Plasma Assisted Catalytic Conversion of Carbon Dioxide (CO_2) and Propane to Propylene and Carbon Monoxide (CO)

DE-FE0031917

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U.S. Department of Energy
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Project Overview

Title	**Plasma Assisted Catalytic Conversion of Carbon Dioxide (CO_2) and Propane to Propylene and Carbon Monoxide (CO)**
Award No.	DE-FE0031917
Period of Performance	10/01/2020 – 09/30/2022
Project Funding	DOE: $999,722 Cost-Share: $255,642
Project Participants	Susteon Inc., North Carolina State University, Newcastle University, SoCalGas
DOE/NETL Project Manager	Dr. Sai V. Gollakota

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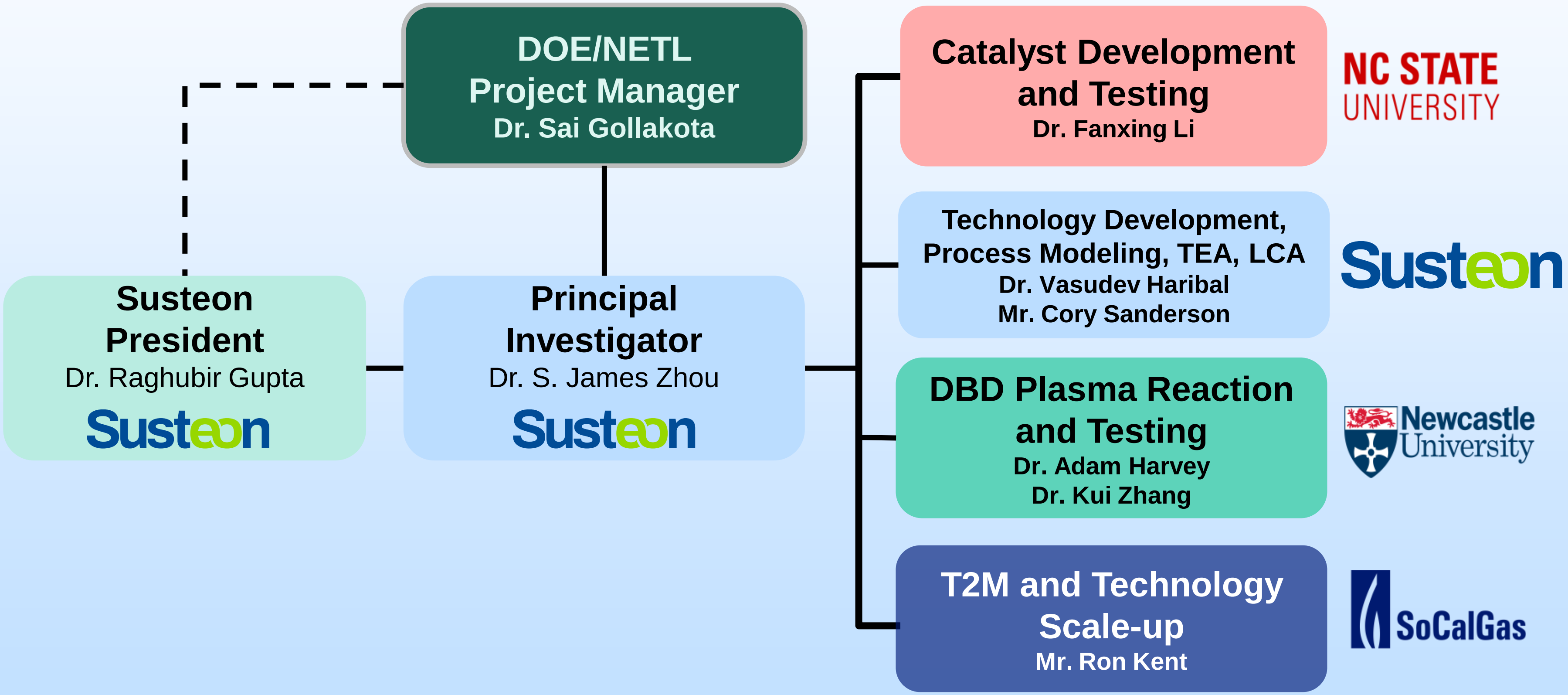
Team Members and Organizational Structure



Project Objectives

Utilize CO_2 as a soft-oxidant with propane and ethane in a catalytic non-thermal plasma reactor to produce propylene/ethylene

- Modular design
- Negative CO_2 footprint of the overall process
- Production of ’green” carbon monoxide with large market potential
- Commercially competitive production costs due to low capex

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Background Information - Steam Cracking Process for Olefin Production

$$C_2H_6 \text{ or } C_3H_8 \text{ or Naphtha} \xrightarrow{\text{Heat}} C_2H_4 / C_3H_6 + x.H_2$$

ΔH_{298K} = +134 kJ/mol
Ethane to ethylene

ΔH_{1048K} = +319.6 kJ/mol
Naphtha to ethylene

- Feed is a mixed stream of ethane and steam.
- A high-temperature reactor (750°– 875 °C)
- Reactor residence times of 0.1–0.5 s
- Reaction limited to practical single-pass ethane-conversion of 67–70% and an ethylene yield of around 55%
  - Equilibrium limitation and coke formation
- Periodic shut down and regeneration with air to avoid coke build-up
- Highly endothermic: Total energy demand between **15 and 25 GJ/t ethylene**
- CO_2 intensive: **1–2 t CO_2/t ethylene**
- Considerable amount of NO_x emissions

Source of olefins (*via* steam cracking)	CO_2 Emissions
Ethane	1.2 kg/kg
Propane	1.4 kg/kg
LPG	1.7 kg/kg
Naphtha	2.2 kg/kg

Alternate routes to produce olefins from these sources are needed to reduce their GHG footprint.

-P. Eisele and R. Killpack, "Propene," in Ullmann's Encyclopedia of Industrial Chemistry (2011)
-H. Zimmermann and R. Walzl, "Ethylene," in Ullmann's Encyclopedia of Industrial Chemistry (2009)
-Ren, T et.al., Energy 31.4 (2006): 425-451.

