Sustainable Conversion of Carbon Dioxide and Shale Gas to Green Acetic Acid via a Thermochemical Cyclic Redox Scheme

Fanxing Li research group

North Carolina State University

Partners:

Susteon Inc.

Linde, plc (cost share partner)

NETL Project Manager: *Naomi Oneil*

Background and Project Overview

Project Funding: DOE - $797,244; Cost share - $199,606

Performance Period: 02/01/2019 – 01/31/2022

Project Participants: North Carolina State University; Susteon Inc.; Linde (cost share partner);

Project Objective: To develop a process for sustainable and cost-effective production of acetic acid from carbon dioxide, domestic shale gas, and waste heat.

Proposed Strategy: To perform CO_2-splitting and methane partial oxidation (POx) in a synergistic two-step, thermochemical redox scheme via a hybrid redox process (HRP).

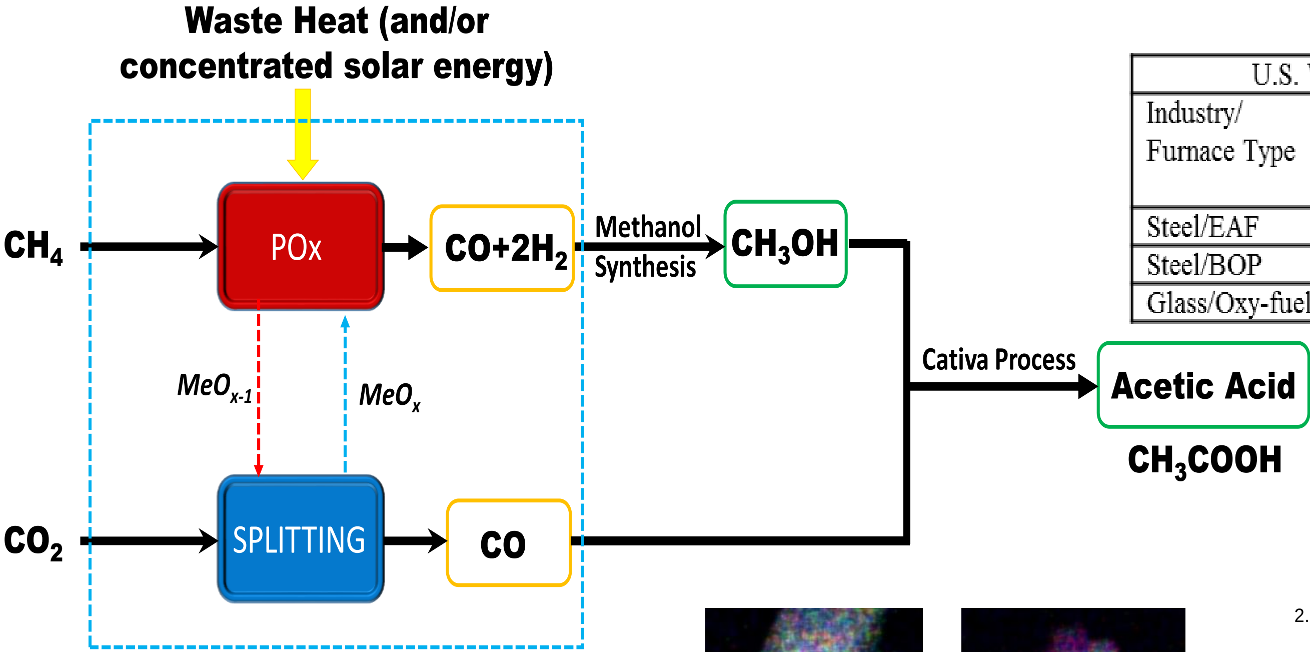
Specific Objectives

(1) Year 1: unveil the optimization strategies for the redox materials to further improve their activity at low temperatures (≤ 700 °C) while maintaining their redox stability;

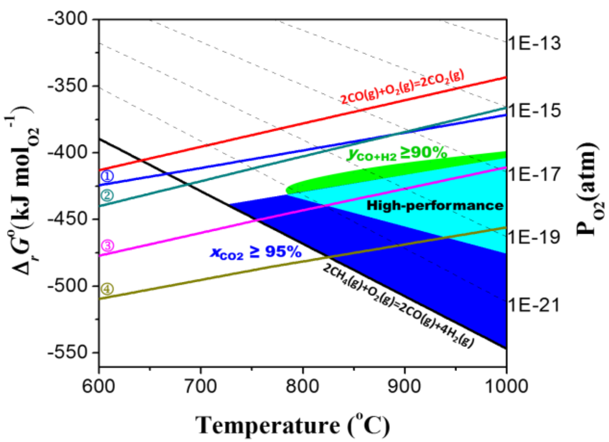
(2) Year 2: comprehensively investigate the robustness and long-term performance of the redox materials. Techno-economic and life-cycle analyses will be updated with new experimental results.

(3) Year 3: Further optimization of the redox materials. Comprehensive reactor and process designs for scale-up and commercialization.

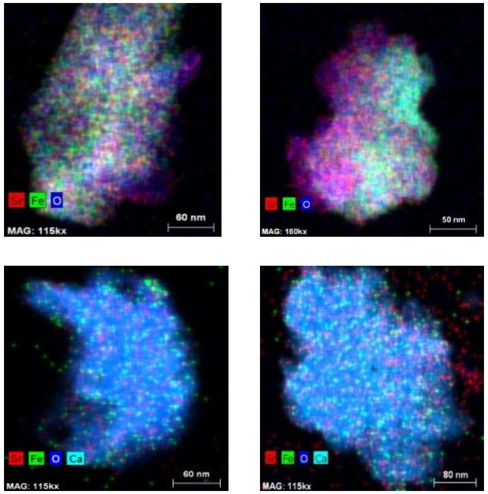
Technology Background

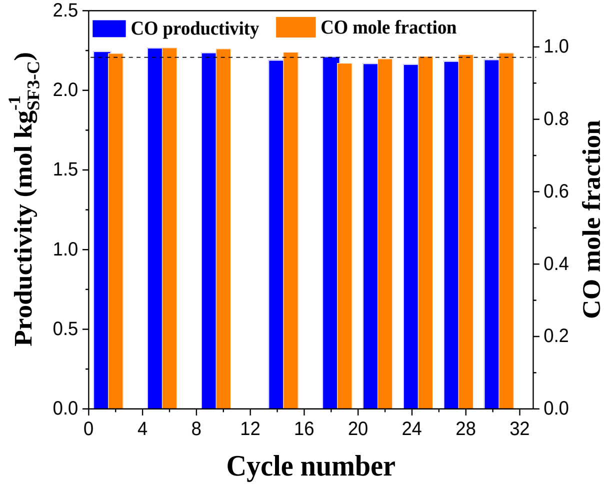


U.S. Waste Heat Sources (Annual)		
Industry/ Furnace Type	Waste Heat @700° C (GJ)	CO_2 Converted (tonne/year)
Steel/EAF	36,547,000	6,180,000
Steel/BOP	14,300,000	2,260,000
Glass/Oxy-fuel	4,033,000	683,000

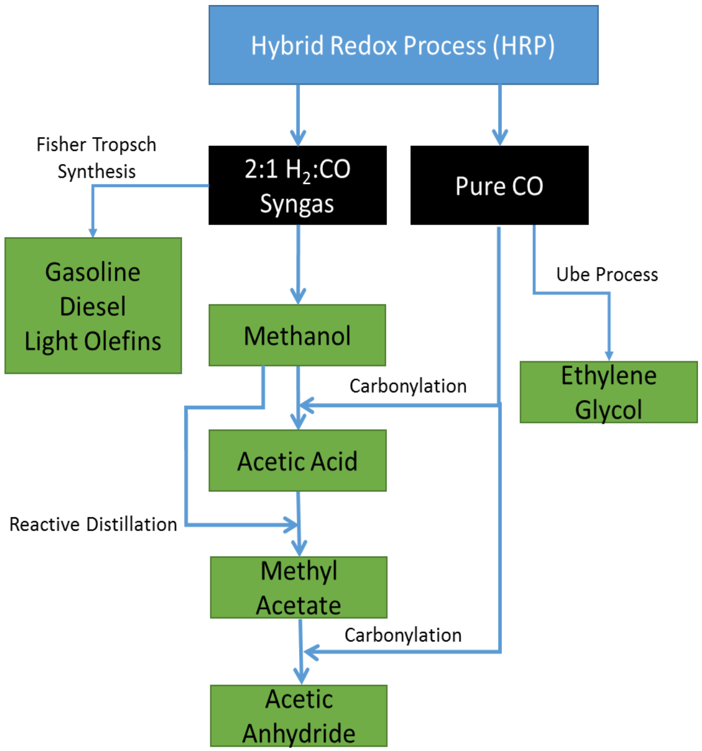


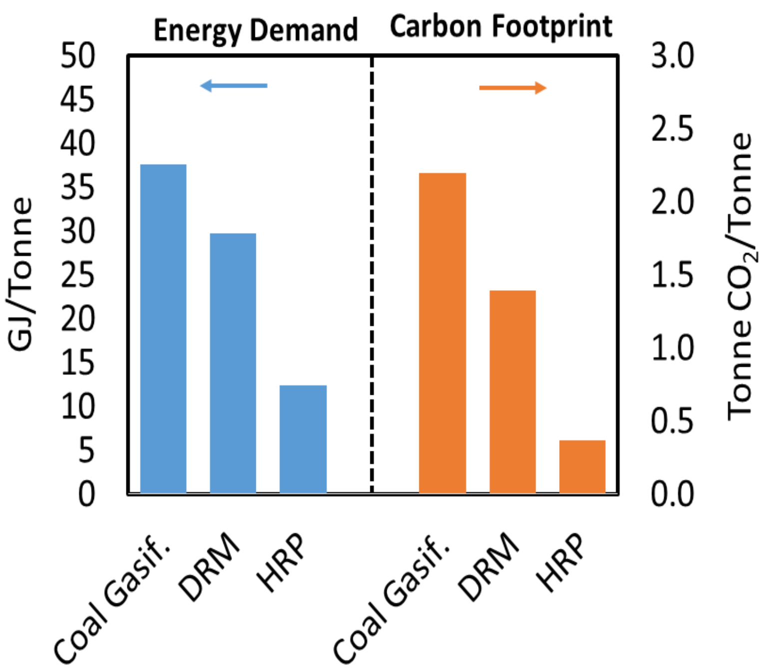
(1) FeO; (2) $SrFe_2O_4$; (3) $Sr_2Fe_2O_5$; (4) $Sr_3Fe_2O_6$





Technology Background





HRP can be a highly versatile and sustainable process for CO_2 utilization and chemical production.

Technology Background

	HRP	Dry Reforming	Coal Gasification
Unit operations for syngas preparation	HRP Reactors Methanol Reactor Acetic Acid Reactor	Reforming Cryogenic Separation WGS High Recycle Methanol Reactor Acetic Acid Reactor	Air Separation Coal Gasifier WGS Reactor CO_2 removal Cryogenic CO recovery MeOH Reactor Acetic Acid Reactor
Energy needs (GJ/tonne) (Figure 3)	20.4*	29.7	38
CO_2 consumed (tonne of CO_2/tonne of AcOH)	0.75	0.75	0
Feedstock including fuel (per tonne of AcOH)	35.4 MM BTU CH_4	44.7 MM BTU CH_4	4 tonnes of coal
Feedstock price	$3/MM BTU	$3/MM BTU	$25/tonne of coal
Capital Recovery ($/tonne of AcOH)	$100[a]	$150[a]	$200[b]
O&M (excluding feedstocks and energy) ($/tonne of AcOH)	$10[c]	$15[c]	$25[d]
Price of CO_2 ($/tonne)[e]	$40	$40	N/A
Cost of Production ($/tonne of AcOH)	$246.20	$329.10	$325.00
Gross Margin	25%	25%	25%
Required Selling Price	$307.80	$411.36	$406.75

Challenges at the project onset: (a) High operating temperature; (b) Long-term redox stability; (c) System design and scale up; (d) Techno-economics.

