CO_2 to Methanol Using Plasma Catalysis at Atmospheric Pressure

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U.S. Department of Energy

National Energy Technology Laboratory

Carbon Management and Natural Gas & Oil Research Project Review Meeting

Virtual Meetings August 2 through August 31, 2021

Project Overview

– **Funding (DOE SBIR)**

Phase-I: $196,990 (07-01-2019 to 03-31-2020)

Phase-II: $1.15 MM (08-24-2020 to 08-23-2022)

– **Project Participants**

Advanced Energy Materials LLC

E^3Tec LLC

TechOpp Consulting

Project Goal & Objectives

Goal

Develop skid mounted unit solutions for on-site production of CO/Syngas and mini GTL plant for methanol production using synergy of plasma and catalyst.

Objectives

- Economical conversion of CO_2 at modular scale to CO (1 – 10 m^3/h), syngas and methanol (1 - 3 ton/day).
- Optimize the tri-reforming process for throughput (lpm/kW) using CO_2, CH_4, H_2O, and O_2, with conversion >80% for syngas H_2/CO > 2.
- Demonstrate the process scaleup with 3 kW plasma and catalyst lifetime for 100 h.
- Develop integrated PFD for mini modular plants for CO and methanol.
- Establish conversion and throughput for economical production at modular scale.
- Process validation with gas feed from a fermenter.

Technology Background

The most significant challenge in CO_2 conversion to CO / Syngas / methanol:

CO_2 is thermodynamically and kinetically inert and its conversion requires high pressures and temperatures.

$$CO_2 + 3H_2 \longleftrightarrow CH_3OH + H_2O \qquad \Delta H_{298k} = -49.5 \text{ kJ/mol}$$
$$CO_2 + H_2 \longleftrightarrow CO + H_2O \qquad \Delta H_{298k} = 41.2 \text{ kJ/mol}$$
$$CO + 2H_2 \longleftrightarrow CH_3OH \qquad \Delta H_{298k} = -90.6 \text{ kJ/mol}$$

Of the above three routes, syngas to methanol (CO, H_2) is commercially implemented using thermal catalysis, but economical only at large scale.

Direct hydrogenation of CO_2 with high rates and selectivity to methanol requires high pressures from 100 to 300 bar.

Improved catalysts and pathways are critically needed for CO_2 to chemicals conversion.

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CO_2 to Methanol Production Technologies

- Direct CO_2 hydrogenation

- Demo pilot plants in Iceland, Japan, Korea using thermal catalysis at high pressures and temperatures
- No commercial plants

- Indirect CO_2 hydrogenation

- Dry reforming of CH_4 and CO_2 to syngas followed by methanol production
- Low lifetime of catalysts limit the commercial implementation

- Electrochemical Conversion

- Low activity and Low stability of electrocatalysts
- Low solubility of CO_2 in the reaction media
- Lab scale, but of interest due to use of H_2O in place of H_2

- ADEM's Plasma catalysis (PlasCat™) US patent – 63/070,197

- No external heat and low-pressure (< 7 bar) operation
- Synergy between plasma and catalysis
- Low capital cost, easy to scaleup and build mini GTL plants

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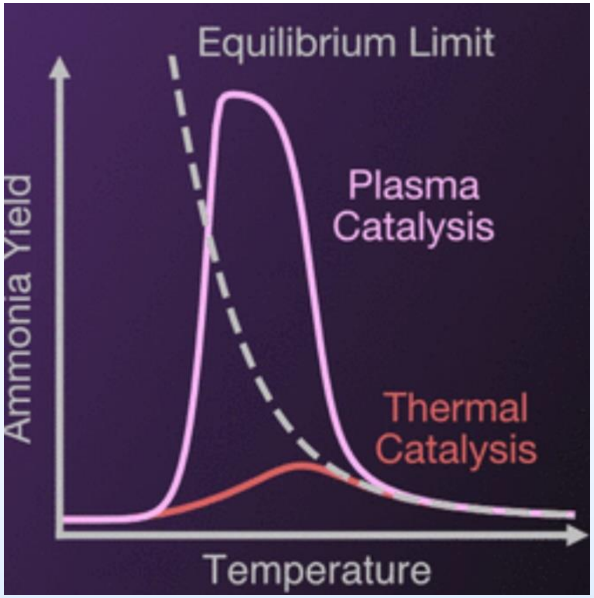
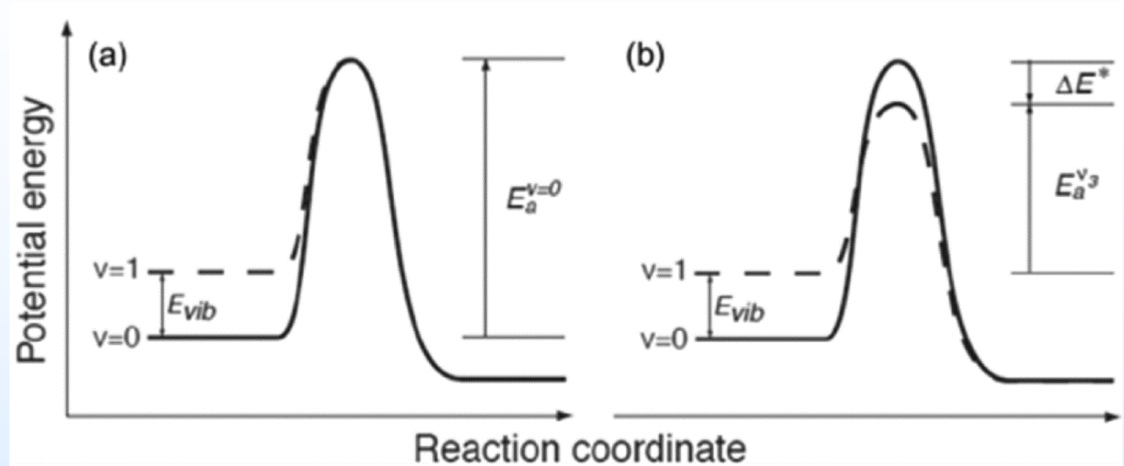
Plasma Catalysis