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CO_2 Oxidative Dehydrogenation (CO_2-ODH) of Alkanes

Oxidative Dehydrogenation (ODH) using O_2

$$C_2H_6 + 0.5\ O_2 \rightarrow C_2H_4 + H_2O \qquad \Delta H_0 = -105\ \text{kJ/mol}$$

- high temperatures
- need for pure oxygen
- safety concerns
- higher energy losses

Oxidative Dehydrogenation (ODH) using CO_2

$$C_3H_8 + CO_2 \rightarrow CO + C_3H_6 + H_2O \qquad \Delta H_0 = +60.3\ \text{kJ/mol}$$

- Mildly endothermic and is catalyzed by a variety of catalysts

- Consumption of CO_2 as a feedstock
- CO_2 reduction to CO works in tandem with alkane dehydrogenation to its corresponding olefin
- CO_2-ODH catalysts perform the dual function of activating both the hydrocarbon and CO_2.
- Supported Ni-Fe, Cr and Ga systems are promising.

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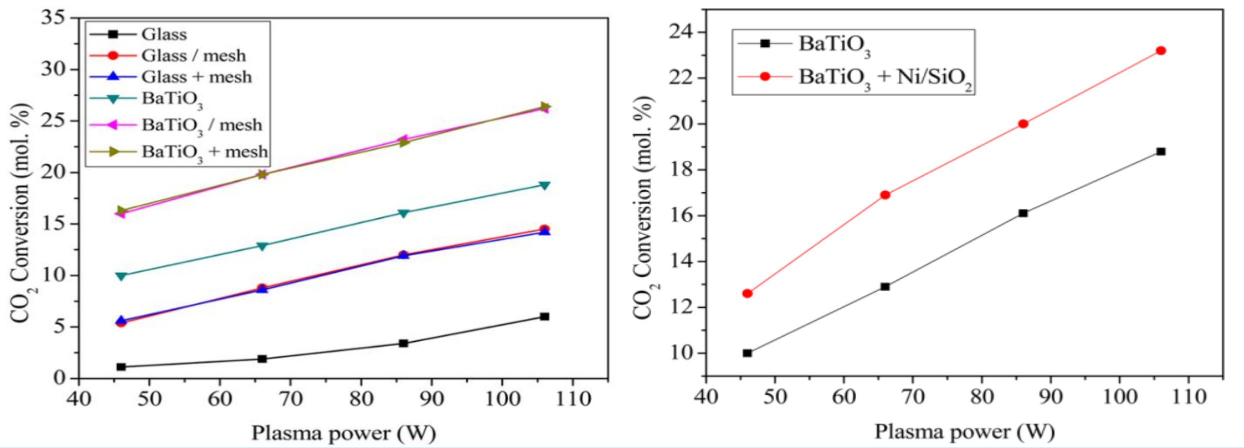
Plasma-Assisted Catalytic Conversion of CO_2

- Catalyst enables interplay of gas phase and gas–solid reactions on the catalyst surface
- Dielectric-barrier discharge (DBD) is a form of non thermal plasma
  - average temperature of the energetic electrons is in the range of 10,000–100,000 K
  - actual gas temperature remains near ambient
- CO_2 conversion increases with plasma power over glass and $BaTiO_3$ beads.
- Addition of Ni/SiO_2 catalyst increases conversion by almost 1.5 times.
- Absence of plasma led to no CO_2 conversion



K. Zhang, G. Zhang, X. Liu, A. N. Phan, and K. Luo, *Ind. Eng. Chem. Res.*, vol. 56, no. 12, pp. 3204–3216, Mar. 2017

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Technical Approach and Key Milestones

- Catalyst preparation, characterization, and evaluation under thermal and plasma conditions
  - Focus on the formulation and synthesis conditions for maximum alkene yield and catalyst stability
- CO_2 oxidative dehydrogenation in the plasma reactor with and without catalyst
  - Obtain optimal process conditions
- Process modeling, TEA and LCA
  - Determine process economics and CO_2 footprint
  - Design pilot-scale plasma reaction system for the next phase of technology development

Key Milestones

- Demonstrate >50% propane and CO_2 conversion and at least 80% propylene selectivity
- Demonstrate >50% ethane conversion and CO_2 conversion and at least 80% ethylene selectivity
- Achieve <25% catalyst deactivation during 24 hours of continuous testing

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Success Criteria

Parameter	Criteria	Testing Tool
Production costs of ethylene, propylene and carbon monoxide	≤ 20% of the market price	Final TEA
CO_2 utilization potential (with renewable power)	≥ 0.92 kg CO_2/kg olefin (70% ethylene, 30% propylene)	Final LCA
Total CO_2 avoidance	≥ 2.12 kg/kg olefin	Final LCA
Utilization of distributed CO_2 resources	Design of a modular system	Design package

