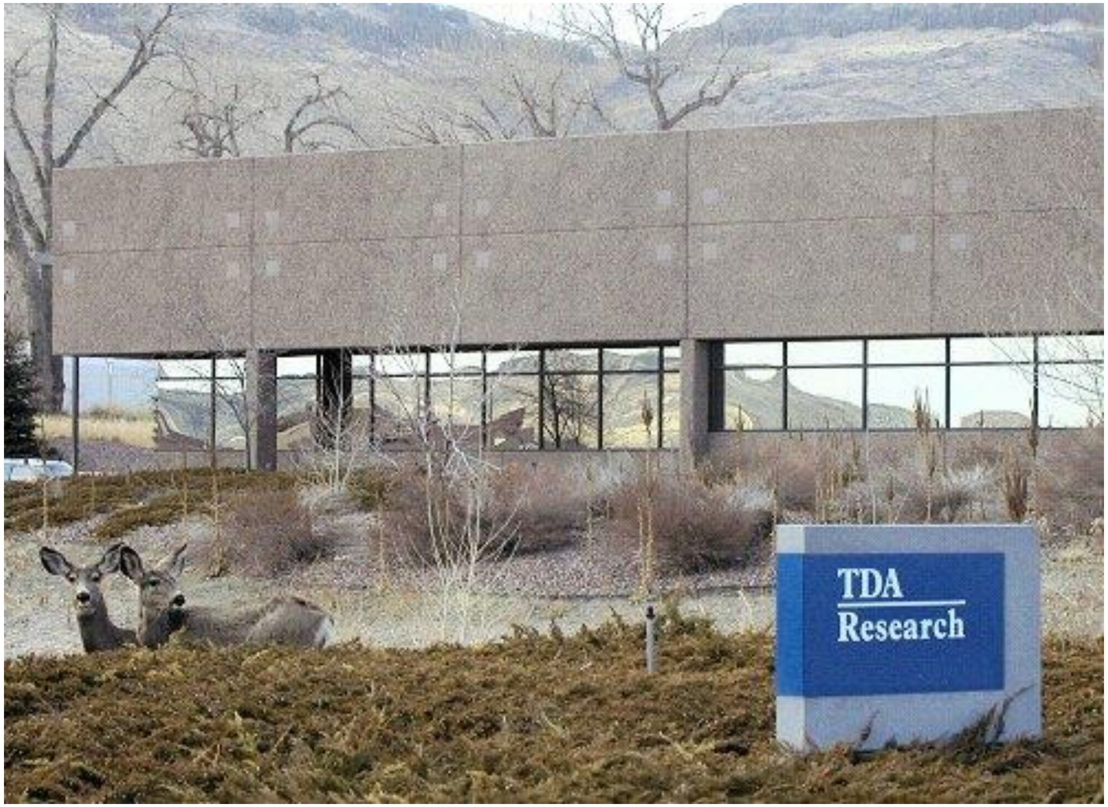
A High Efficiency, Modular Pre-combustion Capture System for CoalFIRST Poly-generation Process (Contract No. DE-FE0031926)



Gökhan Alptekin
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2021 Carbon Management and Oil and Gas Research Project Review Meeting

Point Source Capture — Lab, Bench, and Pilot-Scale Research

August 13, 2021

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

Project Objectives

- **Demonstrate techno-economic viability of a modular coal-to-energy-and-chemicals process with a focus on syngas treatment and processing**
  - A high temperature PSA adsorbent/WGS process is used for CO_2 removal above the dew point of the synthesis gas
  - A fixed-bed TSA based sulfur removal system will be used to remove H_2S
  - A catalytic CO_2 purification process
- **Main Project Tasks**
  - Design a fully-equipped slipstream test unit with 10 SCFM raw synthesis gas treatment capacity
  - Demonstrate the operation of the integrated system with high CO_2 removal efficiency and contaminant removal using coal synthesis gas
  - Detailed design of the integrated WGS/pre-combustion capture system
  - Complete a high fidelity process design and economic analysis

<u>Project Duration</u>

Start Date = October 1, 2020

End Date = September 30, 2023

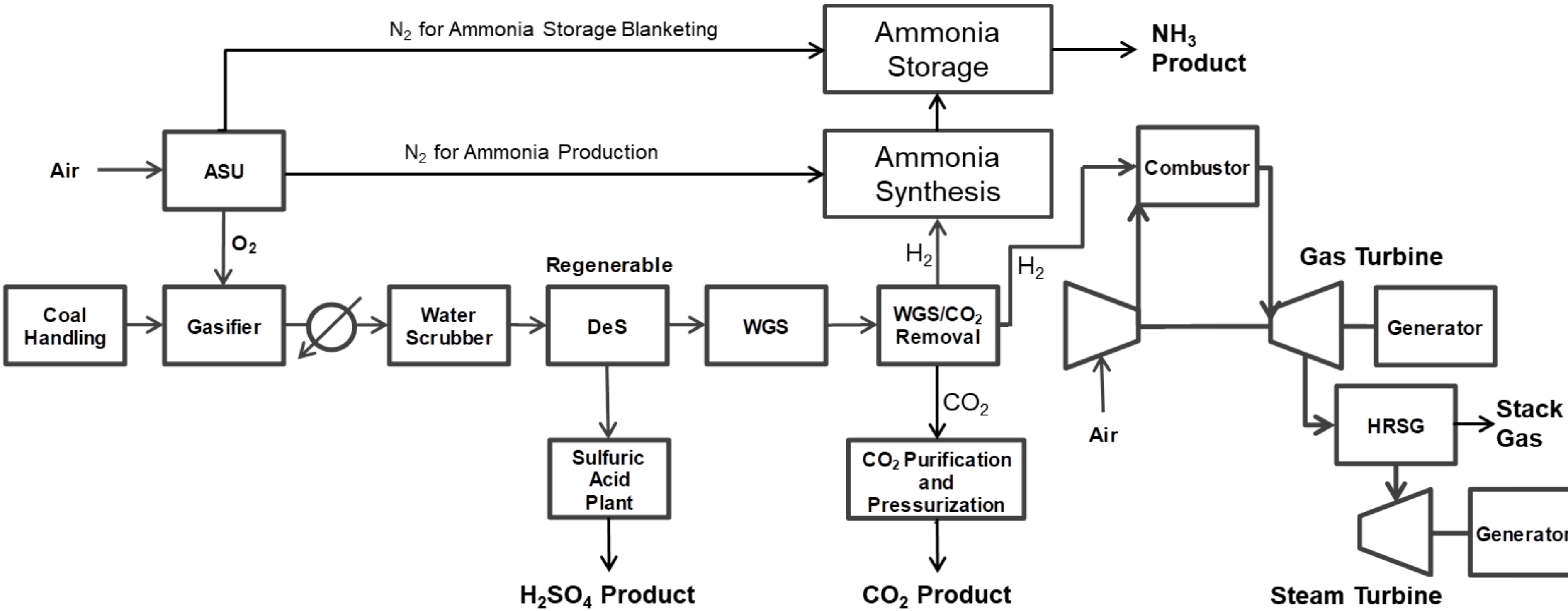
<u>Project Funding</u>

Total Budget = $3,750,000

Federal Share = $3,000,000

Cost Share = 750,000

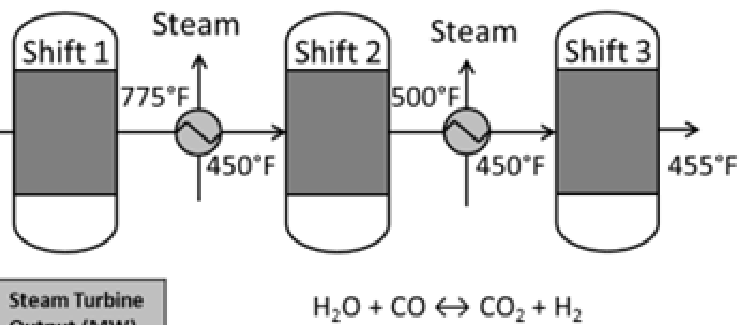
IGCC with Integrated Ammonia Storage



- **Warm gas removal of CO_2, sulfur and contaminants improves efficiency**
- **Reducing the use of excess steam improves power cycle efficiency**
  - Lower energy consumption to raise the steam
- **Process intensification could potentially reduce the number of hardware components and cost**