NC STATE UNIVERSITY

Technical Approach and Project Scope

Research Plan:

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

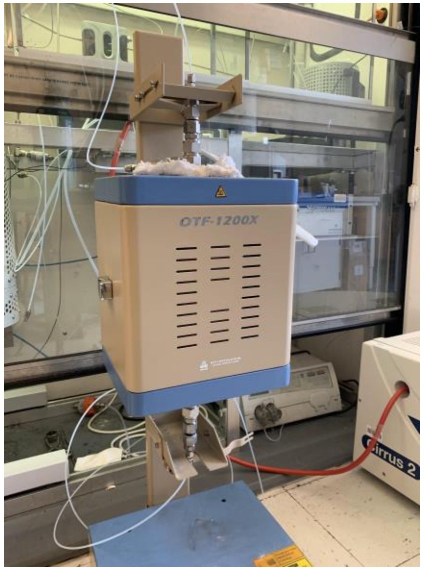
Year II. Stability validation of redox catalysts; Refined TEA and LCA models.

Year III. Redox catalyst demonstration and reactor design; Process scale-up and high fidelity techno-economics.

Key Milestones/Successful Criteria and Timeline:

Q3 Oct.2019	**Title: Milestone 2.2: *Redox material down selection*** Select at least 4 redox catalyst with >20% CO_2/PO_x kinetics improvements and/or >40% per cycle CO yield increase vs the CaO-$SrFeO_3$ reference material.
Q4 Jan.2019	**Title: Milestone 3.2 *Redox performance & stability (decision point)*:** Show CO_2 and methane conversions of >85% at temperatures ≤700 °C after 50 cycles.
Q8 Jan.2021	**Title: Milestone 5.2 *Large lab-scale performance verification (decision point)*:** Show methane and CO_2 conversions of >85% at temperatures ≤700 °C after 500 cycles in a .75" I.D. packed bed.
Q10 Jul.2021	**Title: Milestone 7.1 *Optimized reactor Sizing:*** Report modified reactor sizing based upon TEA optimized catalyst.
Q12 Jan.2022	**Title: Milestone 7.2 *Scalable up material validation:*** Report CO_2 and methane conversions of >85% at process optimized temperature and cycle timing for redox material over 500 Cycles for a one pot synthesize catalyst.

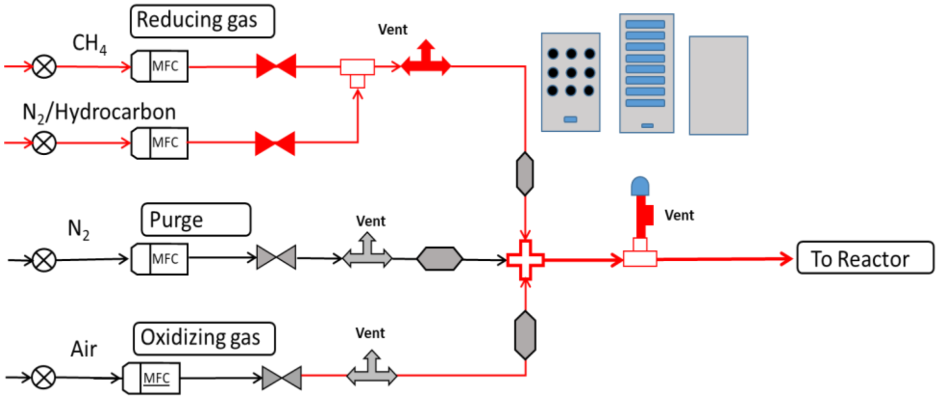
Project Progress: Experimental Set-up



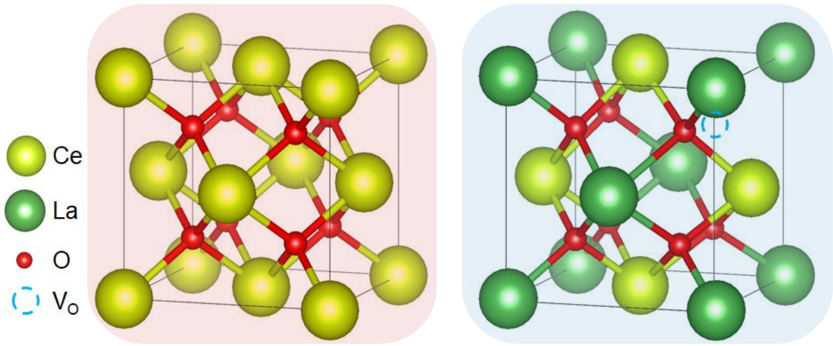
Lab-Scale U-Tube Reactor

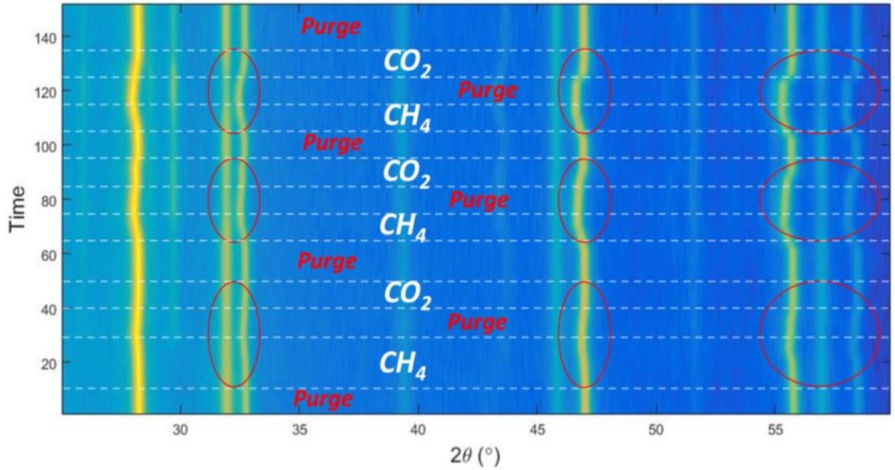
Large packed bed reactor

Bench/small pilot setup

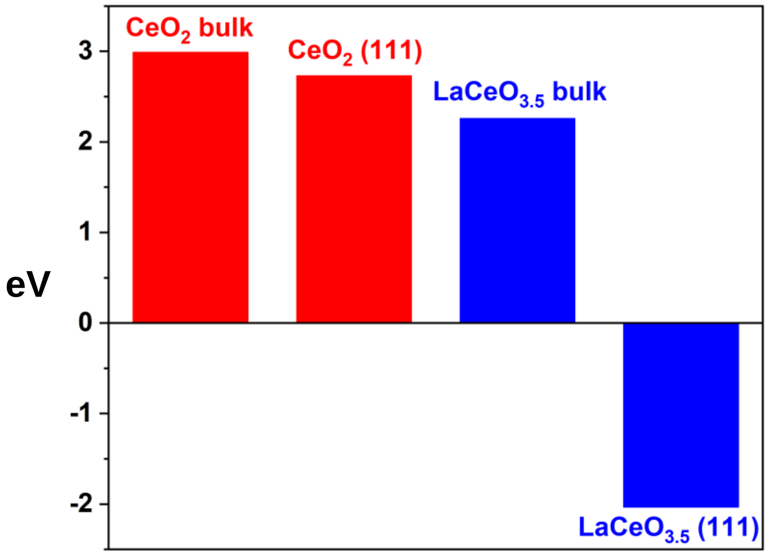


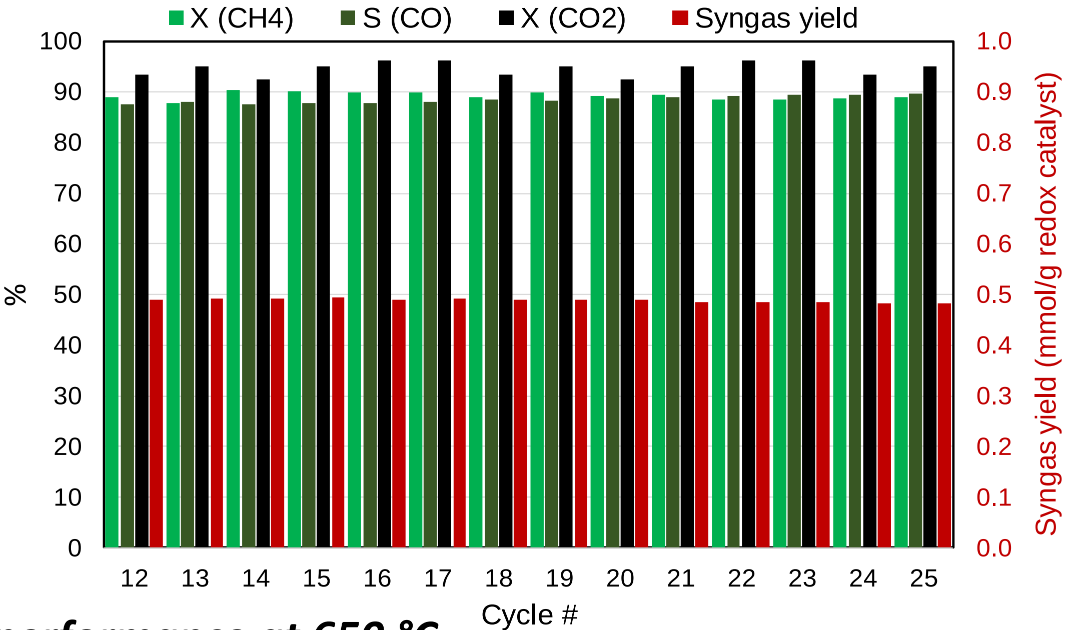
Task 2. Redox Materials Synthesis and Characterizations





Oxygen Vacancy Formation Energy (ΔE_v)