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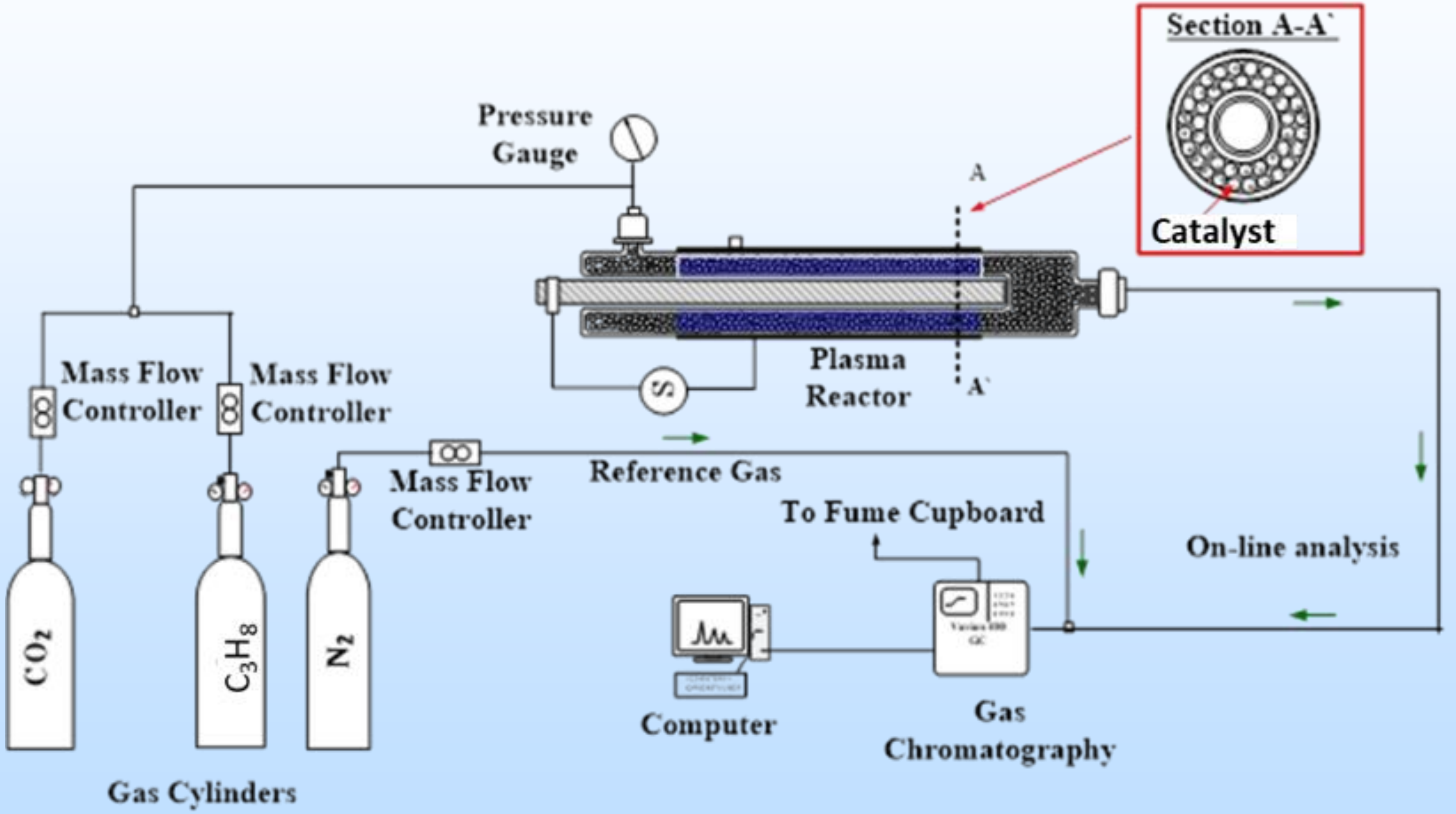
Plasma Test Equipment



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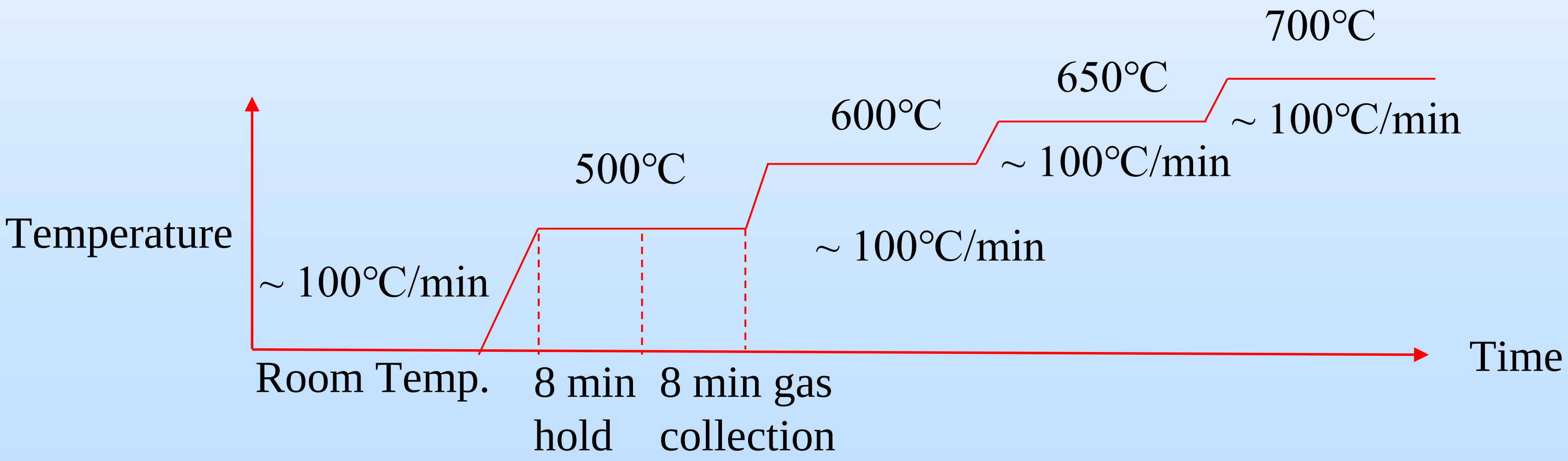
Catalyst Synthesis and Testing

- Sol-gel CeO_2 supported N_1Fe_3 catalyst
- Ce dopant stabilized $Cr/Ce_XZr_{1-X}O_2$ catalyst
- Ga-ZrO_2 Catalyst

