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DE-FE0031918

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

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NC State University

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

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

CBE
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01/17/2024

Outline

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

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Project Overview: Molten-salt mediated oxidative dehydrogenation (MM-ODH) of ethane

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*

Molten Salt Mediated CO_2-ODH:

CO_2-Capture:

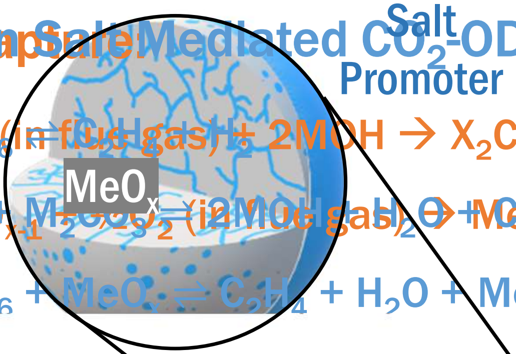
1) $C_2H_6 \rightleftharpoons C_2H_4 + H_2$ *Cracking/Dehydrogenation*

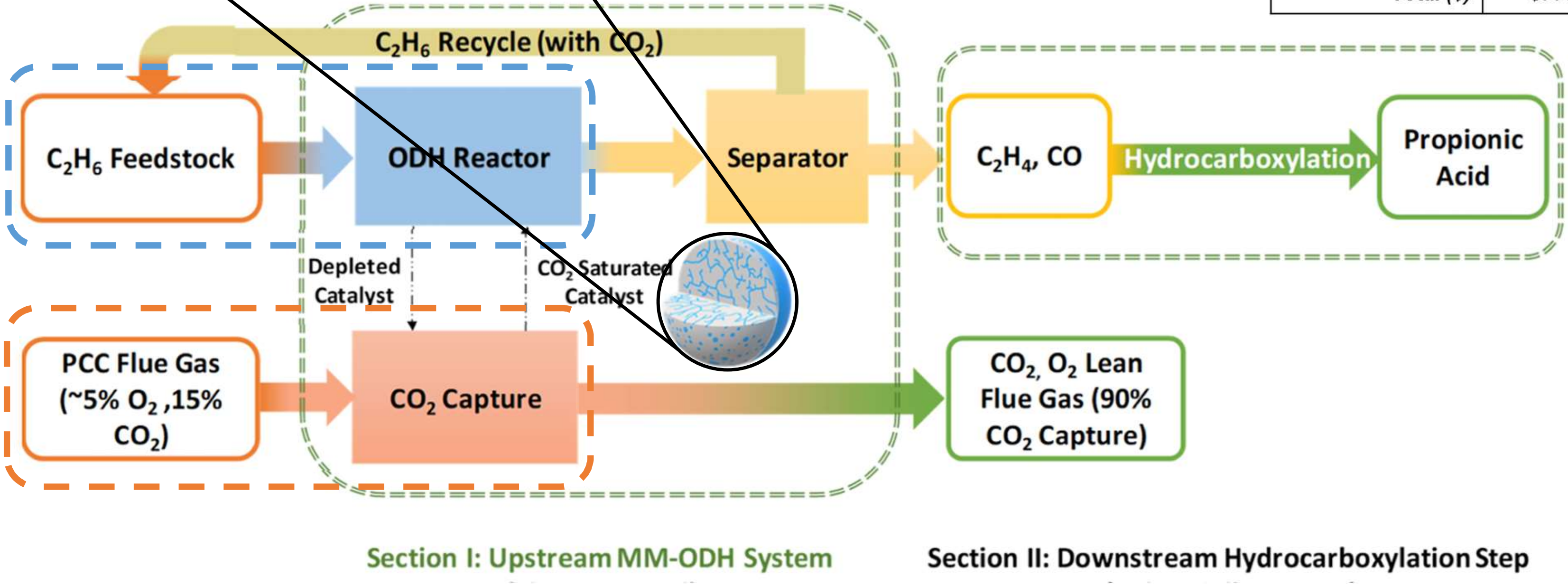
1) CO_2 (in flue gas) + $2MOH \rightarrow X_2CO_3 + H_2O$

2) $H_2 + M_2CO_3 \rightleftharpoons 2MOH + H_2O + CO$ *Modified RWGS*

2) $MeO_{x-1} + CO_2$ (in flue gas) $\rightarrow CO + MeO_x$

2) $C_2H_6 + MeO_x \rightleftharpoons C_2H_4 + H_2O + MeO_{x-1}$ *ODH*





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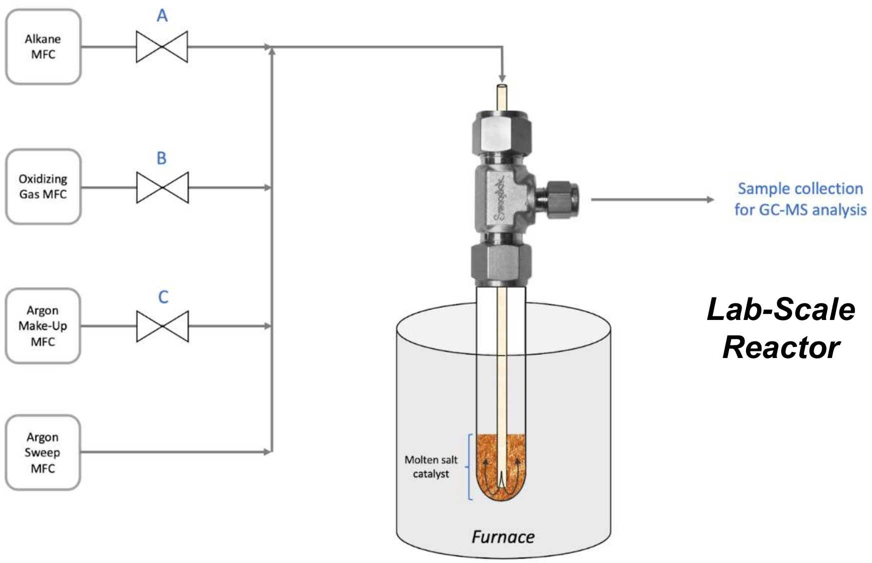
Experimental Set-up



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) $\rightarrow$ X_2CO_3

$MeO_{x-1} + 1/2O_2$ (in flue gas) $\rightarrow$ 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 $CH_3\text{-}CH_2$)

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

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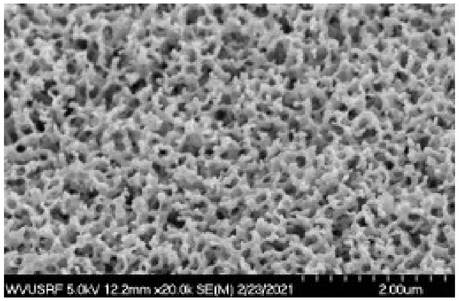
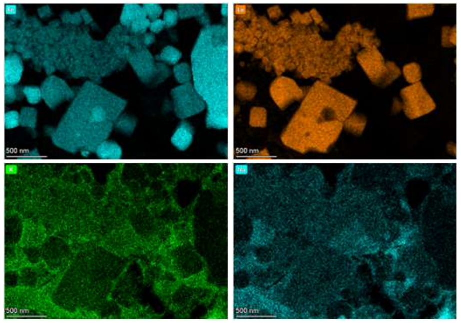
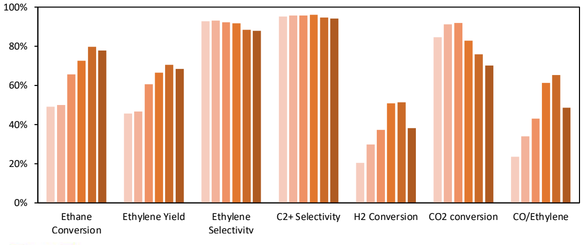
Overview of the Key Results

Material Synthesis, Testing, and Characterizations

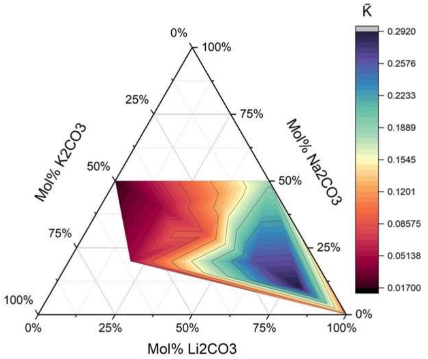


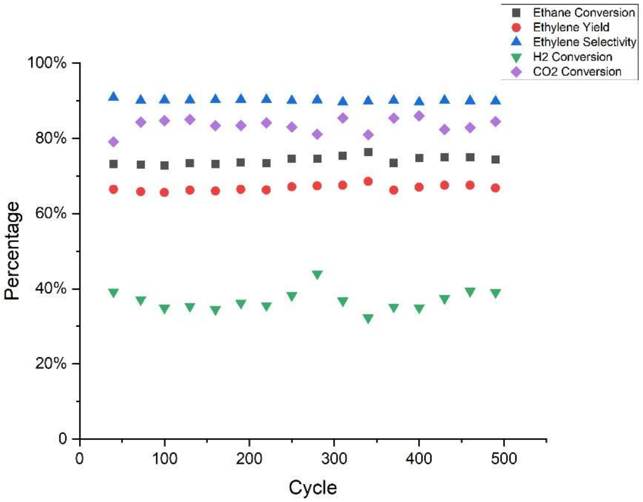




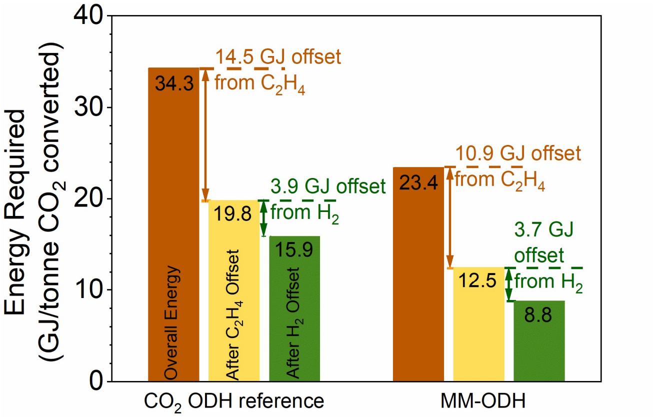
WestVirginiaUniversity

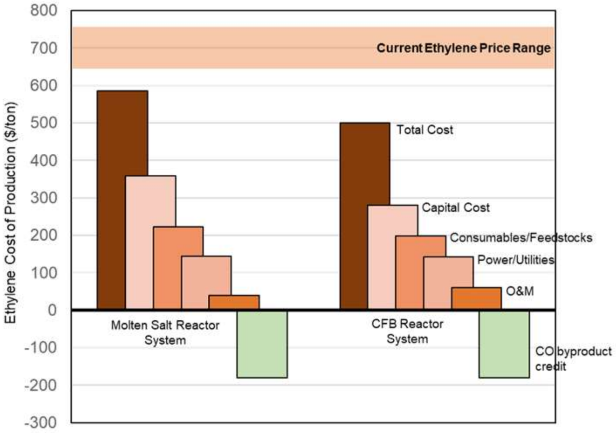
Material Optimizations and Long-Term Stability





