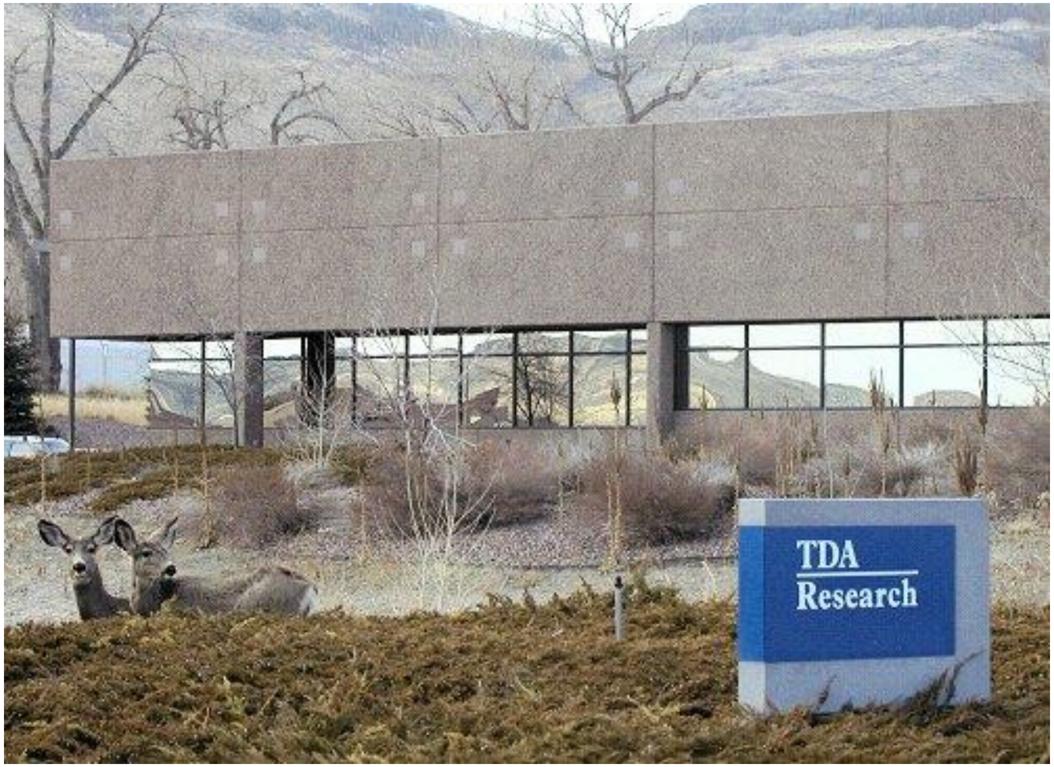
A New Process for Carbon Dioxide Conversion to Fuel (DE-FE0029866)



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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