TDA's Approach – Carbon Capture

- **In conventional coal-to-hydrogen or coal-to-power applications, a multi-stage WGS process with inter-stage cooling is used**
  - WGS is an equilibrium-limited exothermic reaction
- **Water is supplied at concentrations well above required by the reaction stoichiometry to completely shift the CO to CO_2**
- **Excess water is also used to suppress carbon formation**



H2O/CO Ratio[1]	
GE	1.3
E-Gas	0.4
Shell	1.5

[1]Prior to shift steam addition

	Relative HP Steam Flow	Steam Turbine Output (MW)
GE	1.0	275
E-Gas	2.4	230
Shell	0.9	230

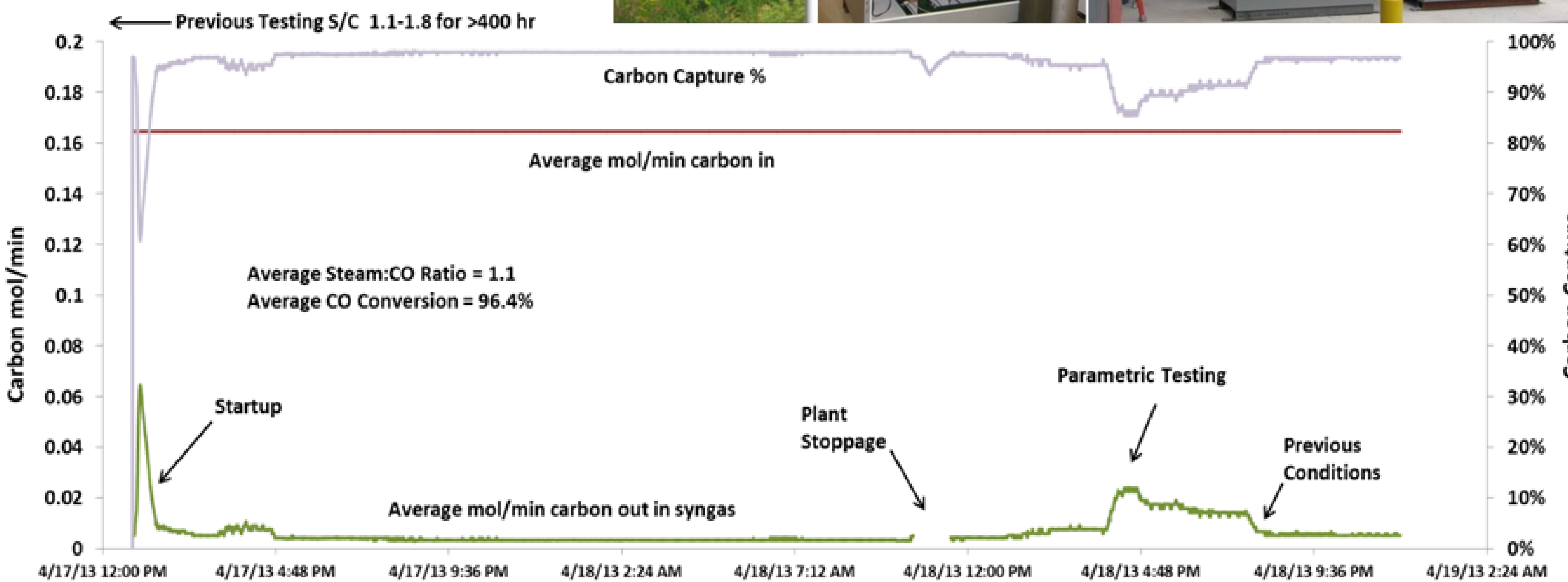
3-stage WGS unit as described in the DOE/NETL-2007/1281

- **In our process, the WGS catalyst is combined with a high temperature CO_2 adsorbent to achieve high CO conversion *__at low steam:carbon ratios__***
- **Reduced water addition increases process efficiency**

Background on Integrated WGS/CO_2 Capture

TDA's CO_2 sorbent integrated with a LT WGS catalyst in the same bed



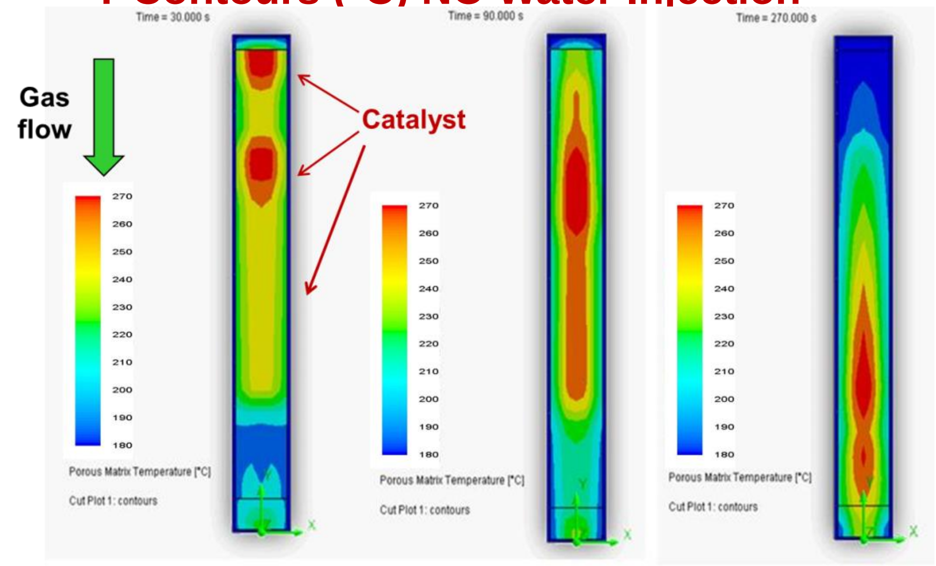


- 90+% capture at steam:CO ratio= 1:1.1 with average 96.4% CO conversion
- All objectives met (no coking etc.) but high reactor T was observed

