-tube:** Quartz U-tubes used to contain pure molten salts, but corroded by molten salt samples, and shattered during molten-solidification transition.
- **b) Straight Tube:** The height of the sleeved sample in the straight alumina tube will change during the test, slow testing gas/sample interaction resulting in long and inaccurate results.
- **c) Trough crucible:** gold (or platinum) paste and gold wire on both ends. After the test, the gold (or platinum) paste melt in the sample and interfere with the test results.
- **d) Standalone button:** Zirconia and molten salt mixture at a mass fraction of 6:4 to provide sample integrity. Gold paste with gold wires on both sides. Most reliable results from this setting.

Standalone button sample Schematic diagram

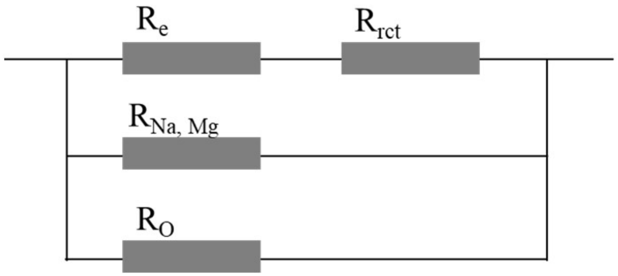


When stable, pure electronic resistance

When stable, mixed oxygen, electronic, and interface reaction resistance, extrapolation to separate interface resistance from mixed oxygen & electronic resistance

Equivalent circuit

Mixed resistance: Oxygen ion resistance//electronic resistance + interface resistance



- ❖ Measure one dense sample to obtain the electronic resistance.
- ❖ Test 3 different thickness porous samples to obtain the mixed interface resistance and oxygen//electronic resistance.

Task 7 Redox Catalyst Optimizations (Composite Catalysts)

- Composite catalysts synthesized using LSF synthesized from reactive grinding, calcined at 700°C
  - Estimated pore volume ~ 0.6 mL g^{-1}, max weight loading ~ 50 wt. %

- 45% weight molten salt with varying molar compositions of carbonate, ball milled and calcined

- 2.5 g, 425-850 µm, GHSV = 150 h^{-1}, 20% C_2H_6/Ar, flue gas regeneration

- Carbonate decomposition is observed during Ar purge steps

- Hydrogen is generated upon introduction of flue gas
  - Hypothesized to be partial reoxidation of LSF by steam generated from recarbonation of alkali hydroxides (or alkali hydroxide decomposition)

- All of the samples exhibited ~100% O_2 uptake (~0.15% wt LSF)