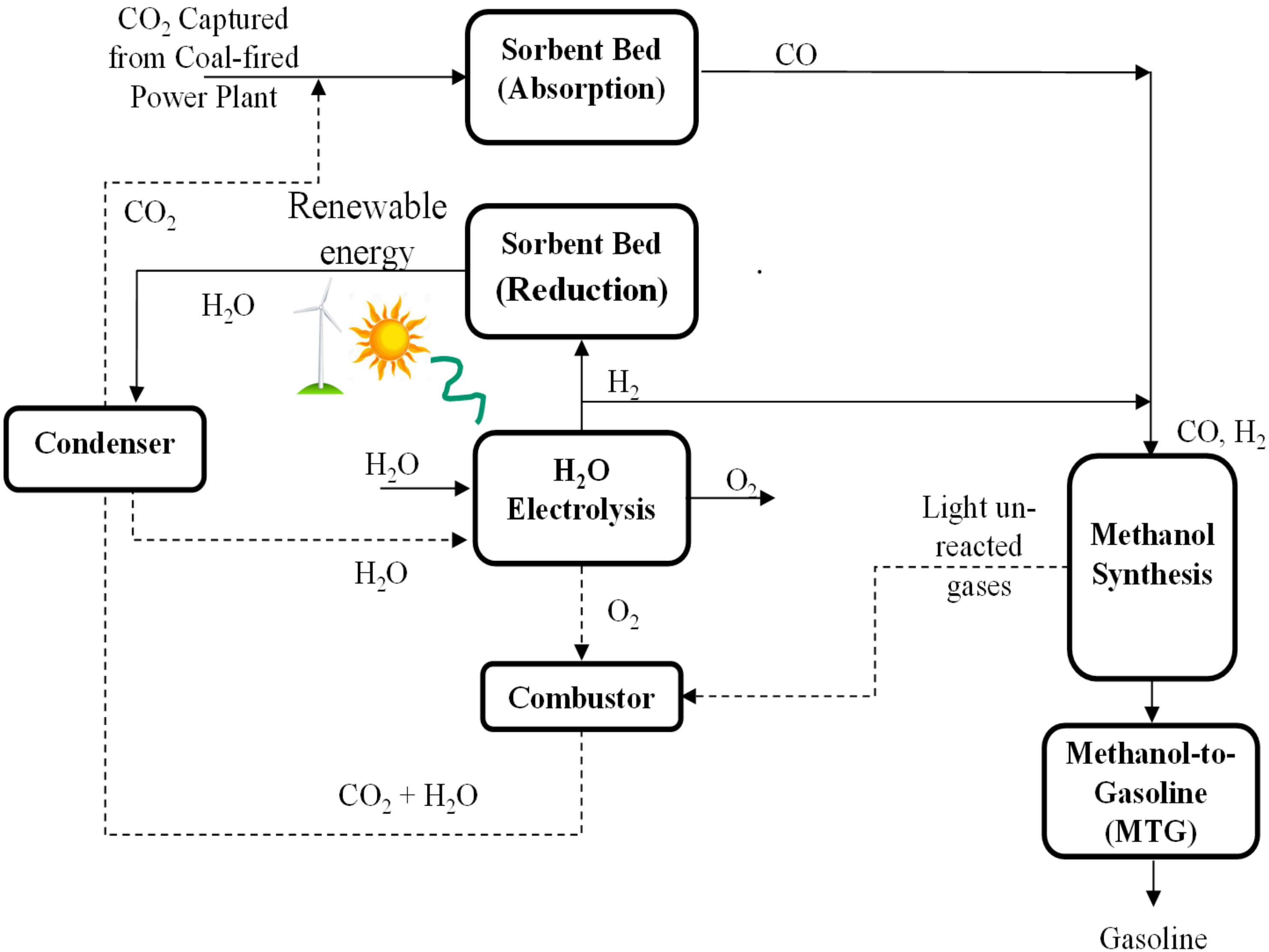
Project Duration

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

Budget

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

Overall Process Schematic



Preliminary Cost Estimate

- **In a process that emits less than 1% of the CO_2 utilized may deliver gasoline fuel at $3.25/gallon**
  - Based on energy costs only
  - Capital cost burden is not included
- **A potential commercial application will be using 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 DOE target to emit less than 1% of the CO_2 utilized cannot be achieved

Estimated energy consumption for CO_2 to methanol 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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TDA's Sorbent

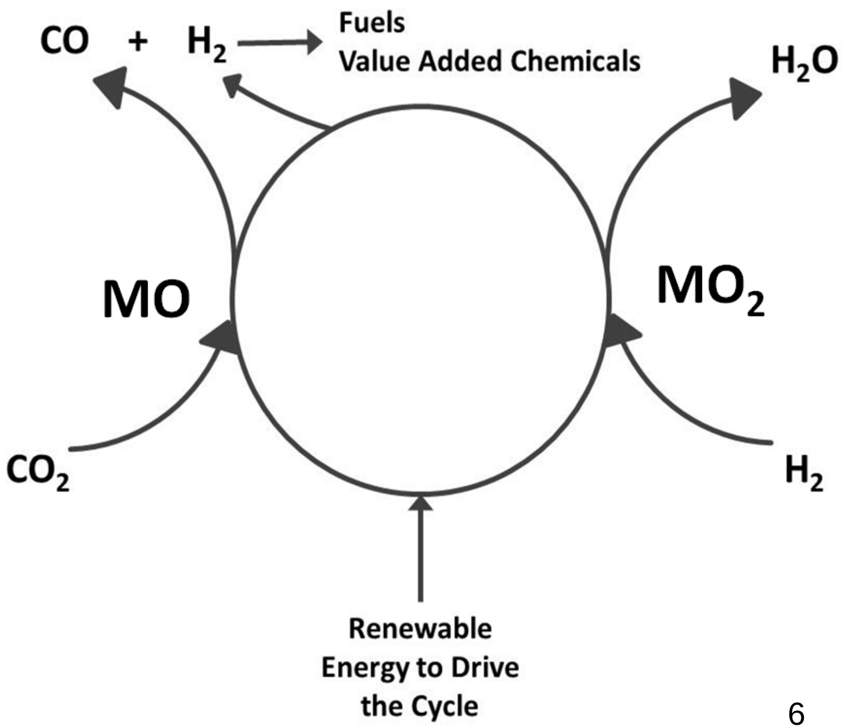
- Our process uses a unique mixed metal oxide phase to reduce CO_2 A low oxidation state metal oxide phase directly reacts with CO_2, stripping off the oxygen to form CO and a higher oxidation state metal oxide forms
- In a subsequent step the sorbent material is contacted with H_2 to reduce it to complete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