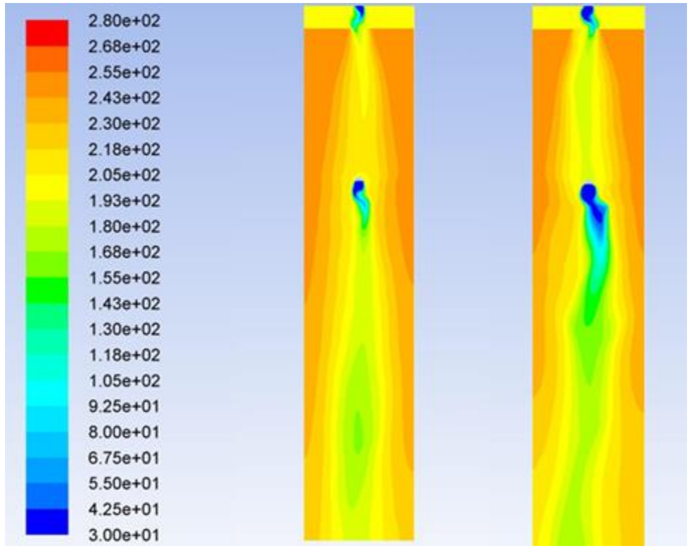
Heat Integrated WGS & CO_2 Capture

- Integrated WGS & CO_2 capture results in higher ΔT , not ideal for CO_2 capture (the WGS heat accumulates in the beds)
- Advanced heat management based on direct water injection has proven to achieve much better temperature control
- Objective is to achieve a more uniform cooling without having hot or cold spots
- The temperature rise is optimal when the catalyst is distributed into two layers with water injections before each layer

T Contours (°C) NO Water Injection



T Contours (°C) Multiple Injection Layers



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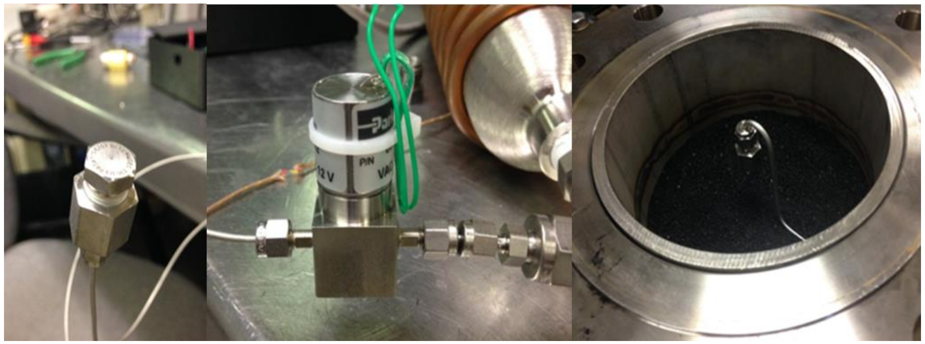
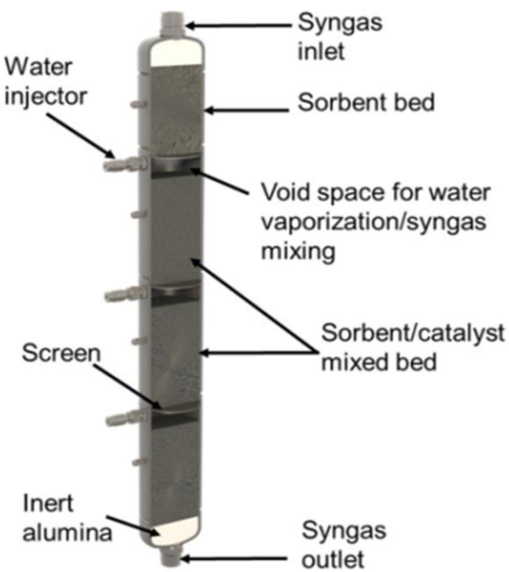
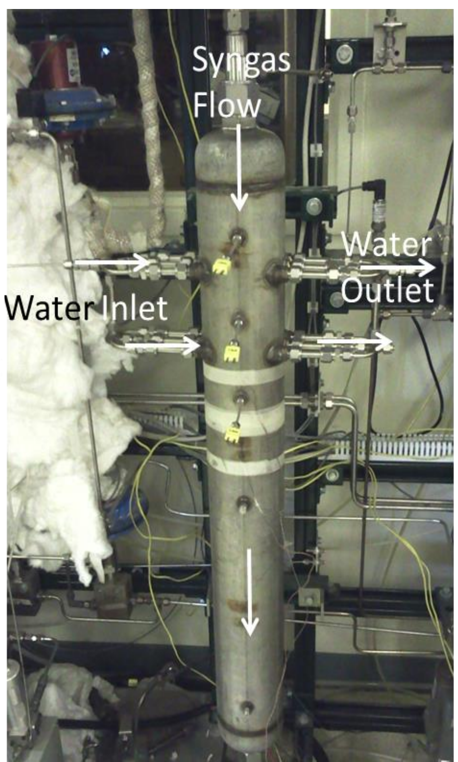
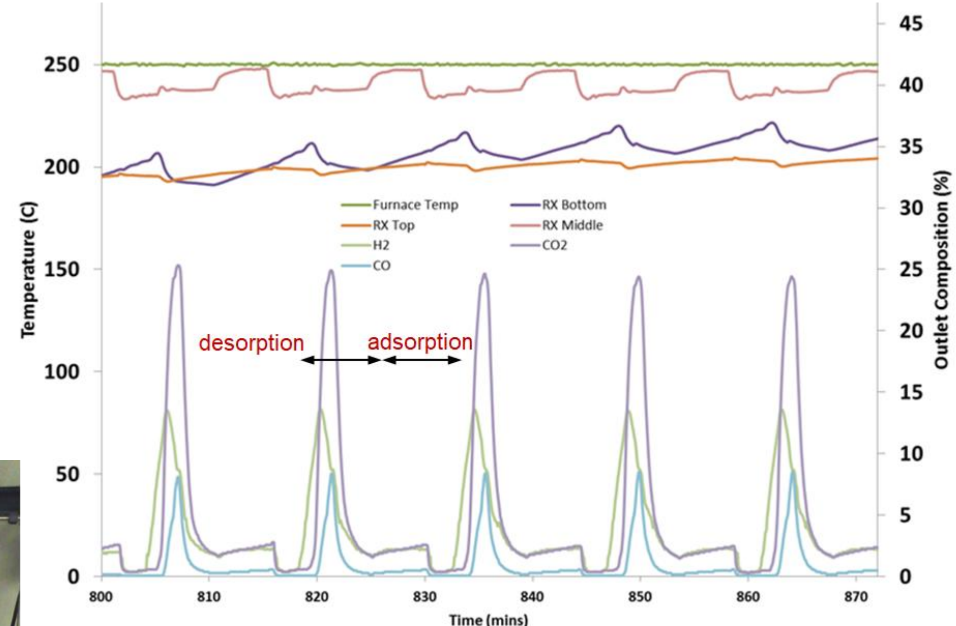
Bench-Scale Evaluations