Techno-Economics and System Design

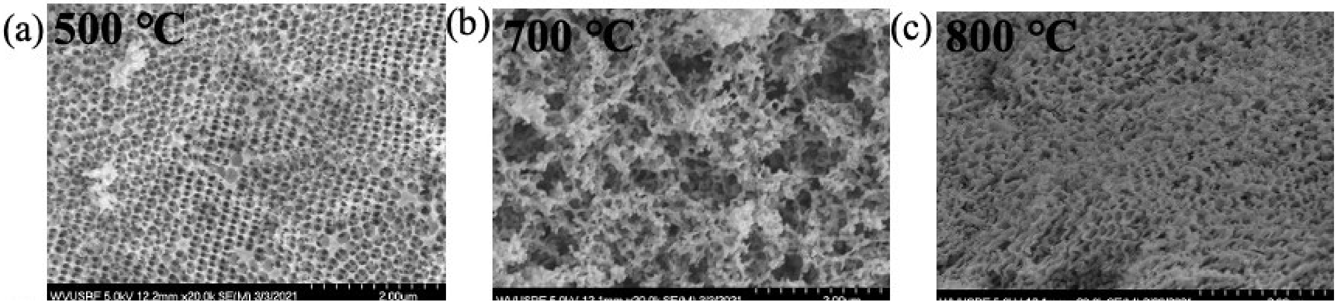




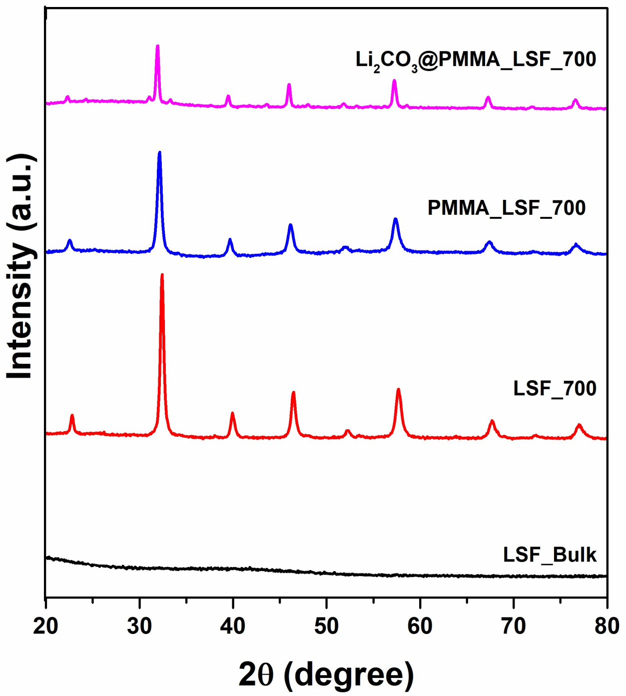
Susteon

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 (Batch 1)	0.7	62%
Reactive Grinding LSF (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.

Redox Catalyst Synthesis and Testing

Effect of Ethane Space velocity

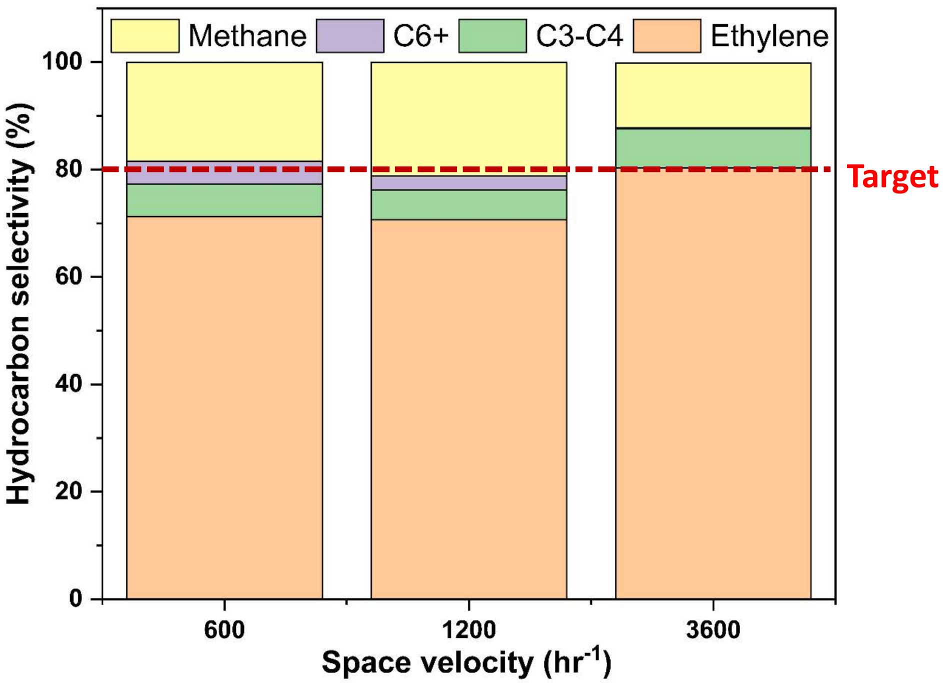


Figure: Hydrocarbon Product distribution during ethane injection (5th injection cycle)

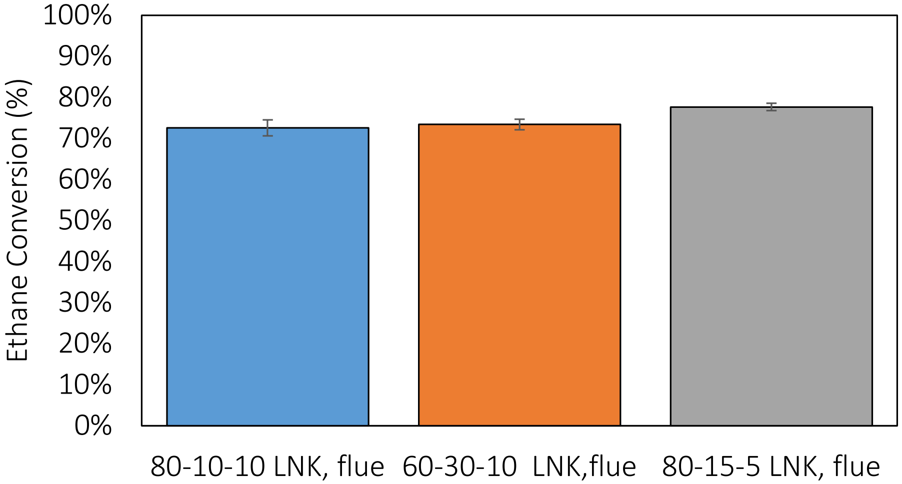
Catalyst: **60%Li_2CO_3@LSF**, Temperature: 750 °C
Injection: Reducing agent: 30 sec, Oxidizing agent: 90 sec
Oxygenate S.V = 600 hr-1