CO_2 Reduction Step

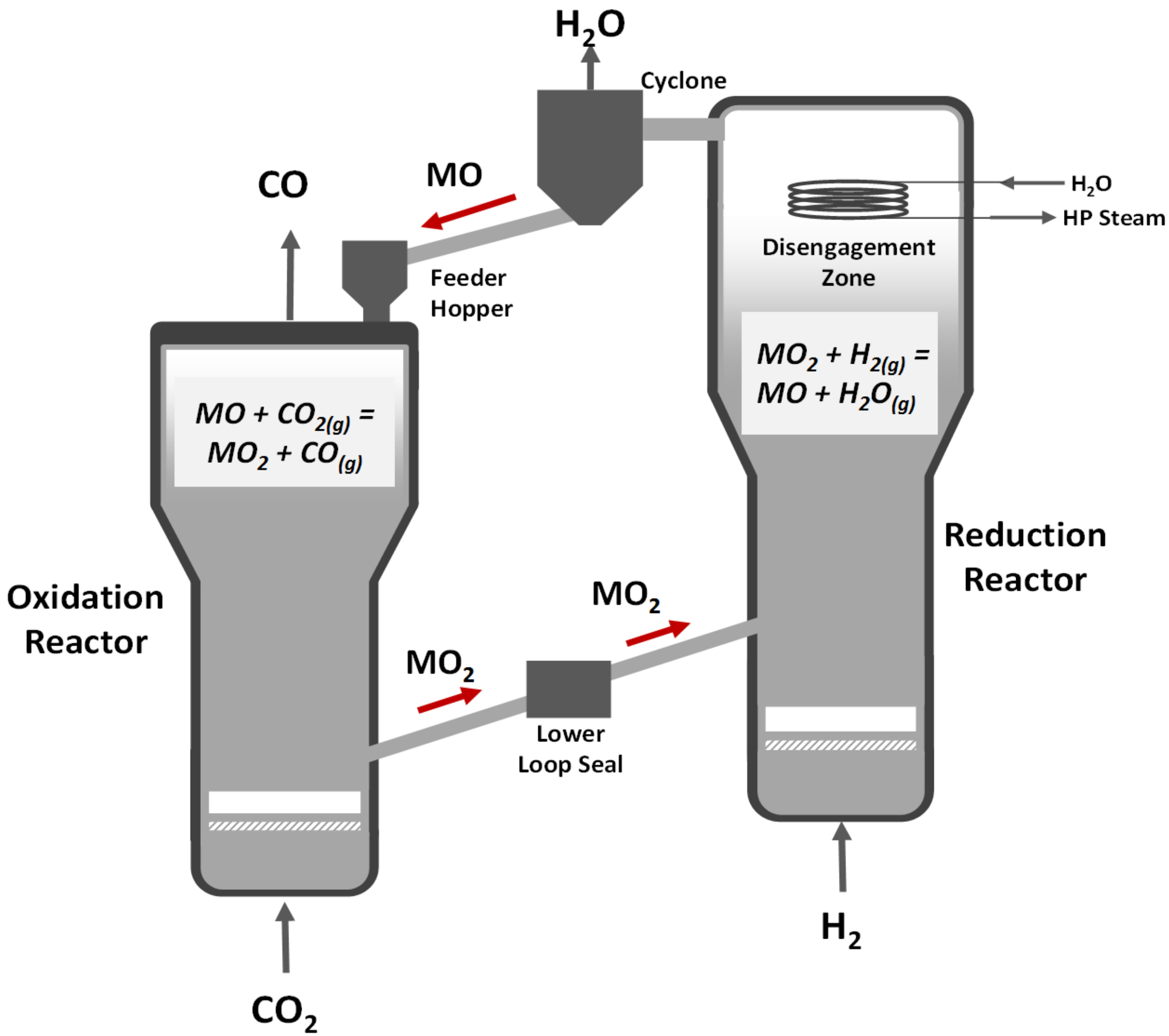
$$MO + CO_{2(g)} = MO_2 + CO_{(g)}$$

Sorbent Reduction Step

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



Sorbent Contactors