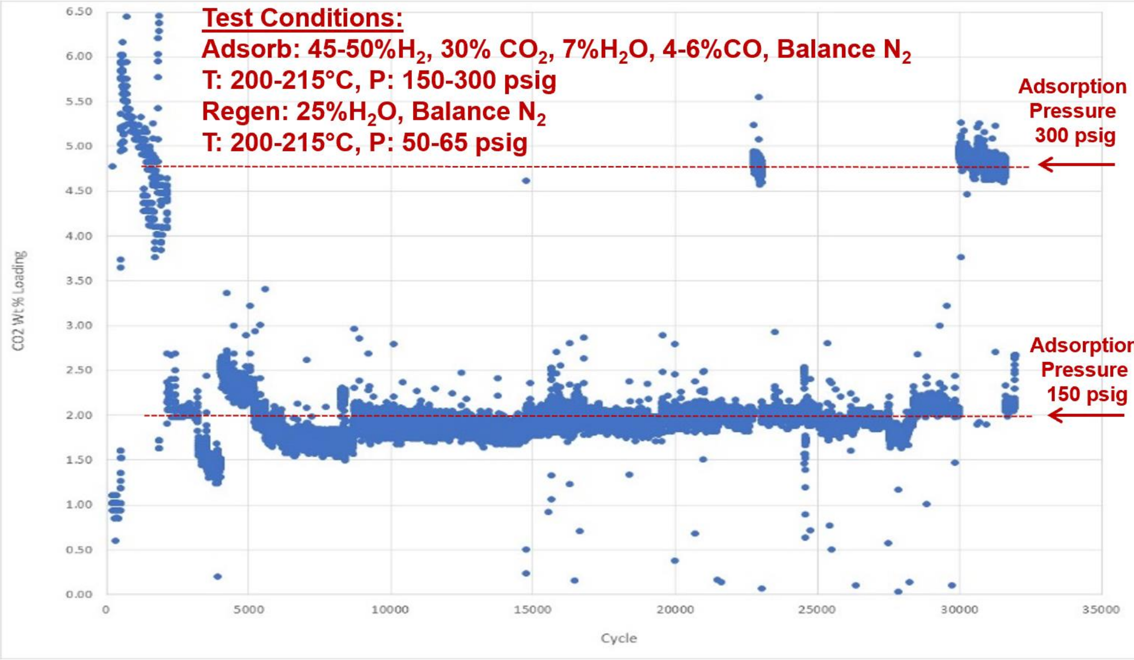


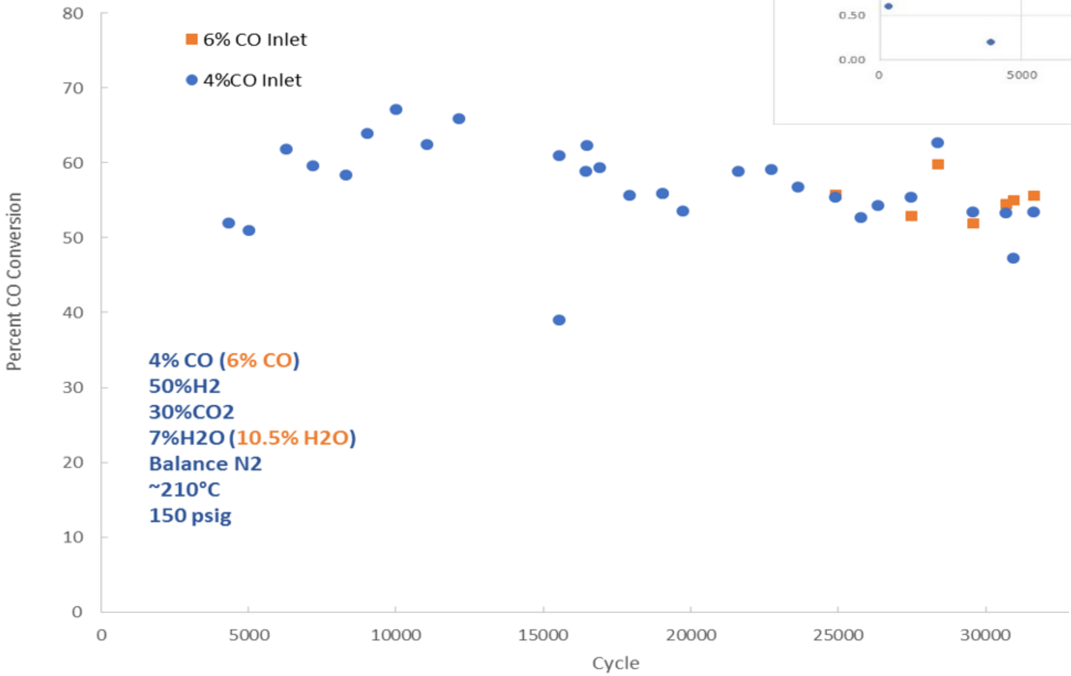


- **Successful proof-of-concept demonstrations have been completed at bench-scale**
- **ΔT <10°C was maintained over extended cycling (much lower than those in early field tests)**

Life Tests

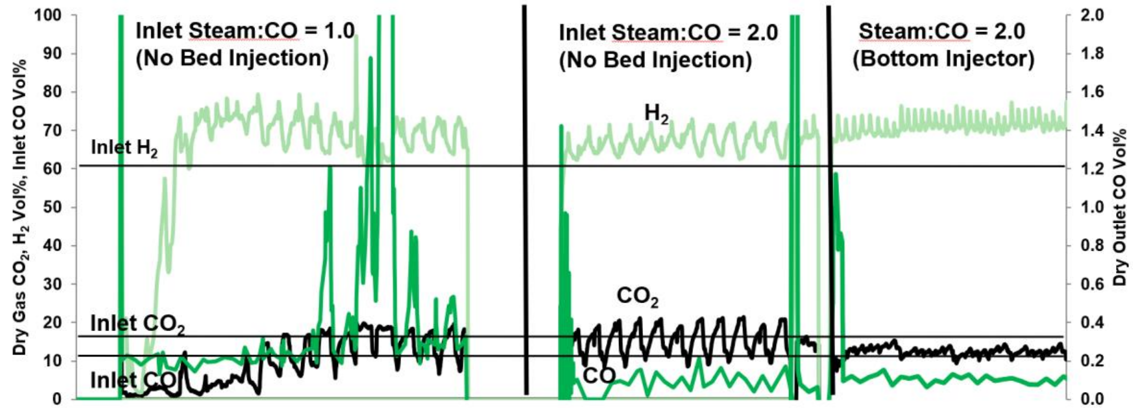
- **We completed 32,000 cycles showing stable performance for the WGS catalyst and CO_2 sorbent**

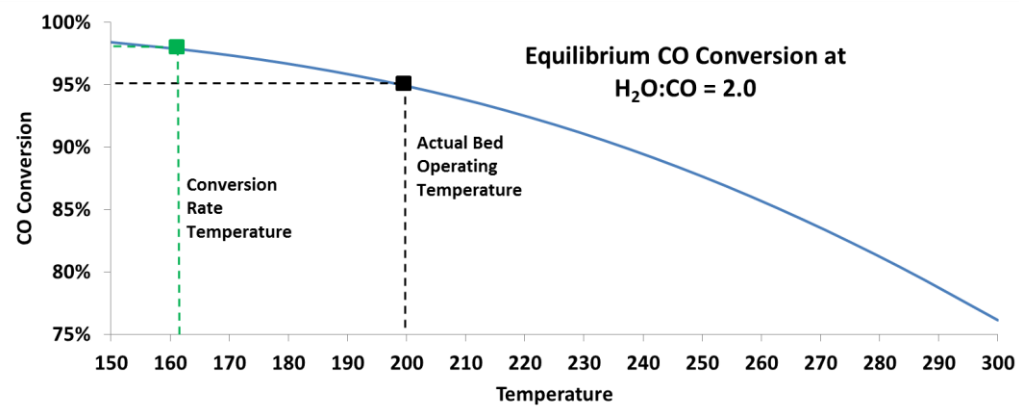




- **By evaluating catalytic activity alone we showed that cycling between reducing and oxidizing conditions (i.e., steam exposure) had no adverse effect on the WGS catalyst**

Integrated WGS/CO_2 Capture System





- **Two campaigns were completed in 2019-2020 at Praxair R&D Center (Tonawanda, NY) integrated with an OTM running on natural gas**
  - By coupling the WGS with the CO_2 sorbent and water injection, we were able to operate the beds at 200^{o}C but achieve the equilibrium CO conversion of a 40^{o}C cooler bed