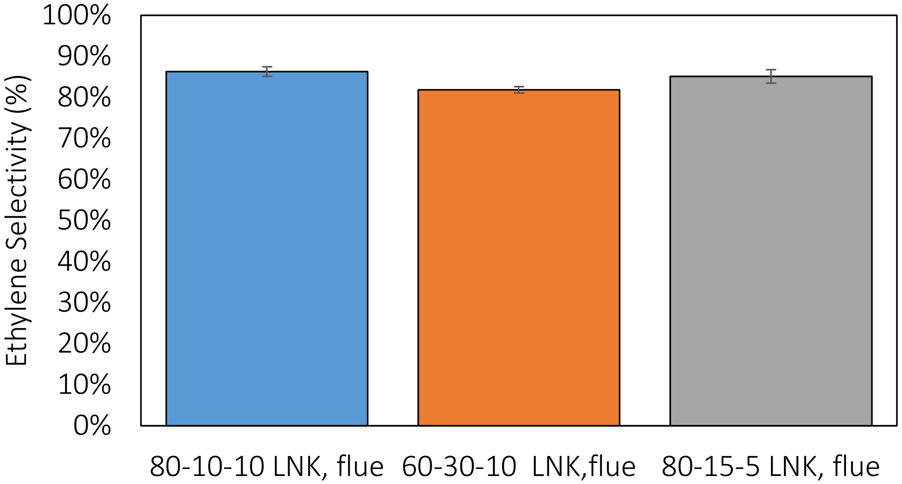
Reactive Performance

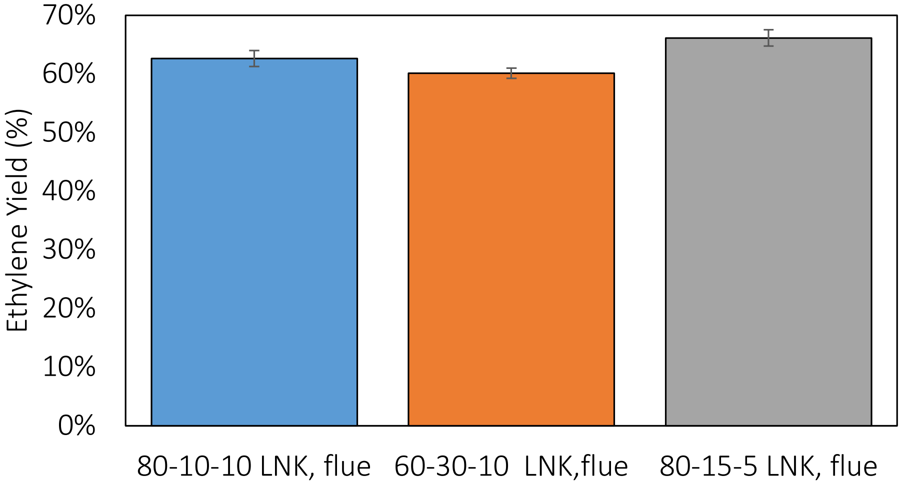
60% Li_2CO_3/ LSF	Ethane Conv. (%)	Ethylene Select. (%)	Methane Select (%)	H_2 Conv. (%)	CO_2 Conv. (%)	CO_2 Capture (%)
600	71.5	71.2	18.4	39	**93.7**	36.4
1200	70.5	70.6	21.3	27	**93.4**	44.5
3600	67.5	**80.3**	12	28	**93.8**	48.1

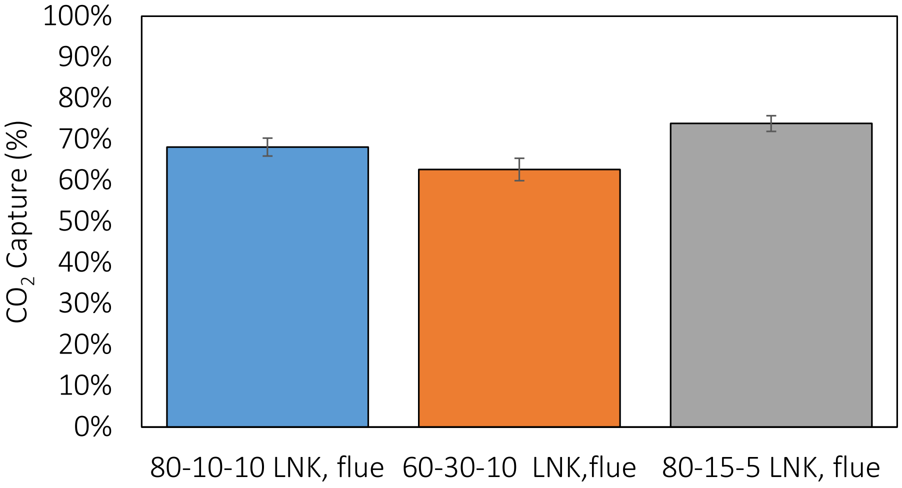
- Increase in residence time promotes ethylene side reaction which results in decrease of ethylene selectivity
- Increase in space velocity hydrogen produced would have less time to react with CO_2 in the molten salt, resulting in lower H_2 conversion
- Ethylene yield at 3600 hr^{-1} SV is **~55 %**

