

A Novel Molten Salt System for CO₂ 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: Naomi O'Neil



08/15/2022

- Project Overview and Technology Background
- Technical Approach and Current Status
- Future development plan
- Summary

Project Overview

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

	DOE Funds	Cost Share
NC State Univ. <i>Dr. Fanxing Li</i>	\$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.





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



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Molten Salt Mediated CO₂-ODH:

1) $C_2H_6 + H_2 \rightleftharpoons C_2H_4$

 $H_2 + M_2CO_3 \rightleftharpoons 2MOH + H_2O + CO$

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

Cracking/Dehydrogenation

Modified RWGS



ODH

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

CO₂-Capture:

- 1) CO_2 (in flue gas) + 2MOH \rightarrow X₂CO₃ + H₂O
- 2) $MeO_{x-1} + \frac{1}{2}O_2$ (in flue gas) $\rightarrow MeO_x$



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



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Preliminary Data for MM-ODH



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 $^{\circ}$ C, and 75% CO₂ conversion with 85% CO₂ 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% CO₂ conversion, and 90% CO₂ 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 5(Q2-Q8). 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.

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.

Perceived Risk	Risk Rating			Mitigation/Response Strategy			
	Probability						
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 Over	rsight 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.			

Risk Mitigation

NC STATE UNIVERSITY Project Progress: Experimental Set-up





In-line QMS

Gas Chromatography

*CO*₂-*Capture (Step 1):* CO₂ (in flue gas) + X₂O (dissolved alkali metal oxide in the molten salt) → X₂CO₃ MeO_{x-1} + 1/2O₂ (in flue gas) → MeO_x

*CO*₂-*ODH* (*Step 2*) R-CH₂-CH₃ + X₂CO₃ → R-CH=CH₂ + CO + H₂O + X₂O (R can be H for ethane, CH₃, or CH₃-CH₂) R-CH₂-CH₃ + MeO_x → R-CH=CH₂ + H₂O + MeO_{x-1}

Project Progress: Experimental Set-up at WVU











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Overview of the Key Results









Task 2 Redox Catalyst Synthesis and Characterizations Porous Oxide Synthesis



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.

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Reactive Performance



Effect of Ethane Space velocity

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

Catalyst: 60%Li₂CO₃@LSF, Temperature: 750 °C Injection: Reducing agent: 30 sec, Oxidizing agent: 90 sec Oxygenate S.V = 600 hr-1 WestVirginiaUniversity.

60% Li ₂ CO ₃ /LSF	60% Ethane ^{Eff} CO ₃ /LSF conversion ^{Se} (%)		Methane Selectivity (%)	H ₂ conversion (%)	CO ₂ conversion (%)	CO ₂ capture (%)		
600	71.5	71.2	18.4	39	93.7	36.4		
1200	70.5	70.5 70.6		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 % ₁₆

Reactive Performance



Effect of CO₂ Space velocity

Ethylene Methane H₂ conversion 60% Ethane CO₂ CO₂ selectivity **Selectivity** (%) Li₂CO₃/LSF conversion conversion capture (%) (%) (%) (%) (%) 80.3 12 28 67.5 93.8 48.1 600 76.3 13.3 17.5 56.1 89.4 28 1200 13.8 17.8 75.6 53.2 89.4 22.4 2400 76.4 13.4 17.4 3600 48.1 89.4 22.1

• An increase in CO₂ space velocity leads to less residence time to replenish molten carbonate salt which results in decrease in CO₂ capture on the molten salt

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

Catalyst: **60%Li₂CO₃@LSF**, Temperature: 750 °C Injection: Reducing agent: 30 sec, Oxidizing agent: 90 sec Ethane S.V = 3600 hr-1

West Virginia University.

Reactive Performance

Effect of oxygenate molecule



Oxygenate	Ethane conversion (%)	Ethylene selectivity (%)	Methane Selectivity (%)	H ₂ conversion (%)	CO ₂ conversion (%)	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

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

Catalyst: 60%Li₂CO₃@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 West Virginia University.









Observations from Li_2CO_3 study (0 – 80 mol%):

> Ethane conversion increases.





Observations from Li_2CO_3 study (0 – 80 mol%):

- **>** Ethane conversion increases.
- > Ethylene yield increases.