Technology Status/R&D Needs

- **Evaluation in a high fidelity prototype to fully demonstrate the concept using actual coal-derived synthesis gas**
  - A 10 kg/hr CO_2 removal is being developed

- **Modular/scalable sub-systems**
- **Warm Gas Sulfur Removal**
  - Need to demonstrate operation in a simple fixed bed regenerable process
- **CO_2 Purification Needs**
  - CO and O_2 levels in CO_2 used for EOR are very stringent
  - Requires additional purification steps/processes

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Current Project Objectives

Elevate from TRL 4+ to TRL 5

Budget Period 1 (BP1: 10/1/2020 – 9/30/2021) – in progress

- Design modifications to integrated slipstream test unit: regenerable sulfur and CO_2 purification subsystems
- Commercially produce CO_2 and sulfur sorbents
- Complete initial techno-economic analysis of the CoalFIRST Poly-generation process integrated with warm gas cleanup

Budget Period 2 (BP2: 10/1/2021 – 9/30/2022)

- Fabricate regenerable sulfur removal and the CO_2 purification subsystems
- Integrate them to the 10 cfm 8-bed integrated WGS/carbon capture unit
- Long term testing of the desulfurization sorbent (300 cycles)

Budget Period 3 (BP3: 10/1/2022 – 9/30/2023)

- Carry out a 3 week field test at GTI at their pilot gasification facility
- Complete the process development and the full scale system design
- Complete an economic evaluation to accurately estimate: Overall process efficiency, CO_2 removal cost and the RSP of NH_3

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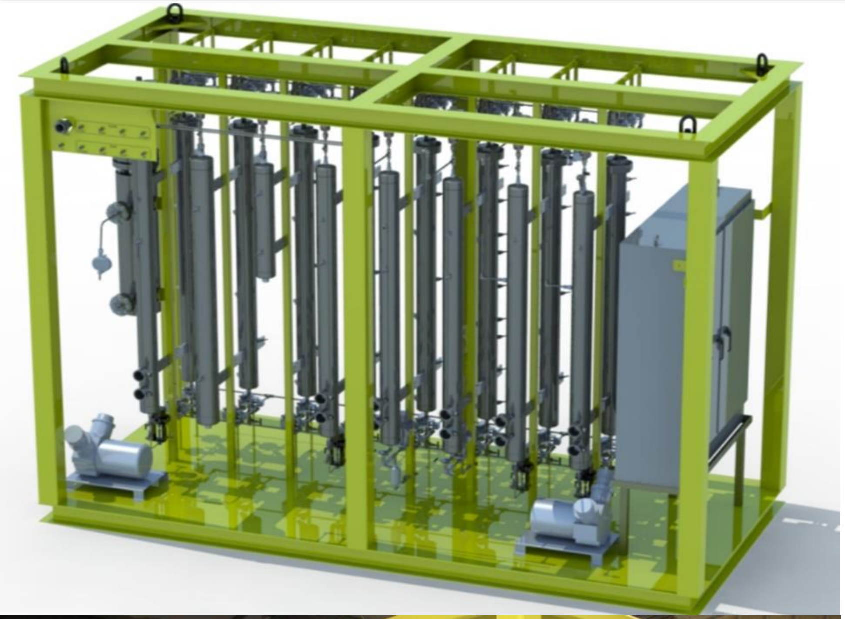
Test Site for Carbon Capture Testing

- **Design data are shared with our testing partner GTI**
- **We will have a full HAZOP for the test unit completed in December 2021**

Operation Conditions	U-GAS®	R-GAS™
Nominal Feed Rate	20 tpd	18 tpd
Capacity	6 MW_{th}	5 MW_{th}
Syngas Production	3000 lb/hr	2500 lb/hr
Pressure	8 – 15 bar	15 – 27 bar
Nominal Temperature	1400°F – 1800°F	2500°F – 4000°F
Diameter	11 in.	6 in.
Technology	Fluidized bed	Entrained-flow
O_2 – Blown Test Campaigns Performed	Yes	Yes
Air – Blown Test Campaigns Performed	Yes	No

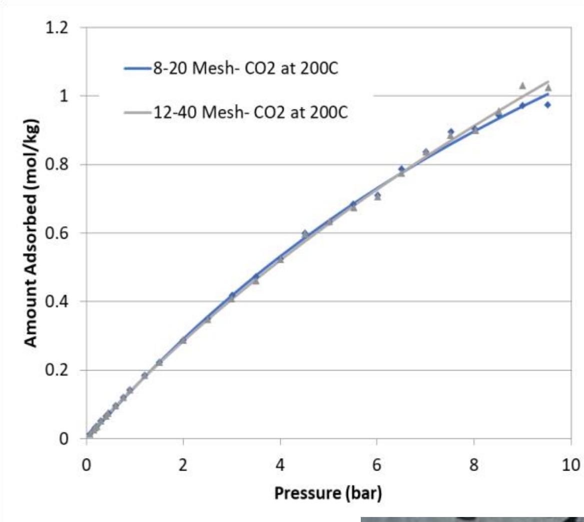
Detailed Design of 10 CFM Test Skid

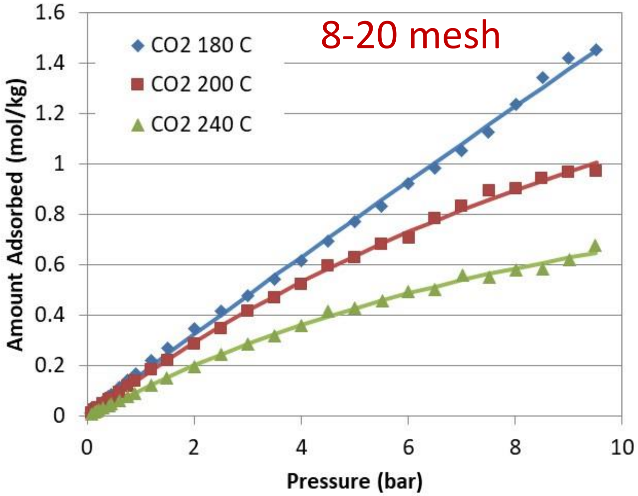


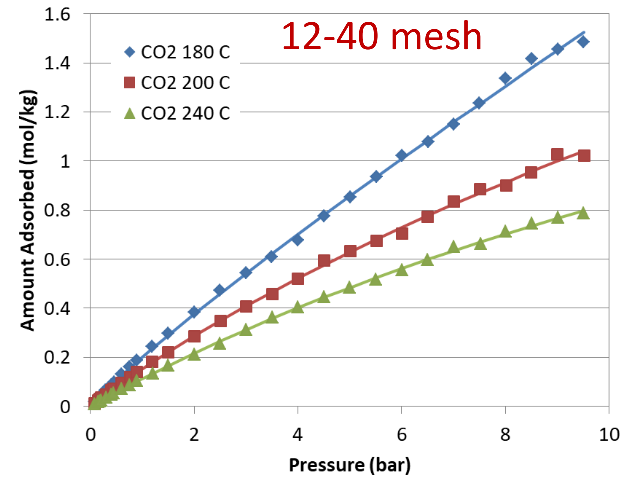
- Test unit is designed to treat 10 SCFM (280 SLPM) of syngas flow
- 8 sorbent beds and 2 accumulator tanks are used to show:
  - 10-20 kW equivalent gas treatment (10 CFM unit)
  - High CO_2 removal efficiency
  - High CO_2 purity (i.e., high H_2 recovery)
- The will contain three sub-assemblies/ skids:
  - Integrated WGS/CO_2 Separation Skid (new updated reactor design)
  - Gas Processing Skid (new regenerable warm gas desulfurization)
  - CO_2 Purification Skid (new skid to demonstrate 95+% CO_2 purity)