[1]**Plasma enhanced catalytic vs Thermal catalytic process**



[2]**Lowering activation barrier**

❖ Reduces activation barrier - Plasma excitation can in principle bypass kinetic bottlenecks of thermal catalytic transformations.

❖ Enhance net reaction rates and conversions.

❖ Plasma heating of gas.

❖ Surface temperature of catalyst is high while bulk temperature is low.

1. *ACS Catal. 2020, 10, 6726−6734*
2. Chem. Rev. 2015, 115, 13408−13446

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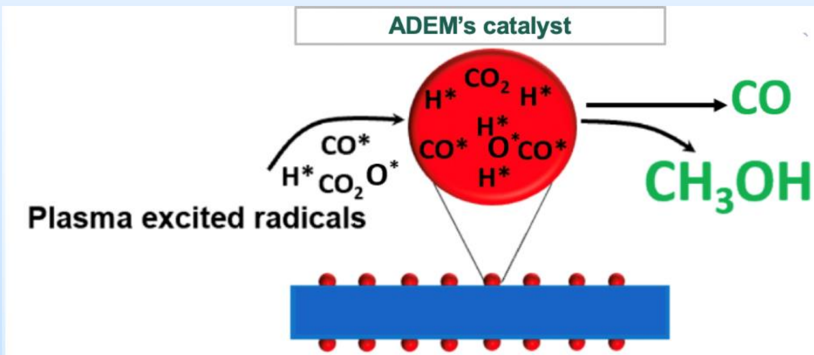
ADEM's PlasCat™ Process

Warm plasmas such as microwave plasma (MW) can simultaneously provide:

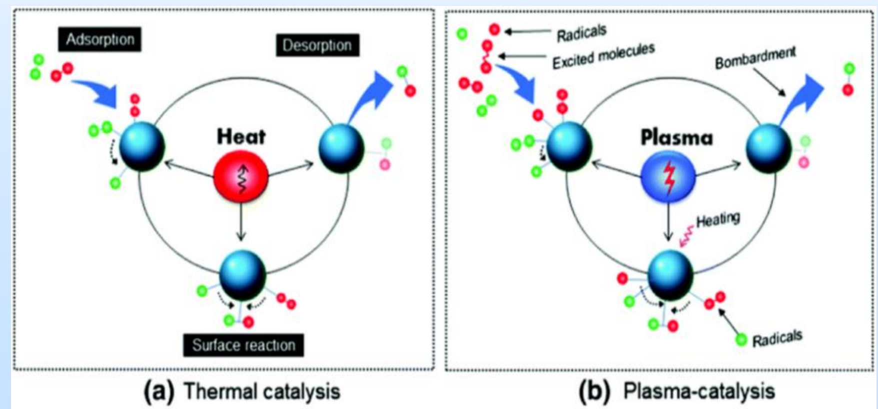
❖High degree of non-equilibrium and a high electron density which translates to efficient reactor productivity.

❖Selectively populate certain vibrationally excited species might be very promising for CO_2 conversion.

❖Plasma activates gas by energetic electrons instead of heat, allowing the thermodynamically difficult reactions such as CO_2 conversion to occur with reasonable energy costs.



Synergism of plasma excitation of CO_2 and H_2 and recombination reactions on catalyst surface to products.



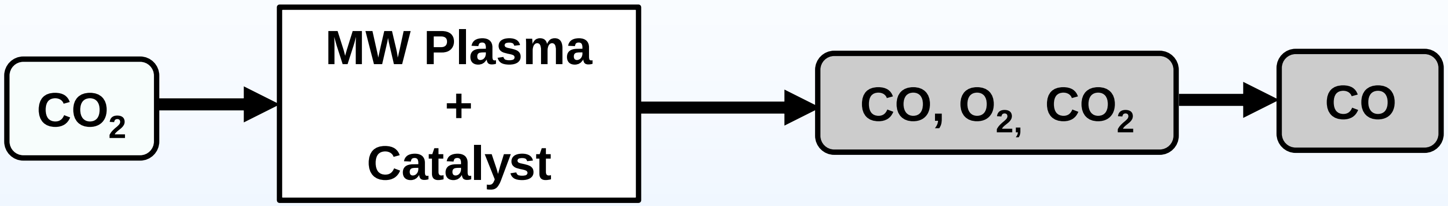
[1]**Comparison of thermal vs plasma catalysis**

