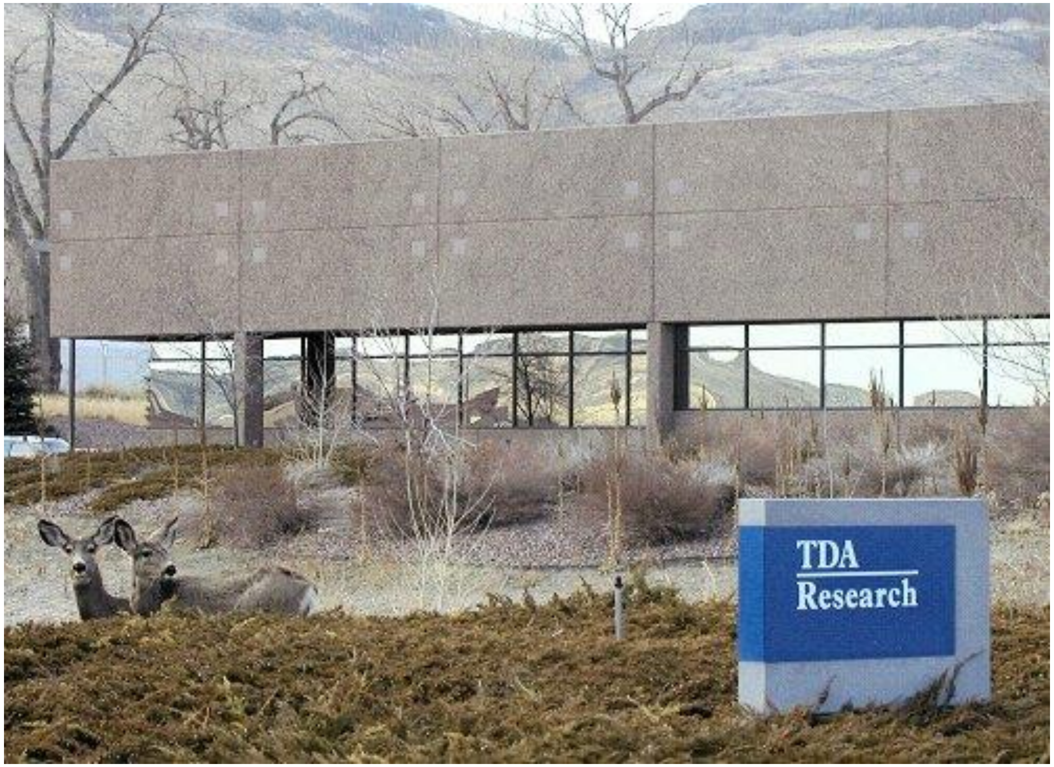
A New Process for Carbon Dioxide Conversion to Fuel (DE-FE0029866)



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2018 NETL CO_2 Capture Technology Project Review Meeting

DE-FE0029866

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TDA Research Inc. • Wheat Ridge, CO 80033 • www.tda.com

Project Objectives

- **The objective is to develop a new sorbent and the process around it for CO_2 utilization**
- **The sorbent converts CO_2 into CO in a redox process using H_2 generated by water electrolysis**
  - **CO and H_2 mixture (referred to as synthesis gas) is then used to synthesize a wide range of synthetic fuels and chemicals, via Fischer-Tropsch and oxo-synthesis processes**

- **Specific objectives**
  - **Sorbent synthesis and development**
  - **Bench-scale tests to assess technical feasibility**
  - **Long-term cycling**
  - **Reactor design (supported by modeling and CFD analysis)**
  - **Prototype fabrication to carry out proof-of-concept tests**
  - **Process design and development**
    - Gasoline synthesis via methanol-to-gasoline process
    - Diesel fuel synthesis via Fischer-Tropsch