Impact of Particle Size on CO_2 Adsorption

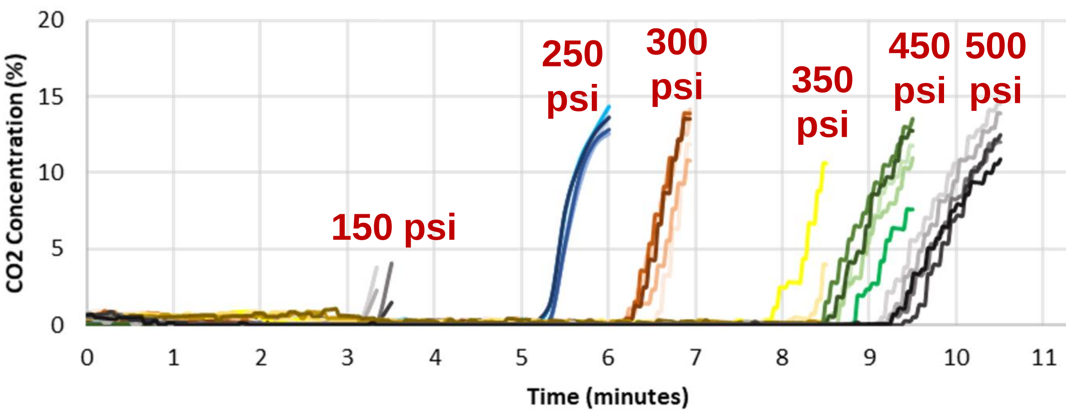
- We used a particle size of 8-20 mesh and measured CO_2 isotherms at 30°C, 180, 200 and 240°C)
- At lower temperatures (e.g., 30, 180, 200°C) both 12-40 and 8-20 mesh size particles achieved similar capacity
- Heat of Adsorption is calculated to be between 5-7 kcal/mol

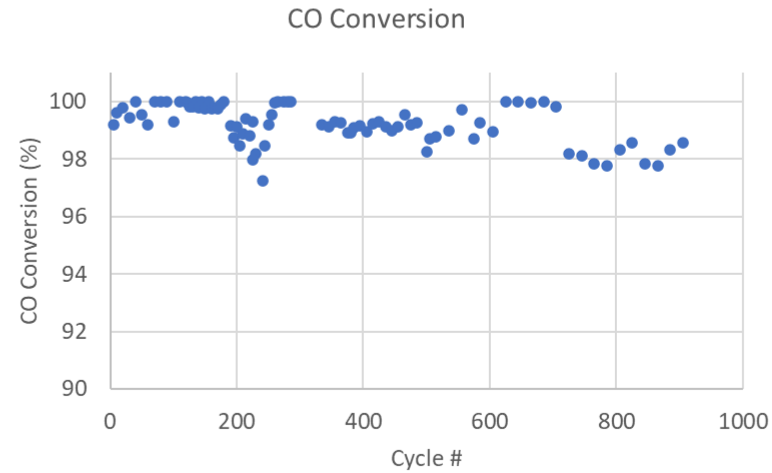




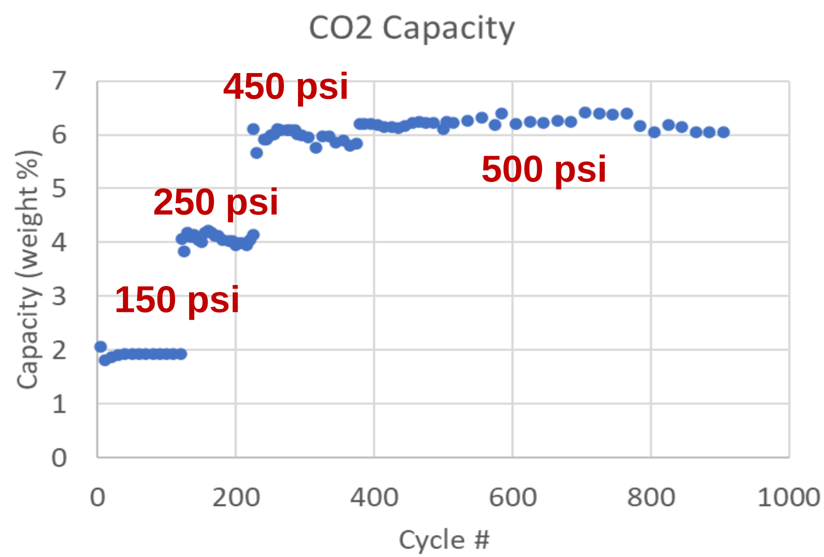


Qualification of the New CO_2 Sorbent

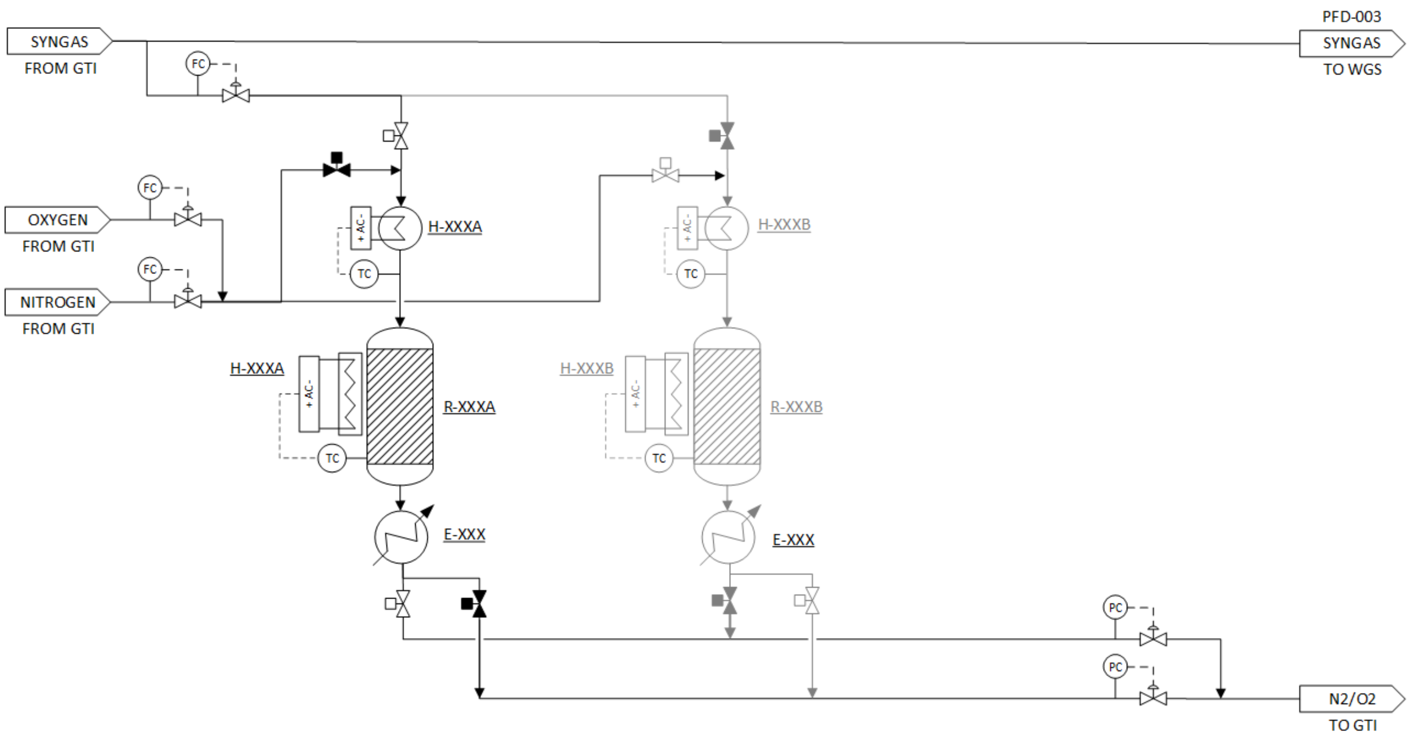




- At the highest pressure of 500 psi, the WGS/CO_2 sorbent bed achieved 6.2 % wt. CO_2 capacity and 99% CO conversion, far exceeding our Milestone (1-1) target of 4% wt. CO_2 capacity at 500 psi
- We completed over 500 adsorption/ desorption cycles at 500 psi