1. *Chemical Society Reviews* **2017,** *46* (19), 5805-5863

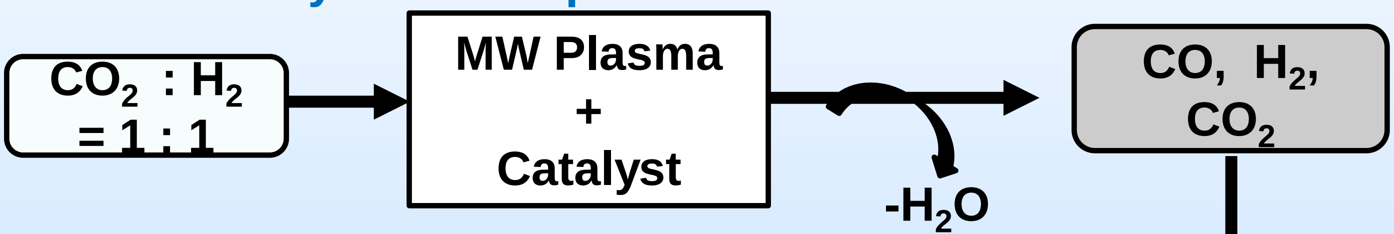
ADVANCED ENERGY MATERIALS

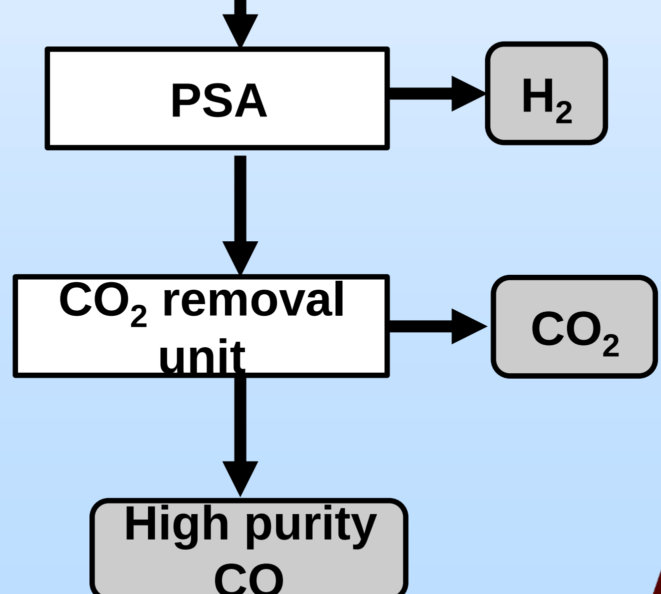
Technical Approach/Project Scope: CO_2 to CO