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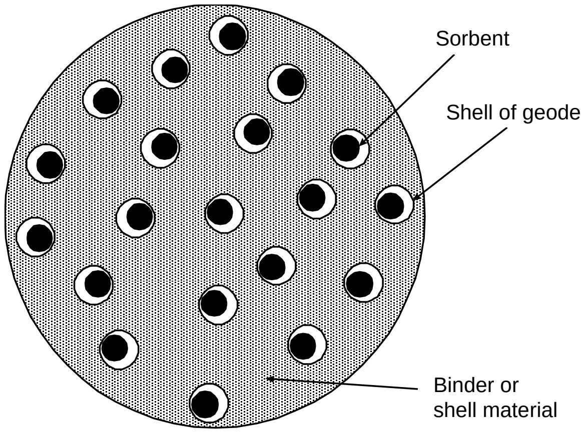
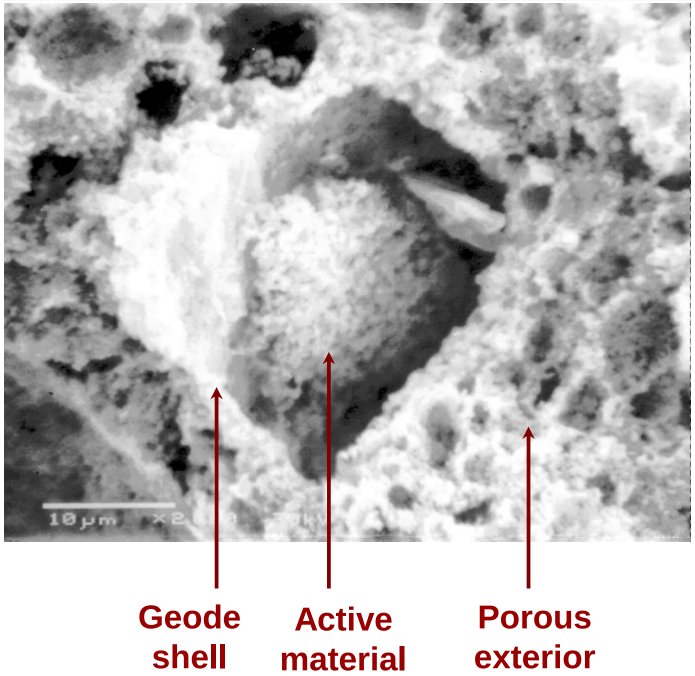
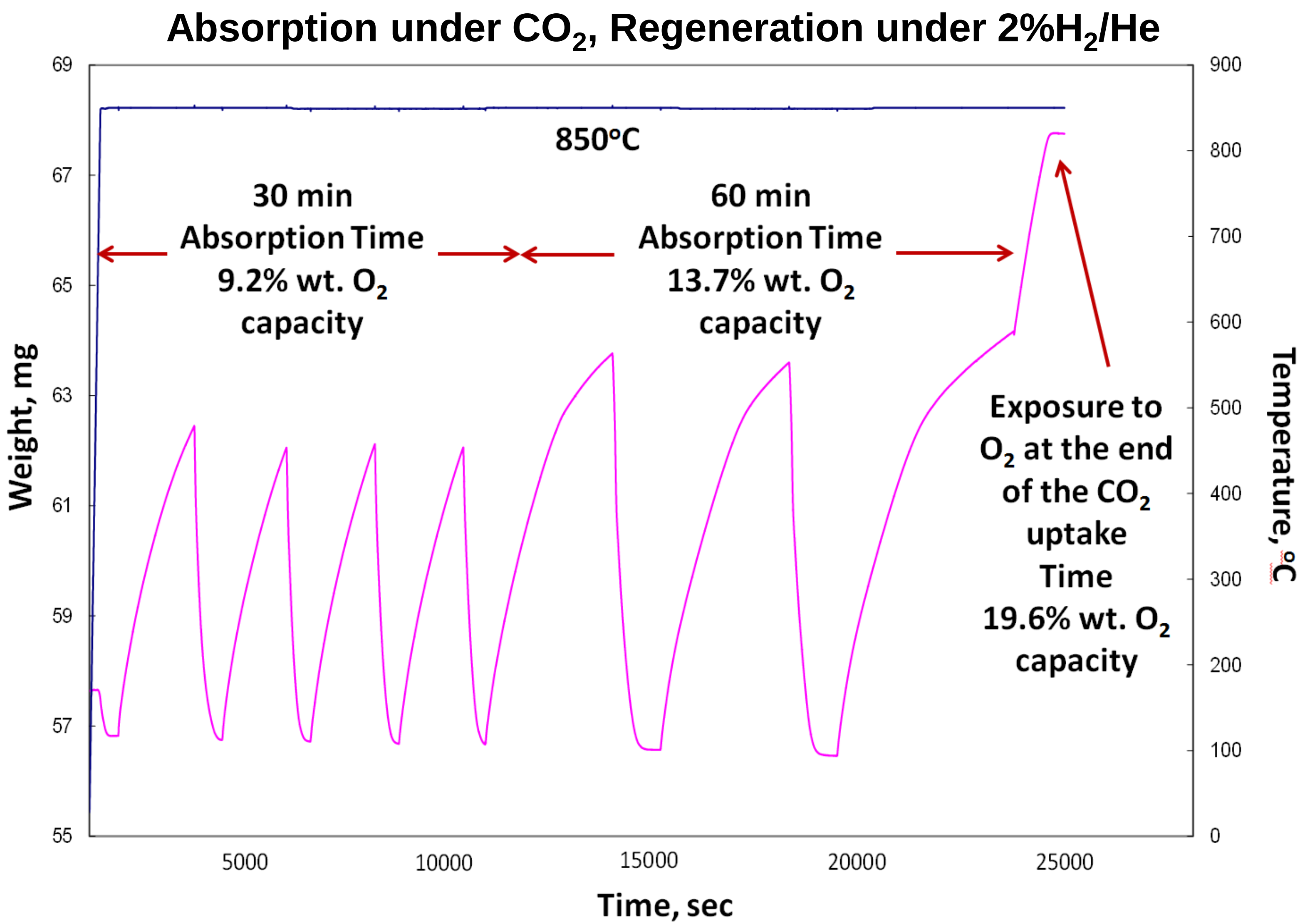
TDA's Sorbent