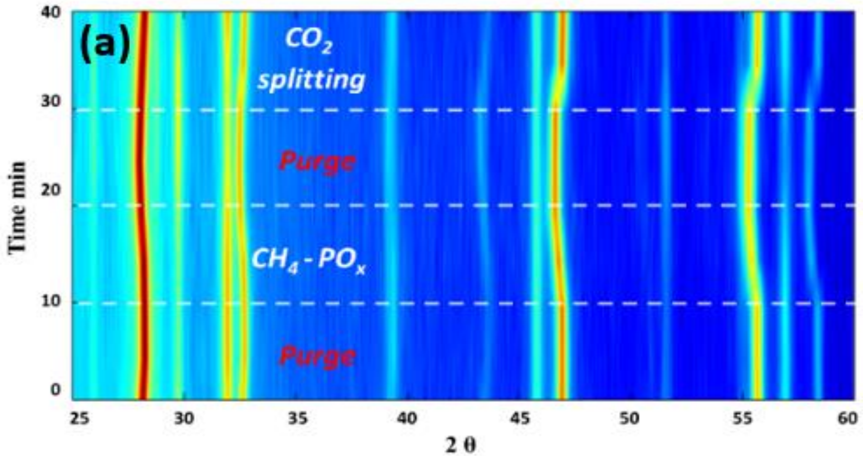


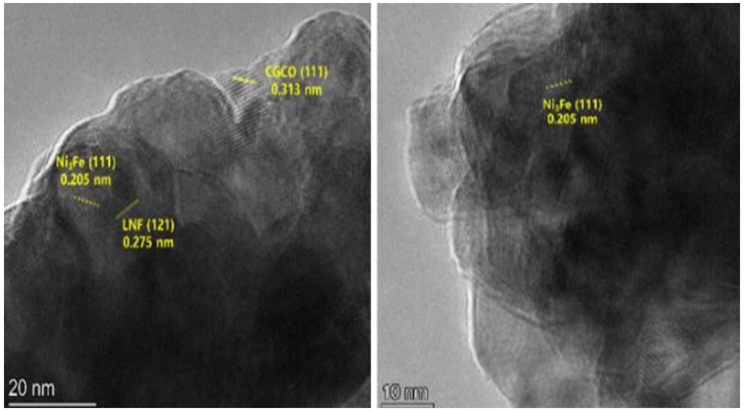
Satisfactory performance at 650 °C

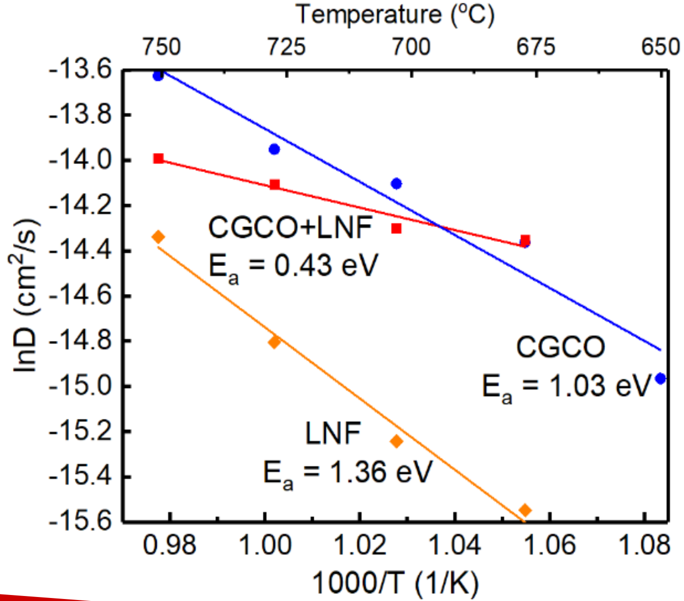
Haribal, et al. ***Advanced Energy Materials***. 1901963:1-10.

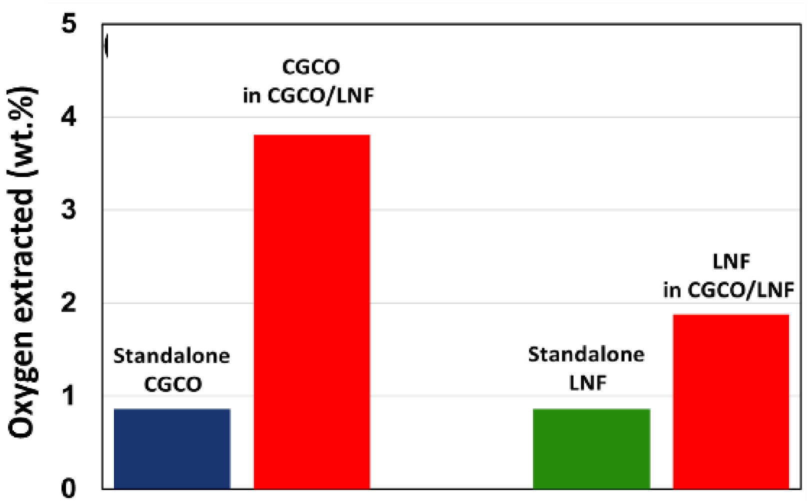
Task 2. Redox Materials Synthesis and Characterizations

PGM Free Mixed Conductive Composites as the Redox Catalyst $Ce_{0.85}Gd_{0.1}Cu_{0.05}O_{2-\delta}$ (CGCO)+$LaNi_{0.35}Fe_{0.65}O_3$(LNF)







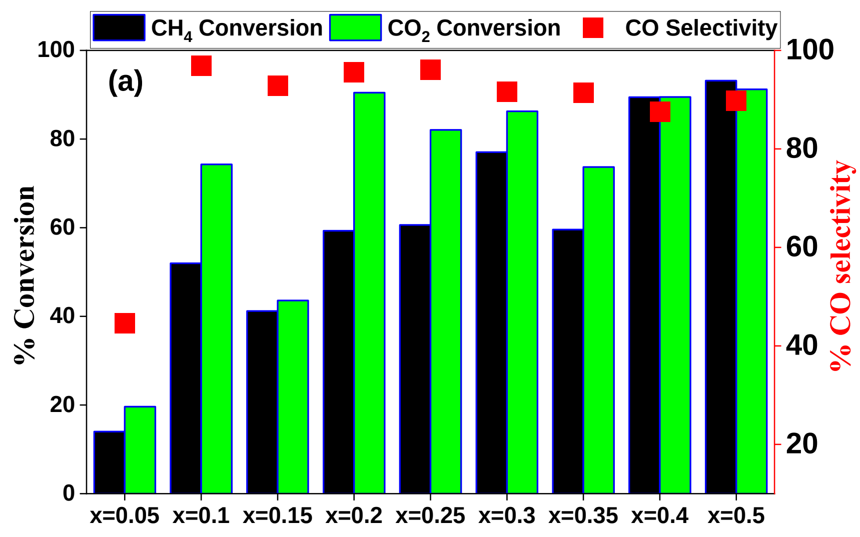


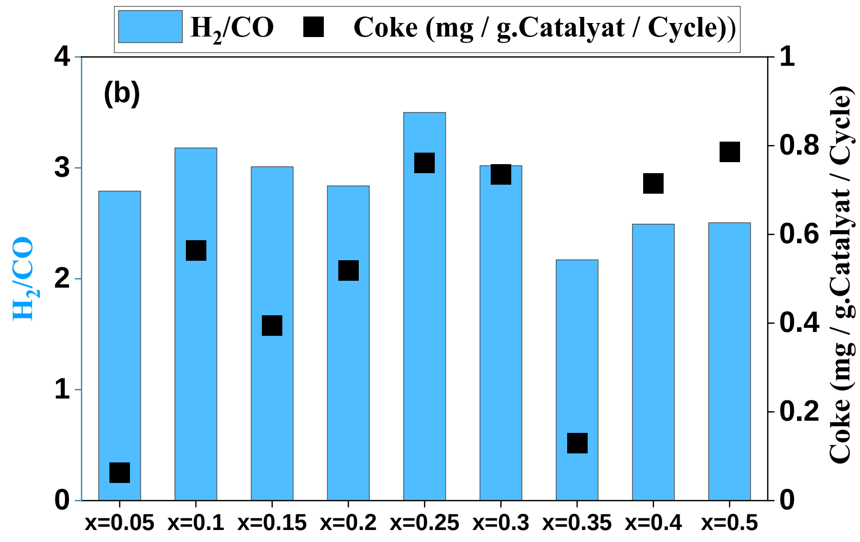
Jiang, et al. ***Journal of Materials Chemistry A***. DOI: 10.1039/D0TA03232H.

Task 3. Further Development of Redox Materials

$LaNi_xFe_{1-x}O_3$ with Different Ni Loading (x≤ 0.5)

Redox Catalyst: $LaFe_{1-x}Ni_xO_3$



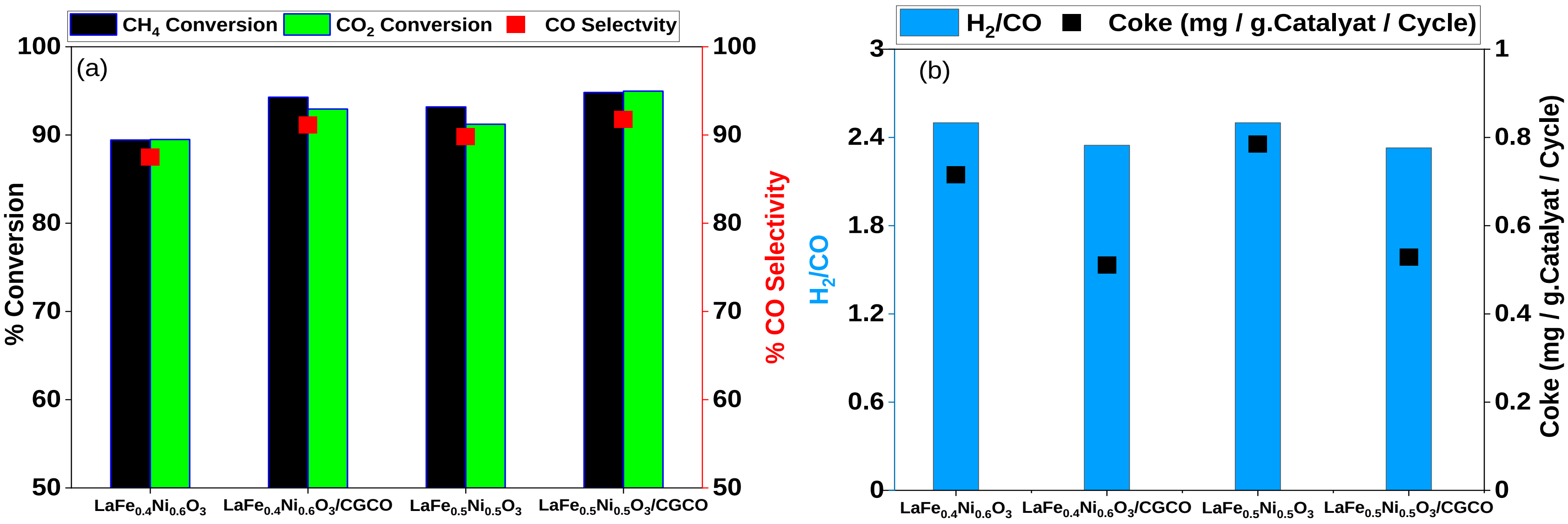


- Partial substitution of Ni into $LaFeO_3$ substantially improved the redox performance in both methane and CO_2 conversion steps.
- CH_4 conversion was merely 15% for $LaFe_{0.05}Ni_{0.95}O_3$. Increase in the Ni content improved the redox performance by up to 6 folds.