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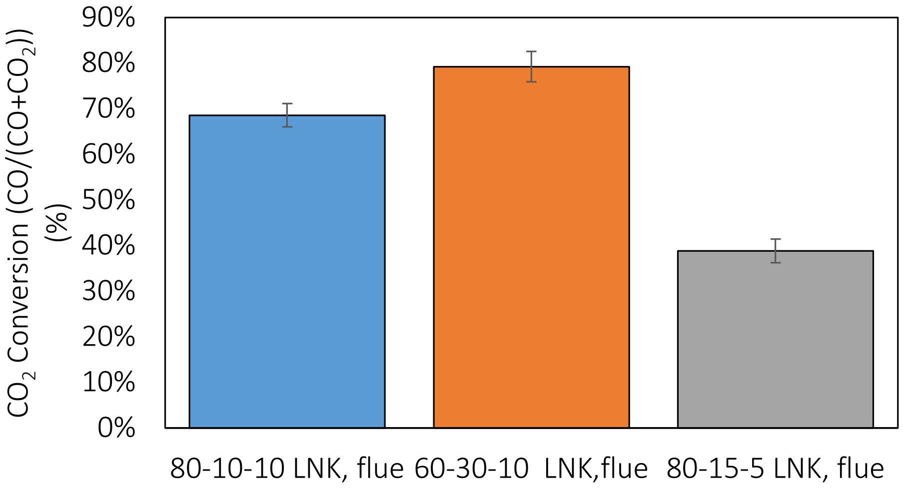
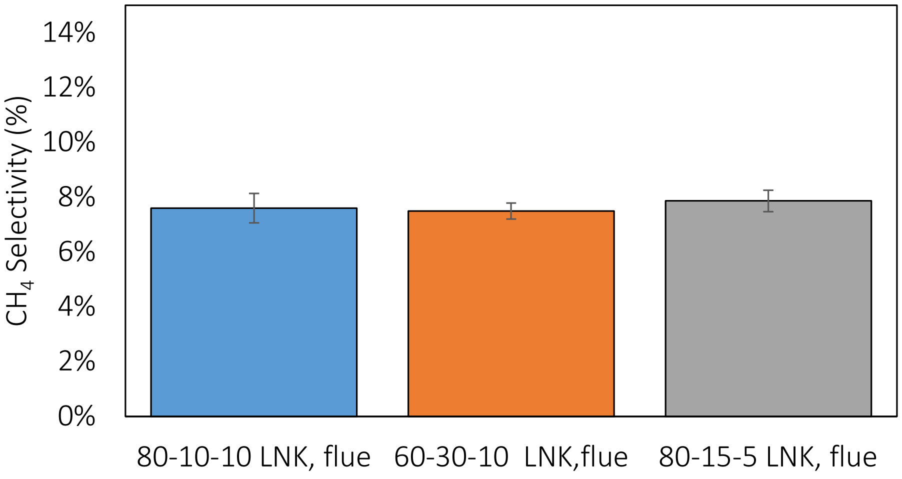
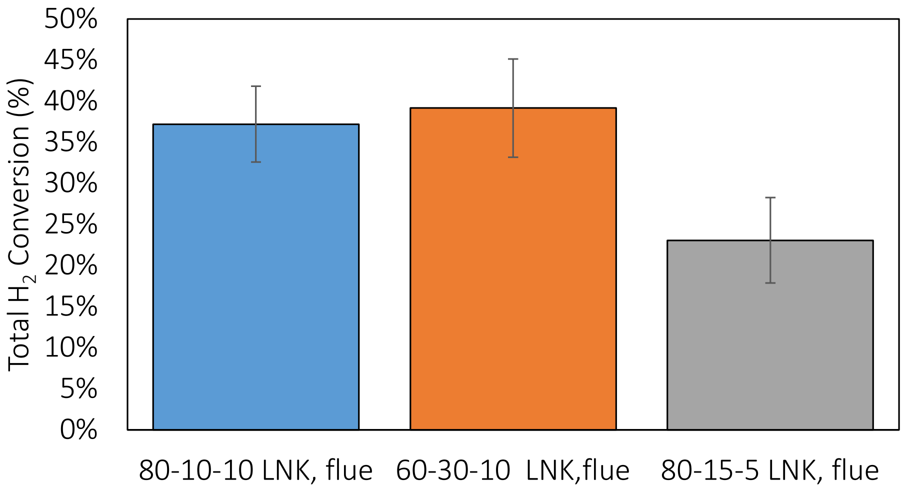
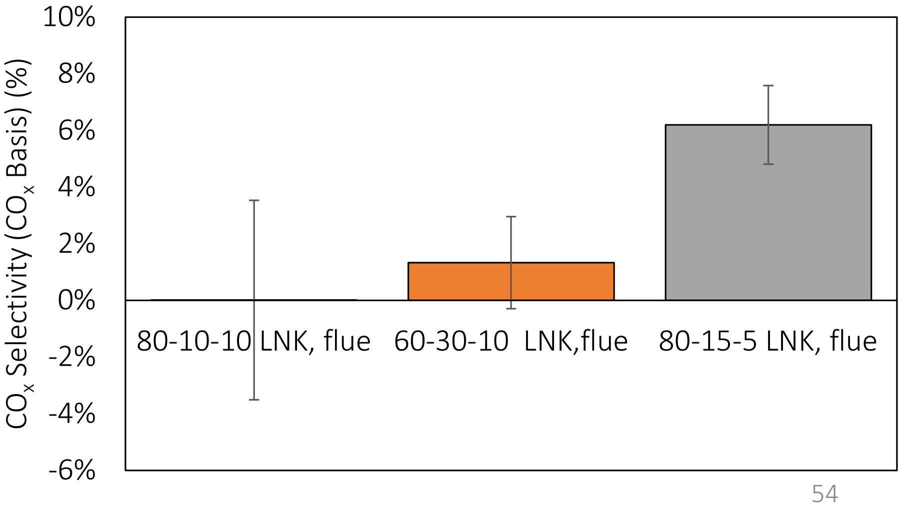
Task 7 Redox Catalyst Optimizations