Project Partners

UNIVERSITY of CALIFORNIA · IRVINE

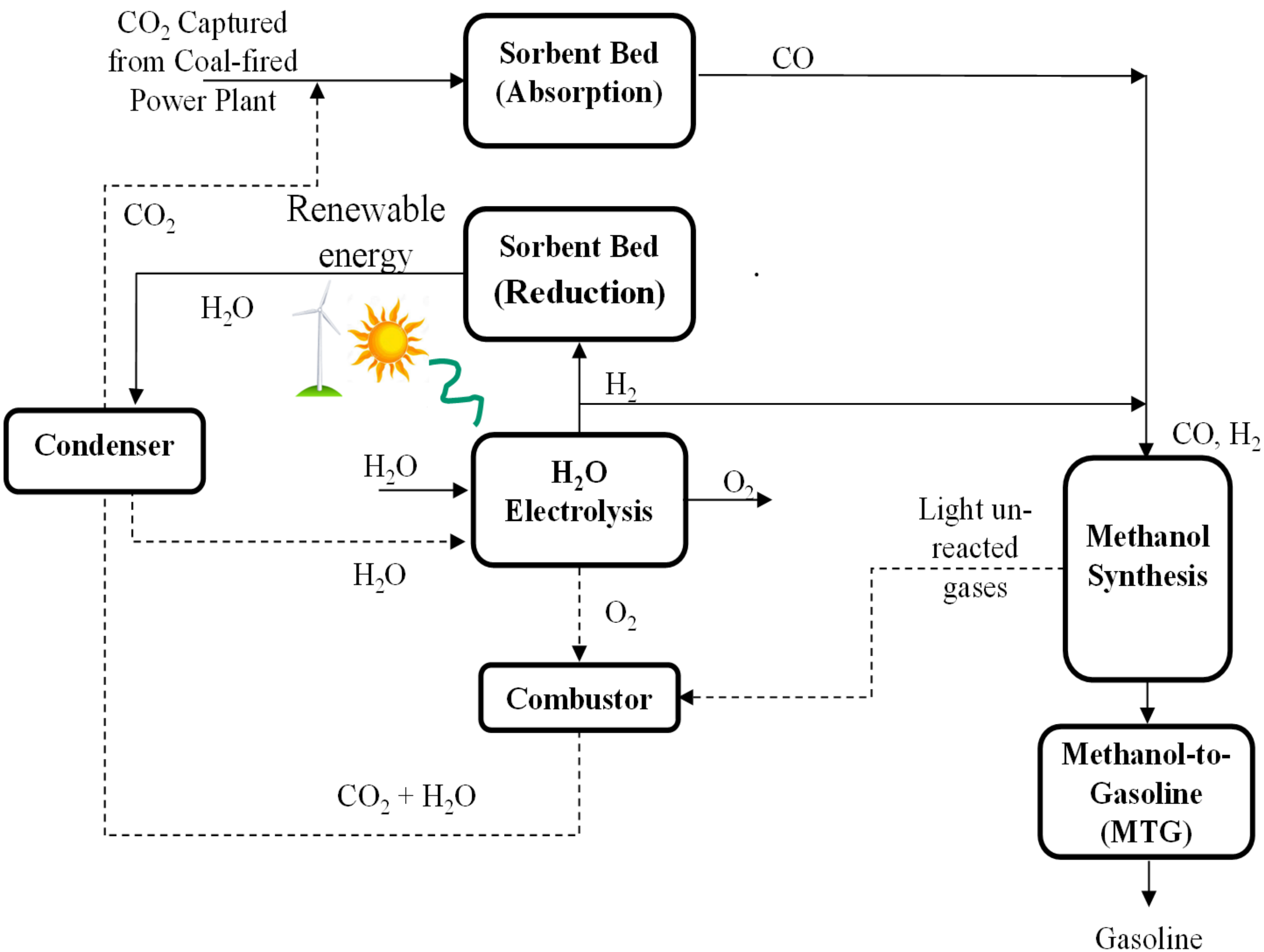
Project Duration

- **Start Date = June 15, 2017**
- **End Date = July 14, 2019**

Budget

- **Project Cost = $1,000,000**
- **DOE Share = $800,000**
- **TDA and its partners = $200,000**

Process Schematic



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Preliminary Cost Estimate

- **In a process (which utilizes over 99% of the CO_2 processed in the system) may deliver gasoline fuel at $3.25/gallon**
  - Based on energy costs only
  - Capital cost burden is not included
- **A potential more near-term commercial application may use natural gas in place of H_2 to carry out the sorbent reduction**
  - While there will be a net reduction in the overall CO_2 emissions, the final product will not contain only captured CO_2

Estimated energy consumption for CO_2 to gasoline conversion

Power	Purpose
331.64	MW_e for Electrolysis
23.57	MW_e for CO2 Reduction
-11.41	MW_e from Methanol Synthesis
-12.85	MW_e from Combustor
-6.20	MW_e from MTG process
324.75	MW_e net power needed (Total)
64.95	kWh per gallon gasoline
3.25	$/ga gasoline

- energy cost assumed to be $0.05 per kWh
- 80% eff. used for electrolysis
- 45% thermal to electric conversion eff. used for high temperature processes ~ 800°C
- 33% thermal to electric conversion eff. used for low temperature processes ~ 200-300°C

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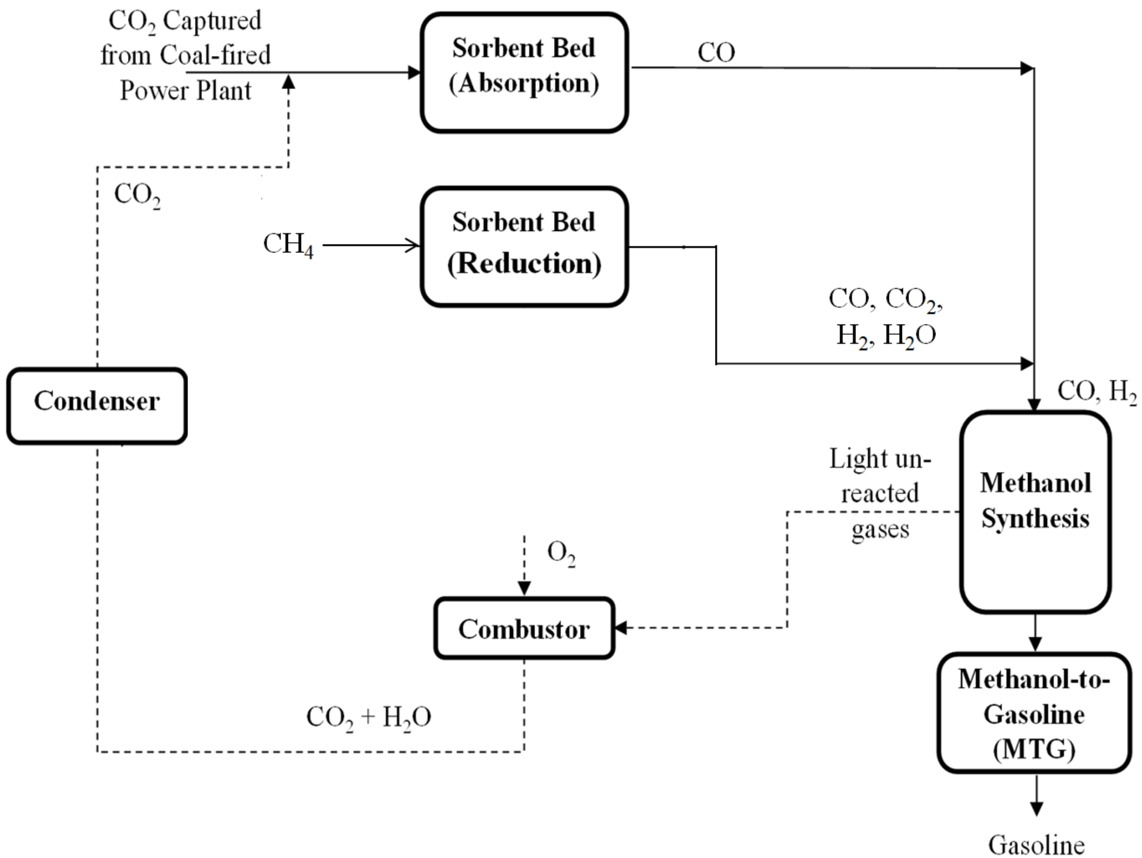
Process Schematic – NG Reduction



Reduction:	$CO_{2(g)} + M = CO_{(g)} + MO$
Partial Oxidation:	$CH_{4(g)} + MO = CO_{(g)} + 2H_{2(g)}$
Net Reaction:	$CH_{4(g)} + CO_{2(g)} = 2CO_{(g)} + 2H_{2(g)}$

