A High Efficiency, Modular Pre-combustion Capture System for 21st Century Power Plant Poly-generation Process
(Contract No. DE-FE0031926)

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Project Objectives

- **The objective is to 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
  - A fixed-bed TSA based sulfur removal system will be used to remove H_2S
  - High temperature process to remove contaminants from product CO_2
- **Project Tasks**
  - Design/build a fully-equipped slipstream test unit with 10 SCFM treatment capacity
  - Demonstrate the operation of the integrated system in achieving high CO_2 and contaminant removal efficiency
  - Design of the integrated system
  - High fidelity process design and economic analysis

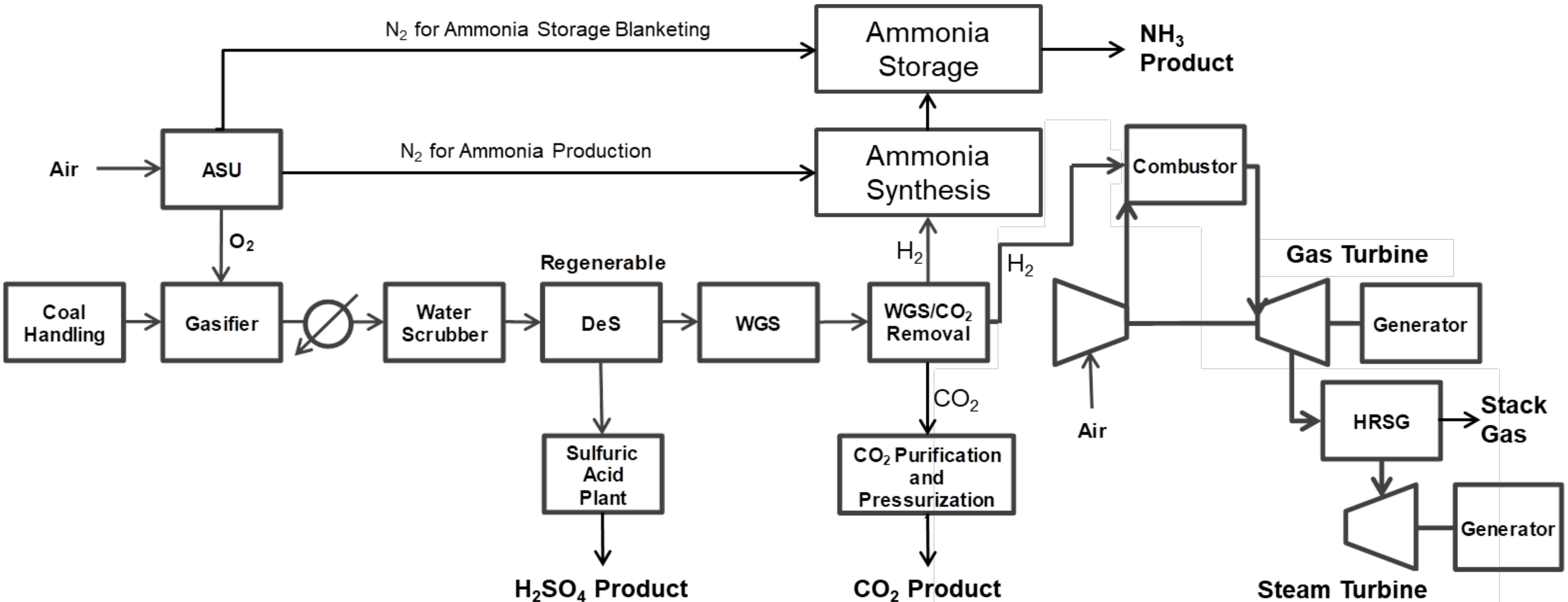
<u>Project Duration</u>

Start Date = October 1, 2020

End Date = September 30, 2024

	DOE Share	Cost Share	Total
BP 1	$1,007,692	$251,850	$1,259,542
BP 2	$738,746	$184,743	$923,489
BP 3	$1,253,562	$313,407	$1,566,969
Total	$3,000,000	$750,000	$3,750,000