Redox Catalyst Optimizations

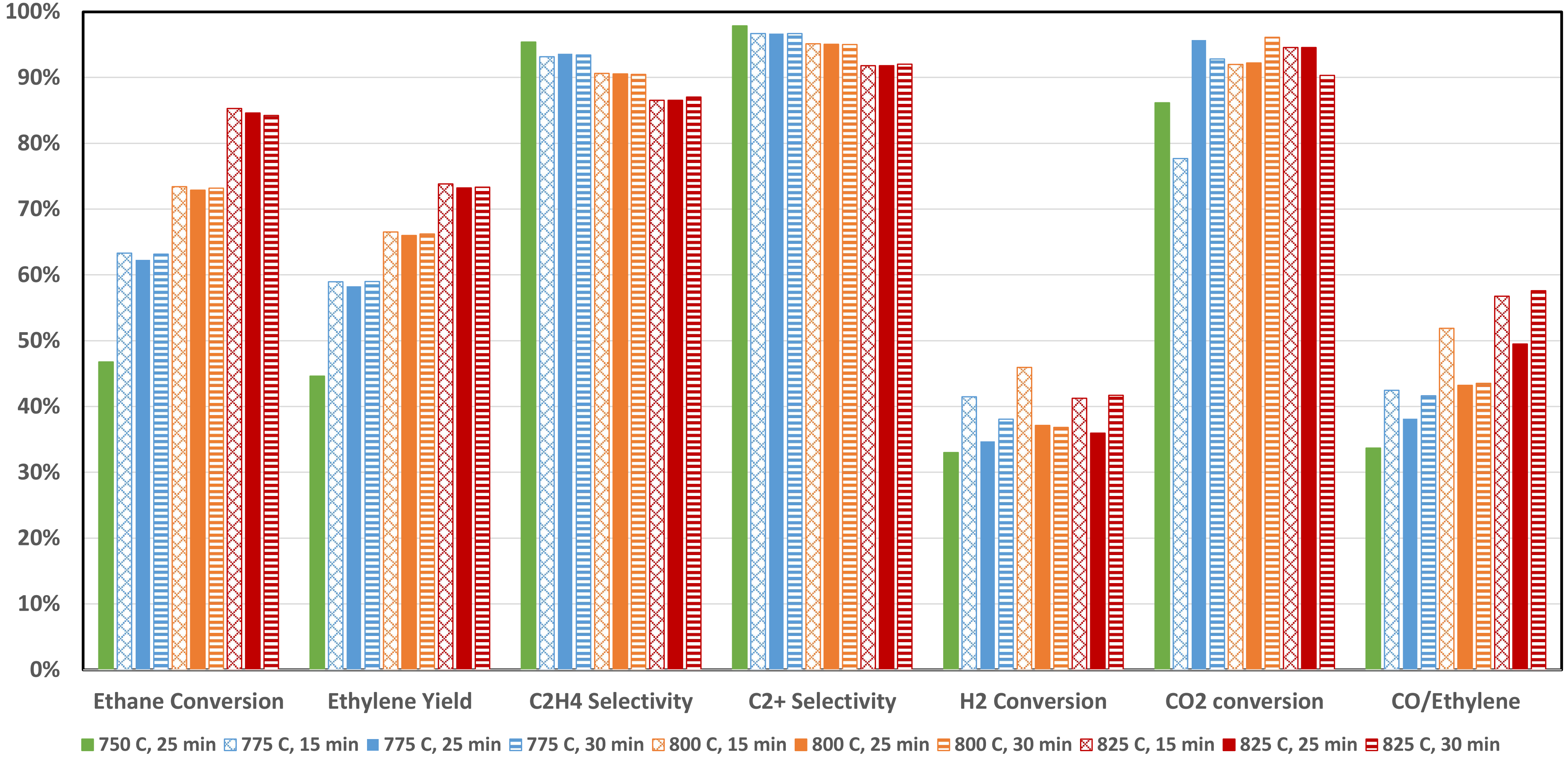






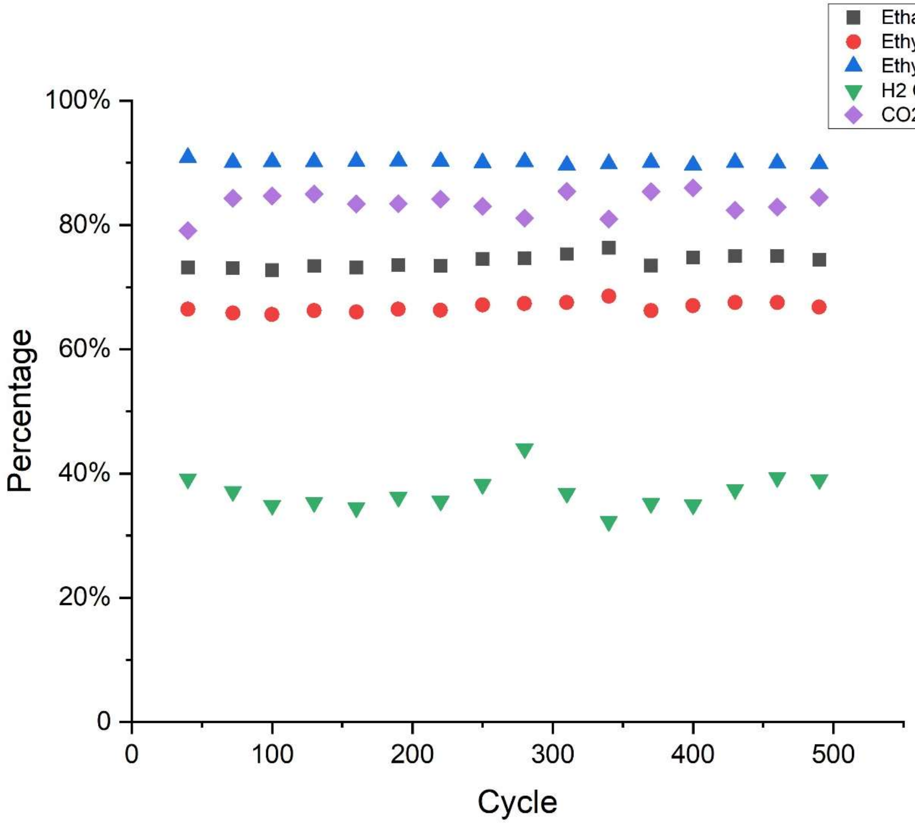


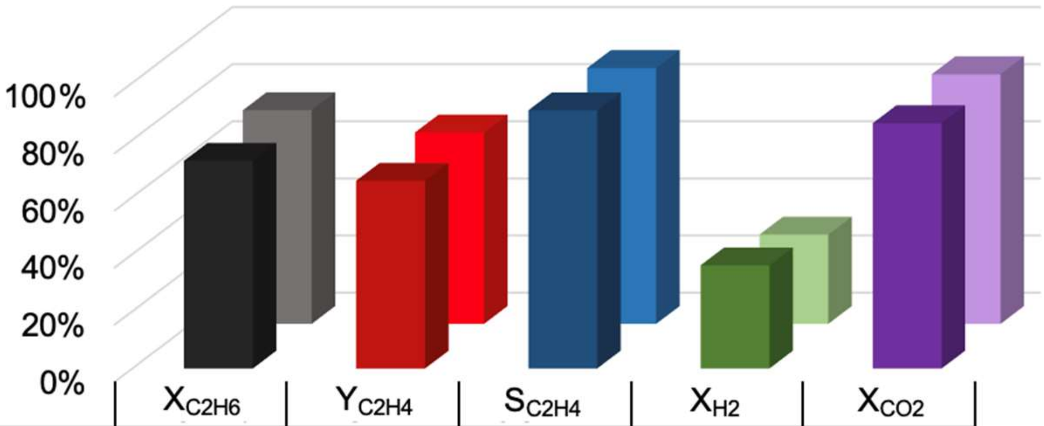
Optimizations of the Molten Salt Compositions



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

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%

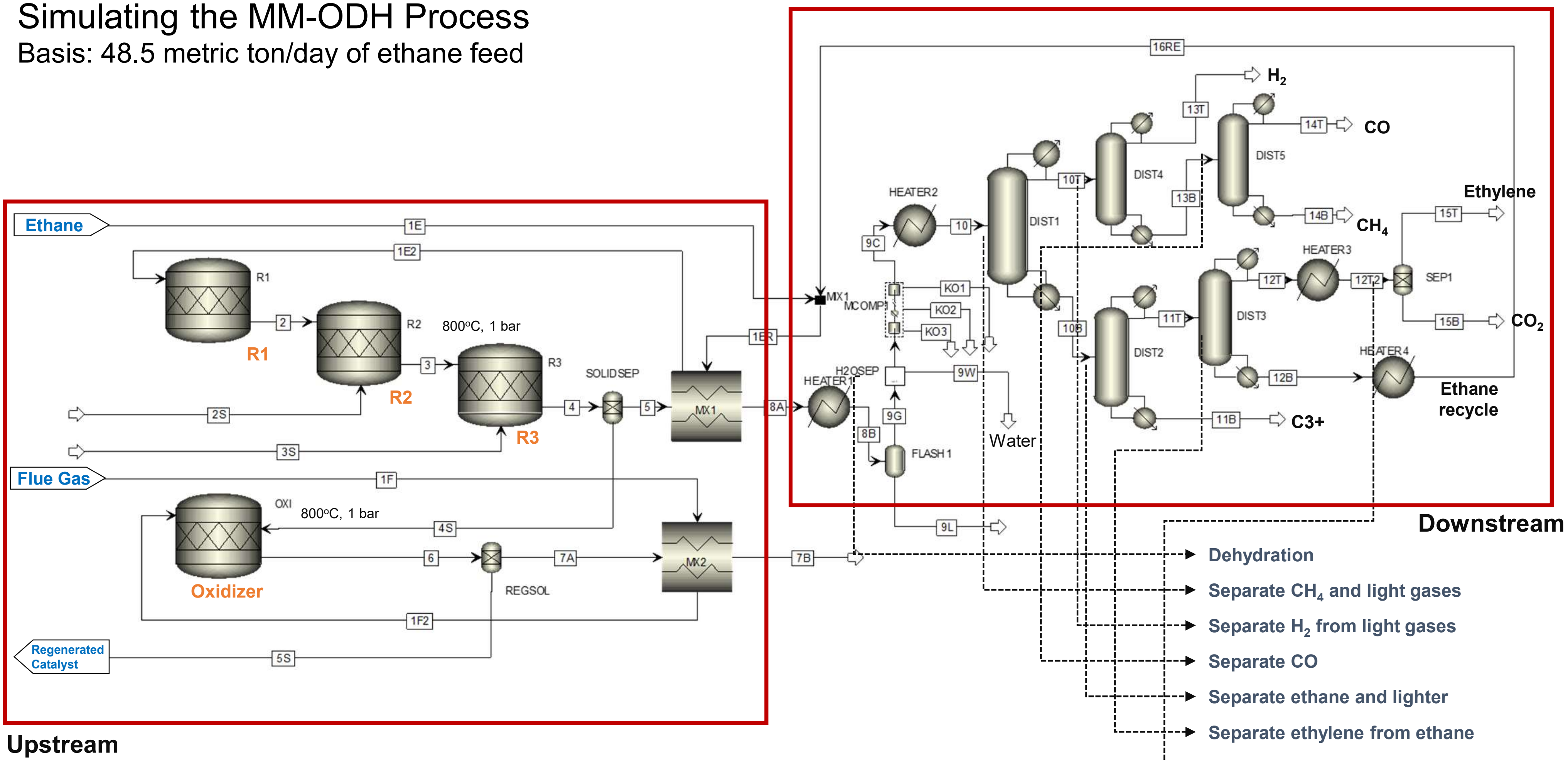
Excellent stability was observed throughout the 500 reaction cycles

TEA and LCA

Process Modeling in AspenPlus™

Simulating the MM-ODH Process

Basis: 48.5 metric ton/day of ethane feed



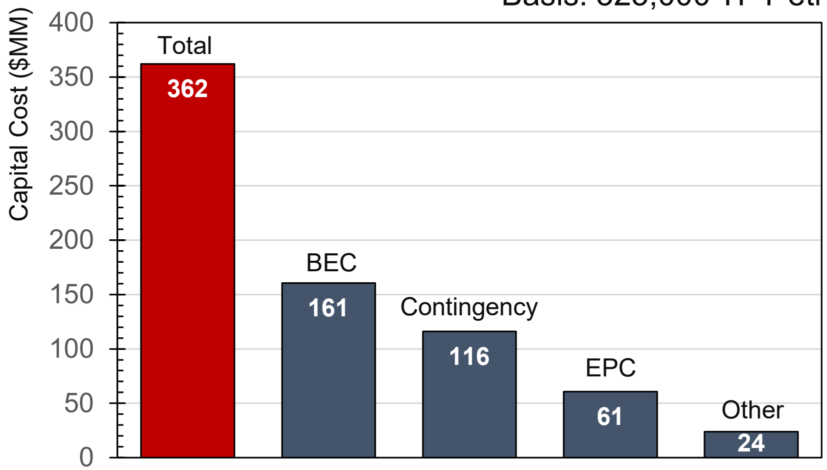
- Dehydration
- Separate CH_4 and light gases
- Separate H_2 from light gases
- Separate CO
- Separate ethane and lighter
- Separate ethylene from ethane
- CO_2 removal

Task 8 Techno-Economic and Lifecycle Analysis

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%**

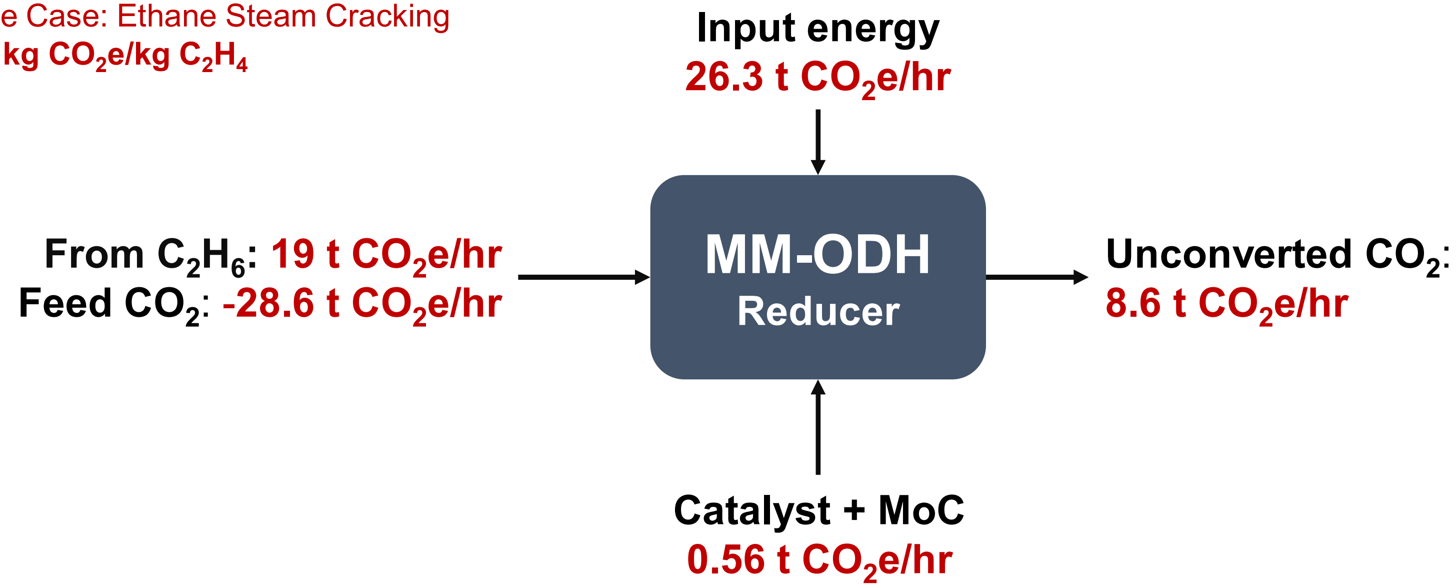
Task 8 Techno-Economic and Lifecycle Analysis