Dry reforming can be achieved with very high level of conversion

TDA's Sorbent

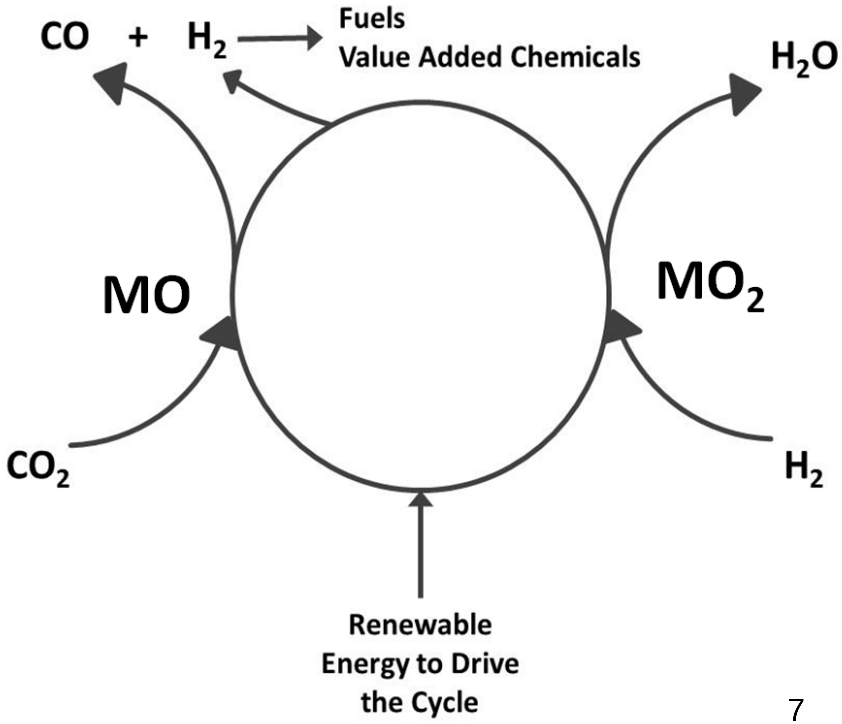
- Our process uses a unique mixed metal oxide phase to reduce CO_2
- A low oxidation state metal oxide phase directly reacts with CO_2, stripping off the oxygen to form CO and a higher oxidation state metal oxide forms
- In a subsequent step the sorbent material is contacted with H_2 to reduce it to complete the redox cycle

<u>CO_2 Reduction Step</u>

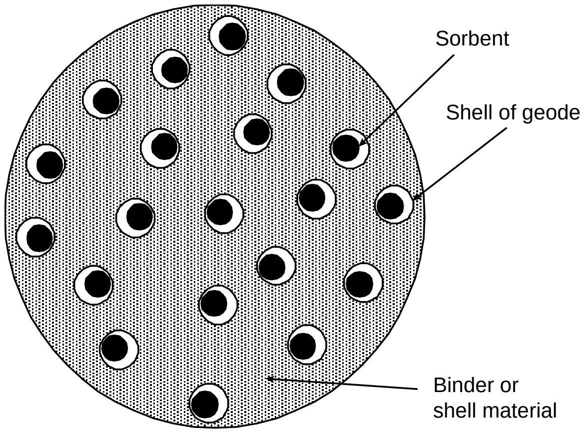
$$MO + CO_{2(g)} = MO_2 + CO_{(g)}$$

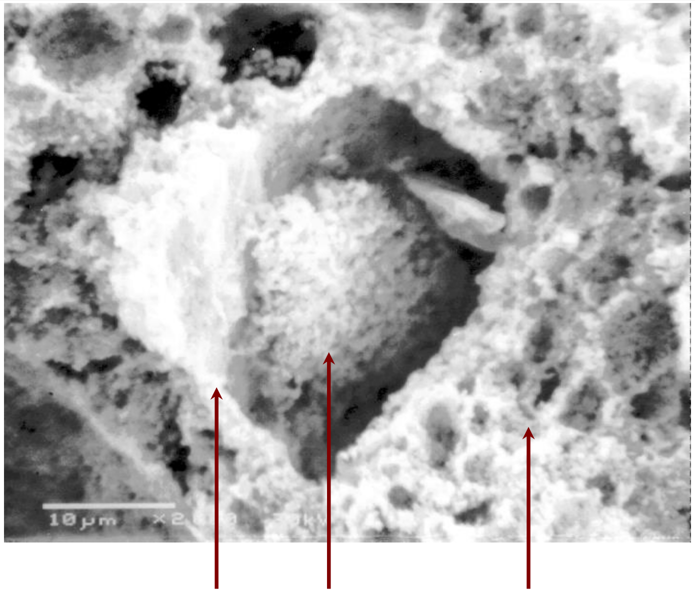
<u>Sorbent Reduction Step</u>

$$MO_2 + H_{2(g)} = MO + H_2O_{(g)}$$



TDA’s Sorbent



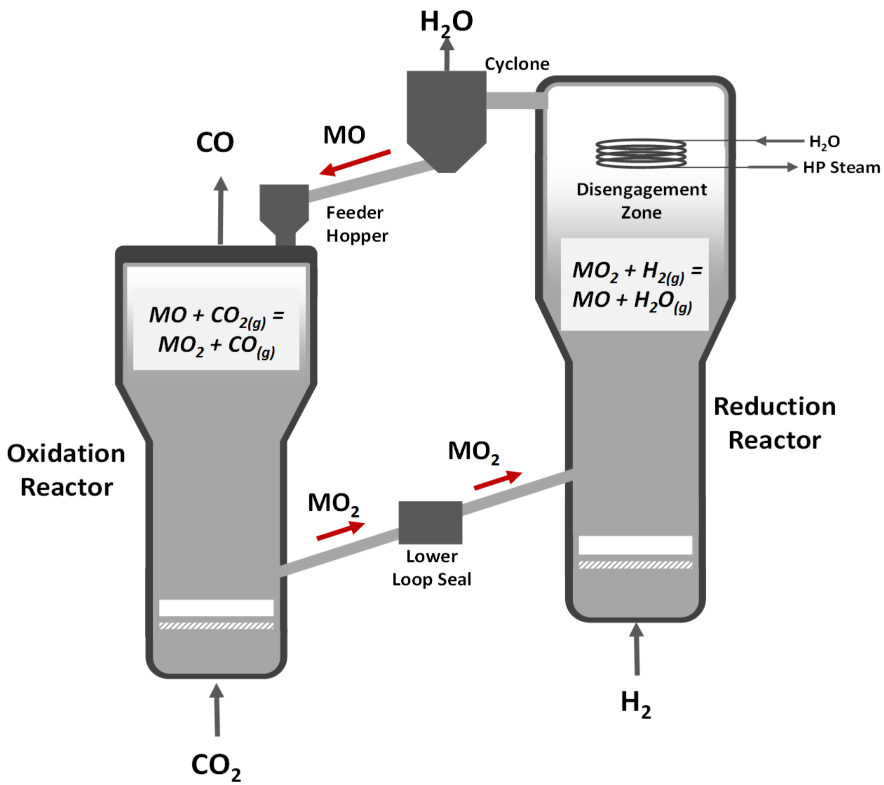


- **The sorbent will be prepared using a structure referred to as a “geode”, based on a TDA proprietary synthesis technique**
  - A large amount of active ingredients (to ensure a high oxygen uptake)
  - A high mechanical integrity during the large expansions and contractions associated with changes in molar volume of the active material in oxygen absorption and desorption
  - A high chemical stability
  - A high surface area maintained through repeated cycles