Testing Protocol: ***20 sccm Ar, 10 sccm propane, and 10 sccm CO_2***



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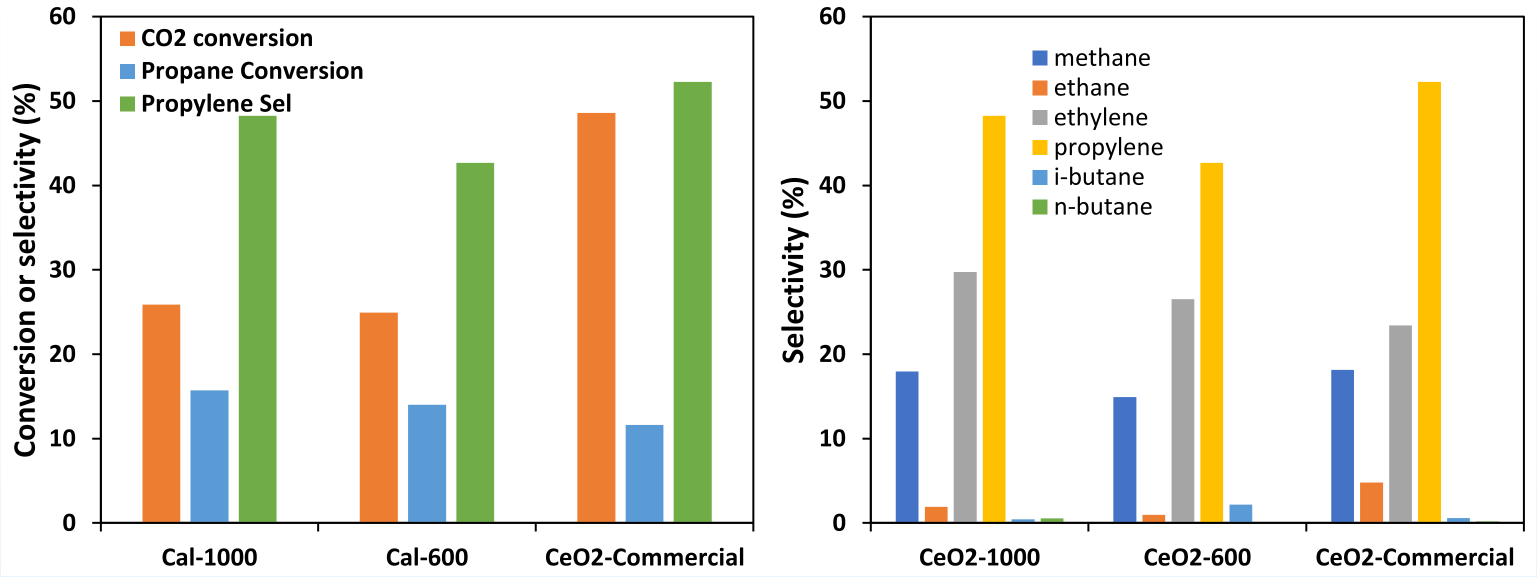
Effect of Catalyst Support



Temperature (°C)	CO_2 conv. (%)	Propane conv. (%)	Methane sel. (%)	Ethane sel. (%)	Ethylene sel. (%)	Propylene sel. (%)	i-Butane sel. (%)	n-Butane sel. (%)
Cal-1000	25.9	15.7	18.0	1.9	29.7	48.3	0.4	0.6
Cal-600	24.9	14.0	14.9	1.0	26.5	42.7	2.2	0.0
CeO2-Commercial	48.6	11.6	18.1	4.8	23.4	52.3	0.6	0.2

Sol-gel CeO_2 supported $NiFe_3$ catalyst exhibits the highest propylene yield of 7.6% at 700°C

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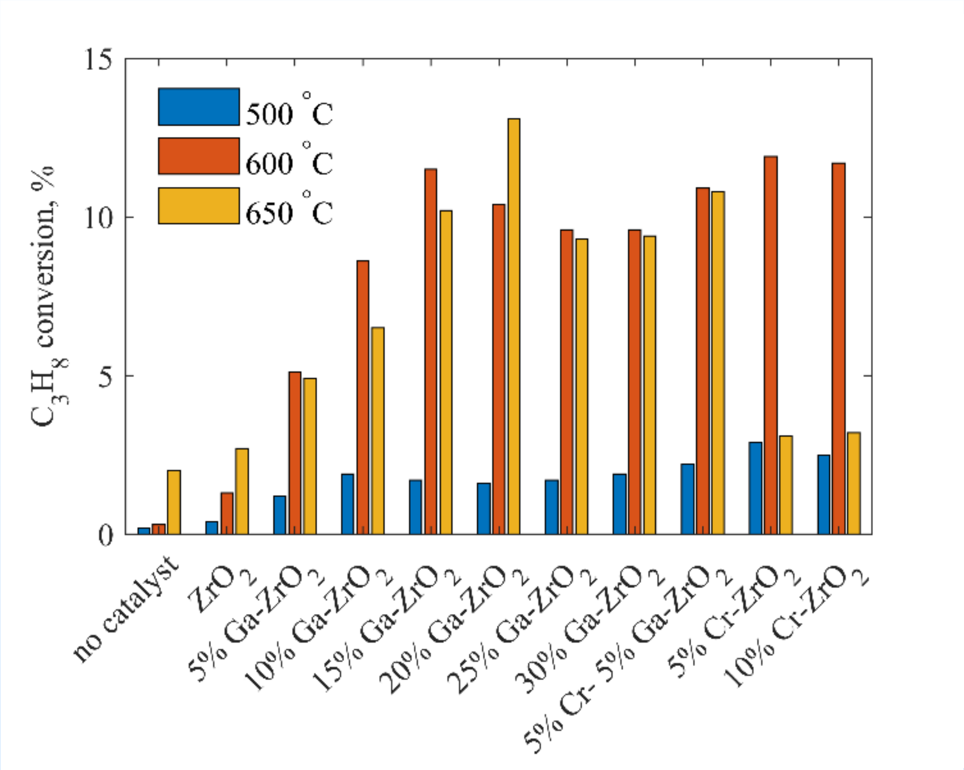
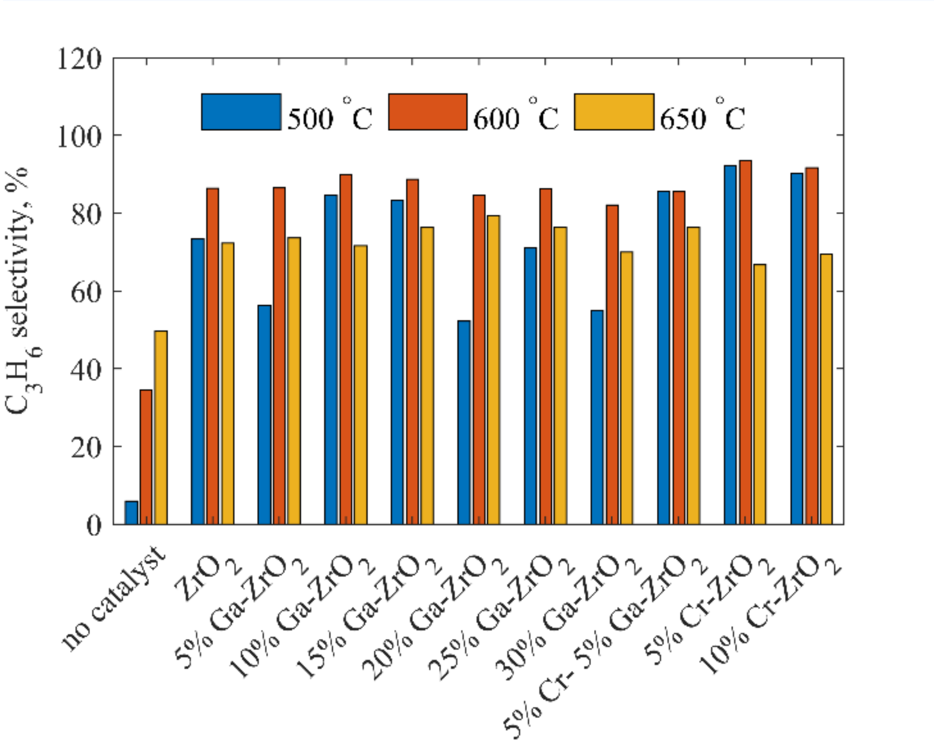
C_3H_8 Conversion and C_3H_6 Selectivity for Ga-ZrO_2 Catalysts