A: Plasma catalytic splitting of CO_2 to CO



B: Plasma catalytic RWGS process



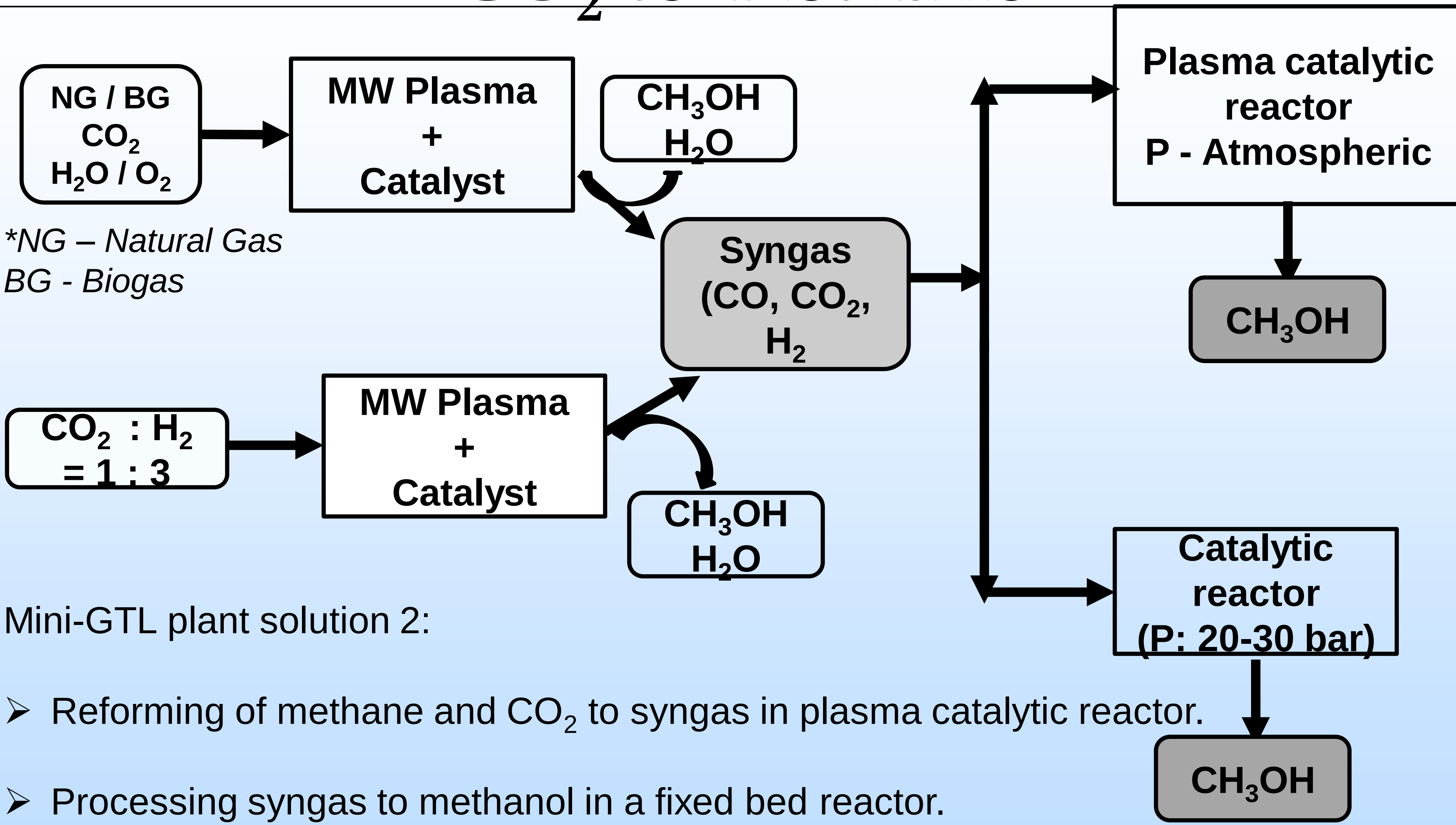


ADEM's mini-GTL plant solution 1:

Plasma catalytic production of CO through splitting of CO_2 or through RWGS.

- On-site & on-demand production.
- Commercially available plasma power sources can be used to produce up to 10 m^3/h on a modular basis.

Technical Approach/Project Scope: CO_2 to Methanol



Mini-GTL plant solution 2:

- Reforming of methane and CO_2 to syngas in plasma catalytic reactor.
- Processing syngas to methanol in a fixed bed reactor.
- Modular unit to produce methanol at 500 - 1,000 ton/yr.

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Project Success Criteria

- Achieve ADEM's PlasCat™ process for CO production from CO_2 at near atmospheric pressure economically (<<$600/ton) and energy efficient (>50%).
- Demonstrate catalyst lifetime > 100 h.
- Show syngas production with $H_2/CO = 2$ at a throughout of 0.5 – 1 m^3/h.
- Optimize production of methanol with 10% yield at atmospheric pressure
- Fully integrated PFD and techno-economic models for mini-GTL plants for further scale up.
- Establish metrics (production scale, conversion, and energy efficiency) necessary for economical production for CO and methanol using Plascat process.

Project Risks and Mitigation Strategies

Project Risks	Mitigation Strategy
High power plasma source for scaleup	Make agreement with equipment manufacturers for supply
Process scalability: control bed T	Manipulate the contact between catalyst and plasma
Cost of production: H_2 price	Mitigating by using NG and H_2O
Delays due to Covid19	No cost project extension

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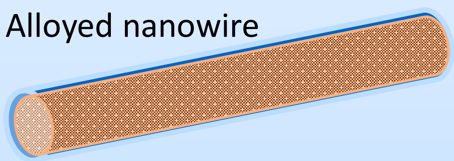
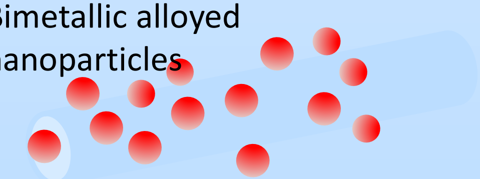
Progress and Current Status: ADEM's Catalysts

- 1-D nanowires as supports, or nanowires alloyed with active metals
- Active and high temperature stability
- Precision composition control
- Uniform loading

Alloyed nanowire



Bimetallic alloyed nanoparticles



Porous nanowire support

Patent Number	Issue Date	Patent Title
9,409,141	8/9/16	Methods for synthesizing metal oxide nanowires
10,030,201	7/24/18	Catalyst compositions and methods for desulfurization
10, 584,289	3/10/20	Nanowire based Hydrodesulfurization Catalysts for Hydrocarbon Fuels
62/457,695	2/10/17	Nanometal oxide Adsorbents for Desulfurization of Hydrocarbon Fuels
PCT/US17/47002	8/15/17	International PCT - Flame based Fluidized Bed Reactor for Nanomaterials Production
PCT/US18/12006	1/1/18	International PCT - Nanowire based Hydro-desulfurization Catalysts for Hydrocarbon Fuels
PCT/US18/17355	2/14/18	International PCT- Nanowire based Adsorbents for Desulfurization of Hydrocarbon Fuels
62/775,150	12/4/18	Catalyst Compositions for Conversion of Furfural to 2-Methylfuran and their applications
62/554,619	8/29/19	Spinel Lithium Titanium Oxide (LTO) Nanowire Anode Material for Lithium Ion Batteries
17/139,821	1/3/20	Novel CO2 Materials for Advanced Carbon Capture Technologies & DBD Plasma Based Processes
16/841,401	4/6/20	Nanowire based Hydrodesulfurization Catalysts for Hydrocarbon Fuels - Continuation
16/841,714	4/6/20	Desulfurization and Sulfur Tolerant Hydrogenation Processes of Hydrocarbon Feedstocks
63/070,197	8/25/20	Plas-Cat Plasma Assisted Distribution of Chemical Production
63/010,477	4/15/20	Non-Passive Anti-viral and Nanofilter based Respirators

Progress and Current Status : Catalyst Stability in Plasma

Developed stable and active metal oxide alloy catalysts

Catalyst - A

Before exposing

After exposing to MW Plasma

Catalyst - B

Before exposing

After exposing to MW Plasma, 1 h

The CO_2 conversion drops from 52.4% to 47.8% on catalyst-A in 1 h.