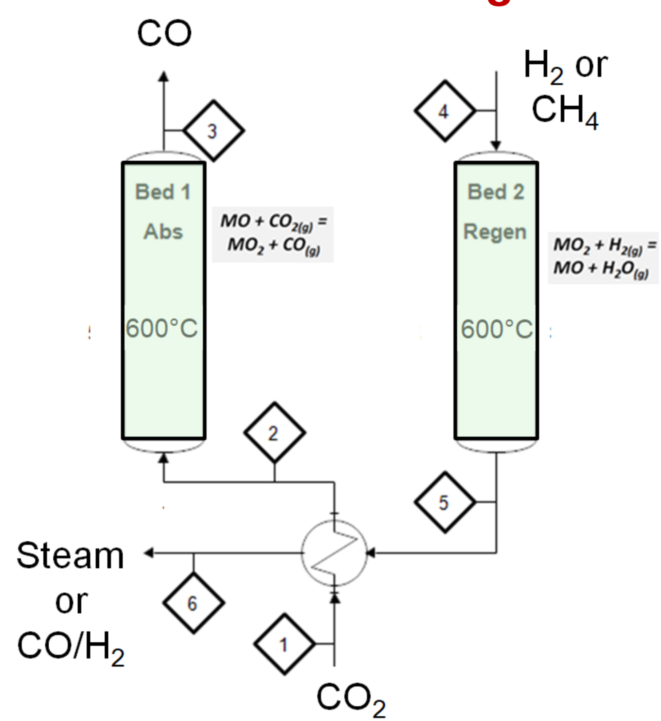
Moving Bed Contactors

- **Early designs were based on circulating beds due to the high temperature needed for CO_2 activation**
  - To eliminate the need for high temperatures flow selection valves
- **Advances in increasing material activity enables the use of fixed bed reactors**