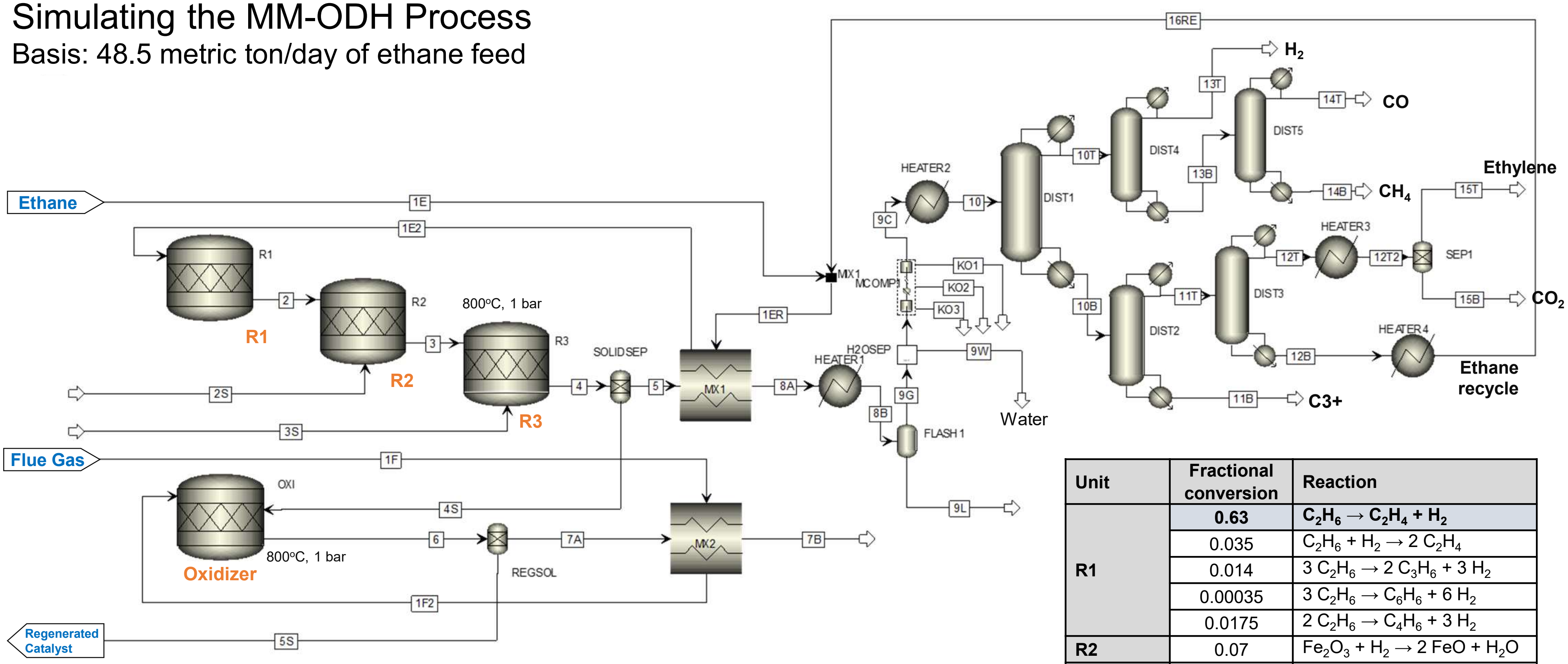


Task 8 Techno-Economic and Lifecycle Analysis

Process Modeling in AspenPlus™

Simulating the MM-ODH Process

Basis: 48.5 metric ton/day of ethane feed



Unit	Fractional conversion	Reaction
R1	**0.63**	**$C_2H_6 \rightarrow C_2H_4 + H_2$**
	0.035	$C_2H_6 + H_2 \rightarrow 2\ C_2H_4$
	0.014	$3\ C_2H_6 \rightarrow 2\ C_3H_6 + 3\ H_2$
	0.00035	$3\ C_2H_6 \rightarrow C_6H_6 + 6\ H_2$
	0.0175	$2\ C_2H_6 \rightarrow C_4H_6 + 3\ H_2$
R2	0.07	$Fe_2O_3 + H_2 \rightarrow 2\ FeO + H_2O$
R3	0.09	$Li_2CO_3 \rightarrow Li_2O + CO_2$
	0.7	$CO_2 + H_2 \rightarrow CO + H_2O$
OXI	1	$CO_2 + Li_2O \rightarrow Li_2CO_3$
	1	$4\ FeO + O_2 \rightarrow 2Fe_2O_3$

- ☐ Li_2CO_3 → Li_2O and Fe_2O_3 → FeO are the assumed transitions
- ☐ SrO and La_2O_3 are inert
- ☐ The composition is varied to mimic 60% LNK + 40% LSF system