- **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

TGA Tests



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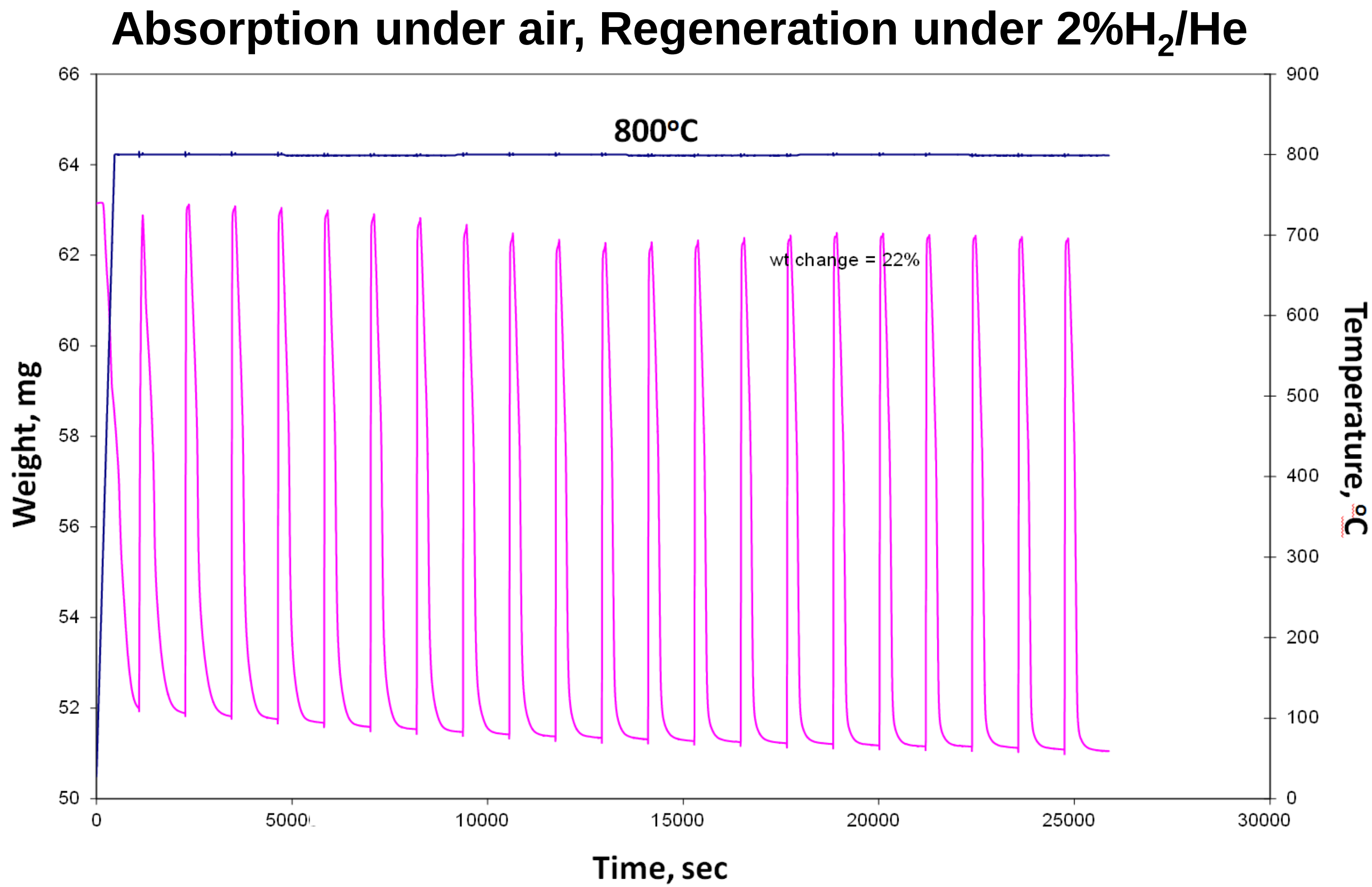
Multiple Cycles at TGA