Process Schematic



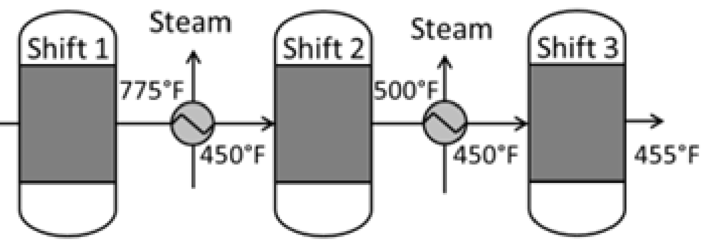
Advantages

- Higher mass throughput to gas turbine – higher efficiency
- Lower GT temperature – Reduced need for HP N_2 dilution hence lower NO_X formation
- Elimination of heat exchangers needed for cooling and re-heating the gas
- Elimination of gray water treatment problem
- Efficiency improvements/process intensification via integration with WGS

TDA RESEARCH

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 commonly used**
  - WGS is an equilibrium-limited exothermic reaction
- **Water is supplied at concentrations well above that is required by the reaction stoichiometry to completely shift the CO into 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

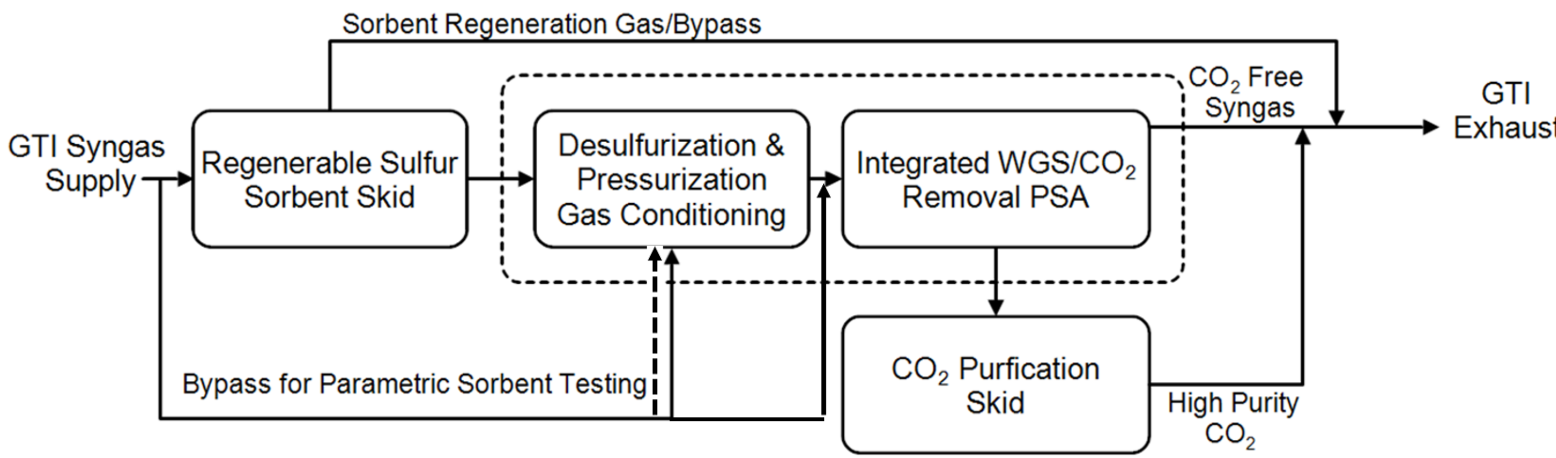
$$CO + H_2O = CO_2 + H_2$$

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

- **In our process, WGS catalyst is combined with a high temperature CO_2 adsorbent to achieve high CO conversion *<u>at low steam:carbon ratios</u>***
- **Reduced water addition increases process efficiency**