- C_3H_8 conversion is about 15-20% for the Ga-ZrO_2 catalysts.
- C_3H_6 selectivity is similar among the Ga-ZrO_2 catalysts.

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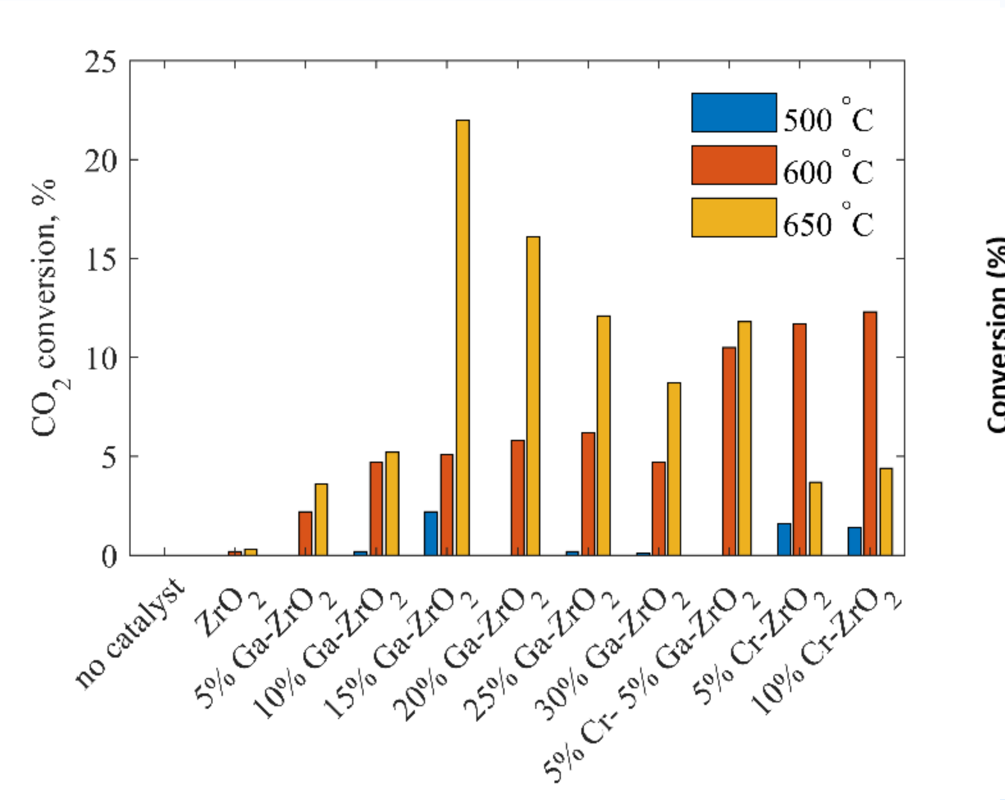
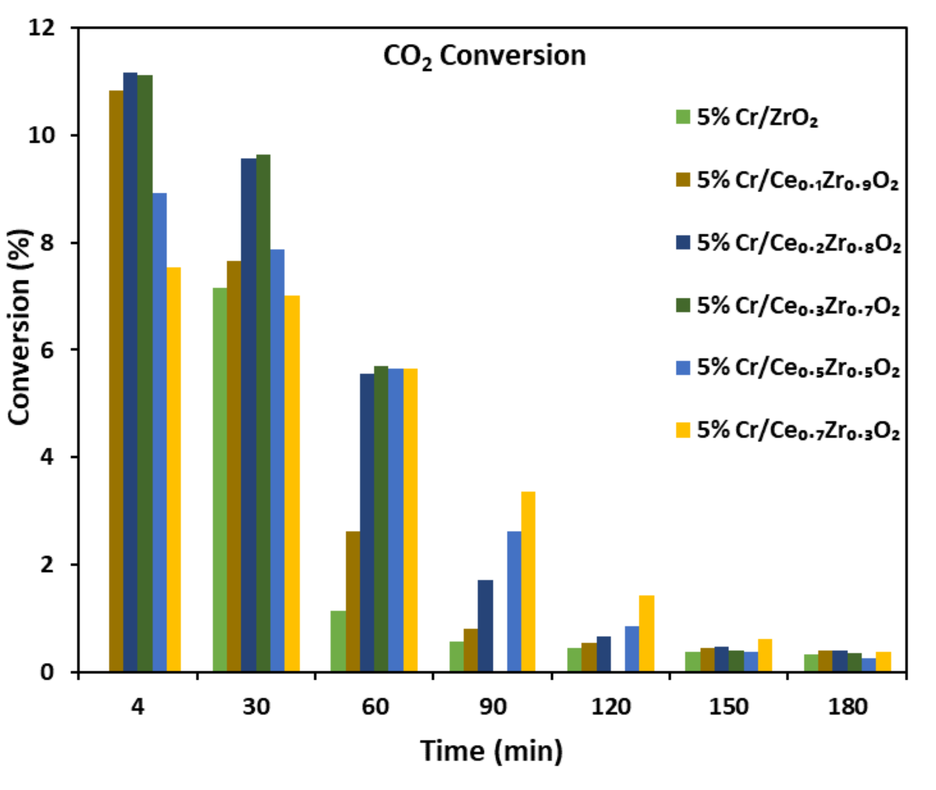
CO_2 Conversion for Ga-ZrO_2 and Cr-ZrO_2 Catalysts