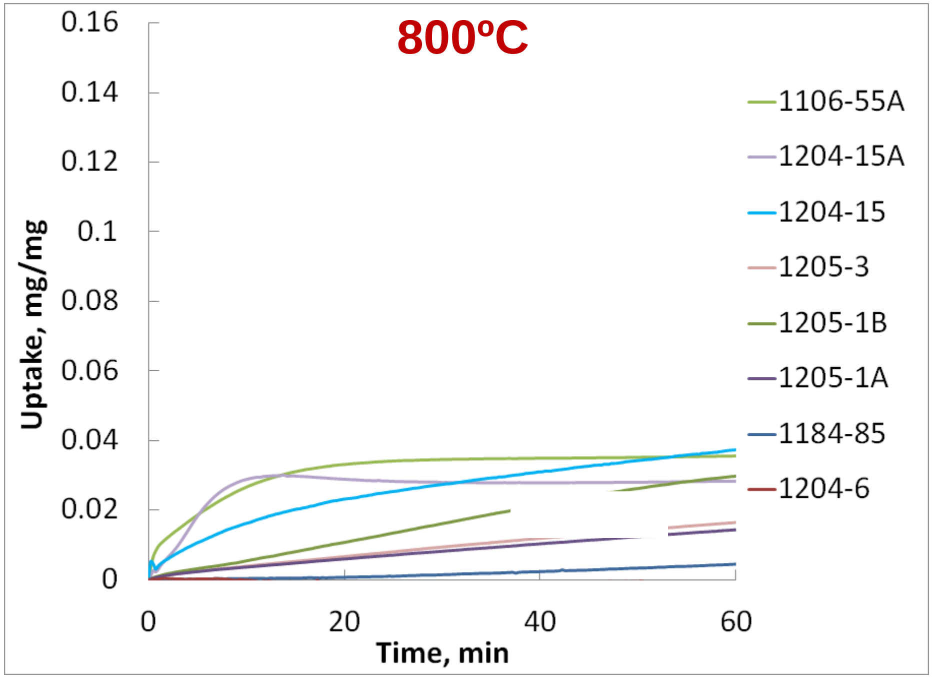
Circulating Bed Design

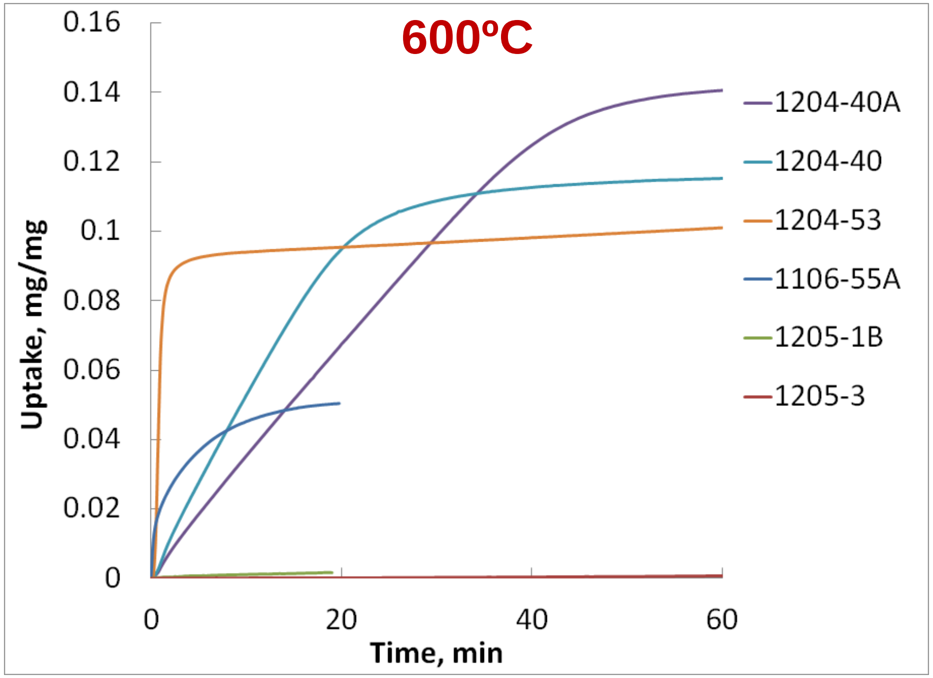


Fixed Bed Design



TGA Screening Results





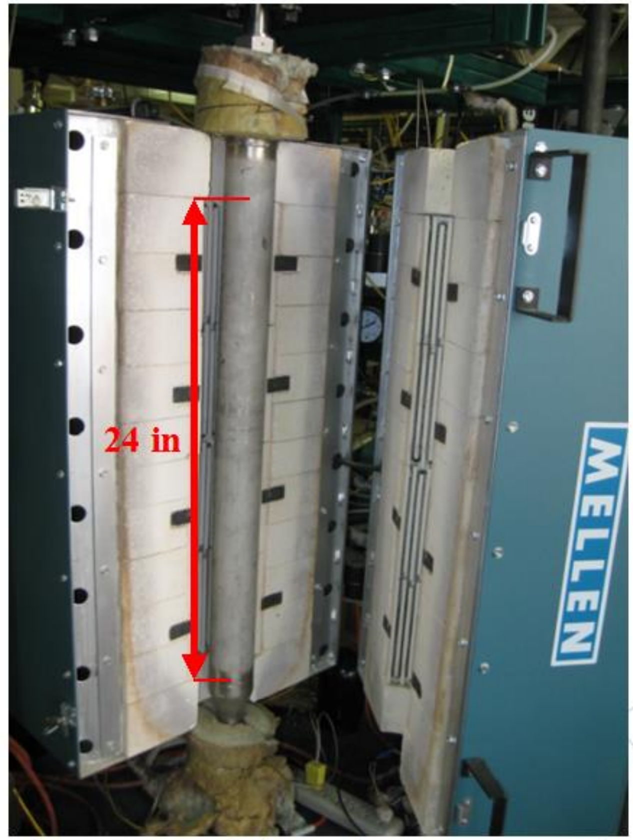
- New materials based on the use of different promoter phases were evaluated to improve:
  - Solid diffusion rates
  - Increase in the oxygen uptake and the rate of reduction
  - Decrease the onset temperatures for these process
- The new materials allowed operation at lower temperatures down with high oxygen uptake at 600°C

Sorbent Evaluation

- **Sorbent samples that meet our physical properties and chemical activity requirements was then evaluated in a micro-reactor**

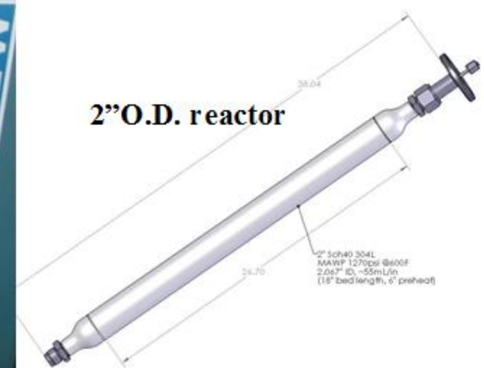
- **We compared the activity of these formulations under representative conditions**

- **Parametric tests to identify optimum operating conditions**
  - Temperature
  - Pressure
  - Gas-solid contact time



2 in Schedule 40 Stainless Steel Reactor
2.07 in Internal Diameter
24 in Heated Bed Length
1324 cm^3 Sorbent Bed

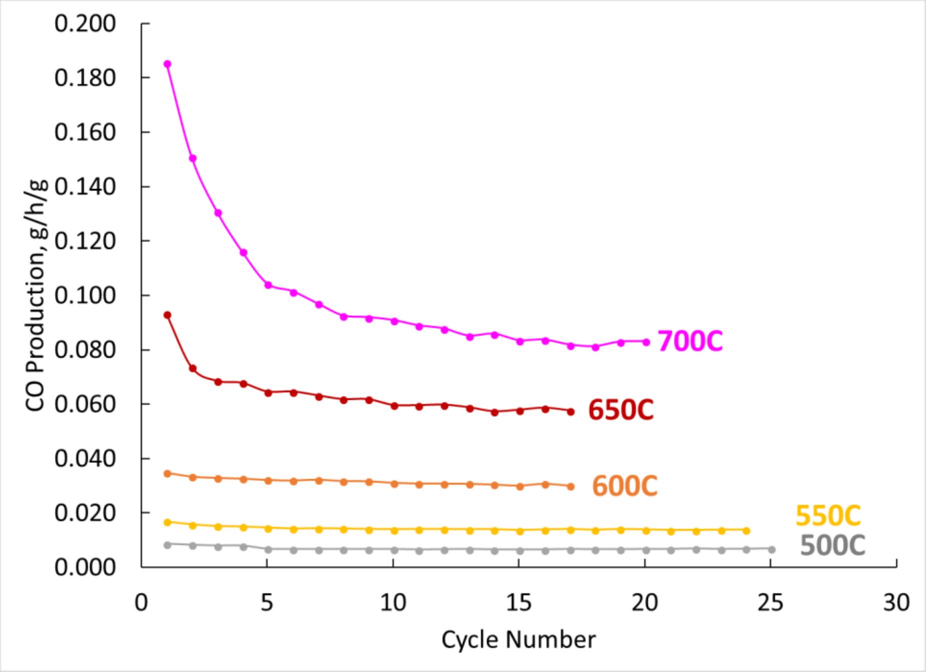
Schedule 40 2" Pipe Reactor		
Internal Diameter	2.07	in
Cross Sectional Area	3.37	in^2
Heated Length	24.00	in
Bed Volume	80.77	in^3
	1323.56	cm^3