Task 3. Further Development of Redox Materials

$LaNi_xFe_{1-x}O_3$ with Different Ni Loading ($x \leq 0.5$)

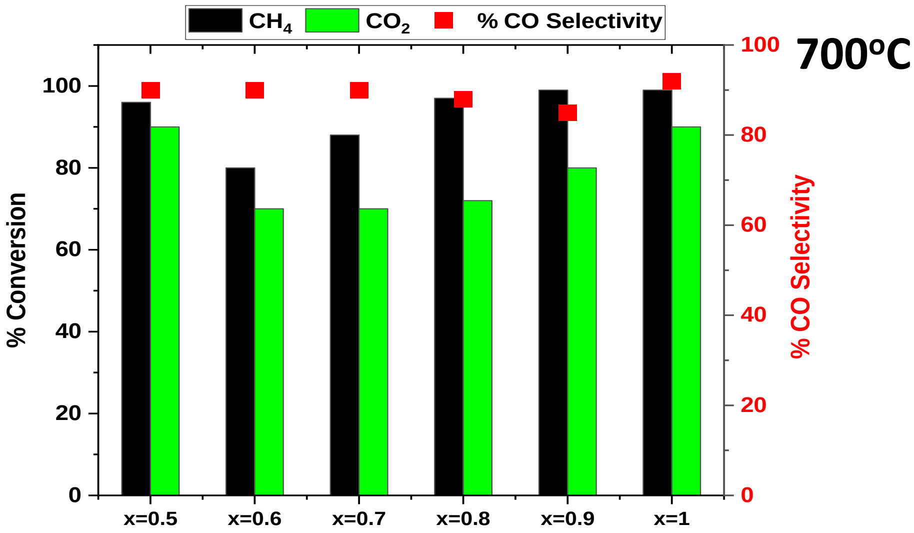
Redox Catalyst: $LaFe_{1-x}Ni_xO_3$ and CGCO / $LaFe_{1-x}Ni_xO_3$

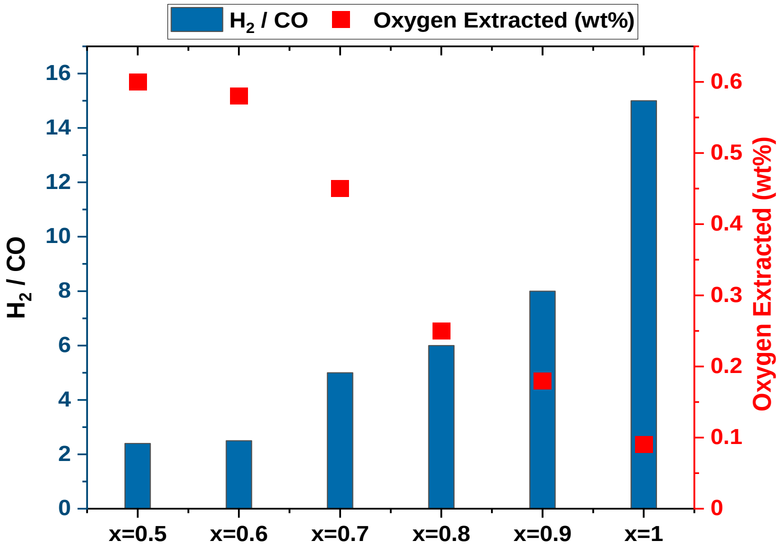


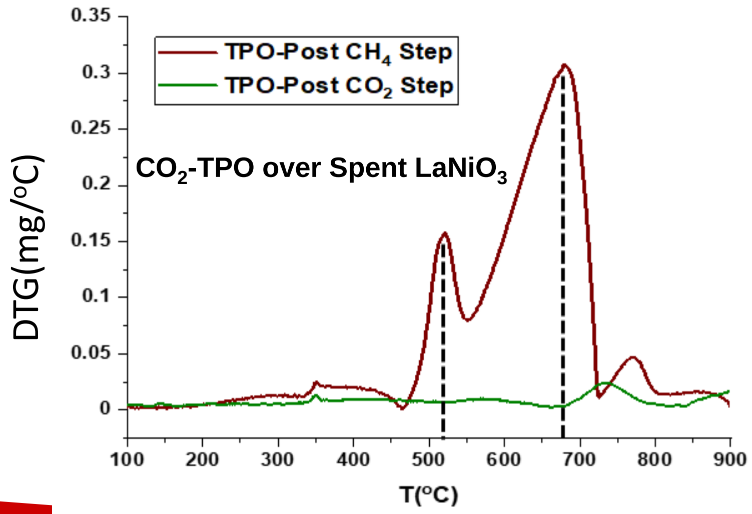
- Redox performances of standalone LNFs are only slightly inferior to those of the composite CGCO/LNFs.
- Considering the simplicity and potential cost savings, standalone $LaNi_{0.5}Fe_{0.5}O_3$ can be a very promising candidate.

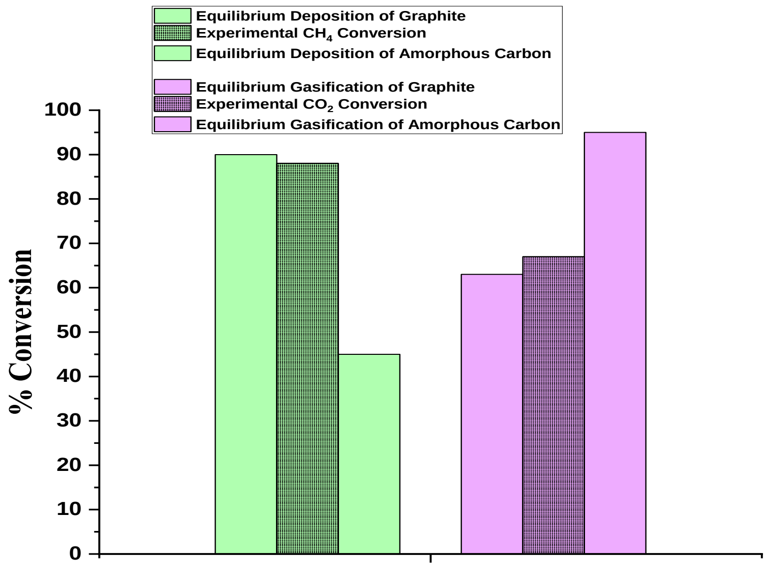
Task 3. Further Development of Redox Materials

$LaNi_xFe_{1-x}O_3$ with Different Ni Loading (x≥ 0.5)



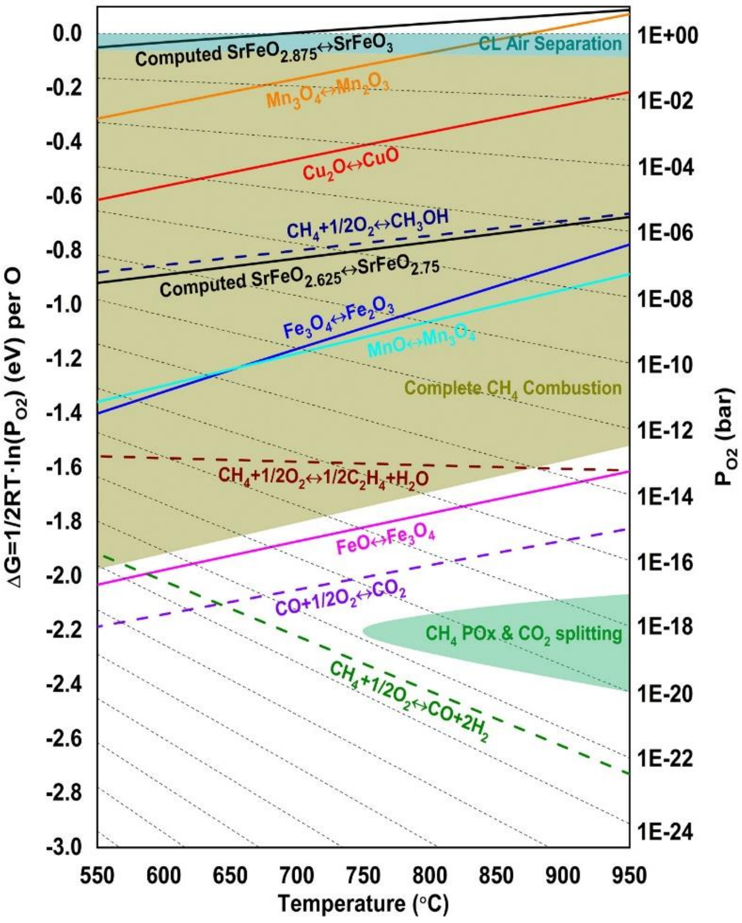


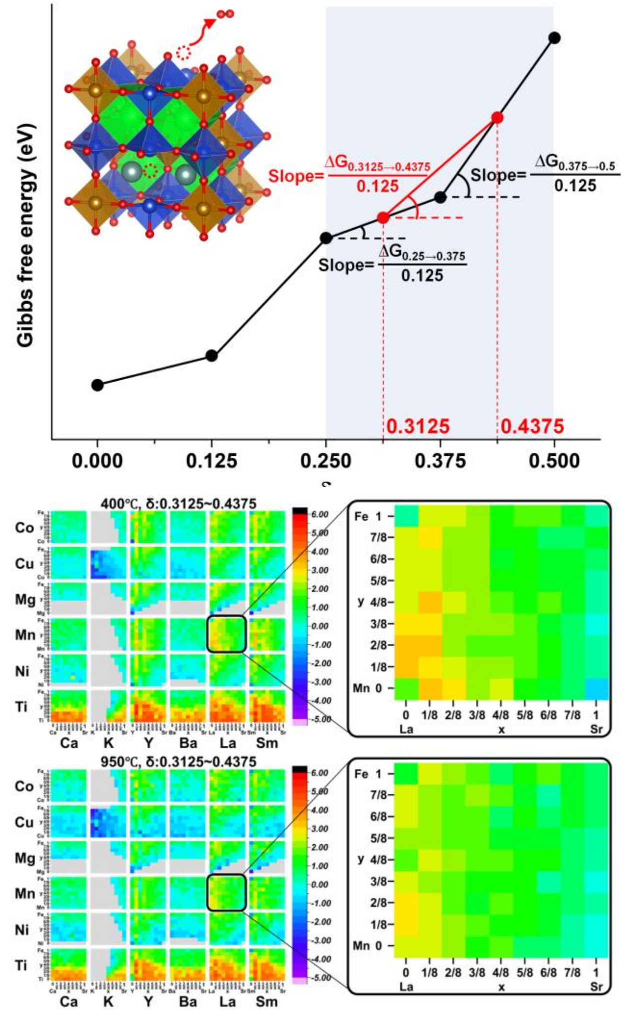




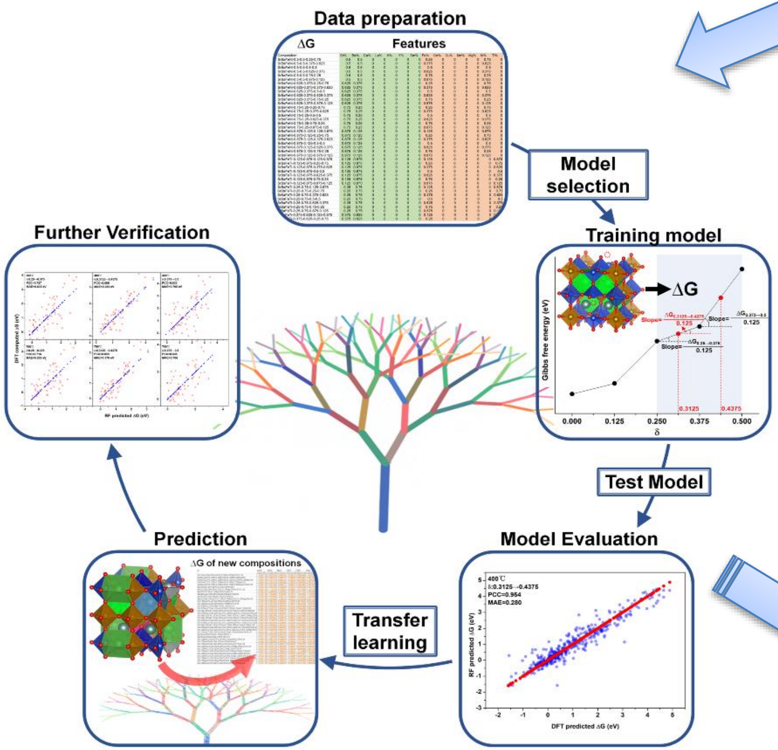
Task 3. Further Development of Redox Materials