Integrated Synthesis Gas Treatment System

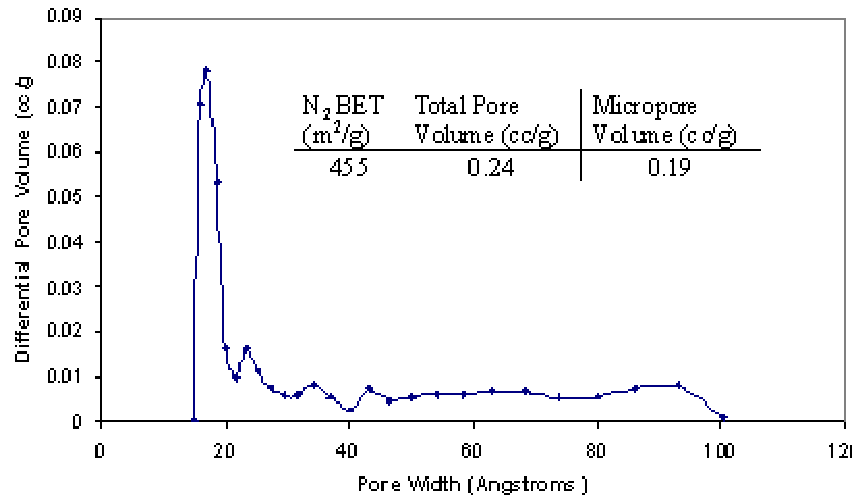
- **Pre-combustion capture using a high temperature PSA adsorbent integrated with low temperature WGS process**
  - Sorbent Development (DE-FE-0013105); Reactor Development (DE-FE-0012048); Proof-of-Concept Evaluations (DE-FE0023684)
- **Removal of sulfur compounds (H_2S, COS, CS_2)**
  - Fixed-bed sulfur sorbents (DE-AM26-99FT40463)
  - DOE/NETL holds the patents (US5,703,003, US5,866,503)
- **Removal of trace contaminants (As, Hg, Se, HCN) (DE-FC26-05NT42460)**
- **CO_2 Purification - Trace Oxygen Removal (DE-FE0029090)**



TDA RESEARCH

TDA's Sorbent

- **TDA's uses a mesoporous carbon with surface functional groups to remove the CO_2 via strong physical adsorption**
  - CO_2-surface interaction is strong enough to allow operation at elevated temperatures
  - Because CO_2 is not bonded via a covalent bond, energy input for regeneration is low
- **Heat of CO_2 adsorption is 4.9 kcal/mol for TDA sorbent**
  - Net energy loss in sorbent regeneration is similar to Selexol; much higher IGCC efficiency can be achieved due to high temperature CO_2 capture
- **Favorable material properties**
  - Mesopores (10 to 100 A) reduce diffusion limitations



US Patent 9,120,079, Dietz, Alptekin, Jayaraman "High Capacity Carbon Dioxide Sorbent", US 6,297,293; 6,737,445; 7,167,354 US Pat. Appl. 61790193, Alptekin, Jayaraman, Copeland "Pre-combustion CO_2 Capture System Using a Regenerable Sorbent"

Sorbent Development Work

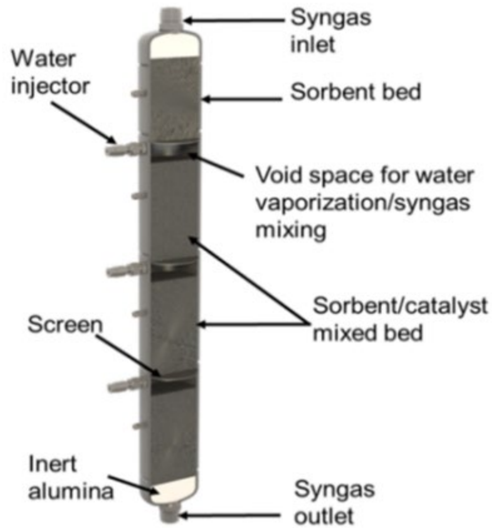
TDA 0.1 MW pre-combustion carbon capture unit installed at the National Carbon Capture Center

- **0.1 MW_e test in a world class IGCC plant to demonstrate full benefits of the technology**
    - Field Test #1 at NCCC
    - Field Test #2 at Sinopec Yangtze Petro-chemical Plant, Nanjing, China
- **Full operation scheme**
    - 8 reactors and all accumulators
    - Utilize product/inert gas purges
    - H_2 recovery/CO_2 purity