Catalyst-B shows 60% conversion and structural stability with time.

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Progress and Current Status: CO_2 to CO Conversion

$$SEI(Jcm^{-3}) = SEI\ (kJL^{-1}) = \frac{power\ (kW)}{Flow\ rate\ (L\ min^{-1})} x60$$

$$SEI(ev/mol) = 0.254 * SEI\ (kJL^{-1})$$

ΔH for
RWGS: 0.425 eV/mol
CO_2 splitting: 2.93 eV/mol

Energy efficiency = (Total conversion X ΔH_{298K} eV/mol) / SEI(eV/mol)

❖ The CO_2 splitting to CO at a throughput of 6 NLpm/kW, SEI – 2.6 eV/mol has showed 8-20% conversion depending on process variable.

❖ The CO_2 hydrogenation to CO at a total throughput of 12 NLpm/kW, CO_2/H_2 – 1, and SEI – 1.34 eV/mol shows 54% conversion.

❖ The CO_2 hydrogenation to CO in MW plasma and catalyst (catalyst –B) at a total throughput of 12 NLpm/kW, CO_2/H_2 = 1, and SEI = 1.33 eV/mol shows 60% conversion.

❖ The addition of catalyst to plasma enhanced the CO_2 conversion by 6-7%. With the new reactor configuration we expect to achieve greater energy efficiency (>50%).

CO_2 Hydrogenation to CO: PlasCat™ vs State of the Art

$CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$ $\Delta H^0 = +41.2$ kJ/ mol

<table>
<tr><th>ADEM's PlasCat™</th><th>State of the Art RWGS</th></tr>
<tr><td rowspan="4">Atmospheric pressure and plasma energy input.

High throughput (current):12-14 Lpm/kW
Target throughput: 30 Lpm/kW

High CO_2 conversion-60% at H_2/CO_2-1 and >99% selectivity .

Current status: 1 m^3 CO_2 at 2 kWh</td><td>[1]Lu et al. 40% conversion of CO_2 over Ni/CeO_2 catalyst, H_2/CO_2-1 and T-750 °C.

Materials Research Bulletin 2014, 53, 70-78.</td></tr>
<tr><td>[2]Nature Catalysis, 2020 18% conversion of CO_2 and 95% selectivity to CO over Ni-Au bimetallic catalyst using H_2/CO_2 – 3 and T-600 °C.

Nature Catalysis 2020, 3 (4), 411-417.</td></tr>
<tr><td>[3]Electrochemical reduction of CO_2

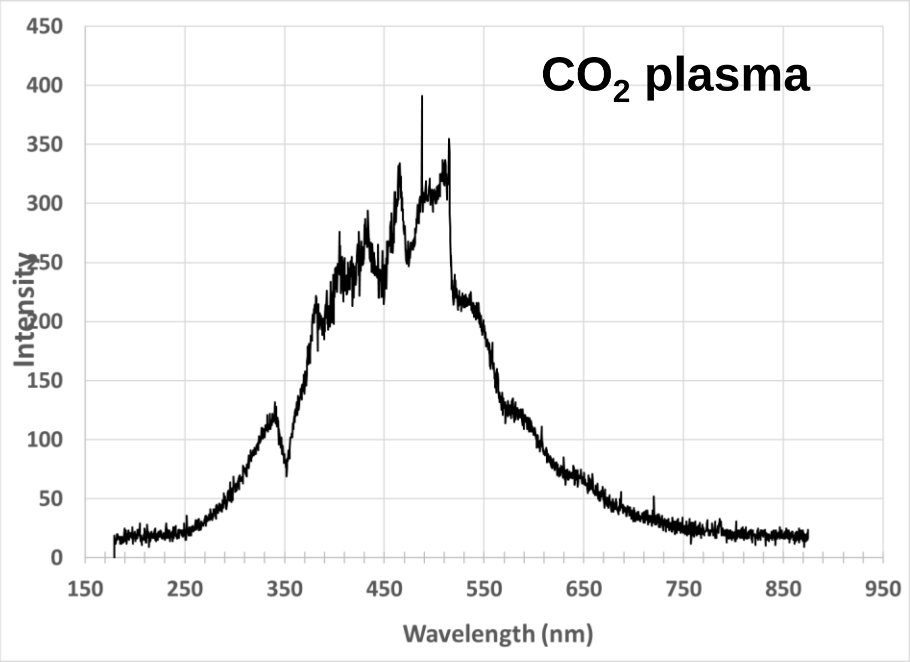
Solidoxide fuel cell operating at 850 °C and processes 1 m^3 CO_2 at 6-8 kWhr
https://www.topsoe.com/processes/carbon-monoxide/site-carbon-monoxide.</td></tr>
<tr><td>DBD Plasma+Catalyst Pd/ZnO