DFT Guided Redox Materials Optimization

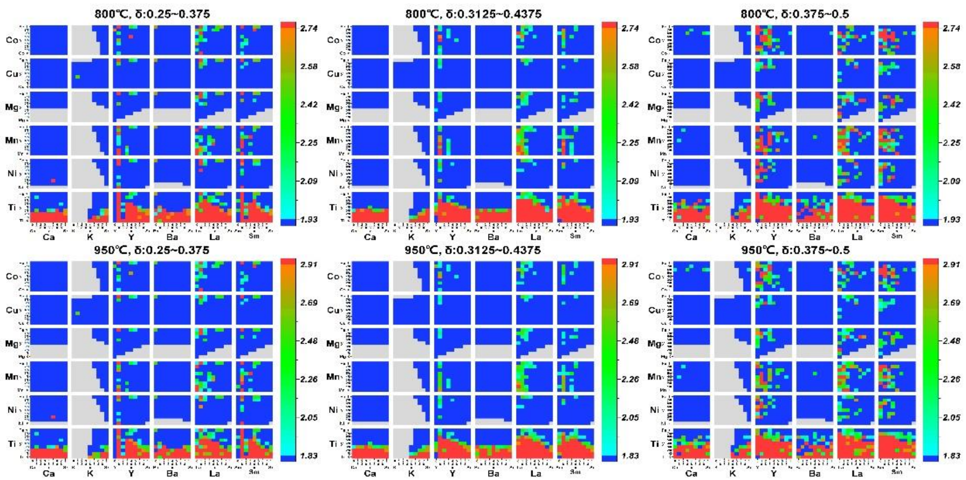




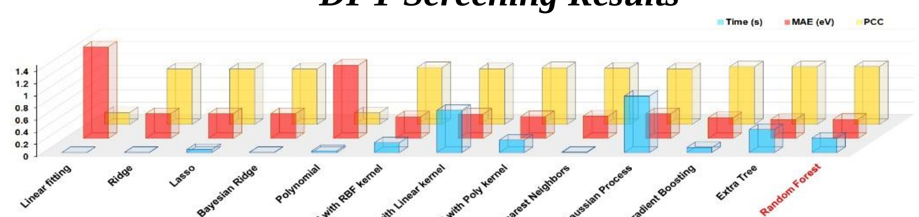
Tailoring Oxide Thermodynamic Properties via High Throughput Screening

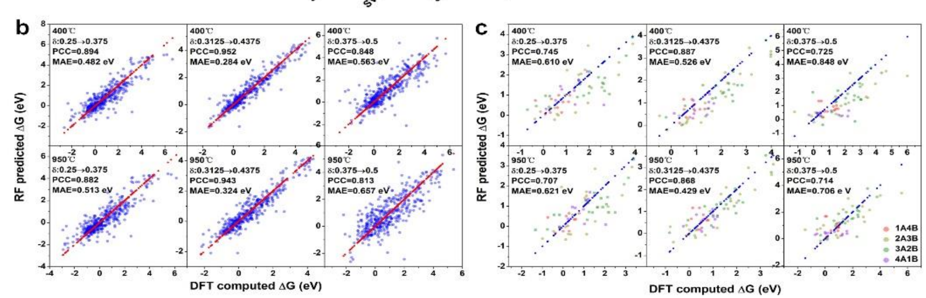


ML Driven Material Optimization



DFT Screening Results



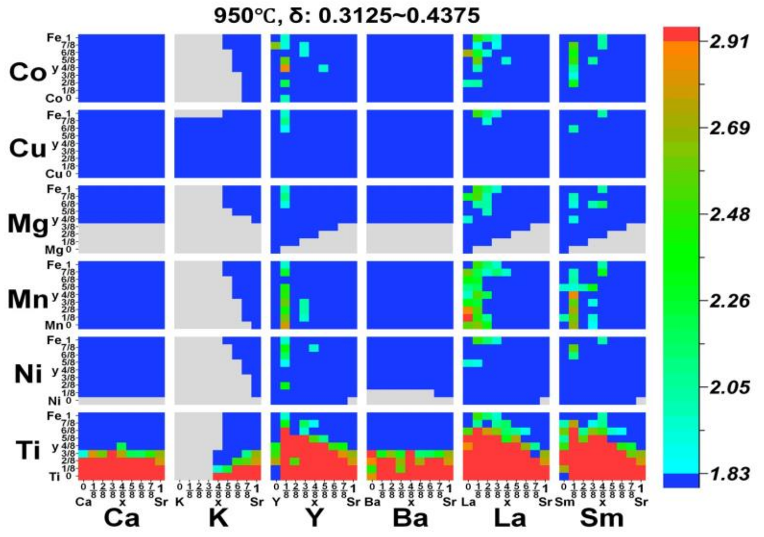


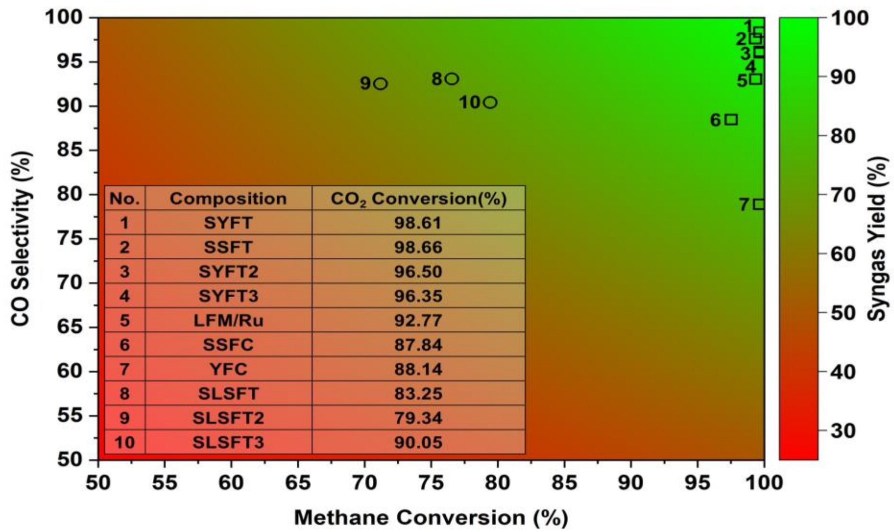
ML Fitting Results

ML based model, verified by DFT, covered 227,273 high entropy perovskites with ease

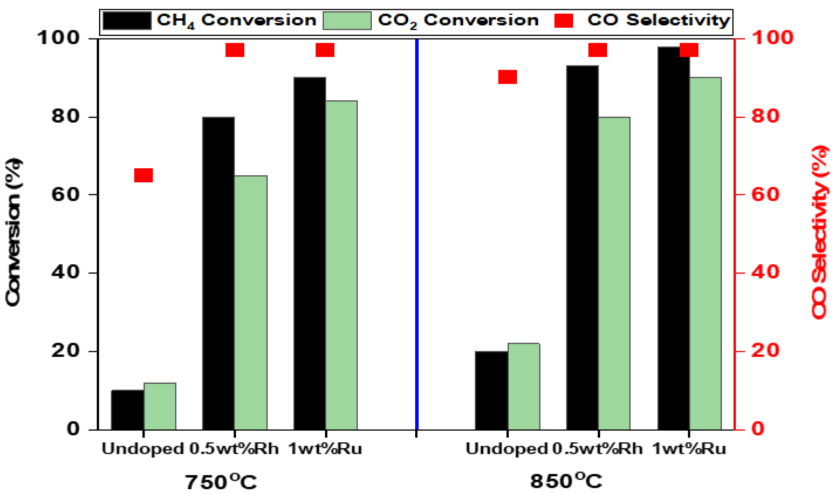
Task 3. Further Development of Redox Materials

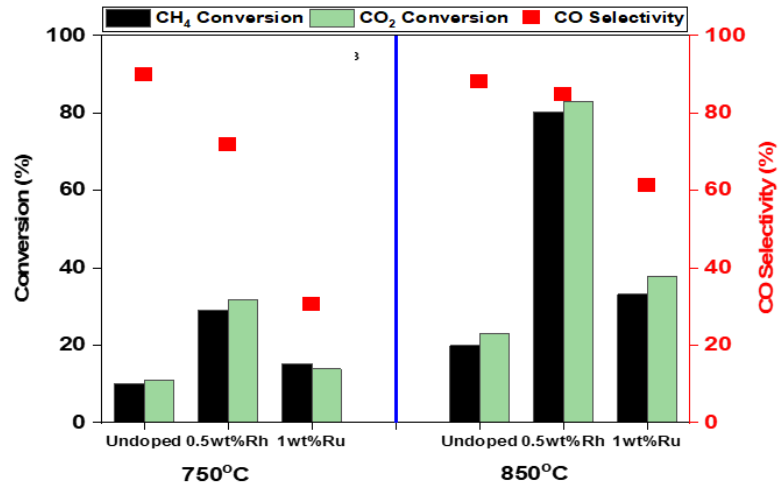
DFT Guided Redox Materials Optimization





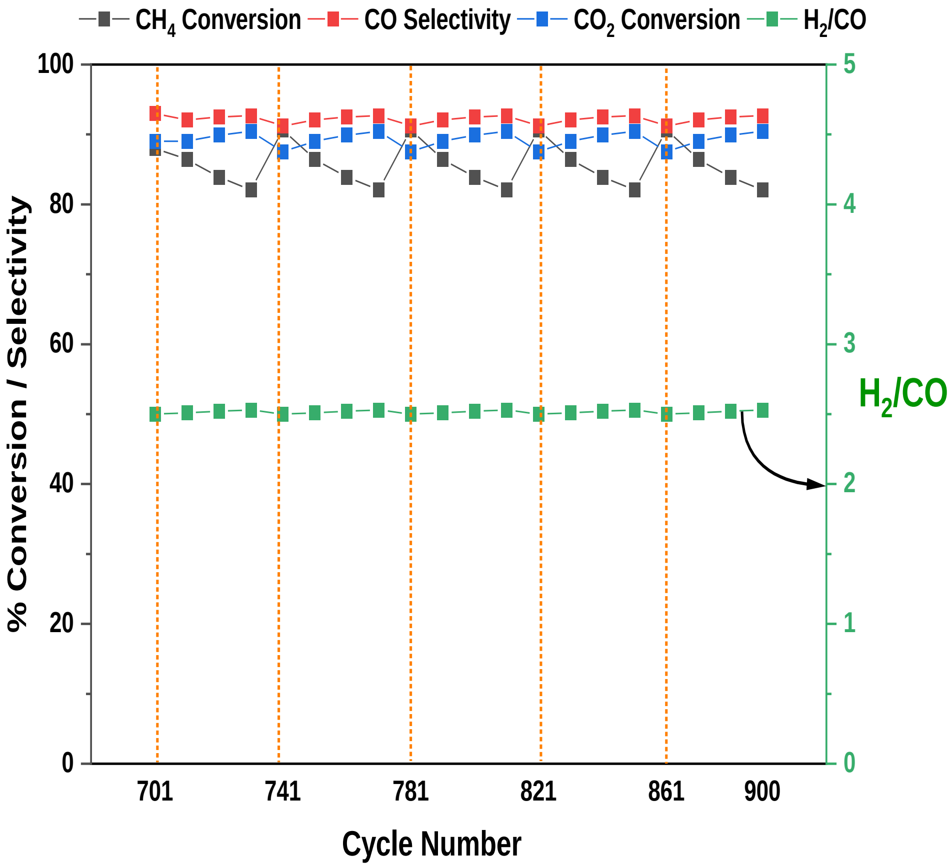
No.	Composition	CO_2 Conversion(%)
1	SYFT	98.61
2	SSFT	98.66
3	SYFT2	96.50
4	SYFT3	96.35
5	LFM/Ru	92.77
6	SSFC	87.84
7	YFC	88.14
8	SLSFT	83.25
9	SLSFT2	79.34
10	SLSFT3	90.05