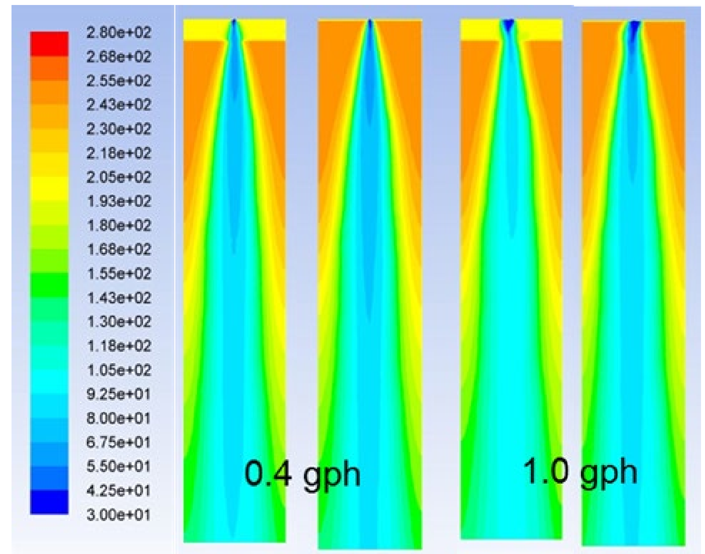
Yangtzi Petro-chemical Plant

Heat Integrated WGS & CO_2 Capture

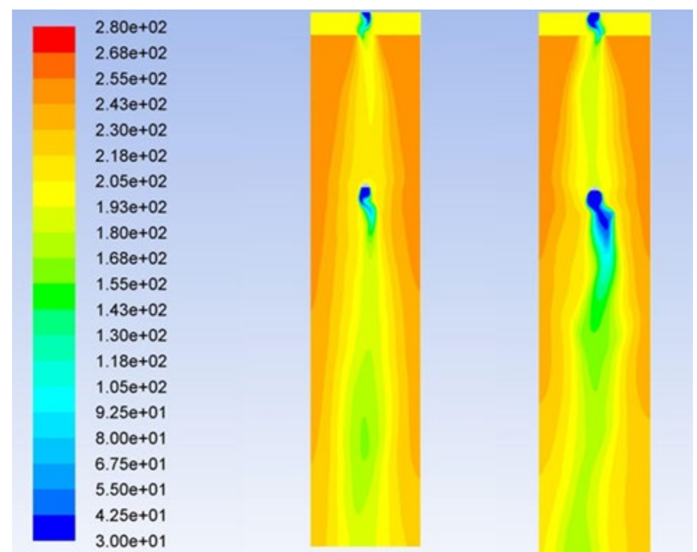
- **Advanced heat management concept based on direct water injection has proven to achieve much better temperature control**
    - Also much better heating efficiency (i.e., kJ heat removed per kg water)
- **Uniform cooling without hot or cold spots**
- **The temperature rise is optimal when the catalyst is distributed into multiple layers with water injections before each layer**