- **15-20% Ga-ZrO_2 can provide high CO_2 conversion which is around 1.5 times higher than Cr-ZrO_2 catalysts.**
- **10-30% Ce doping into ZrO_2 support enhances both propane and CO_2 conversion.**

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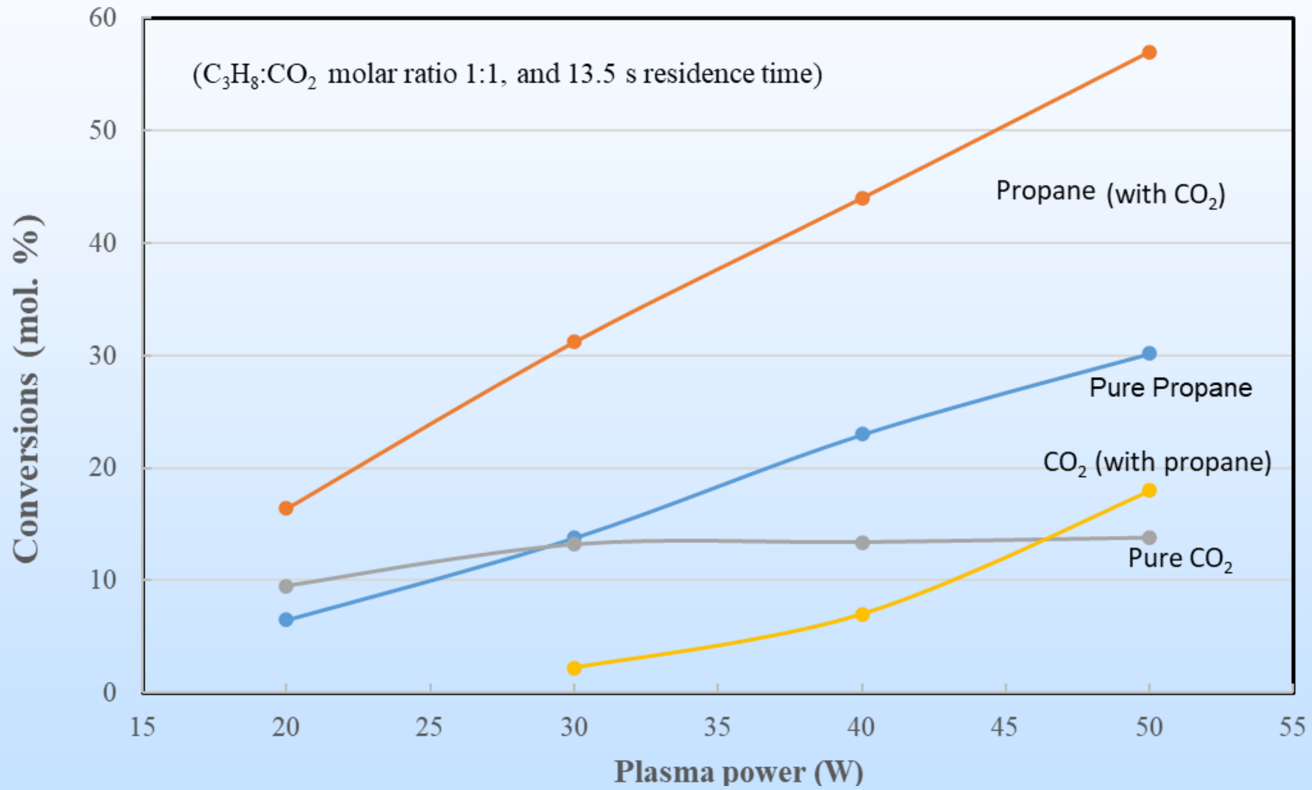
Effect of Plasma Power on Propane and CO_2 Conversion



- Presence of CO_2 enhances propane conversion without a catalyst.
- Both propane and CO_2 conversion increase with increasing plasma power.