Observations from Li_2CO_3 study (0 – 80 mol%):

- **>** Ethane conversion increases.
- > Ethylene yield increases.
- > H2 and CO2 conversion attain maxima at intermediate loadings.









Observations from K_2CO_3 study (0 – 60 mol%):

> Ethane conversion decreases.





Observations from K_2CO_3 study (0 – 60 mol%):

- **>** Ethane conversion decreases.
- > Ethylene yield decreases.





Observations from K_2CO_3 study (0 – 60 mol%):

- Ethane conversion decreases.
- > Ethylene yield decreases.
- > H₂ conversion decreases as CO₂ conversion increases.

Task 3 Redox Catalyst Optimizations

Catalyst	Reaction Metric	Current Performance	DOE Milestone			
	Temperature	750°C	<u><</u> 750°C			
	Ethylene Yield	~55%	<u>></u> 50%			
1) Molten LNK-LSF	Ethylene Selectivity	~81%	<u>></u> 80%			
slurry	CO ₂ Conversion	~93%	<u>></u> 75%			
	CO ₂ Capture	~50%	<u>></u> 85%			
	Temperature	800°C	<u><</u> 750°C			
	Ethylene Yield	60.7%/66.6%	<u>></u> 50%			
2) Molten LNK bath with two compositions	Ethylene Selectivity	92.4%/91.7%	<u>></u> 80%			
	CO ₂ Conversion	91.9%/83%	<u>></u> 75%			
	CO ₂ Capture	>85%	<u>></u> 85%			

Milestone 2.2 *Catalyst Synthesis Screening*: four redox catalysts giving at least 80% selectivity and 50% yield for ethylene at <750 °C, and 75% CO₂ conversion with 85% CO₂ capture)

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Excellent stability was observed throughout the 500 reaction cycles

Task 7 TEA driven redox catalyst optimizations



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



Tasks 4 and 6 Techno-Economic and Lifecycle Analysis

Preliminary Process Models in AspenPlus™

Comparing ethane CO₂-ODH with MM-ODH







Tasks 4 and 6 Techno-Economic and Lifecycle Analysis

Preliminary Process Models in AspenPlus™

Comparing ethane CO₂-ODH with MM-ODH



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.





Tasks 4 and 6 Techno-Economic and Lifecycle Analysis

Preliminary Process Models in AspenPlus™

Estimating the cost of ethylene production using MM-ODH



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.

State Point Data Table

Synthesis of Value-Added Organic Products

Technology Performance Data

	Units	Measured/Current Performance	Projected/Target Performance			
Synthesis Pathway Steps						
Step 1 (based on CO ₂)	mol ⁻¹	X ₂ O+CO ₂ •	→X ₂ CO ₃ [#]			
Step 2	mol ⁻¹	X ₂ CO ₃ +C ₂ H ₆ → CO	$+C_2H_4+H_2O+X_2O$			
Step 3	mol ⁻¹	$CO+C_2H_4+H_2O_2$	→C ₂ H ₅ (COOH)			
Source of external intermediate		Ethane from	n shale gas			
Reaction Thermodynamics						
Reaction		Thermoc	chemical			
AH CLESS	KJ/mol	-205 (Step 1), 382 (S	tep 2), -166 (Step 3)			
$\Delta G^{\circ}_{\mu\nu}$	KJ/mol	-154 (Step 1), 283 (St	tep 2)&, -296 (Step 3)			
Conditions		$700 - 800 \ ^{\circ}\mathrm{C}$	650 – 750 °С			
CO ₂ Source		Simulated Flue Gas	Simulated Flue Gas			
Catalyst/Reaction Medium		Alkali oxide or Alkali oxide/Perovskite	Alkali oxide or Alkali oxide/Perovskite			
Pressure	bar	1	1-2			
CO ₂ Partial Pressure	bar	0.15	0.02-0.15			
Temperature	<u>~</u>	750 - 800 °C	750 °C			
Performance		(range)	(minimum)			
Nominal Residence Time	sec	1	0.5			
Selectivity to Desired Product	%	92.4%	>90%			
Product Composition		(range)	(optimal)			
Product: Ethylene*	mol%	65.7%	>55%			
Co-Product: CO*	mol%	83% >75%				
Desired byproduct: C3+ olefins*	mol%	3.3% n/a				
Unwanted byproduct*: CO ₂ ; CH ₄	mol%	17% (CO ₂); 3.6% (CH ₄) <25%				
Unconverted Feed*: Ethane	mol%	27.5%	<45%			
Grand Total	mol%	100% (HCs); 100% (CQ _x) 100% (HCs); 100% (CQ				