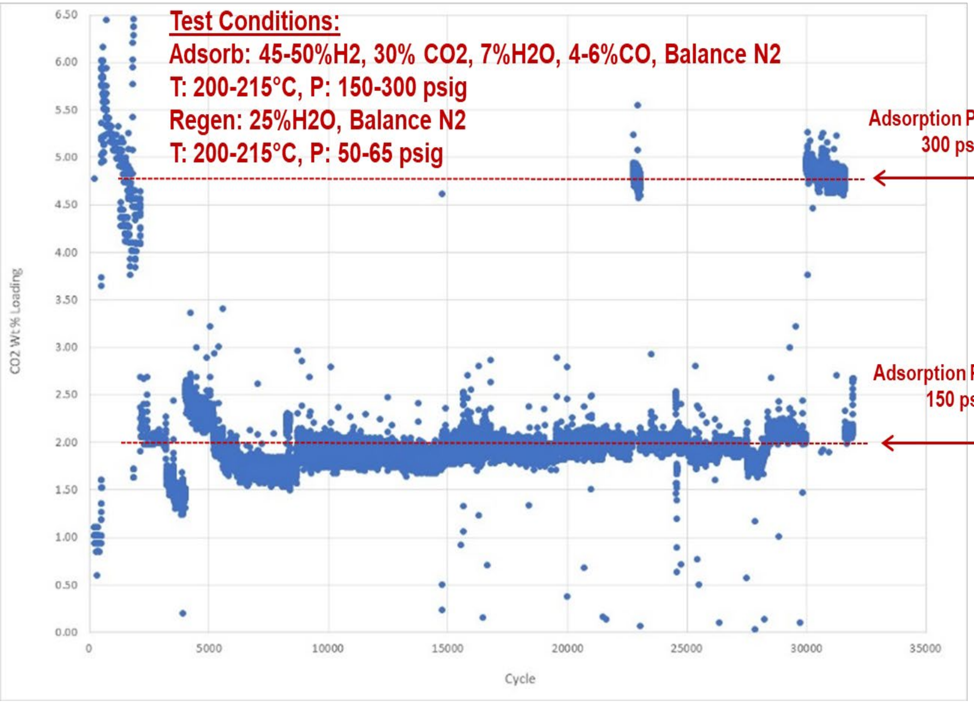
T Contours (°C) Single Injection Layer

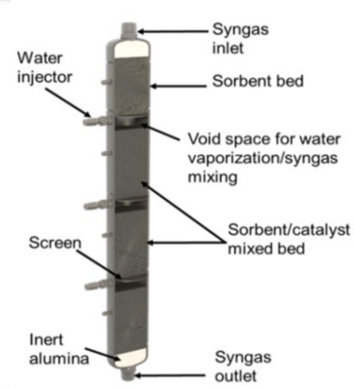


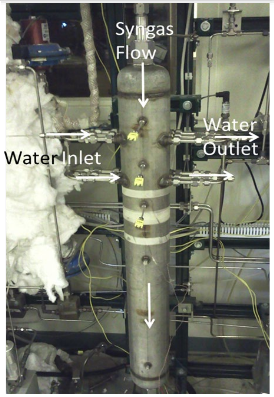
T Contours (°C) Multiple Injection Layers