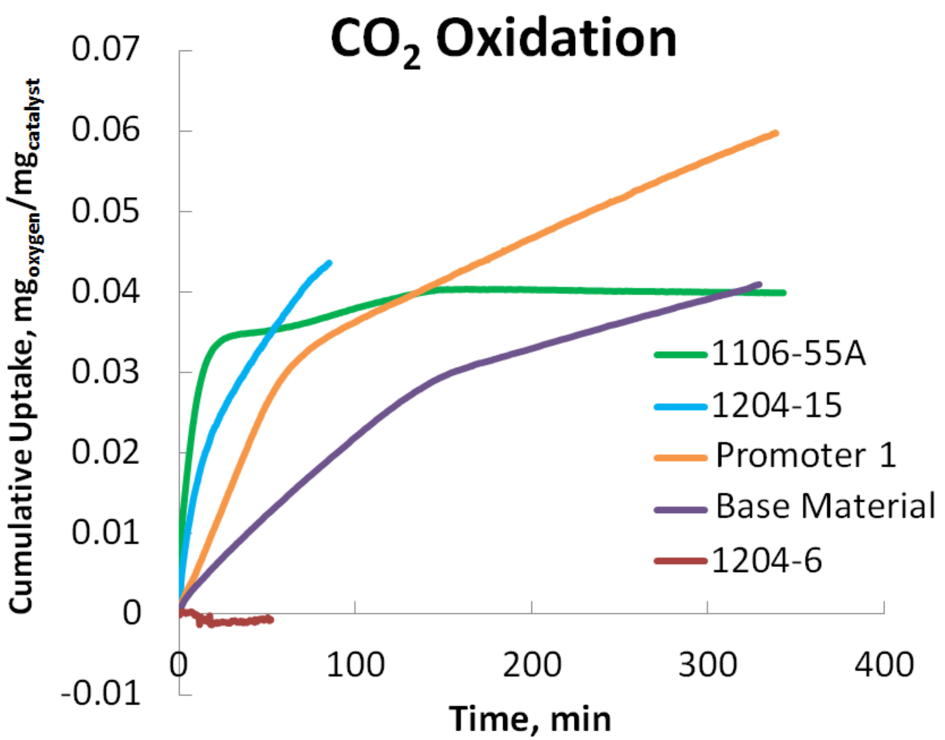
- **Stable oxygen uptake for 20 cycles (following 150 cycle parametric tests) suggests long-term chemical stability**
  - 22% wt. O_2 uptake (air is used as the oxidizer to expedite cycling time)

Sorbent Modifications

Various promoters are being explored to impact:

- CO_2 oxidation capacity and uptake rate
- H_2 reduction rate
- CO_2 Oxidation and H_2 reduction onset temperature