Design of Warm Gas Sulfur Removal



- **Slipstream skid to demonstrate warm gas sulfur removal**
- **Electric heaters to achieve required adsorption and regeneration operating temperatures**
- **Air-cooled exchangers to cool the outlet gas**
  - Product gas and regeneration off-gas will be recombined and returned to GTI
  - Switching valves will be installed in cool gas locations

Qualification of Regenerable Sulfur Sorbent

- **20 cycles complete with Warm Gas Regenerable Sulfur Sorbent**
  - Cycles 5-20: 10 hour adsorption
  - Regeneration until oxygen level >2%

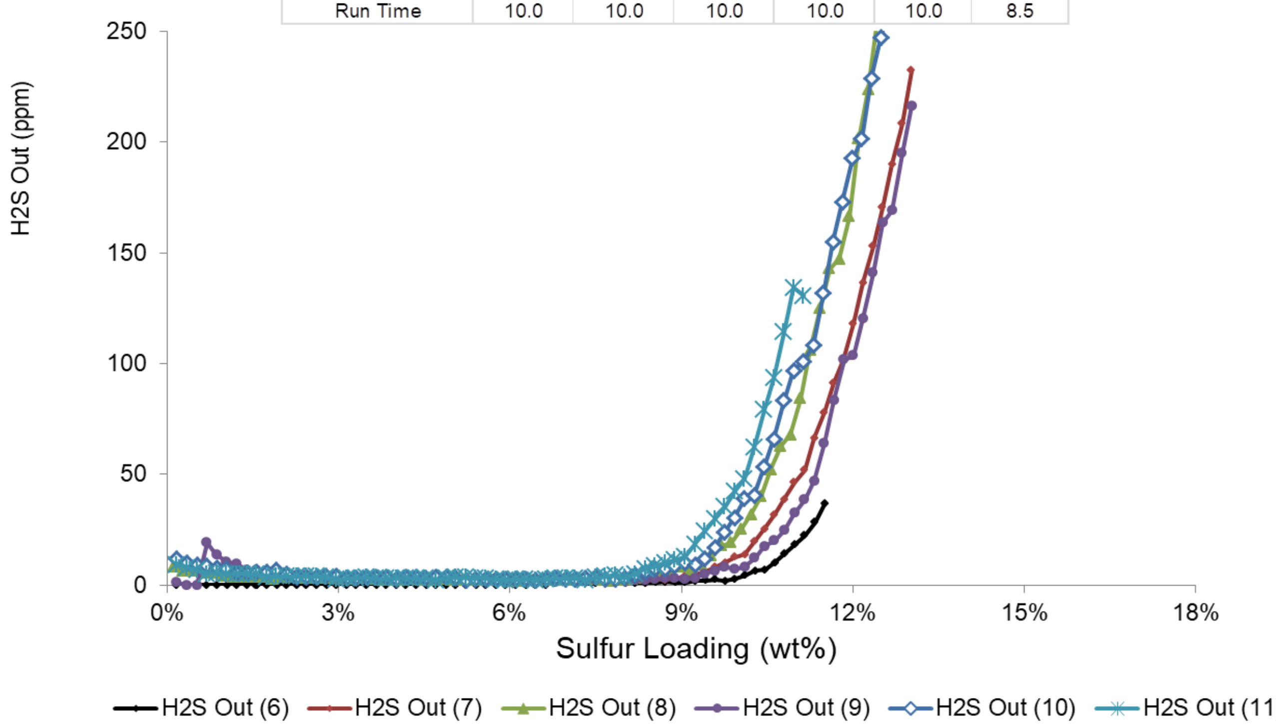
Susteon Regenerable Sulfur Sorbent

306 cc, 344.5 g, 2" id reactor

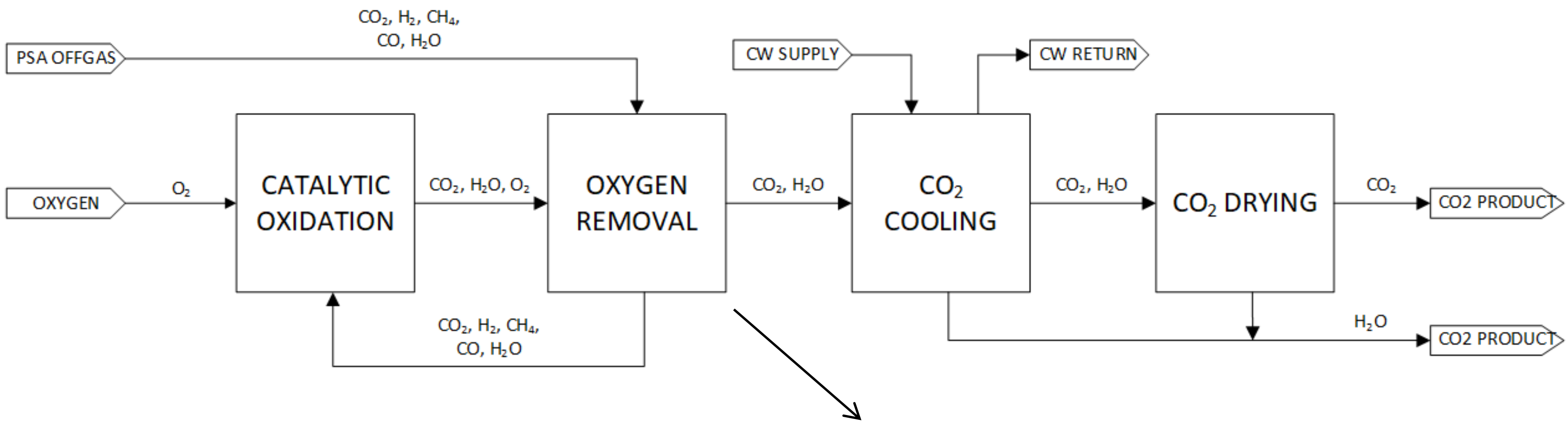
Adsorption: 2,000/h, 538°C, 5k ppm H_2S, 35 psig