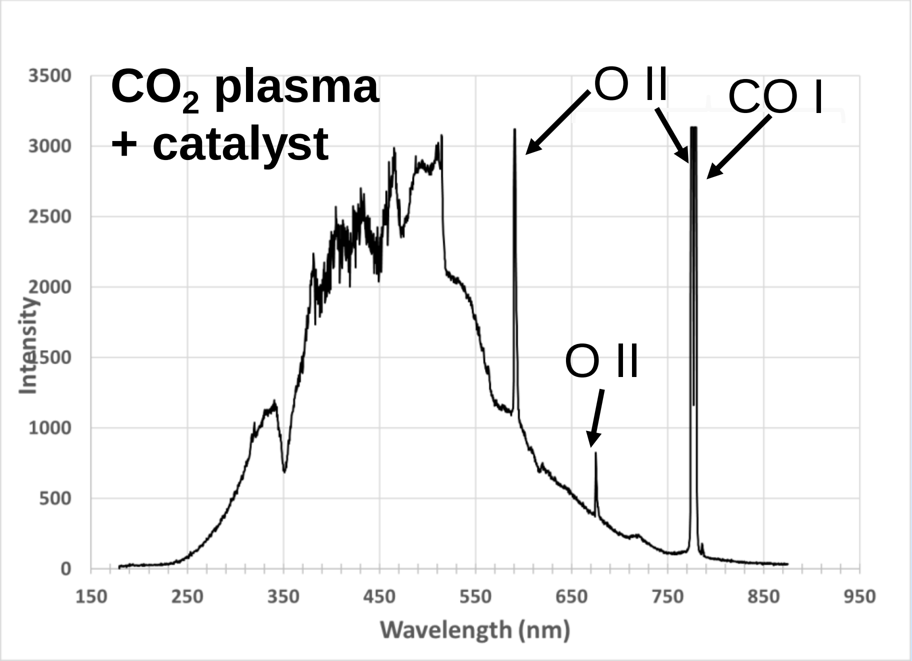
feed: H_2/CO_2-3, CO_2 conversion-32.5%Applied Catalysis A: General 2020, 591, 117407.</td></tr>
</table>

Progress and Current Status: Demonstration of Plasma Catalyst Synergy Using OES

MW power 400 W
CO_2 Flowrate 7 lpm

O II : 590.30nm, 675.12nm , 776.15nm
CO I : 778.62nm





The OES analysis of plasma contacted with catalyst shows the populations of excited species correspond to oxygen and CO.

In this specific configuration ADEM can easily screen and design catalysts for improving the conversion and throughput.

Progress and Current Status: Dry & Tri-reforming

Thermocatalytic dry reforming

- Developed and demonstrated the catalyst in dry reforming test (CO_2/CH_4 – 1, T-800 C, GHSV-7.8 l h^{-1} $gcat^{-1}$) under thermocatalytic conditions.

Catalyst - C: CO_2 conversion - 99%; CH_4 conversion – 80%; 500 h of stability; no coking

Plasma catalytic tri-reforming

- MW Plasma catalytic tri reforming has produced at a throughput of 276 Lph/kW: CO_2 conversion – 78%, methane conversion – 90%, $H_2/CO \geq 2.2$, and methanol yield of 2%.
- The MW plasma tri-reforming with no catalyst at 780 Lph/kW has conversion of CO_2 – 64% and CH_4 – 82%.

ADEM's PlasCat Process vs State of the Art

Process	ADEM's Technology at Atmospheric Pressure					State of the Art
	$CO_2 : CH_4 : H_2O : O_2$	Throughput (Lph/kW)	$\%CO_2$ Conversion	$\% CH_4$ Conversion	H2/CO Ratio	
Plasma catalytic Dry reforming	1 : 1 : 0 : 0	360	90	95	0.9	[1]*Science, 2020*: CO_2/CH_4-1, Catalyst- Ni-Mo/MgO, GHSV-60-300 L/h, T-800 °C, P-1 bar, H_2/CO – 0.8-1 with CO_2 conversion 80-100% and CH_4-70-95%
Thermal DMR T – 800 °C	1: 1: 0: 0	GHSV – 7.8 L/h/gcat	99	80	-	
Plasma Bi-reforming	1 : 1 : 1 : 0	550	69	-	1	[2]***J of American Chemical Society, 2013***: NiO/MgO catalyst, 5-30 bar, T-850 °C, CH_4/CO_2/H2O – 3/1.2/2.4, GHSV-60 L/h. CO_2 conversion-75%, H_2/CO-2
Plasma Tri-reforming	0.4 : 1 : 0.75 : 0.2	276	78	90	2.2	[3]***Nature Scientific Reports*, 2018**: DBD Plasma + T-300 C. CO_2 conversion-18%, H_2/CO-1.4-1.7. CH_3OH yield – 0.24 mol%

1. *Science* **2020,** *367* (6479), 777-781.
2. *Journal of the American Chemical Society* **2013,** *135* (2), 648-650.
3. *Scientific Reports* **2018,** *8* (1), 15929.

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Progress and Current Status: Syngas to Methanol

New high pressure bench scale (catalyst 10 - 100 g) fixed bed reactor
ID: 0.5 – 2″ X L: 25″. Reactor capable to handle up to P: 70 bar.