* To be consistent with yield definitions, the mole percentages for hydrocarbons were calculated on a carbon basis using the feed ethane as the denominator; and the CO and CO_2 percentages were calculated using the captured CO_2 as the denominator

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Plans for Future Development

Future work within the project:

- TEA update;
- TEA driven optimization of the reaction media and redox catalysts;
- Reactor system design, final TEA, and commercialization plan;

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;

Scale-up potential:

- Further scale up/pilot testing (TRL-6, 100 kg/day);
- Demonstration and commercialization with industrial partner(s);

Summary Slide

- Perovskite oxides with high porosity were prepared via various methods;
- Oxide molten salt compatibility were verified and reactive performance exceeded the CO₂ 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% CO₂ capture, >90% CO₂ 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.







Thanks for the support! Questions or suggestions?

Acknowledgement





West Virginia University.

Susteon

NCSU:

Luke Neal, Kyle Vogt-Lowell, Dennis Chacko

WVU:

John Hu, Sonit Balyan, Xingbo Liu, Wenyuan Li

Susteon:

Vasudev Haribal, Raghubir Gupta



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	٥											
Milestone 1.2: TMP	NCSU/Susteon	٥											
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		٥										
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				٥								
Task 4.0: Techno-Economic and Lifecycle Analysis	Susteon												
Subtask 4.1 Process Model Refinement and Analysis	Susteon												
Milestone 4.1: Initial TEA	Susteon				٥								
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						٥						
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										٥		
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												٥
Milestone 8.2: Commercialization Road Map	Susteon												♦

Appendix: Project Organizational Structure



Temperature (°C)	Cycle Time (min)	Ethane Conversion	Ethylene Yield	C ₂ H ₄ Selectivity	C ₂₊ Selectivity	H ₂ Conversion	CO ₂ conversion
	15	-	-	-	-	-	-
750	25	46.80%	44.60%	95.40%	97.80%	33.00%	86.20%
	30	-	-	-	-	-	-
	15	63.30%	59.00%	93.20%	96.70%	41.50%	77.70%
775	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%
	15	85.30%	73.80%	86.50%	91.80%	41.30%	94.50%
825	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 °C, and 75% CO₂ conversion with 85% CO₂ capture)



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).

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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.

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- Targeted 3DOM structure of LSF is
- 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)).



High frequency intercept of EIS is a mixed impedance of ions and electrons. Low frequency intercept is not attainable.

Galvanostatic test was used to obtain sustainable ion conductivity.



Sample: Na₄Mg(WO₄)₃ Sample weight: 4.0g

It is feasible to obtain the EIS of $Na_4Mg(WO_4)_3$ within N₂ & Air atmosphere using Galvanostatic Test





Atmosphere: Air Temperature: 900°C I=0.0001A



Atmosphere: 5% H₂ 3.5% steam bal. N₂



As the temperature increases, the reaction becomes more intense, and the gold paste gradually dissolves in the crucible



Before Test



After Test in N₂&O₂ atmosphere



Crucible After Test in H₂ Atmosphere



Tube After Test in H₂ Atmosphere



Main Problems

Under a 5% H_2 3.5% steam bal. N_2 atmosphere, the reaction is active and vigorous.



1. The gold paste melted and interfered with the normal ionic current.

2. The $Na_4Mg(WO_4)_3$ sample evaporated. No reliable measurement can be made.







Fig. (a) XRD patterns of AN-50wt% composite on heating; (b) and (c) are the backscatter-electron SEM pictures of AN-50wt% samples obtained by furnace cooling and quenching methods, respectively.^[1]

[1] Xu, Jungu, et al. "High oxide ion conduction in molten Na2W2O7." Advanced Electronic Materials 4.12 (2018): 1800352.