Reactor Results – CO_2/H_2 Cycling

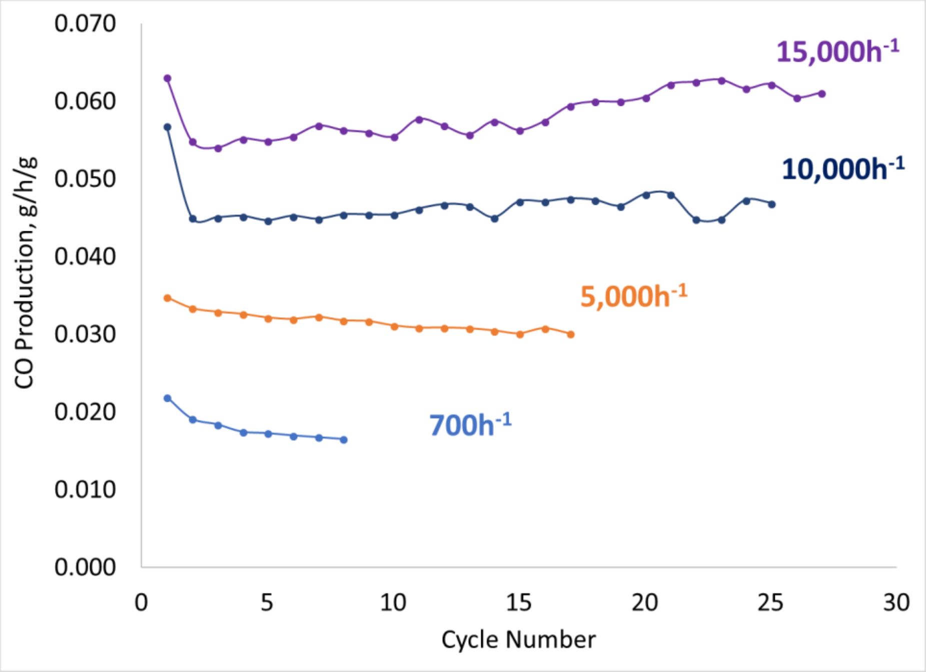
CO Production vs. Temperature

GHSV: 5,000h^{-1}, t_{ox}/t_{red}: 20 min



CO Production vs. GHSV

Temp: 600C, t_{ox}/t_{red}: 20 min



- **Stable sorbent capacity was achieved at a range of temperatures**
  - **At high temperatures after an initial drop performance stabilized**
- **CO production rate increased an order of magnitude increasing the temperature from 500 to 700°C**

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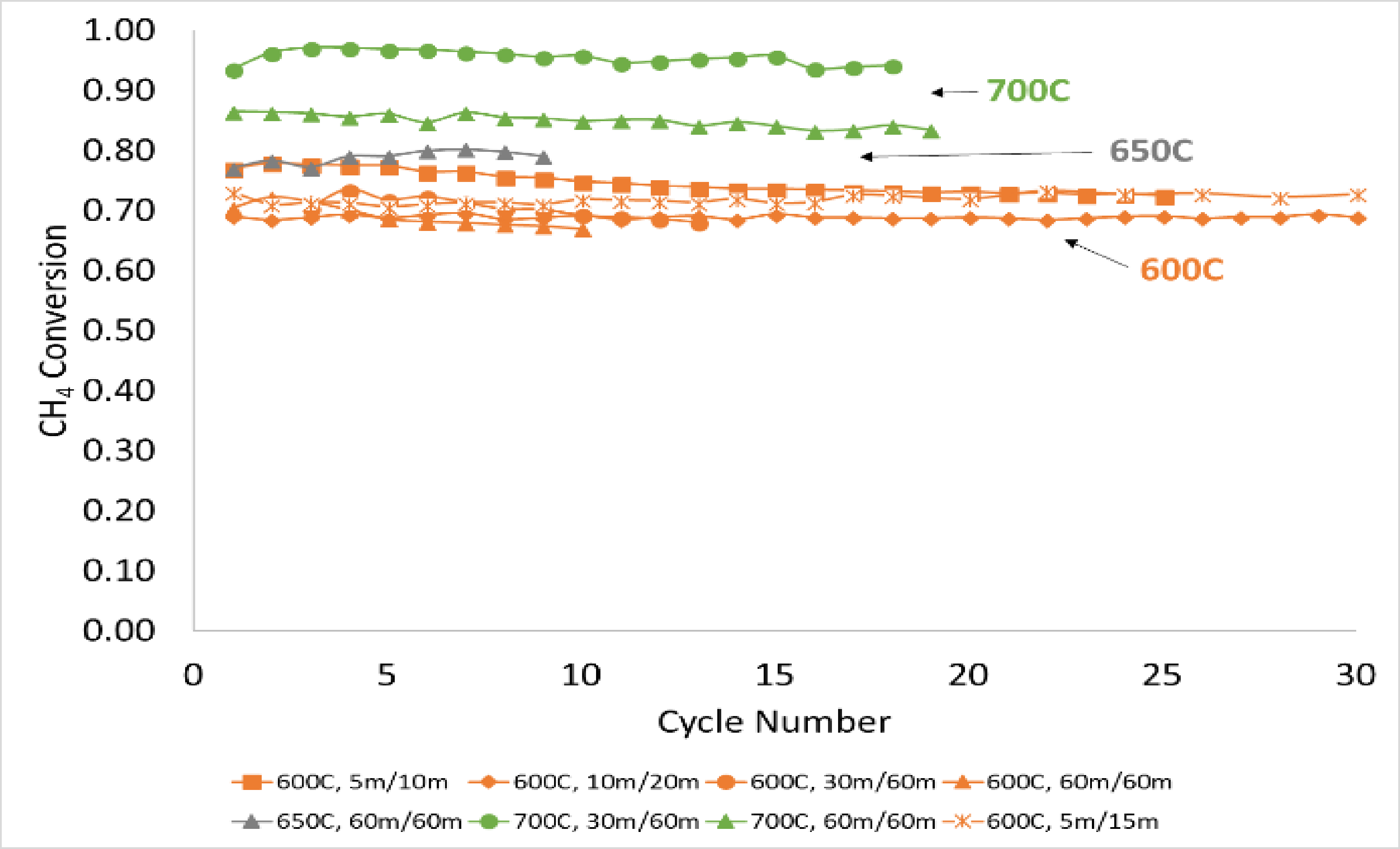
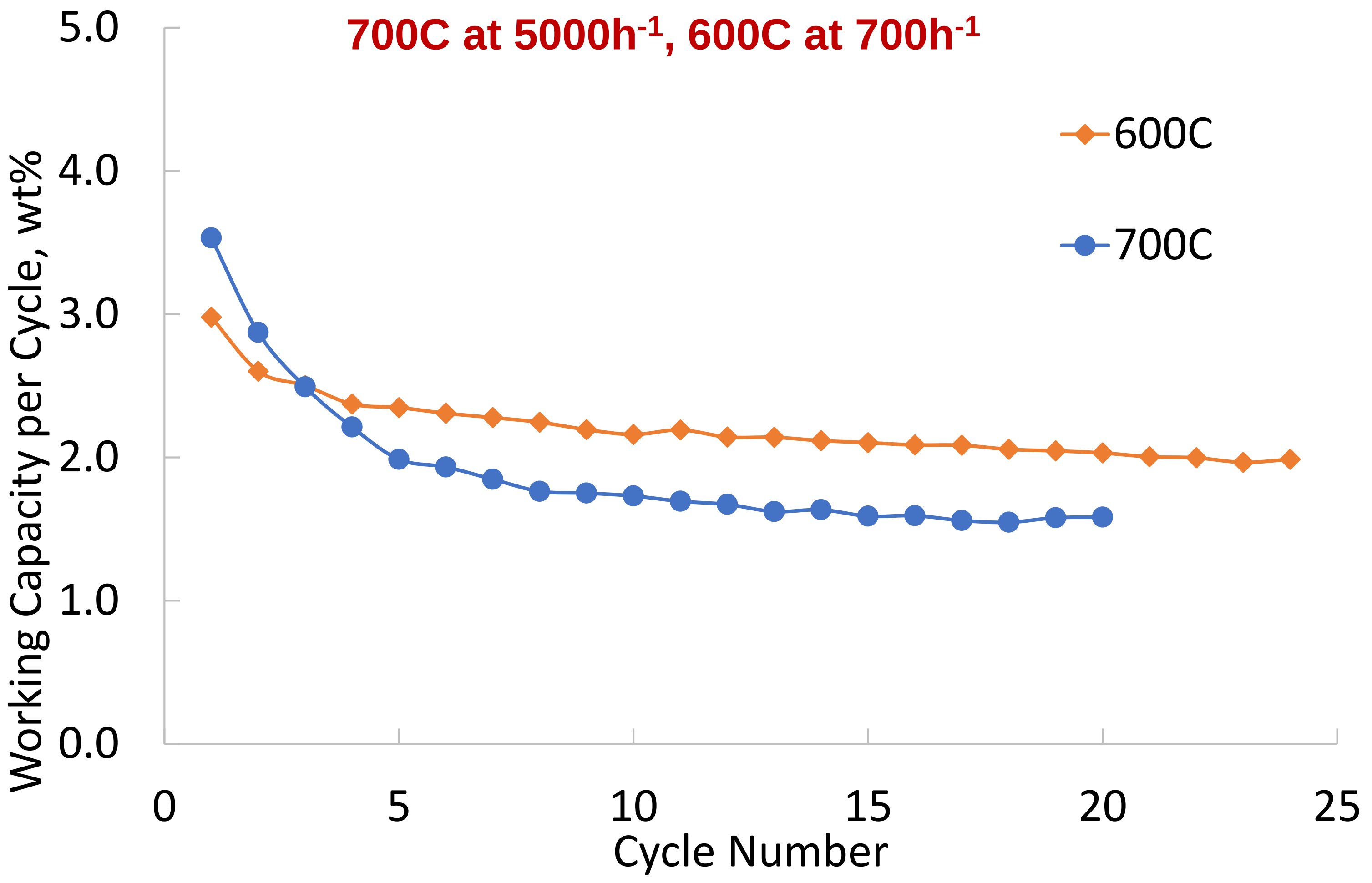
Reactor Results – CO_2/CH_4 Cycling