Tests under progress to develop kinetic model using ADEM's catalyst bimetallic catalyst
P: 20-60 bar, T: 220-260 C, GHSV: 3,000 – 6,000 h^{-1}

ADEM's bimetallic catalyst at H_2-CO_2/CO+CO_2 = 2, T: 220 °C, P: 20 bar and GHSV: 2, 600 h^{-1} $gcat^{-1}$.

- ❖ Showed high 'C' conversion (>38%) closer to equilibrium conversion (40%) compared to catalyst of same composition prepared by conventional methods (20 to 25%) and commercial (Cu-Zn-Al) catalyst shows 18% conversion
- ❖ Good selectivity to methanol (94%) compared to industrial best catalyst (87%).

Progress and Current Status: CO_2 to Methanol

$CO + 2H_2 \rightarrow CH_3OH$, $\Delta H = -90.8$ kJ/mol
$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$, $\Delta H = -49.9$ kJ/mol

Comparison of Plascat process with state-of-the-art plasma catalysis

Parameters	ADEM Plasma unit	DBD Plasma[1]
H_2 and CO_2 flow rates	12 and 6 slpm	30 and 10 ml/min
Power and time	700 W, 1.5 hrs	10 W, 1.5 hrs
Energy efficiency	664 mmol/kWh	306 mmol/kWh
Overall Methanol rate (mmol/h)	465 mmol/h	4.6 mmol/h

1. *ACS Catalysis* **2018,** *8* (1), 90-100.

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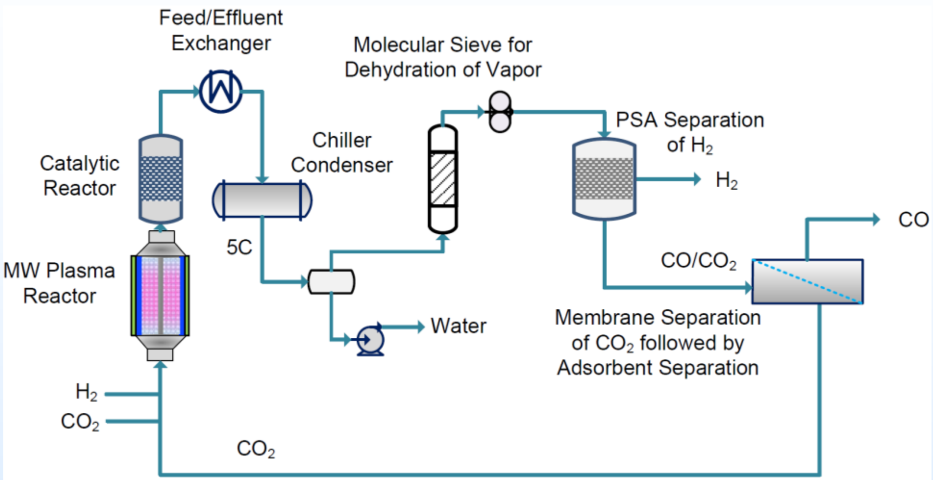
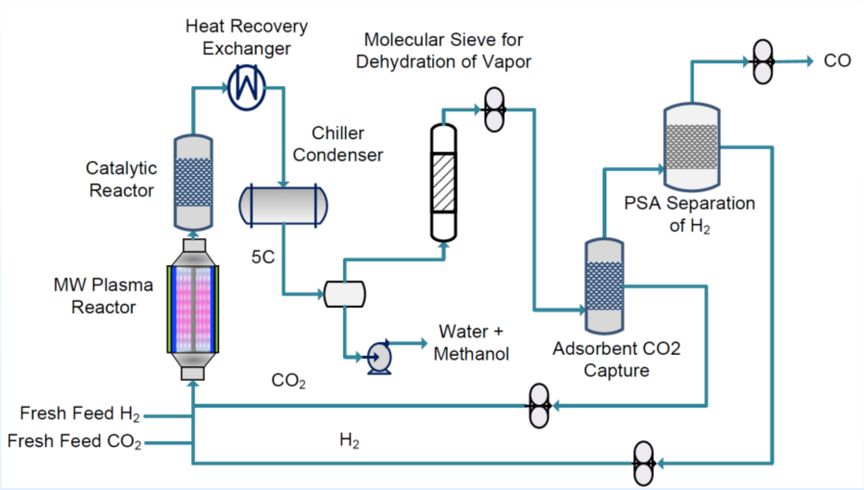
Progress and Current Status: T-E Analysis of Modular Plants





PFDs for mini plant of producing CO from CO_2 and H_2

Currently working on developing the metrics (target conversion and energy efficiency) for both CO and methanol plants that includes fully integrated systems for economical production.

For CO production, will setup the metrics for both CO_2 splitting and CO_2 hydrogenation pathways and the target unit capacity is 1 -10 m^3 h^{-1}.

For methanol, target plant capacity is 500 – 1,000 TPA.

Plans for Future Testing & Development

- Optimize ADEM's Plascat process for CO_2 to CO: throughput from 6 lpm/kW to 30 lpm/kW and conversion from 10-20% to consistently >30% using CO_2 only.