Task 5. Redox Material Long Term Stability

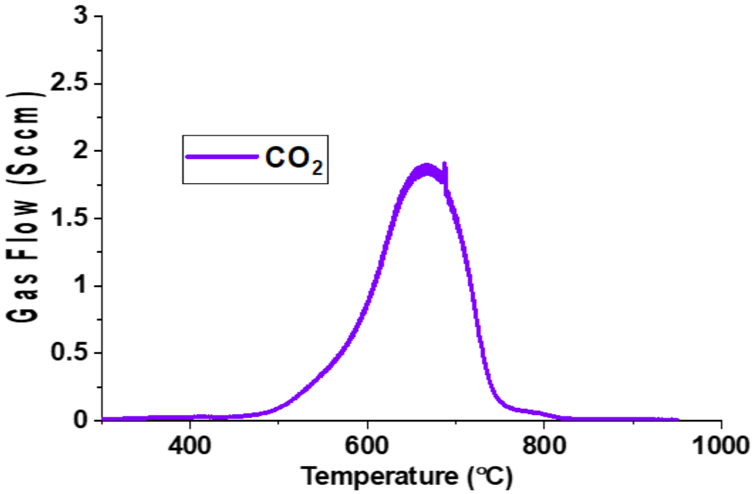
Long Term performance of standalone $LaNi_{0.5}Fe_{0.5}O_3$

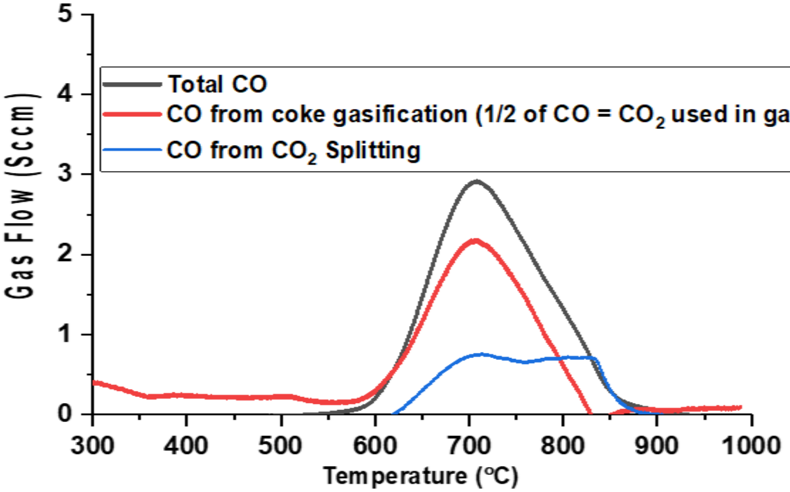


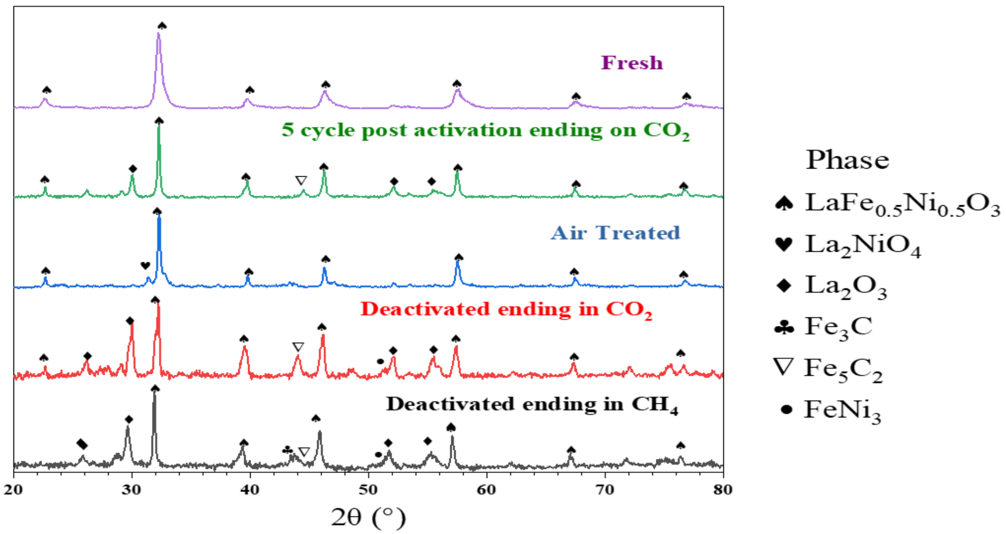
- Near 85% methane conversion, 95% CO selectivity, and ~90% CO_2 conversion were achieved throughout the last 200 cycles with periodic reactivation.
- Sequential air reactivation have a minimal negative impact on the overall syngas and CO yields.
- Both methane and CO_2 conversions, were above 85% over the entire 900 cycles, meeting Milestone 5.2.

Task 3. Further Development of Redox Materials (performance/stability)

TPO and XRD of deactivated and reactivated LNF redox catalyst at various stages







- The deactivated samples, both after methane reduction and CO_2 regeneration, contain iron carbides (Fe_3C and/or Fe_5C_2).
- Iron carbide species are completely absent from the reactivated (air treated sample).
- Net carbon accumulation was 0.325 mg/gram of redox catalyst each cycle.

Summary on Redox Materials Development

Four generations of highly effective redox catalysts were developed:

- **Gen 1.** Platinum group metal (PGM) promoted doped ceria oxide showed high activity for low temperature methane POx and CO_2-splitting;
- **Gen 2.** PGM free CGCO+LNF composite redox catalysts also showed excellent performance;
- **Gen 3.** PGM and rare earth free LNF composite redox catalysts, with optimized Ni:Fe ratios, demonstrated satisfactory performance;
- **Gen 3B.** PGM and rare earth free LNF redox catalysts offers the potential to produce separate streams of concentrated H_2 and CO, with the opportunity to increase CO_2 utilization;
- **Gen 4.** DFT guided selection of mixed-oxides with high activity and high lattice oxygen storage capacity.

Task 6. Update on Techno-Economic Analysis

Susteon

TEA process & approach

Technology
- Define existing state of the art technology
- Build process model with data for novel technology
- Size equipment based on heat and material balance from process model

Economics
- Market analysis of target product- price, volume, growth, players, derivatives
- Determine methodology and quality of cost estimate based on development
- Cost equipment and facility using method matching estimate stage and quality

Analyze
- Utilize cost estimates and assumptions to build unit cost economic model
- Compare breakeven unit cost against current market price
- Perform sensitivities in economic model by varying assumptions

BFD and Energy Flows

Baseline Case

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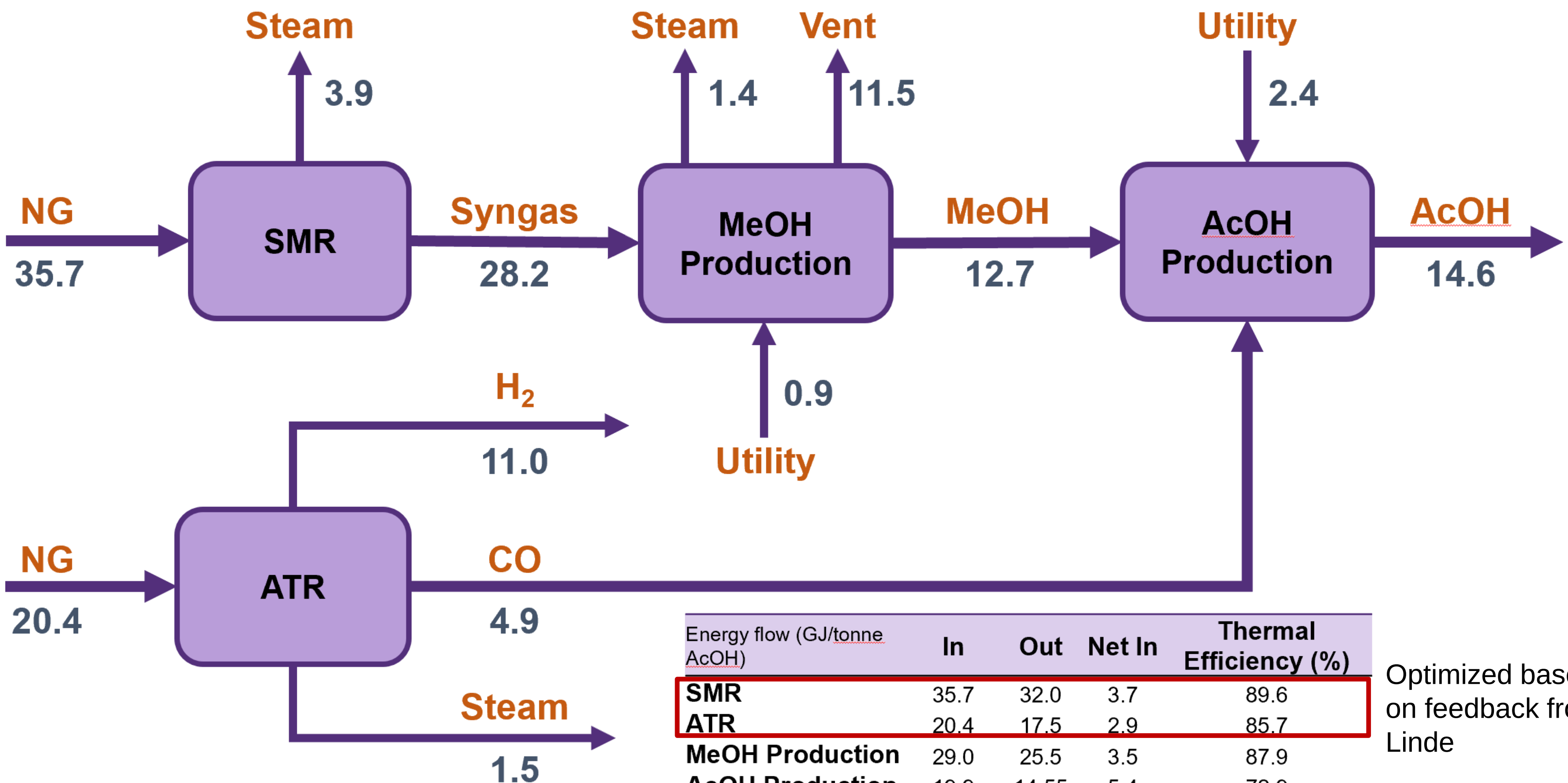
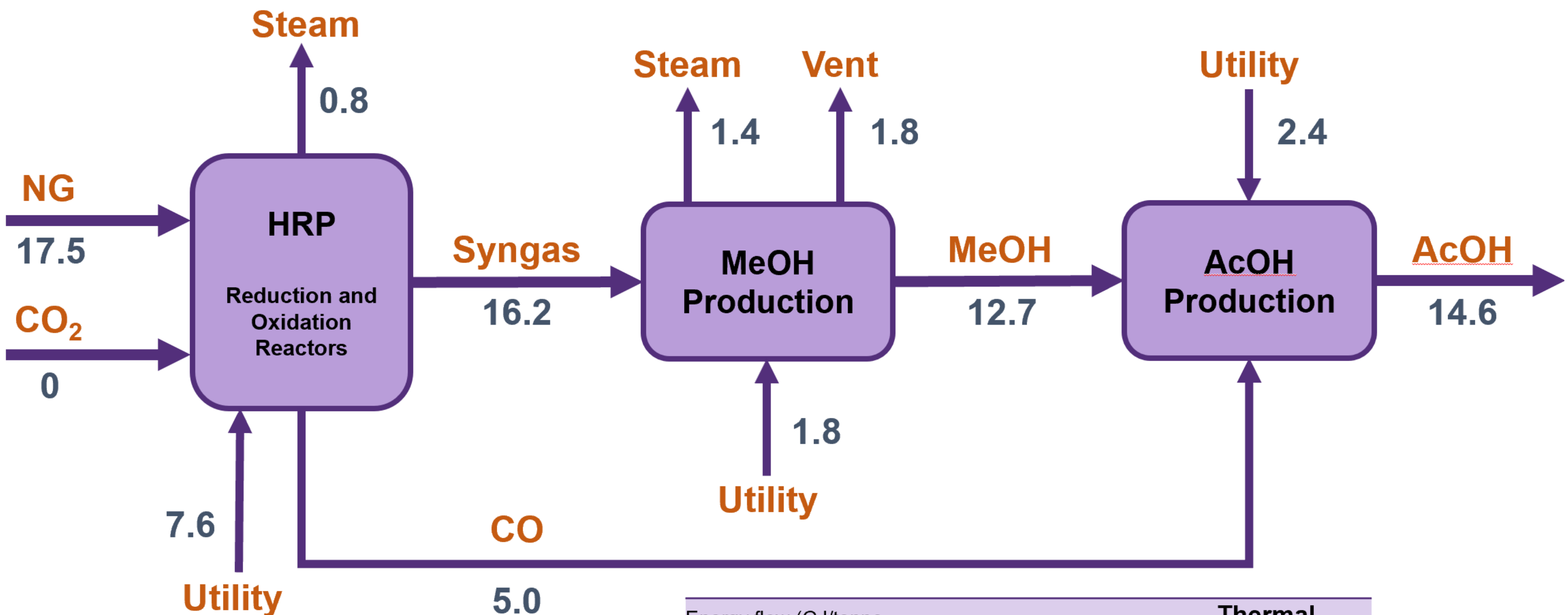