- **High CH_4 conversion was achieved at 600-700°C**

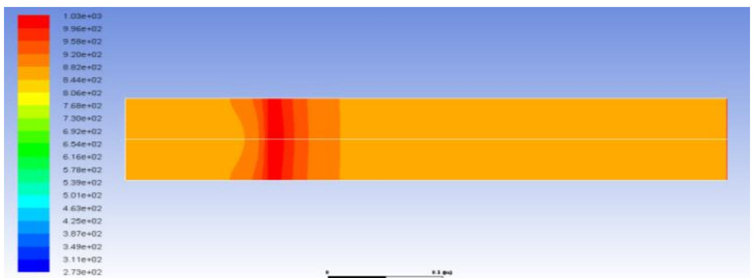
Working Capacity >2% wt. per cycle



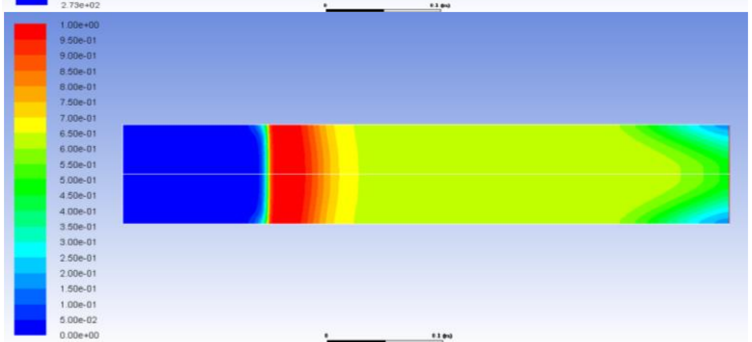
CFD Analysis

- **GTI is supporting a CFD analysis to identify the best configuration for the gas-solid contactor**
  - To provide information on the flow, concentration and temperature distributions in the reactors

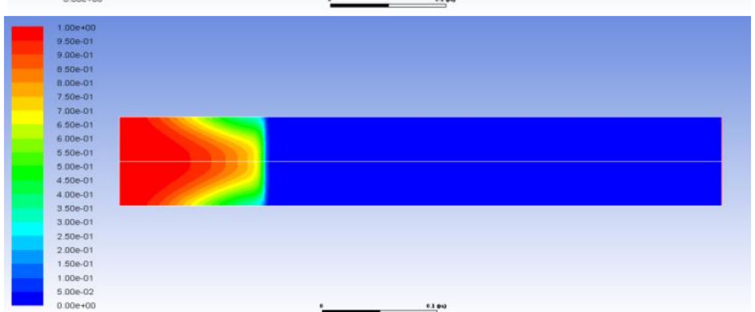
Flow Direction



Temperature

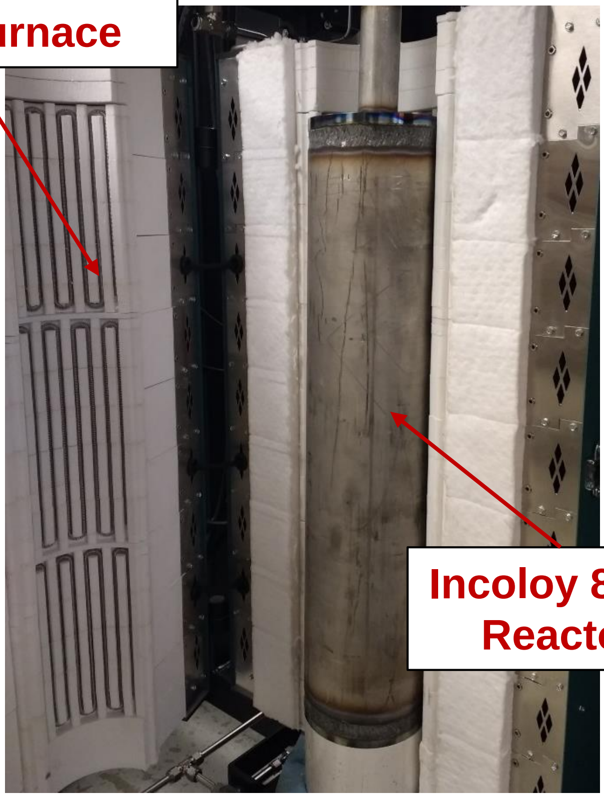


CO Mass Fraction



CO_2 Mass Fraction

Sorbent Life Testing



- **The most promising sorbent will be tested for a minimum of 10,000 cycles (1-10 kg/day)**