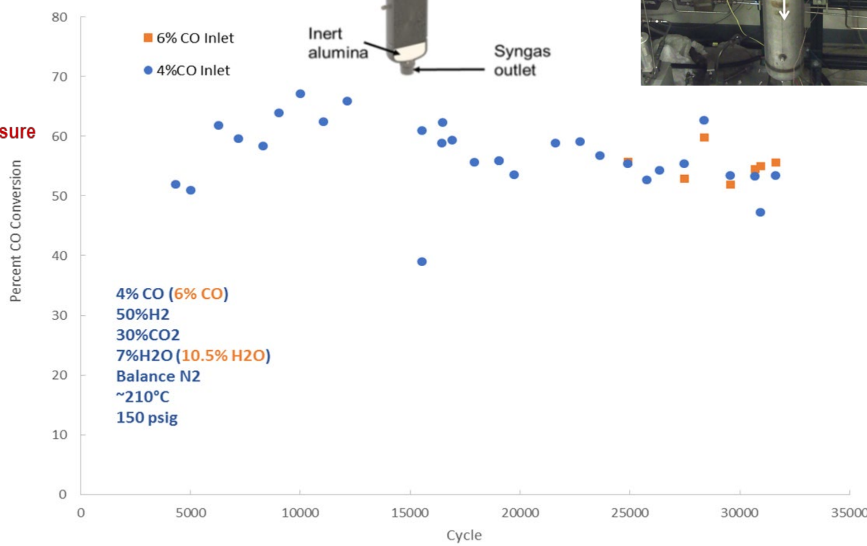


Life Tests – WGS/CO_2 Capture





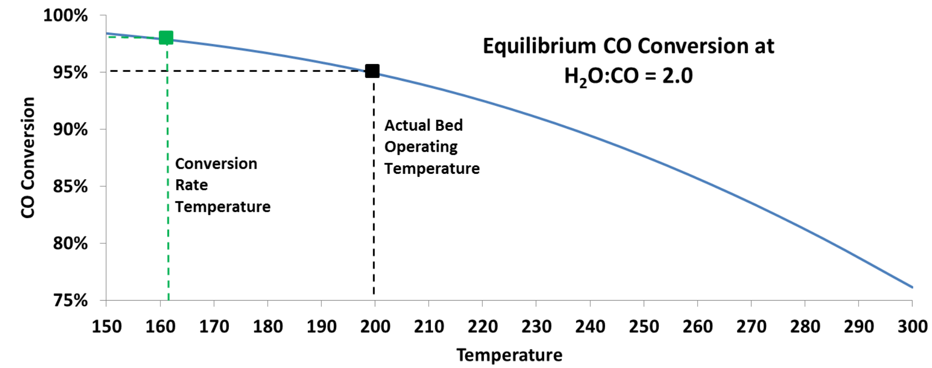


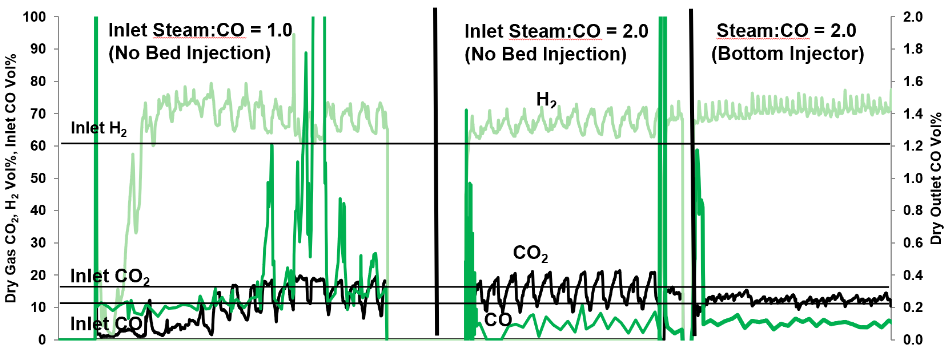


- We completed 32,000 cycles showing stable performance for the integrated WGS catalyst and CO_2 sorbent bed
- Measuring catalytic activity (by itself) through multiple cycles showed that the exposure to the reducing/oxidizing conditions had no adverse effect on the WGS catalyst