Estimating Net *kg CO_2e emitted per /kg ethylene*

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

Task 8 Techno-Economic and Lifecycle Analysis

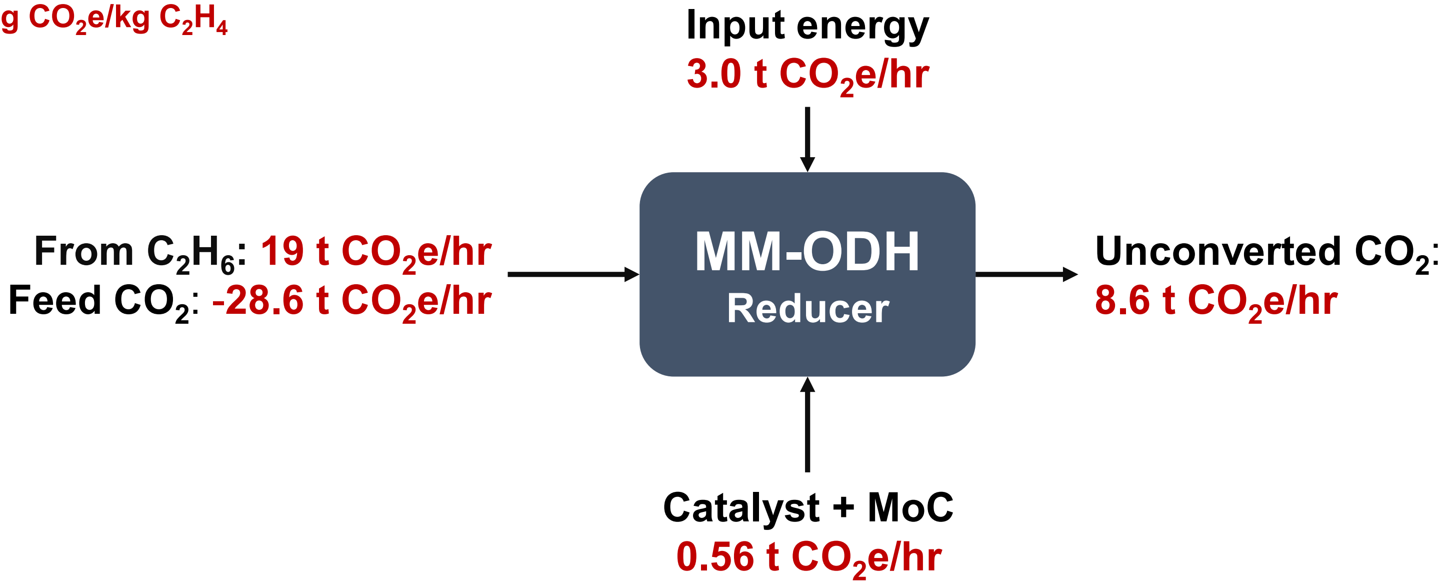
Estimating Net *kg CO_2e emitted per /kg ethylene*

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

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Summary

- Perovskite oxides with high porosity were prepared via scalable methods;
- Oxide – molten salt compatibility were verified and performance exceeded the targets;
- Molten salt with optimized compositions alone were also shown to be highly effective;
- >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 savings and significant economic benefits;
- All the key milestones have been met.

Future work beyond the project:

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

WestVirginiaUniversity

Susteon

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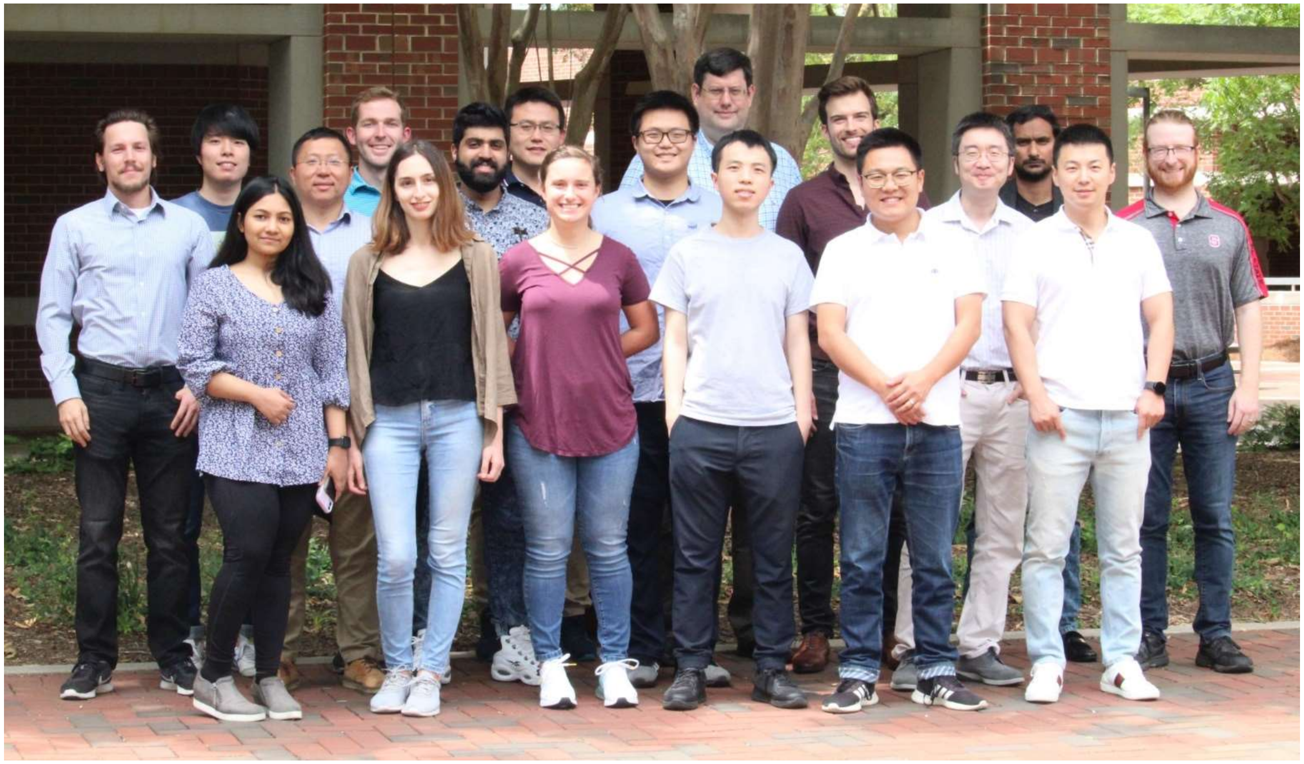
Acknowledgements



NCSU:

Kyle Vogt-Lowell, Dennis Chacko, Luke Neal

WVU:

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Susteon:

Vasudev Haribal, Raghubir Gupta, Andrew Tong, Emma Li

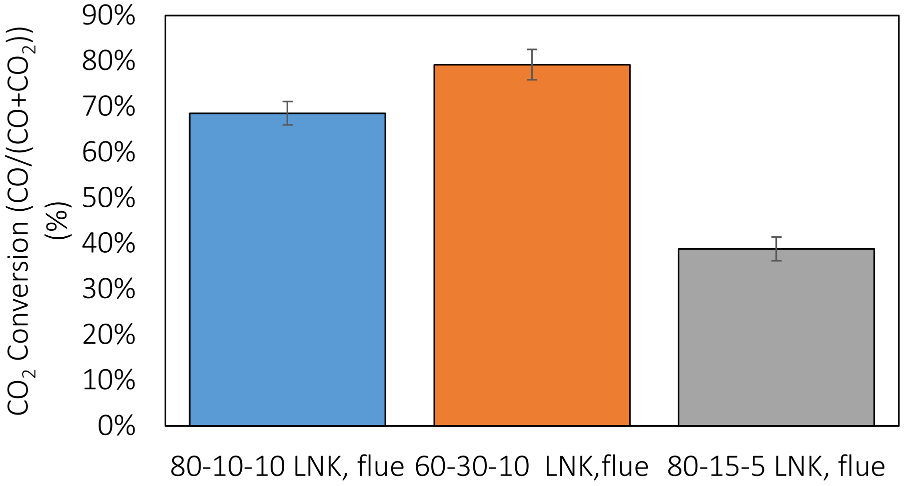
Naomi O'Neil
Greg Imler

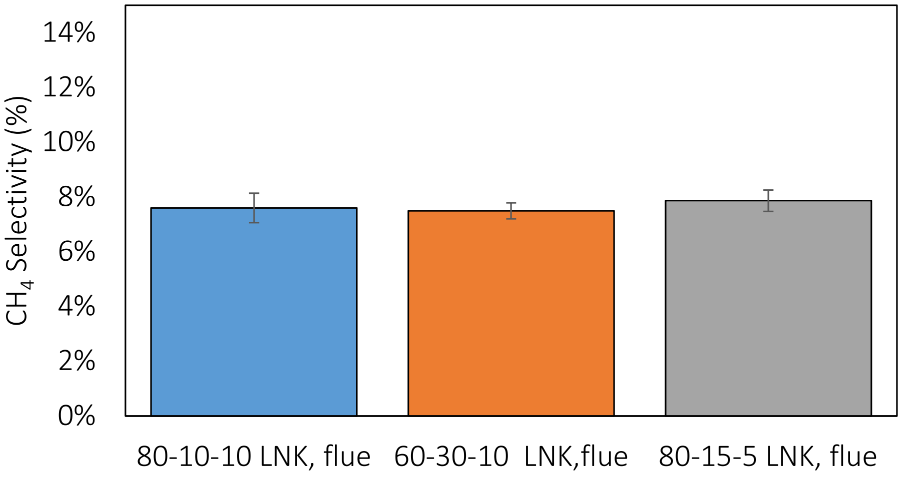
Thanks for the support!
Questions or suggestions?