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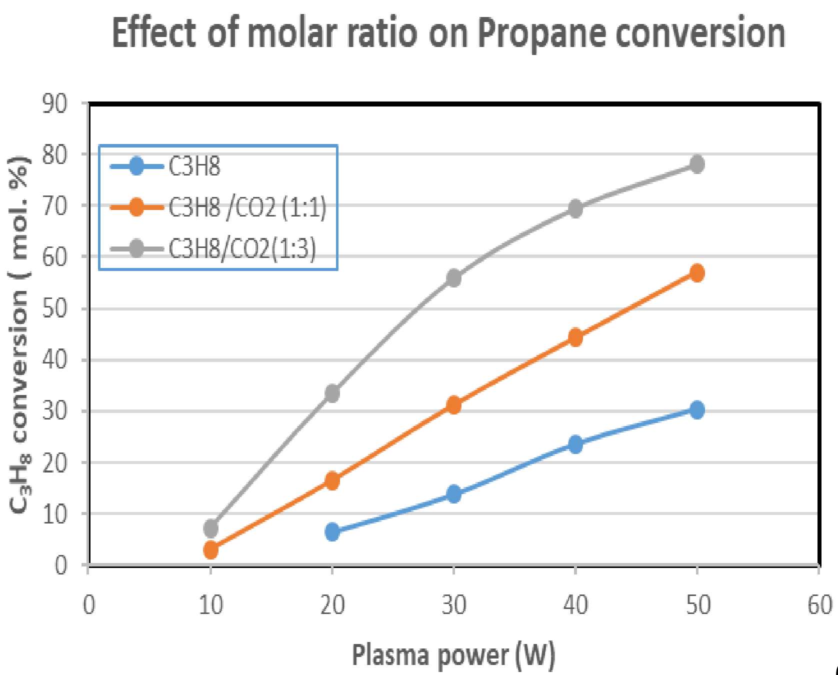
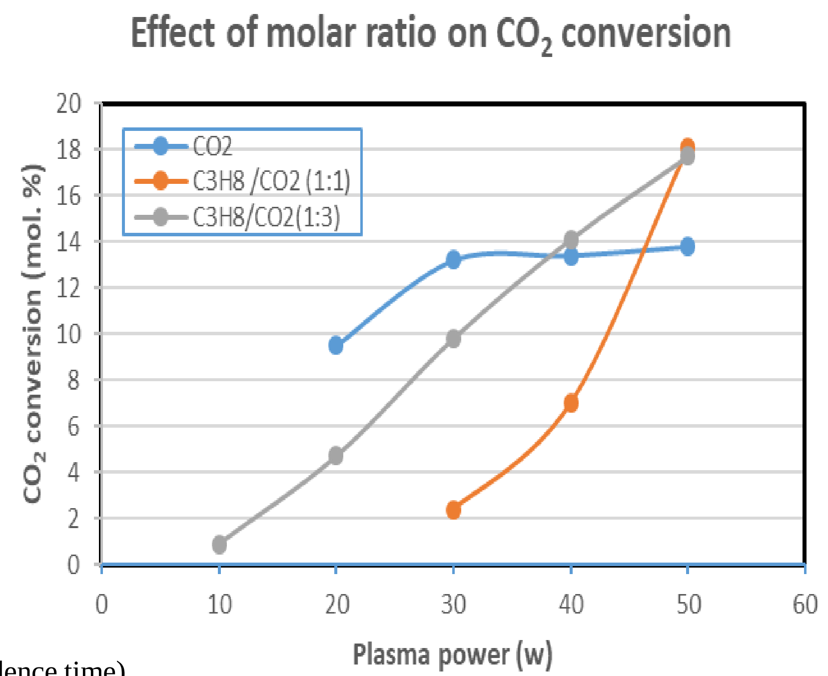
Effect of Propane / CO_2 Molar Ratio on Conversion





(13.5 s residence time)

- **Presence of more CO_2 enhances both propane and CO_2 conversion without a catalyst.**
- **Both propane and CO_2 conversion increase with increasing plasma power.**

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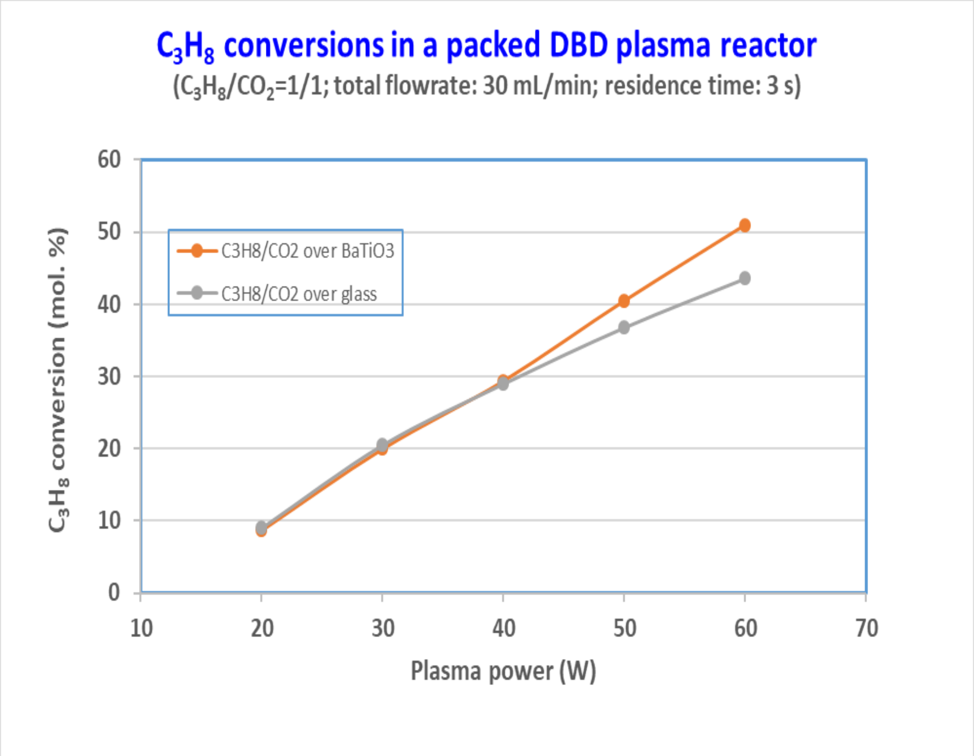
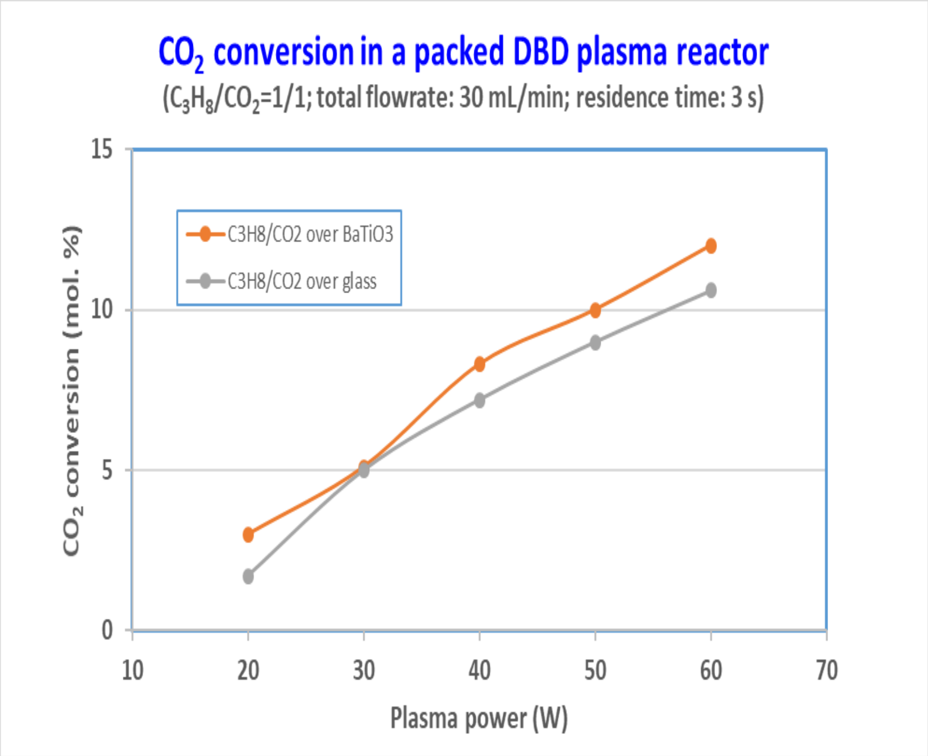
Effect of Packing on Propane and CO_2 Conversion