TDA RESEARCH

Integrated WGS/CO_2 Capture System



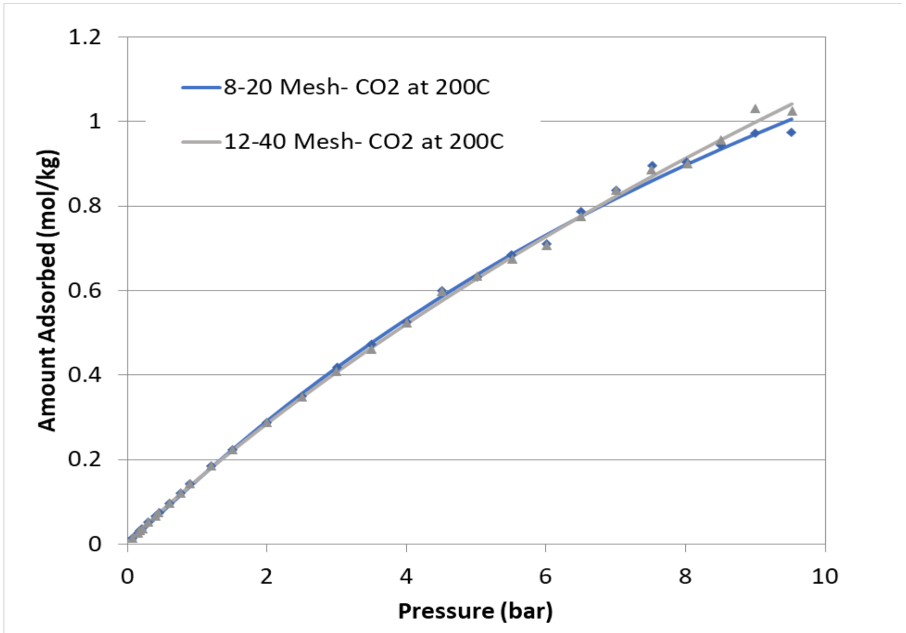


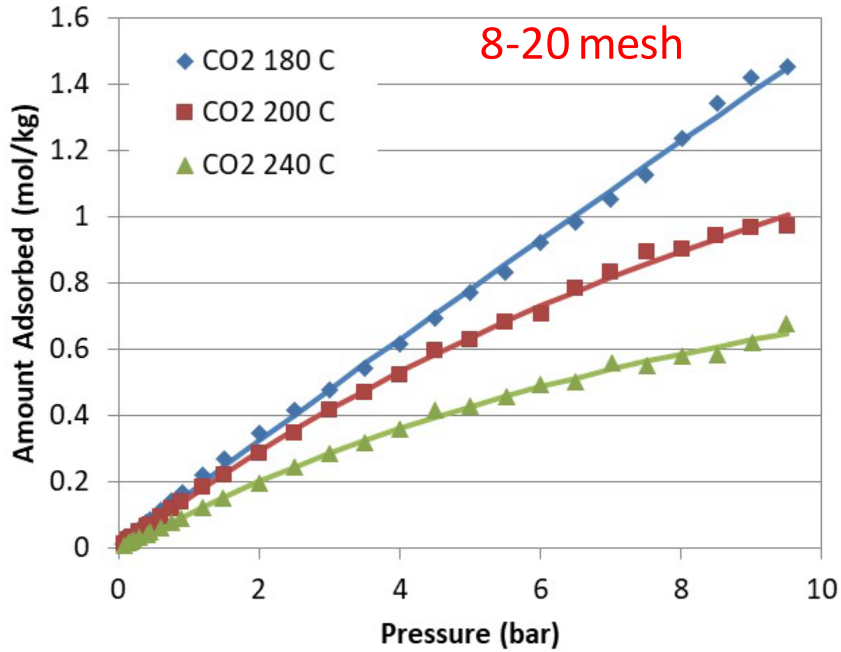
- **Evaluations at Linde/Praxair R&D Center (Tonawanda, NY)**
  - Integrated with OTM on natural gas

- **Overall CO conversion >98% was achieved**
- **By coupling the WGS with CO_2 sorbent and water injection, we were able to operate the beds at 200°C but achieve the equilibrium CO conversion of a 40°C cooler bed**

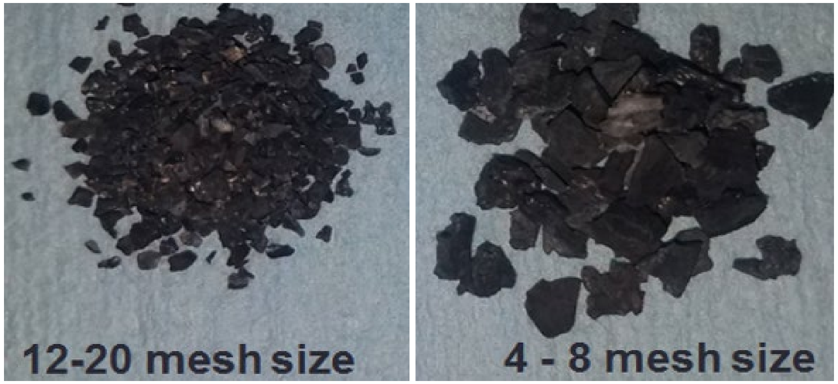
TDA RESEARCH

Modification of the CO_2 Sorbent





- We assessed the feasibility of using 8-20 mesh size sorbent and measured CO_2 isotherms at 180, 200 and 240°C
- Material prepared at 12-40 and 8-20 mesh size achieved similar capacity
- 12-40 mesh particles worked slightly better at 240°C