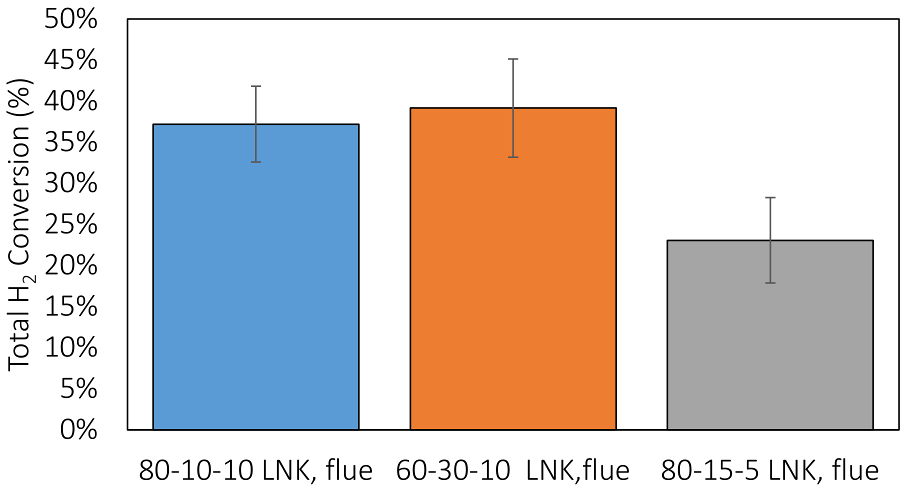
Project Schedule and Milestones

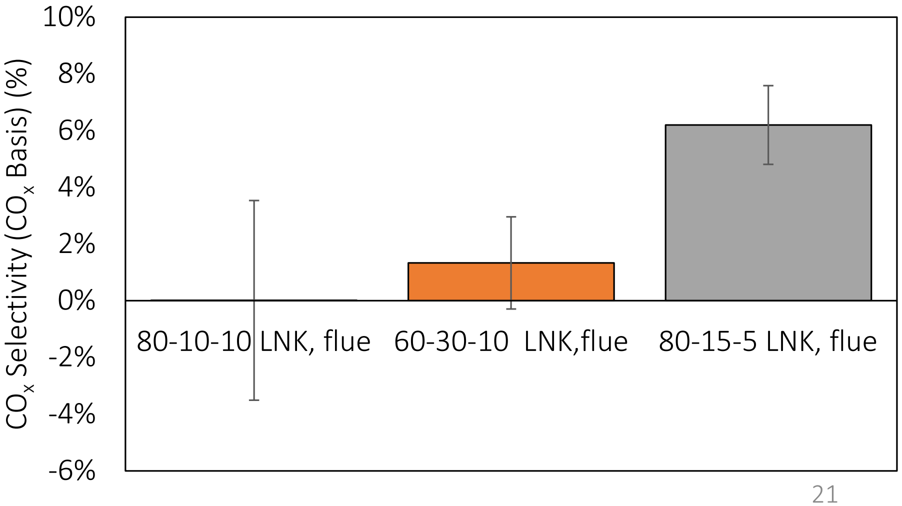
		Stage I				Stage II								
Task Name	Team Member	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12	Q13
Task 1 Project Management and Planning	NCSU/Susteon	■	■	■	■	■	■	■	■	■	■	■	■	■
Milestone 1.1: PMP modification	NCSU	◊												
Milestone 1.2: TMP	NCSU/Susteon	◊												
Task 2.0: Redox Catalyst Synthesis 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													◊

Task 7 Redox Catalyst Optimizations



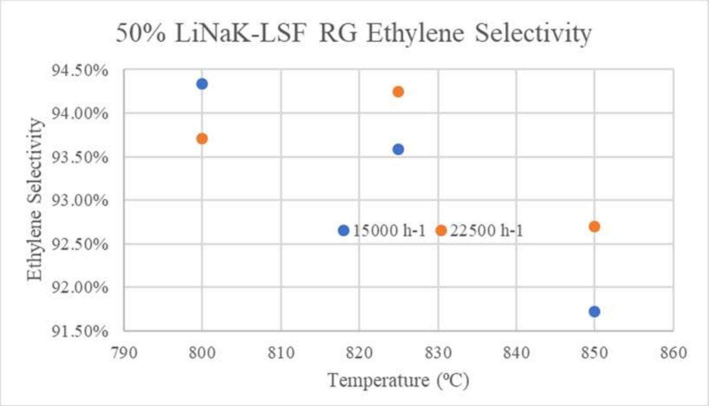


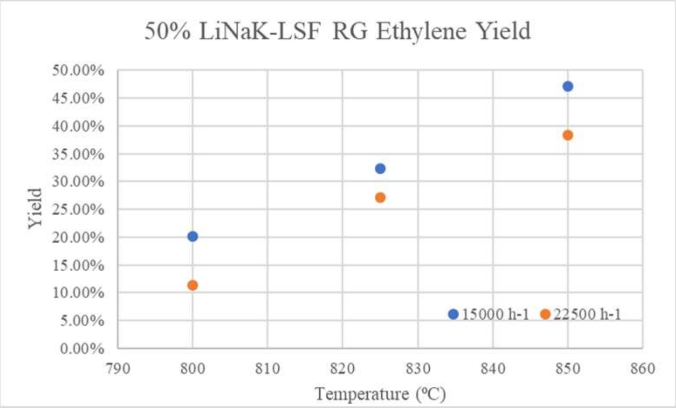


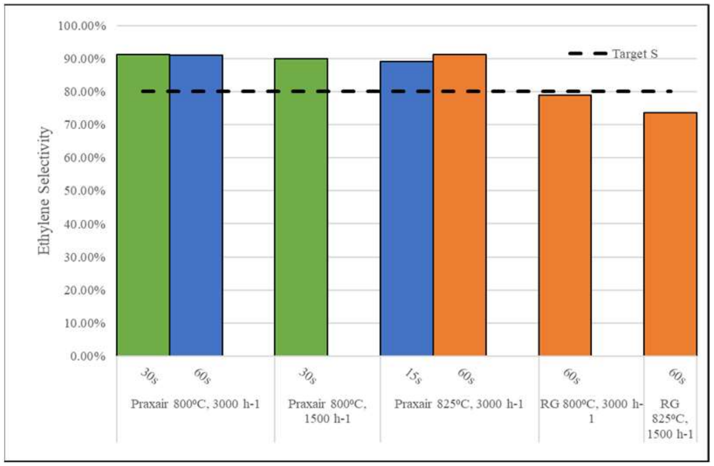


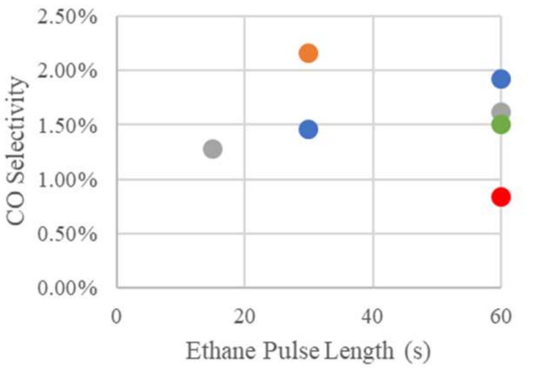
Task 2 Redox Catalyst Synthesis and Characterizations

Reactive Performance









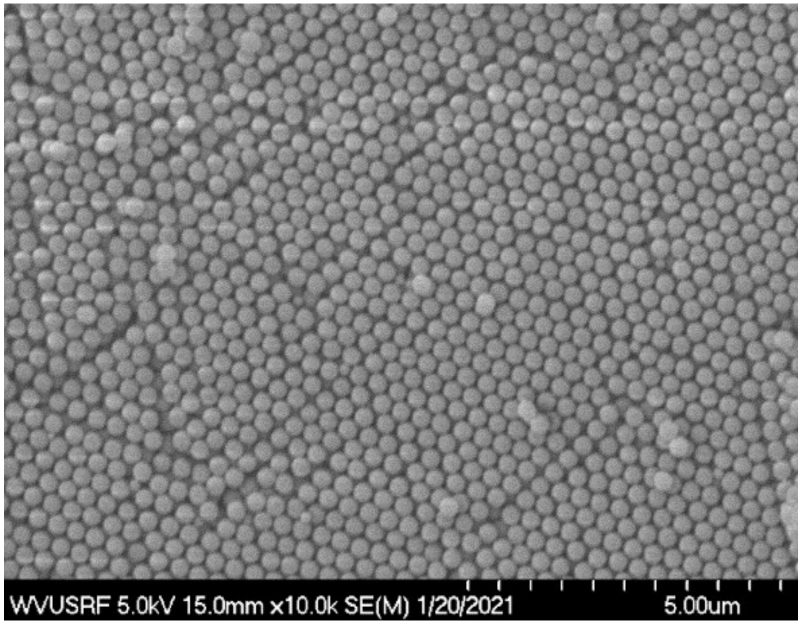
CO yields were unsatisfactory!