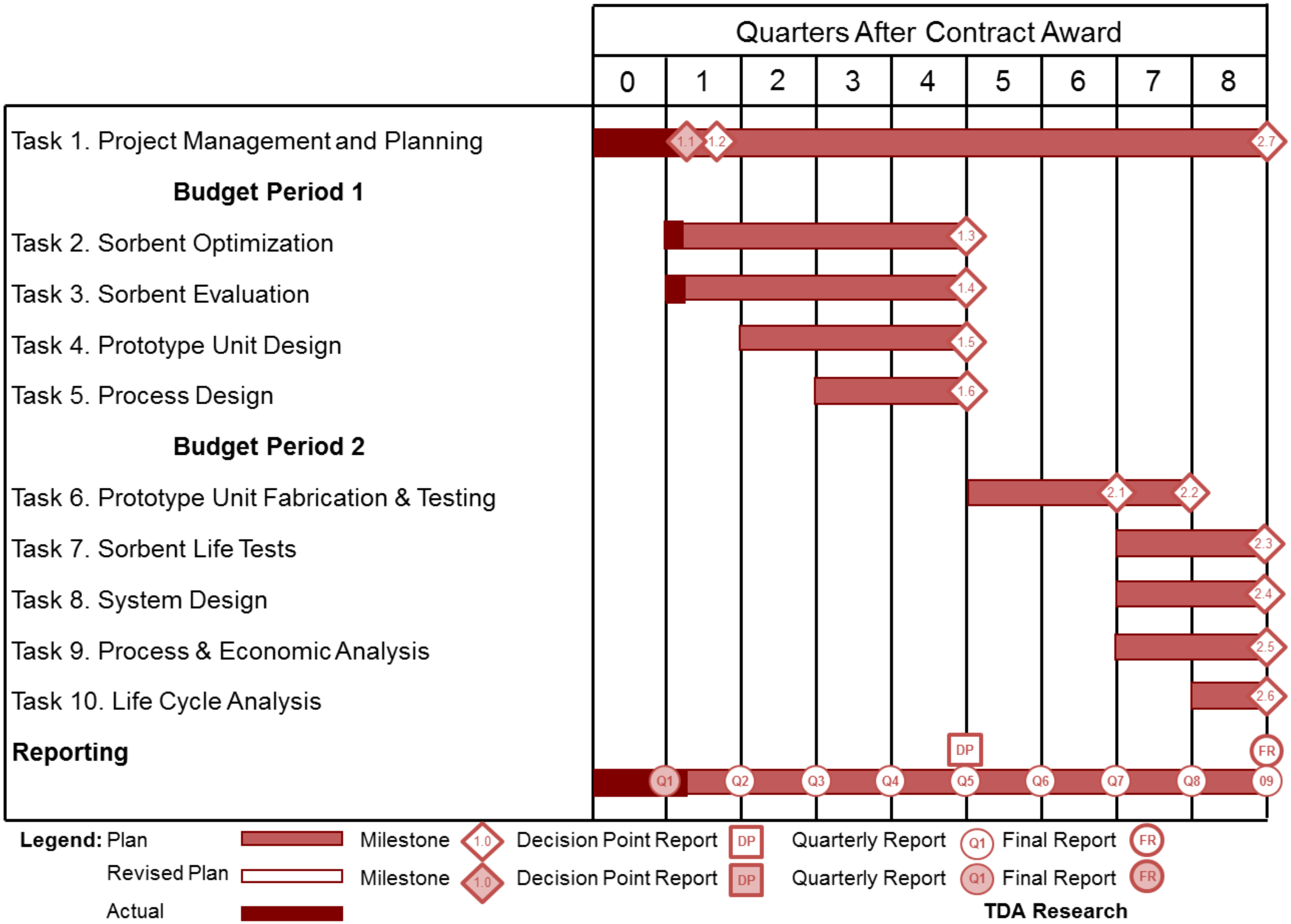
Reduction: Ramp temp. to 800°C in 2% H_2/Balance N_2
Oxidation: 100% CO_2 for up to 360 minutes



H_2 Reduction

Sample No.	Onset T, ºC	Weight %
1106-55A	299	-17.05
1204-15	368	-16.07
Promoter 1	543	-9.26
Base material	635	-10.45
1204-6	290	-3.53

Project Schedule



Sorbent Optimization

- We will explore various preparation approaches to improve the conversion of CO_2 into CO
  - Evaluate the use of different promoter phases to improve the solid diffusion rates
  - Increase in the oxygen uptake and the rate of reduction
  - Decrease the onset temperatures for these process
- Ensure very high mechanical integrity of the sorbents
  - We will evaluate various binder materials to increase crush strength and attrition resistance
  - Maintaining porosity for fast absorption/regeneration rates
- Rapid screening of materials will be carried out in thermo-gravimetric analyzer (TGA)