- $BaTiO_3$ beads produce higher propane and CO_2 conversions at >40W than glass beads.
- H_2/CO ratio is comparable over $BaTiO_3$ beads (about 1.7) and glass beads (about 1.6).

Plans for Future Testing

- Initiated catalyst synthesis for testing in plasma reactor
- Introduce catalyst into the plasma reactor, and explore the effect of catalysts on the conversion and selectivity - CeO_2 first, followed by various supported metal catalysts
- Optimization of selected catalysts for plasma assisted CO_2-ODH
- Optimization of plasma process conditions to maximize CO_2 and propane conversion as well as propylene and CO yields
- Validation of catalyst stability in long-term testing conducted for up to 100 hour
- Completion of TEA and LCA to show process economics and CO_2 reduction potential
- Completion of technology gap analysis and updated TMP

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Plans for Commercialization

- Develop process design and modeling
- Plasma reactor scale up
- Scale-up of the catalyst
- Explore pilot testing of plasma assisted CO_2 reaction system
- Set up partnerships with key stakeholders

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Summary Slide

- Initiated synthesis, characterization and testing of various supported metal catalysts
- Some catalysts show greater than 90% propylene selectivity
- Plasma testing shows greater than 80% propane conversion without a catalyst
- Feasibility of the CO_2-ODH reaction with plasma demonstrated at much lower temperatures than conventional processes
- Presence of CO_2 enhances propane conversion in the plasma reactor

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Acknowledgement

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- Department of Energy (DOE/NETL)
- DOE Project Manager: Dr. Sai V. Gollakota
- SoCalGas
- North Carolina State University
- Newcastle University

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Acknowledgement

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Appendix

- These slides will not be discussed during the presentation but are mandatory.

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Team Members and Organizational Structure

DOE/NETL Project Manager
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DBD Plasma Reaction and Testing
Dr. Adam Harvey
Dr. Kui Zhang
Newcastle University

T2M and Technology Scale-up
Mr. Ron Kent
SoCalGas

Project Timeline

Project Timeline		O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S
		10/01/2020 – 09/30/2022																							
	Assigned Resources	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
Task 1 - Project Management and Planning	**Susteon**																								
Subtask 1.1 - Project Management		■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Subtask 1.2 - Technology Maturation Plan									■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Milestone 1: Kickoff meeting and submission of revised PMP				◆																					
Task 2- Catalyst Preparation, Characterization, and Testing	**NCSU & Susteon**			◆																					
Subtask 2.1 – Catalyst Preparation		■	■	■	■	■																			
Subtask 2.2 – Catalyst Testing for CO_2-ODH Activity and Selectivity				■	■	■	■	■	■	■	■														
Subtask 2.3 – Catalyst Forming					■	■	■	■	■																
Milestone 2: Successful preparation, forming and testing CO_2-ODH catalysts											◆														
TTask 3.0 - Experimental Testing of Plasma Assisted Catalytic CO_2-ODH	**NU**																								
Subtask 3.1 - Plasma Reactor Design and Setup		■	■																						
Subtask 3.2 - CO_2-ODH Process Performance Measurements without Catalyst				■	■																				
Subtask 3.3 - CO_2-ODH Process Performance Measurements with Catalyst						■	■	■	■	■															
Subtask 3.4 - Catalyst Stability									■	■	■	■													
Milestone 3: Successful obtaining process conditions for maximizing CO_2 conversion and catalyst stabiity												◆													
Task 4.0 - Process Modeling	**Susteon**							■	■	■	■	■	■												
Milestone 4: Successful development of process model for process heat and material balances													◆												
Task 5.0 - Catalyst Optimization	**NCSU & Susteon**													■	■	■	■	■	■						
Milesteon 5: Successful optimization of catalyst for CO_2-ODH																			◆						
Task 6.0 - Optimization of Process Conditions	**NU**																	■	■	■	■	■			
Milestone 6: Successful optimization of plasma process conditions to maximize CO_2 and propane conversion as well as propylene and CO yields																						◆			
Task 7.0 - Long-Term Testing	**NU**																		■	■	■	■	■	■	
Milestone 7:Successful validation of catalyst stability in long-term testing conducted for up to 100 hours																								◆	
Task 8.0 - Final Techno-Economic and Life Cycle Analyses	**Susteon**																								
Subtask 8.1 - Process modeling																					■	■	■	■	
Subtask 8.2 - TEA, LCA, and Technology Gap Analysis																							■	■	■
Milestone 8: Successul completion of TEA and LCA to show process economics and CO_2 reduction potentials																									◆