Energy flow (GJ/tonne AcOH)	In	Out	Net In	Thermal Efficiency (%)
SMR	35.7	32.0	3.7	89.6
ATR	20.4	17.5	2.9	85.7
MeOH Production	29.0	25.5	3.5	87.9
AcOH Production	19.9	14.55	5.4	72.9
Overall	59.4	43.8	15.5	73.8

Optimized based on feedback from Linde

Figures in GJ/tonne AcOH

BFD and Energy Flows
HRP Case



Energy flow (GJ/tonne AcOH)	In	Out	Net In	Thermal Efficiency (%)
HRP	25.1	22.0	3.1	87.7
MeOH Production	17.9	15.9	2.0	88.8
AcOH Production	20.1	14.6	5.5	72.5
Overall	**29.2**	**18.6**	**10.6**	**63.7**

2

Figures in GJ/tonne AcOH

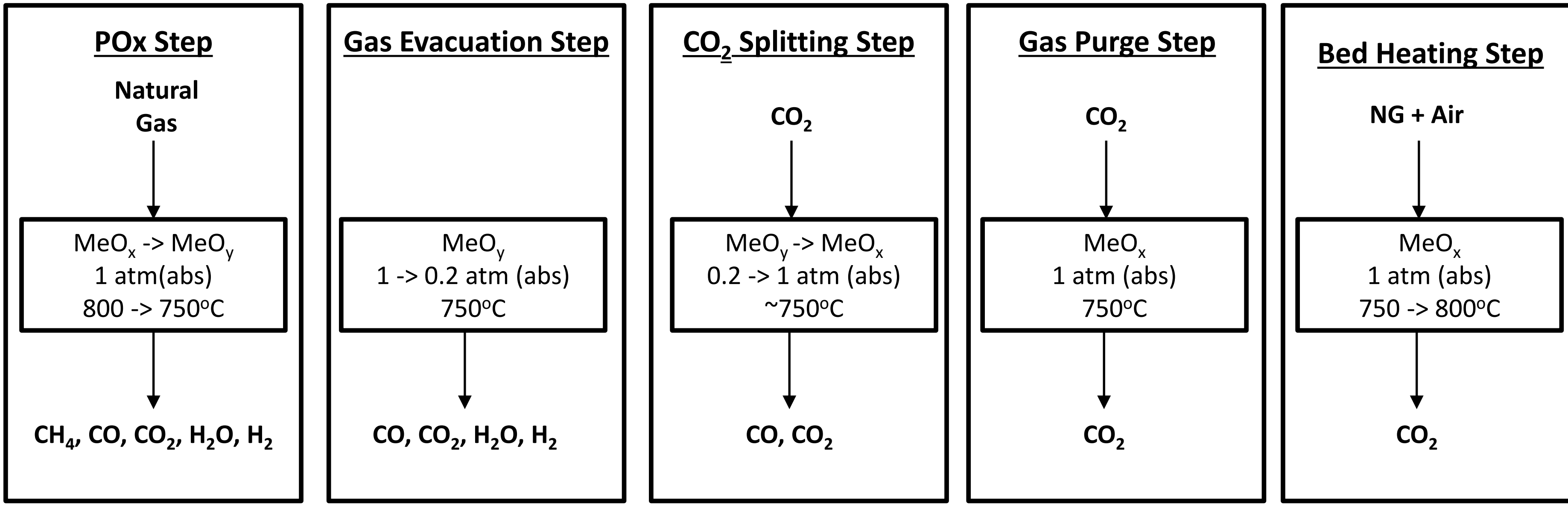
Key Factor Comparison
Baseline Case vs. HRP

Parameter	Baseline (SMR, ATR)	HRP
Net Energy Input GJ/tonne AcOH	15.5	10.6 32% energy savings
Syngas Generation Systems	Two systems: 1) For methanol 2) For CO	Single system produces methanol-ready syngas and CO
Methane (energy) feed GJ/tonne AcOH	56.1	25.1 55% reduction
Auxiliary output streams	Large H_2 and steam flows	Less steam
Thermal Efficiency	Optimized over decades	Conservative unoptimized estimate for FOAK

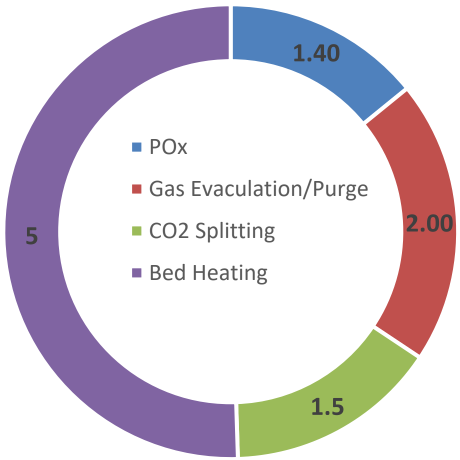
Reactor Design Concept

Susteon

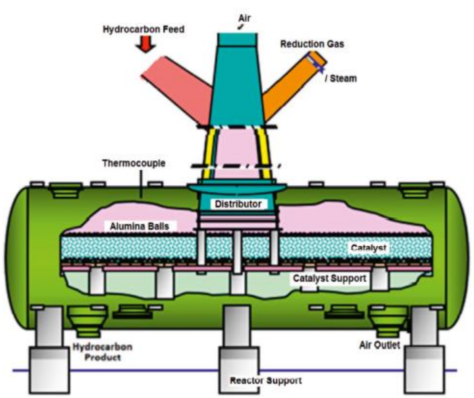
HRP Fixed Bed Steps



HRP Step Durations (min)

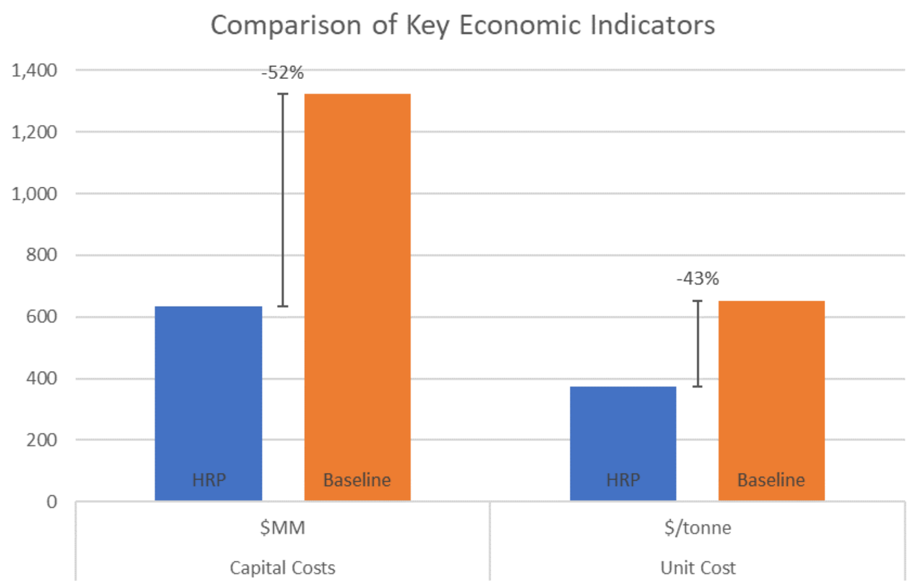


CATOFIN Design



HRP Fixed Bed Operation Modelled after Lummus CATOFIN Propane Dehydrogenation reactor

Techno-Economics



Item	Units	Value
Fabricated Unit price	USD/unit	$3,700,000
Installed costs	factor	2.47
Bare Erected Cost	USD/unit	$9,100,000
Number of Units required		6
Total Reactor cost		$54,600,000
Catalyst Unit Price	USD/kg	$30.00
Initial Catalyst Charge	USD	$12,000,000
Inert Unit Price	USD/kg	$1.00
Initial Inert Charge Cost	USD	$300,000.00
Total bare erected cost	USD	$66,700,000

With respect to Baseline Case

- 52% reduction in capital costs is expected
- Leading to 43% reduction in cost per tonne of acetic acid

Future Work

- Perform detailed sensitivity analysis of operating and capital cost expense and finalize TEA report

Plans for Future Development

Future work within the project:

- TEA driven redox catalyst optimization and stability testing;
- Detailed reactor and system design for optimal performance;
- Scale-up and commercialization roadmap.

Future work beyond the project:

- Further scale up testing (up to 1000 cuft/day);
- Detailed redox catalyst cost and scalability study;
- Demonstration and commercialization with industrial partner(s).

Summary Slide

- Hybrid Redox Process can generate high quality syngas and a separate stream of CO via CO_2 splitting;
- Four generations of high-performance redox catalysts have been developed;
- Computationally guided material development led to promising results;
- >90% methane conversion, 95% CO_2 conversion and 90% CO selectivity;
- Long-term stability for 900 cumulative cycles have been demonstrated;
- Both fluidized bed and packed bed system designs have been developed;
- TEA findings are highly encouraging.

Appendix:

Research Products:

Peer-reviewed publications:

Sherafghan Iftikhar, Qiongqiong Jiang, Yunfei Gao, Junchen Liu, Haiming Gu, Luke Neal, and Fanxing Li*

"$LaNi_xFe_{1-x}O_{3-\delta}$ as a Robust Redox Catalyst for CO_2-Splitting and Methane Partial Oxidation".(2021) ***Energy and Fuels*** (Accepted)

Qiongqiong Jiang, Yunfei Gao, Vasudev Haribal, He Qi, Xingbo Liu, Hui Hong, Hongguang Jin, Fanxing Li*.

"Mixed Conductive Composites for 'Low-Temperature' Thermo-chemical CO2 Splitting and Syngas Generation".

(2020) ***Journal of Materials Chemistry A***. DOI: 10.1039/D0TA03232H.