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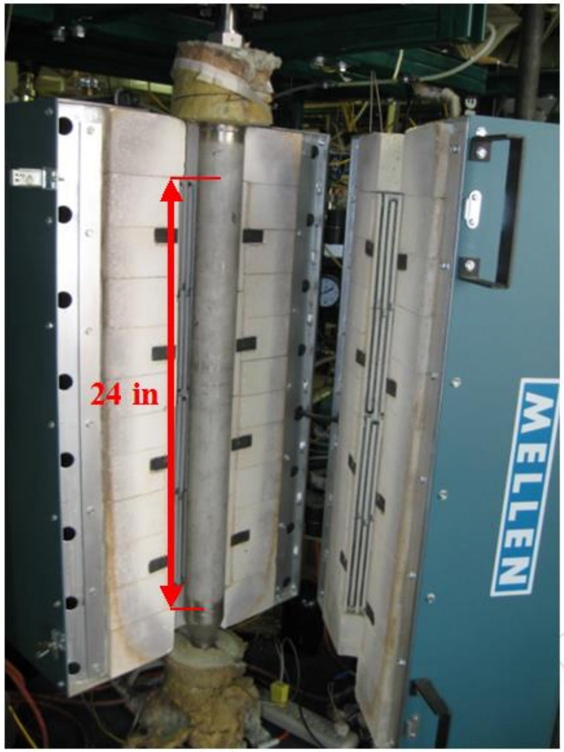
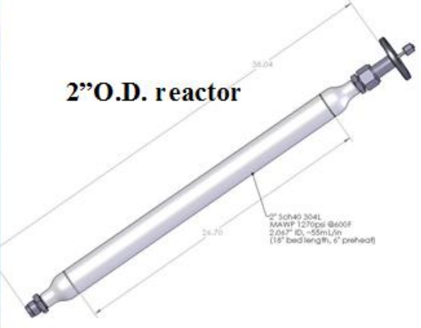
Sorbent Evaluation

- **Sorbent samples that meet our physical properties and chemical activity requirements will be evaluated in a micro-reactor**
- **We will compare 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



Sorbent Life Testing

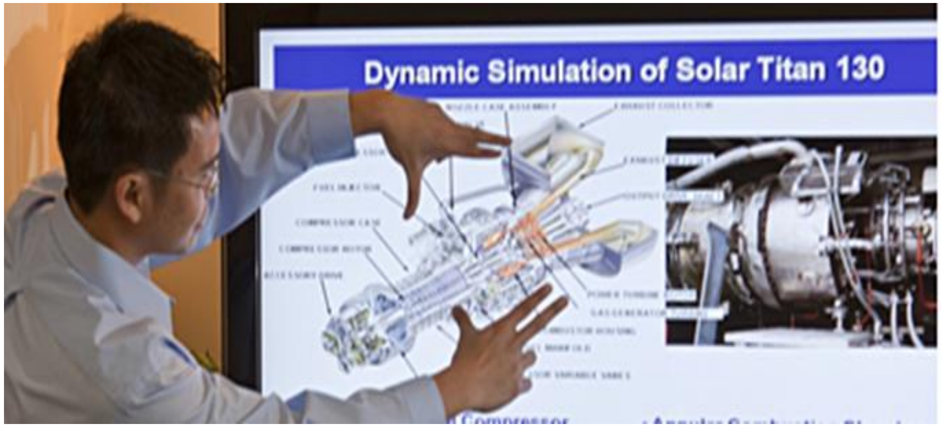
- The most promising sorbent samples will be evaluated for multiple cycles to determine chemical and mechanical stability

- A minimum of 10,000 cycles will be completed to assess sorbent stability

- The most suitable test equipment will be selected based on the final process equipment design (fixed-bed, fluidized bed, circulating bed etc.)

Design of the Gas-solid Contactors

- **We will carry out a detailed design of the sorbent reactors using computer simulation and modelling**
- **In collaboration with GTI, a CFD analysis will be completed to identify the best configuration for the gas-solid contactor**
  - To provide information on the flow, concentration and temperature distributions in the reactors



- **This will provide a complete prototype unit design and preliminary design of the full-scale system**
  - Engineering drawings and 3D layouts

Design and Fabrication of a Proof-of-Concept Test Unit

- **A proof-of-concept test unit will be designed will be fabricated and used to carry out evaluations**
- **We will first complete experiments in a cold-flow visualization system**
  - **A transparent plastic version of the desired size reactors to monitor distribution of sorbent particles within the reactor**
- **We will fabricate the apparatus to carry out proof-of-concept tests**
- **We will carry out shakedown and troubleshooting of the prototype test unit**
- **We will then tests system for CO_2 conversion to CO through multiple absorption/ reduction conditions**
- **The prototype unit will be operated for at least 500 hours of operation under simulated conditions**

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Process Design and Simulations

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

- **We will establish the basis for process design and develop the Aspen Plus^{TM} 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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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**