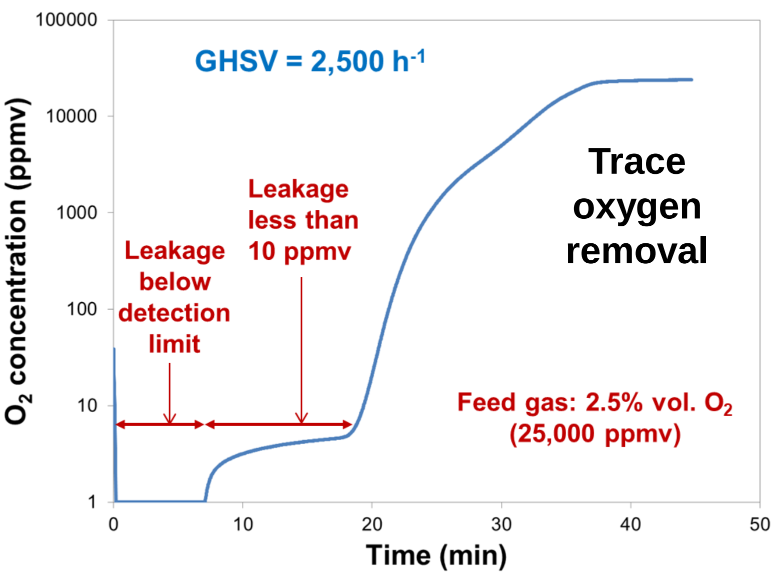
Desorption: 1,000/h, 566°C, 3.5% O_2, 35 psig

Cycle #	6	7	8	9	10	11
Inlet [H2S]	5,000	5,000	5,000	5,000	5,000	5,000
Sulfur Loading	11.5%	12.9%	12.1%	13.0%	12.2%	11.0%
Run Time	10.0	10.0	10.0	10.0	10.0	8.5



CO_2 Purification Subsystem



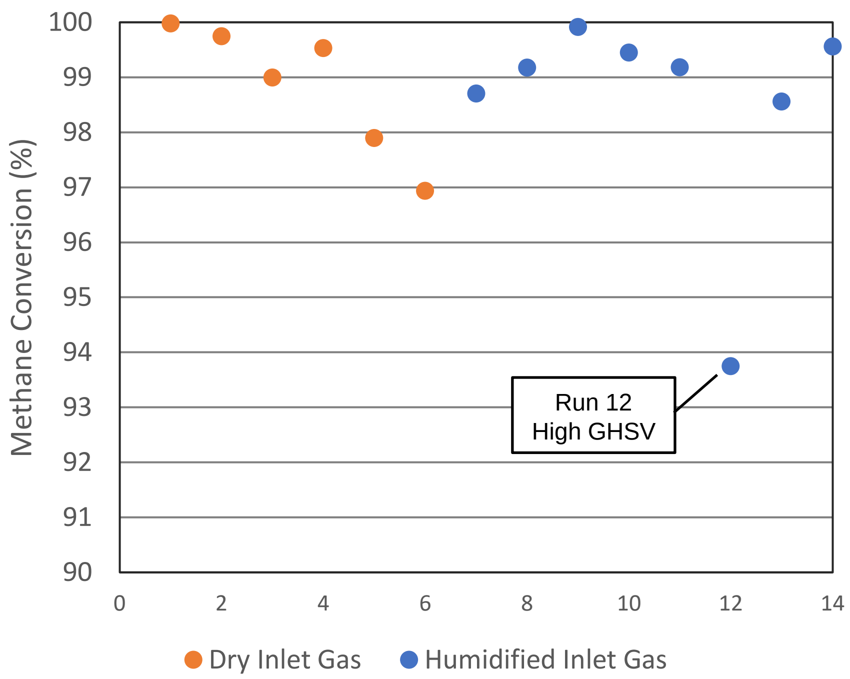


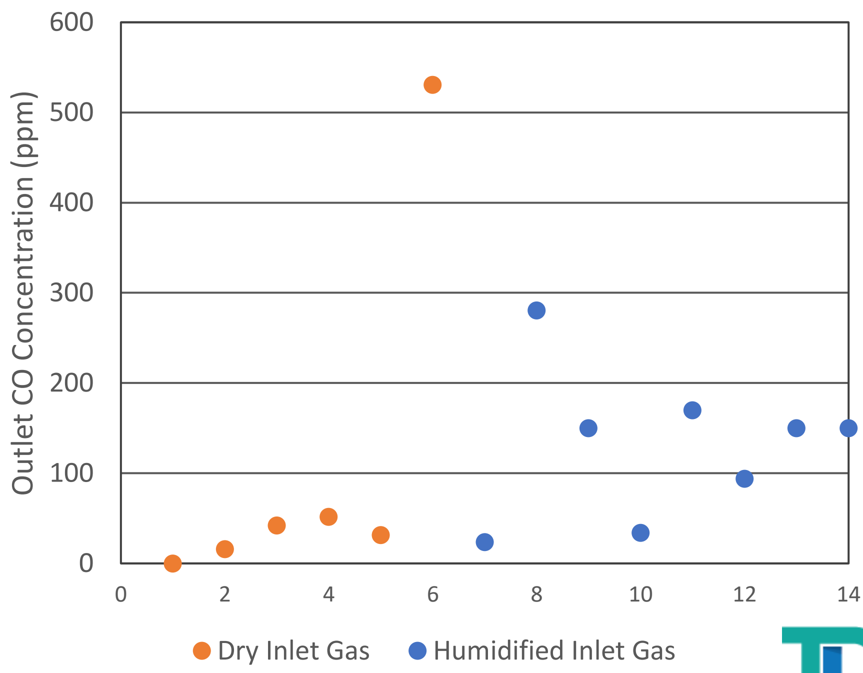
Trace Oxygen removal Sorbents previously developed for removing residual oxygen from oxy-combustion processes under DOE Gasification Group funded Contract DE-FE0029090

- **Breakthrough tests confirmed very high oxygen removal efficiency**
- **O_2 concentration in treated gas can be lowered to <10 ppmv**

CO_2 Purification Catalyst Performance

- We tested simulated CO_2 product gas at varying CH_4 concentration and gas-solid contact times at stoichiometric conditions
  - 4% CH_4, 15k/hr GHSV
  - 6% CH_4, 10k/hr GHSV
  - 2% CH_4, 30k/hr GHSV
- High humidity exposure results in more CO formation
  - Temperature needs to be controlled by cooling the inlet gas





Initial Techno-economic Analysis

	AST Study	UCI Study	UCI Study		
	Actual	Actual	Actual*	Projected+	Projected++
Chemical Storage type	NH_3	none	H_2	H_2	NH_3
ASU Type	Cryogenic	Cryogenic	ITM	Cryogenic	Cryogenic
Carbon Capture Technology	Selexol	TDA	TDA	TDA	TDA
Carbon Capture , %	95%	90%	90%	90%	90%
Electricity: Chemical	30:70	100:0	50:50	48:52	57:43
Coal Feed rate, GJ/h	1412	5763	5422	5422	5422
Gross Electric power, MW_e	96	694	481	481	484
Total Auxiliaries, MW_e	60	139	103	131	131
Net Electric Power, MW_e	36	555	377	350	353
Energy stored as chemical, MW	84	0	377	377	268
Combined Net Power and Chenmical Storage, MW	120	555	754	727	622
HHV Net Plant Efficiency	30.6%	34.7%	50.1%	48.3%	41.3%

* Chen, Q., Rao, A. and Samuelsen, S., 2014. H2 coproduction in IGCC with CCS via coal and biomass mixture using advanced technologies. Applied energy, 118, pp.258-270.

- **Greater than 40% net efficiency for NH_3 co-production is achieved with TDA warm gas capture system and a cryogenic ASU plant**

Acknowledgments

- DOE/NETL Project Manager, Andrew Jones
- Susteon, Raghubir Gupta, Andrew Ton, Cory Sanderson
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- UCI, Ashok Rao