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



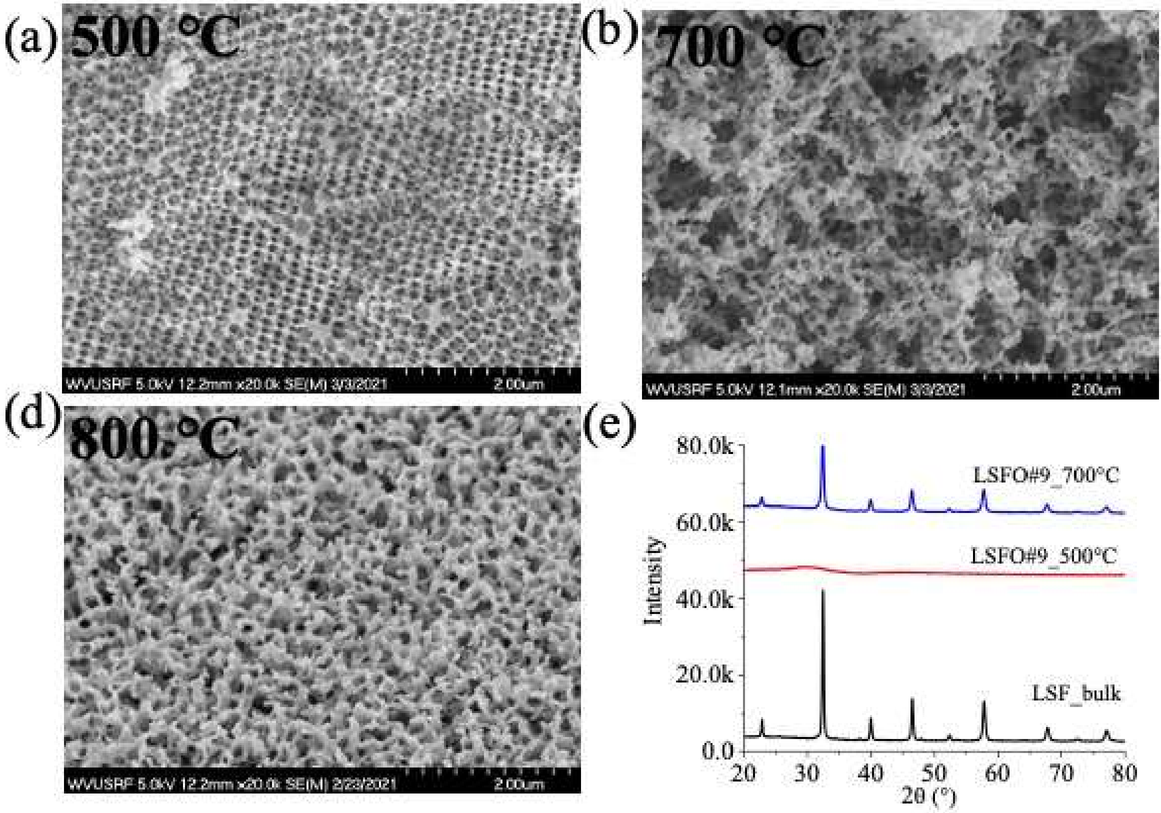
SEM image of the as-synthesized PMMA

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.

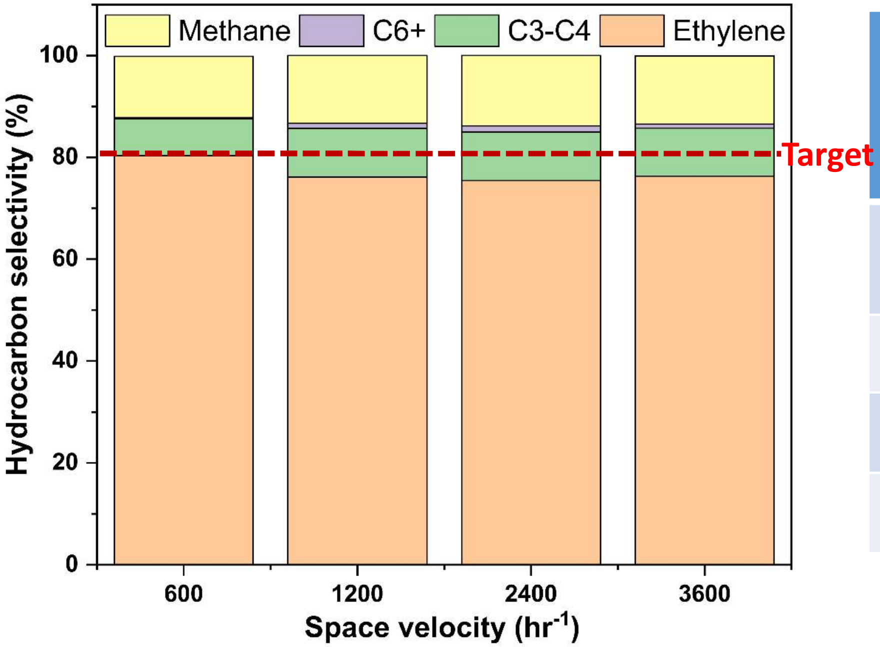
OBSERVATIONS:

- 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)).

Redox Catalyst Synthesis and Testing

Effect of CO_2 Space velocity

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

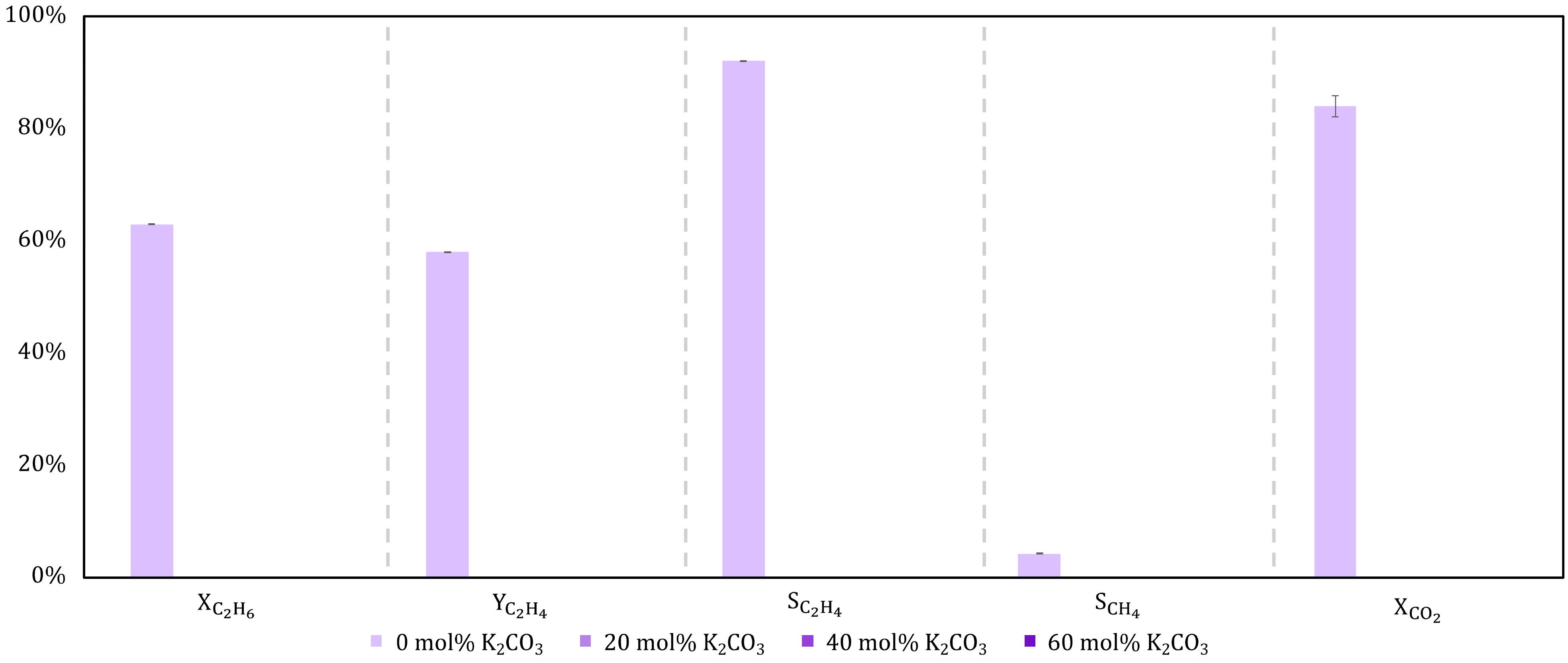
Figure: Hydrocarbon Product distribution during ethane injection (5th injection cycle)

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

- 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 3 Redox Catalyst Optimizations