- **6” diameter 36” height vessels to house 12L (0.4 CF) sorbent**
  - Incoloy HT is chosen for the material with a design temperature of 805°C and pressure of 295 psig

Process Design and Simulations

- **In collaboration with UCI, we are working to configure and optimize the entire CO_2 utilization plant starting at a subsystem level**

- **We established the basis for process design and develop the Aspen Plus™ models that use TDA's CO_2 utilization system integrated with two chemical conversion processes**
  - To diesel fuel via Fisher-Tropsch synthesis
  - To gasoline via MTG process

- **Net process efficiency and the cost of fuel produced will be estimated**
  - **Material and Energy Balances**
  - **Cost Estimates**
    - Capacity Factored Estimates
    - Equipment Modeled Estimates
    - Vendor Supplied Estimates

- **Capital requirements, operating and maintenance costs will be developed in accordance with the DOE NETL's *Cost and Performance Metrics Used to Assess Carbon Utilization and Storage Technologies* document**

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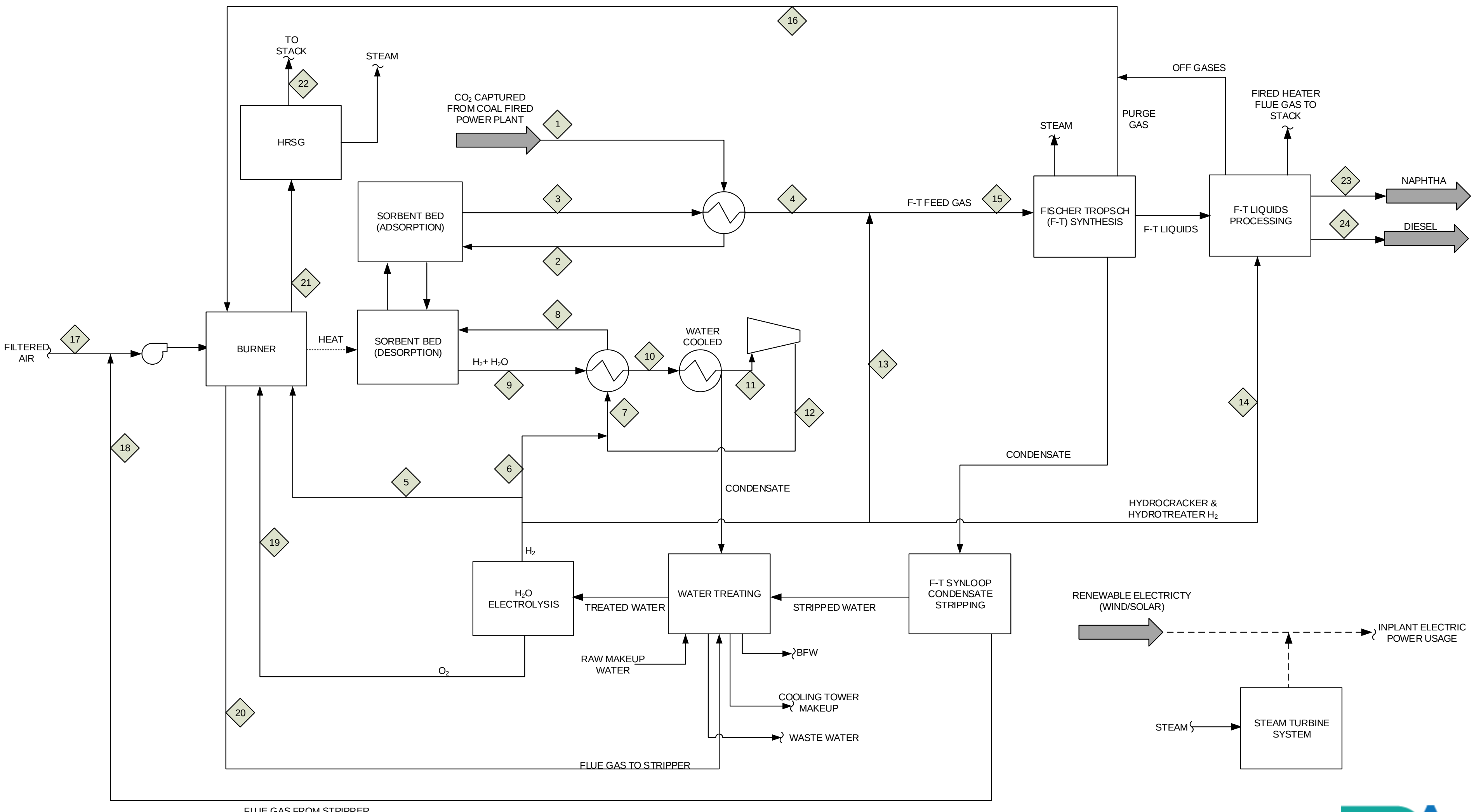
Case 2: H_2-Fischer Tropsch



Preliminary Simulation Results

	CASE		
	Case 1 H2-MeOH	Case 2 H2-FT	Case 2 NG-FT
CO2 Entering Plant, tonne/h	56	56	32
Steam Turbine Power, kWe	10,395	11,793	10,625
Net Electricity Imported, kWe	427,905	375,798	133,505
Product(s), tonne/h	37.54	13.97	13.97
Cost of Product(s), $/tonne	567	1,362	784
Cost of Product(s), $/gal	1.71	3.81	2.19

- **Methanol can be produced at $1.71/gal using H_2 reductant**
- **FT Liquids are produced at $3.81/gal or $2.19/gal based on the reductant source (H_2 or CH_4, respectively)**

Life Cycle Analysis (LCA)

- We will complete a detailed product life cycle analysis to validate that there is a net reduction in carbon footprint
  - To quantify any additional CO_2 or greenhouse gas (GHG) emissions while utilizing the CO_2 generated by the power plants
- The proposed technology's carbon foot print on a percent reduction basis will be compared to that of the state-of-the-art conversion technologies

Acknowledgements

- DOE/NETL funding provided the DE-FE0029866 project is greatly acknowledged
- Project Manager, Steve Mascaro

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