- Optimize ADEM's Plascat process for CO_2 to CO with H_2 (H_2/CO – 1): throughput from 6 lpm/kW to 30 lpm/kW and conversion from 60% to consistently >80%.

- Integrated MW plasma and DBD plasma catalysis processes for methanol production.

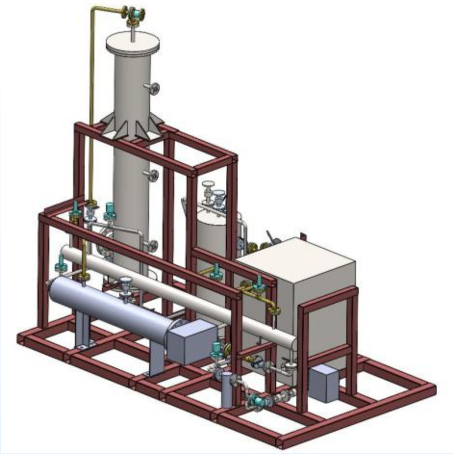
- Develop the kinetic model for syngas to methanol process

- Demonstrate the catalyst lifetime under plasma > 100 h.

- Finalize techno-economic models for mini plants and establish/validate the targets for economical production.

- Life cycle analysis for net CO_2 reduction for the above mini plants.

Plans for Commercialization



- ADEM is currently demonstrating its reactive adsorption-based desulfurization technology for gaseous and liquid hydrocarbons using a skid mounted mini plant.

- Setup a similar demonstration unit for plascat process (processing capacity: 1-3 $m^3 h^{-1}$) in house and later at an on-site of commercial partner (Brown-Forman).

- Develop a fully integrated mini-plant system that includes product separation, purification and gas recycling. (SBIR Phase-IIA).

- Demonstrate the scalability of the process using 6 kW, 915 MHz plasma source (Phase IIA).

- ADEM is planning to raise series-B funding ($3-5 MM) for commercialization.

- Partnering with equipment manufacturers/suppliers such as plasma source manufacturers (iPLAS).

- Reach out to more customers with help from commercialization assistance vendor (Tech-Opp consulting) and our strategic partners.

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Summary

- ❖ Developed alloyed catalysts that are more stable under plasma, and at high temperature.
- ❖ Catalyst – B has showed 60% conversion of CO_2 to CO with 100% selectivity to CO and stability in plasma.
- ❖ The ADEM's proprietary reactor configuration has showed significant synergy between plasma and catalyst supported by plasma diagnostics (OES data).
- ❖ The reforming catalyst has showed good stability over a period of 500 h at CO_2 conv of 99% and 80% CH_4 conversion.
- ❖ The process of CO_2 to methanol with CO as a byproduct will be optimized for high selectivity to methanol.
- ❖ In syngas to methanol process, the bimetallic alloyed catalyst has showed near equilibrium CO_2 conversion and high selectivity to methanol compared to industrial catalyst and by conventional methods.

Appendix

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

Organization Chart

Organization	Tasks	Team
Advanced Energy Materials LLC	Setting up plasma catalytic test reactors, catalyst development, plasma catalysis tests for CO_2 conversion to CO / syngas / methanol and process parameters optimization. Developing skid mounted unit solutions for CO_2 to chemicals.	Dr. Sivakumar Vasireddy
		Dr. Juan He
		Dr. Tu Nguyen
		Luke Guhy
		Ms. Neeti Rastogi
		Dr. Mahendra Sunkara
		Ms. Vasanthi Sunkara
E^3Tec LLC	Plasma catalytic process modeling, CO_2 footprint, Life cycle analysis and Techno-economic analysis.	Dr. C.B. Panchal
		Ms. Kruti Goyal
Tech Opp Consulting	Commercialization Assistance	Mr. Brian Phillips

Gantt Chart

Phase II Tasks	Budget Yr I (Aug27th 2020-Aug26th 2021) Q1	Q2	Q3	Q4	Budget Yr II (Aug27th 2021-Aug26th 2022) Q5	Q6	Q7	Q8
Task 1. High Throughput and High conversion of CO_2								
Sub-Task 1.1 Optimization of catalysts	75%							
Sub-Task 1.2 CO_2 hydrogenation activity in a plasma fixed bed reactor	60%							
Sub-Task 1.3 CO_2 hydrogenation in a plasma fluidized reactor			25%					
Task 2. MW Plasma Catalytic Production of Methanol Through Tri-Reforming Using $CH_4+CO_2+H_2O$								
Sub-Task 2.1 Syngas production from CO_2 reforming of methane			40%					
Sub-task 2.2 Syngas to methanol studies using fixedbed and DBD reactors at different pressures		35%						
Task 3. Process Scaleup and Lifetime Studies								
Sub-Task 3.1 Kilogram scale synthesis of catalysts					80%			
Sub-Task 3.2 Scalability and lifetime studies with MW plasma fluidized bed reactor								
Sub-Task 3.3 Methanol synthesis from syngas in a fixed bed reactor at 100 g scale								
Task 4. Techno-Economic& C-footprint based life cycle								
Subtask 4.1 Process Analysis				40%				
Sub-task 4.2 C-footprint Analysis				35%				
Sub-task 4.3 Techno-Economic Analysis (TEA)				30%				
Task 5. Process Validation of Pilot scale Unit								
Task 6. Project management and reporting								