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



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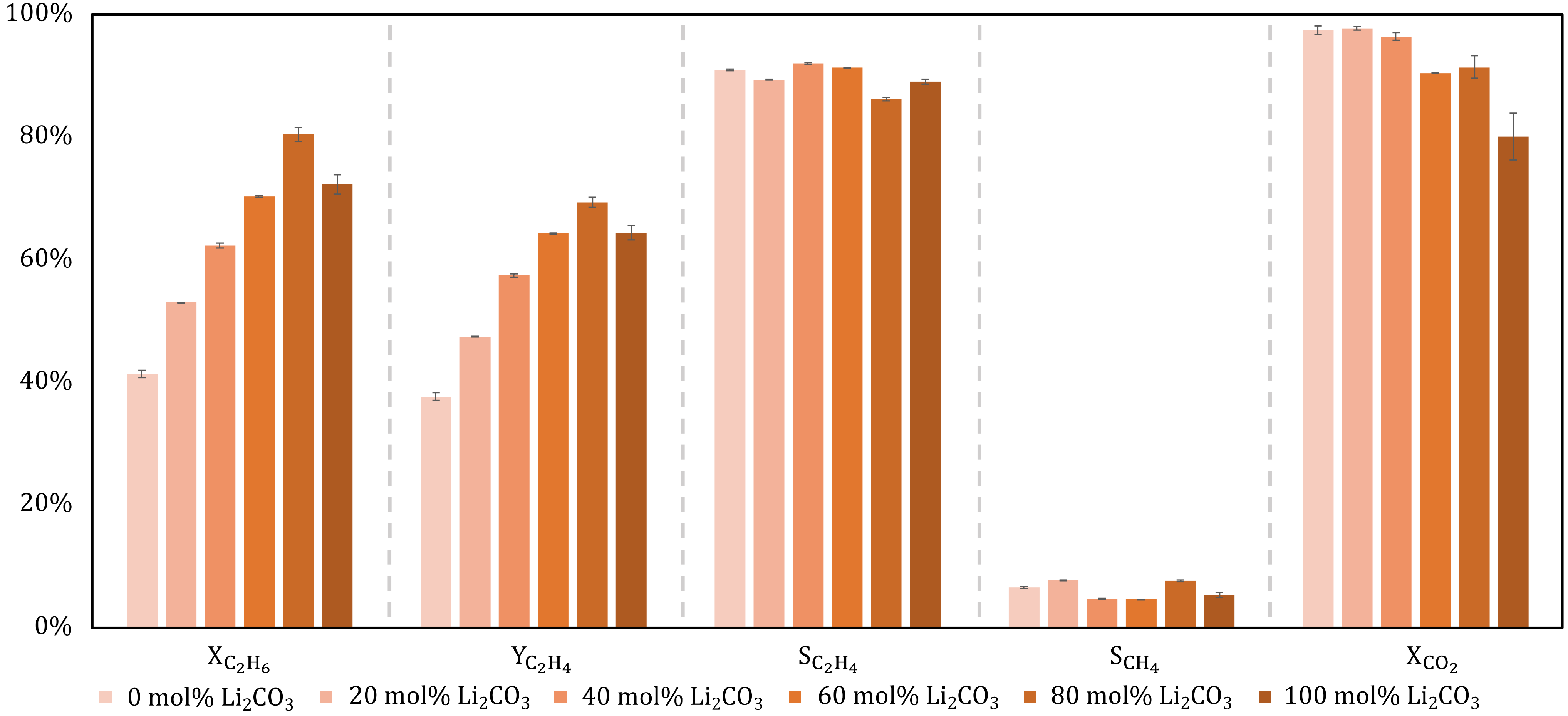
Optimizations of the Molten Salt Composition

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



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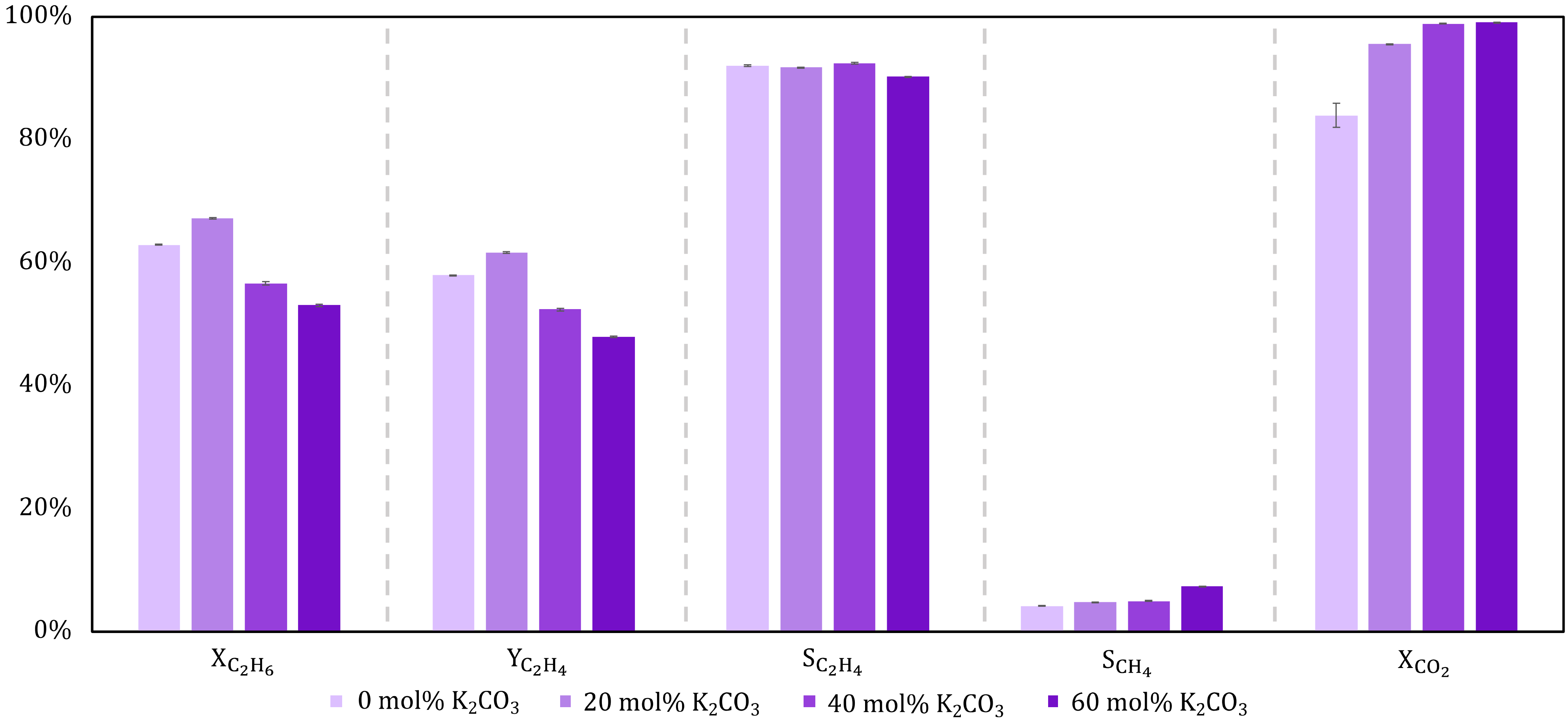
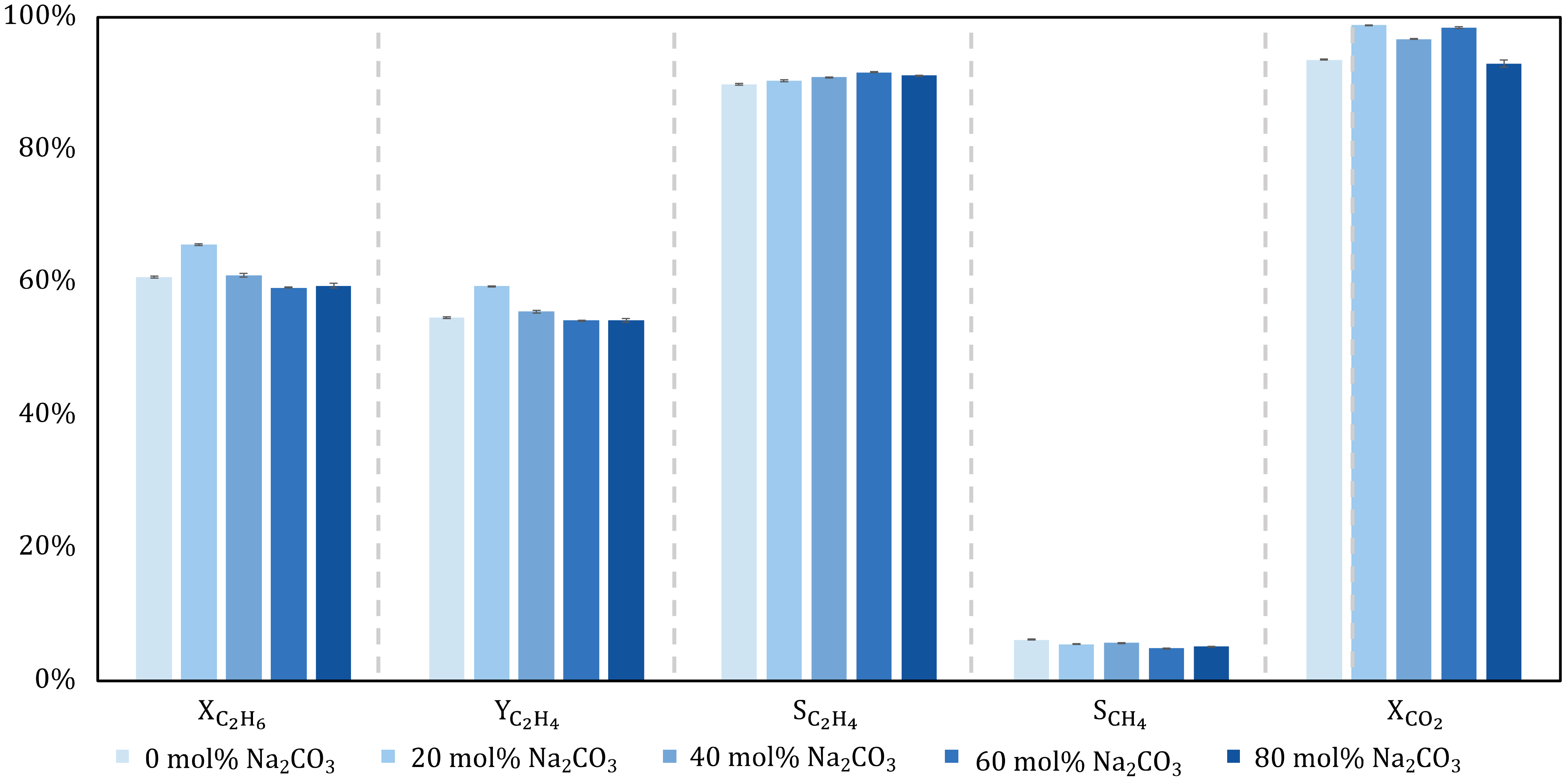
Task 3 Redox Catalyst Optimizations

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



Task 3 Redox Catalyst Optimizations

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



Task 3 Redox Catalyst Optimizations

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