Vasudev Haribal, Xijun Wang, Ryan Dudek, Courtney Paolus, Brian Turk, Raghubir Gupta, and Fanxing Li*****. (2019) "Modified Ceria for "Low-Temperature" CO_2 Utilization: A Chemical Looping Route to Exploit Industrial Waste Heat". ***Advanced Energy Materials.*** 1901963:1-10.

Conference Presentation:

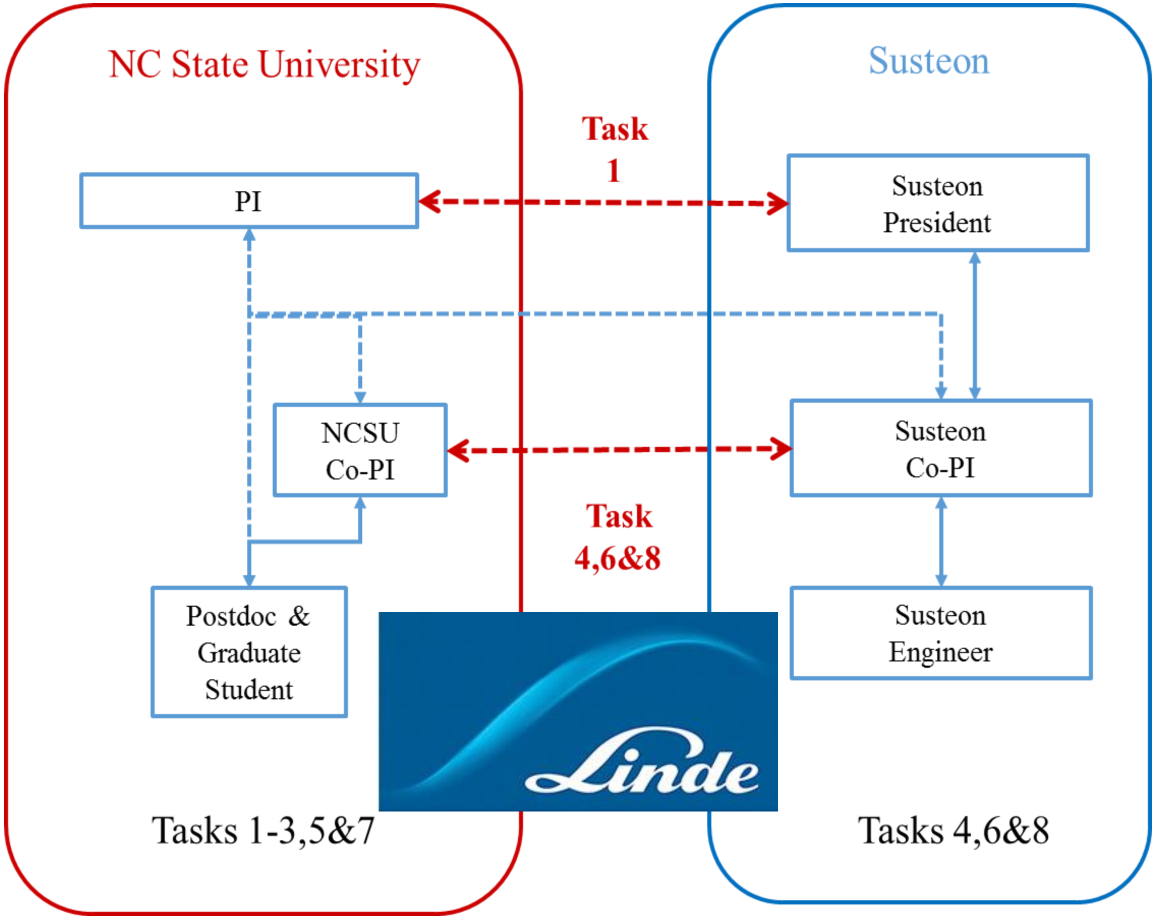
Qiongqiong Jiang, "Composite Mixed Ionic-electronic Conducting Materials for Low-Temperature Thermochemical CO_2 Splitting and Syngas Generation" Advanced Fossil Energy Utilization R&D, 2019 AIChE annual meeting (*Received CRE Division Student Travel Award*)

NC STATE UNIVERSITY

Project Schedule and Milestones

Task Name	Start	End	Resource	2019				2020				2021			
				Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
Task 1 Project Managmant and Planding	2/1/2019	1/31/2022	NCSU/Susteon												
Milestone 1.1: PMP modification		2/28/2019	NCSU	◊											
Milestone 1.2: Project kickoff meeting		3/31/2019	NCSU/Susteon	◊											
Task 2.0: Redox material synthesis and characterizations	2/1/2019	6/30/2021	NCSU												
Subtask 2.1 Redox Material Synthesis	2/1/2019	6/30/2021	NCSU												
Subtask 2.2 Characterization of the Redox Materials	2/1/2019	11/31/2019	NCSU												
Milestone 2.1: Initial Redox material Screening		7/31/2019	NCSU		◊										
Milestone 2.2: Redox material down selection		10/15/2019	NCSU			◊									
Task 3.0: Redox Material Development	4/1/2019	6/30/2021	NCSU												
Subtask 3.1. Further characterization of the activity	4/1/2019	6/30/2021	NCSU												
Subtask 3.2. Optimization Strategy Development	7/1/2019	12/31/2020	NCSU												
Title: Milestone 3.1 Redox kinetics characterized		10/15/2019				◊									
Title: Milestone 3.2 Redox performance & stability		12/31/2019					◊								
Task 4.0: Techno-economic and Lifecycle Analysis	2/1/2019	12/31/2019	Susteon												
Subtask 4.1 Process model refinement and analysis	2/1/2019	12/31/2019	Susteon												
Subtask 4.2 Analysis of Alternatives Commercial Products	7/1/2019	12/31/2019	Susteon												
Milestone 4.1. Initial LCA TEA Report		12/31/2019	Susteon				◊								
Milestone 4.2 Product slate screening		10/15/2019	Susteon			◊									
Task 5.0: Redox Material: Long Term Stability	2/1/2020	6/30/2021	NCSU												
Subtask 5.1. Long term testing of the redox materials	2/1/2020	6/1/2021	NCSU												
Subtask 5.2 Empirical kinetic parameters analysis	2/1/2020	6/1/2021	NCSU												
Milestone 5.1 Reactor sizing		6/30/2020	NCSU						◊						
Milestone 5.2. Large lab-scale performance verification		12/31/2020	NCSU								◊				
Task 6.0: Techno-Economic and Life Cycle Analyses Update	2/1/2020	6/30/2021	Susteon												
Milestone 6.1 Reactor size/sensitivity		9/30/2020	Susteon							◊					
Milestone 6.2 TEA/LCA Update		12/31/2020	Susteon								◊				
Task 7.0: Redox Material : Economics Driven Optimizations	2/1/2021	12/31/2021	NCSU												
Subtask 7.1 Techno-economic Redox Catalyst Optimization	2/1/2021	12/31/2021	NCSU												
Subtask 7.2 Synthesis optimization for scale-up	2/1/2021	12/31/2021	NCSU												
Milestone 7.1 Optimized reactor Sizing		6/30/2021											◊		
Milestone 7.2 Scalable up material validation		12/31/2021													◊
Task 8.0: Development of detailed reactor and process	2/1/2021	12/31/2021	Susteon												
Milestone 8.1 commercialization road map		12/31/2021	Susteon												◊
Milestone 8.2 Final TEA and LCA report		4/30/2022	Susteon												→

Task 1. Project Management and Planning

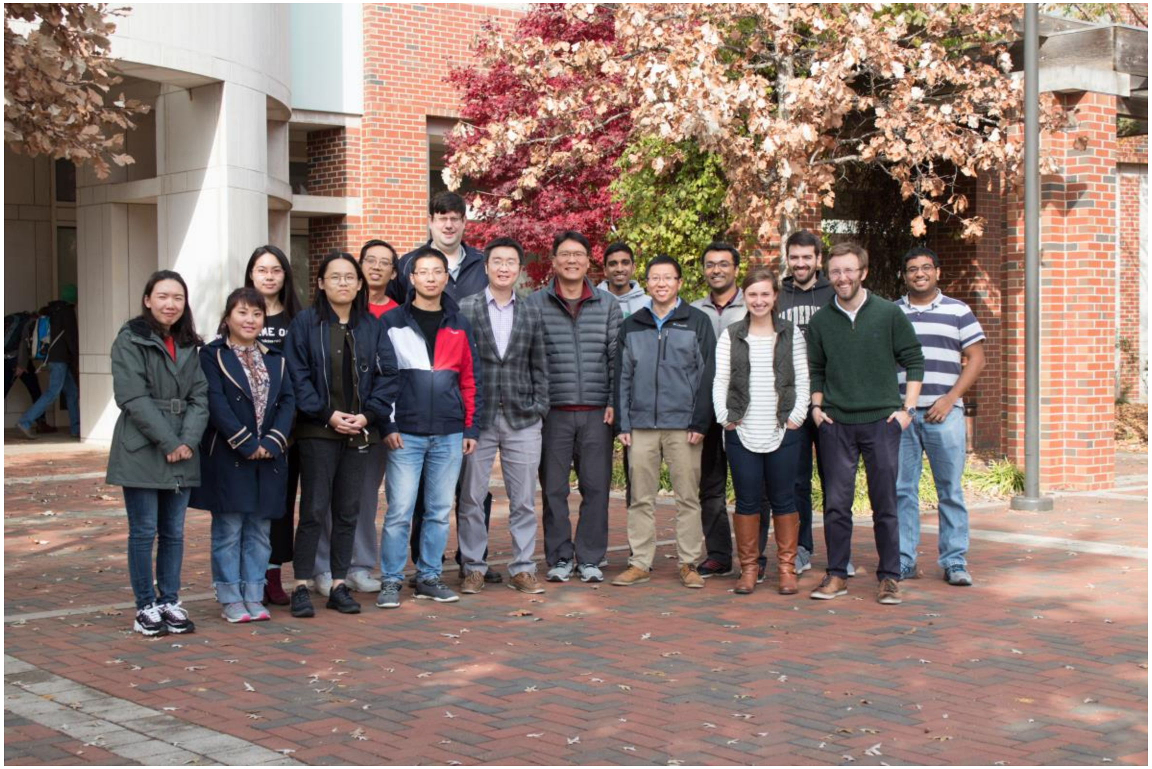


The project has been effectively managed.

Risk Management

Perceived Risk	Risk Rating Probability (Low, Med, High)	Impact	Overall	Mitigation/Response Strategy
Financial Risks:				
Third party funding or cost-share	Low	Med	Low	The project is not dependent upon third party funding Cost-share is provided by NCSU and Susteon.
Cost/Schedule Risks:				
Delayed funding causing project delays	Med	Low	Low	Use of existing equipment and personnel will allow quick ramp up of project upon finalization
Technical/Scope Risks:				
Low redox material performance	Low	High	Med	Extensive preliminary results, and identified alternative systems, and PI expertise will permit rapid identification or risk and mitigation.
Poor techno-economic or LCA results	Low	Med	Low	TEA and LCA will be validated early, and alternative final products screened to identify potentially better economics and or CO_2 utilization.
Management Risks:				
Communications between organizations	Low	Low	Low	Organizations are in the same geographical area and will have bi-weekly conference calls and in-person meetings
Planning and Oversight Risks:				
Personnel hiring	Low	Low	Low	Existing personnel is sufficient to complete early tasks
ES&H Risks:				
Use of Toxic and Flammable gasses	Low	Med	Low	PI laboratories have significant infrastructure in place for the handling of hazardous gasses.
External Factor Risks:				
N/A	Low	Low	Low	Project is not dependent upon third party or external considerations to proceed

Acknowledgement



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