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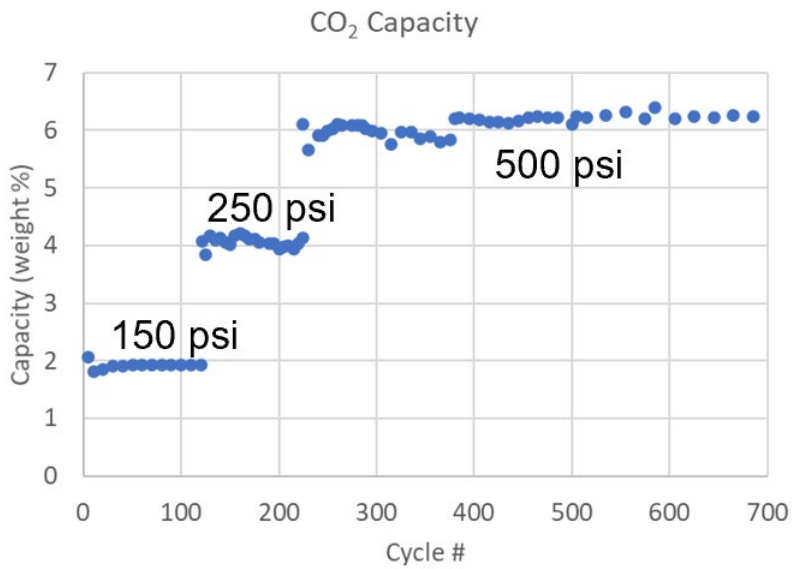
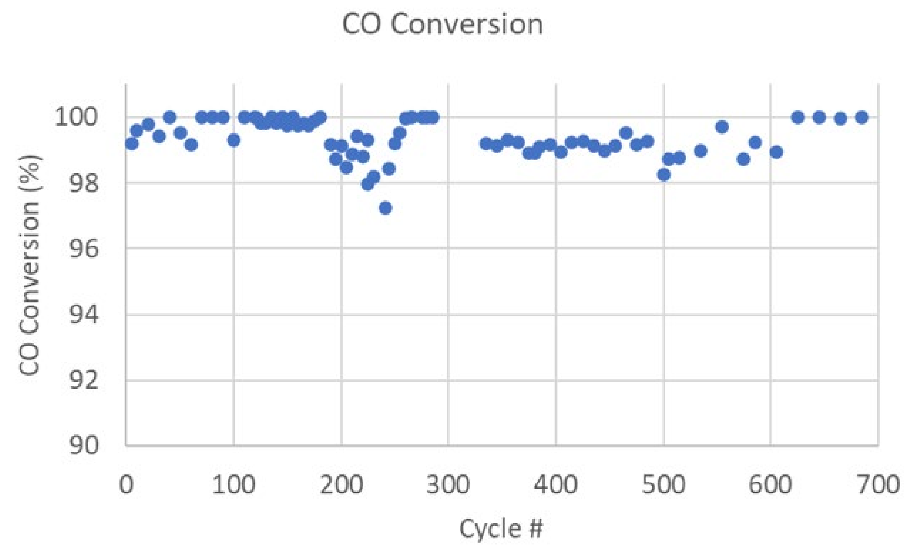
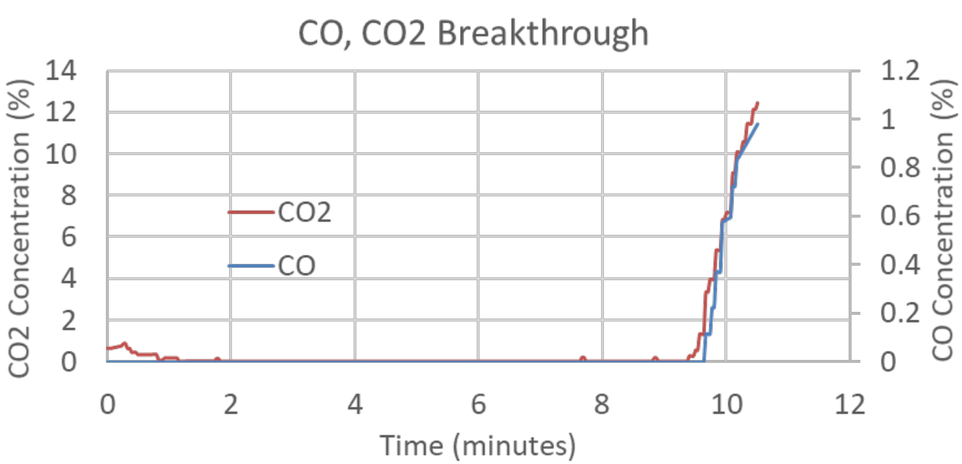
CO_2 Sorbent/WGS Catalyst Testing

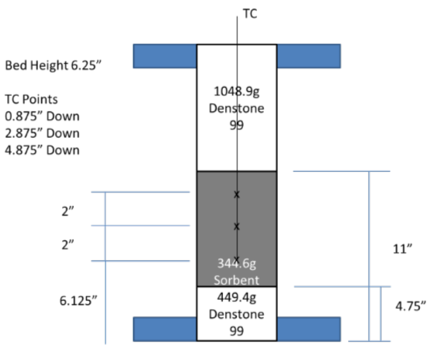


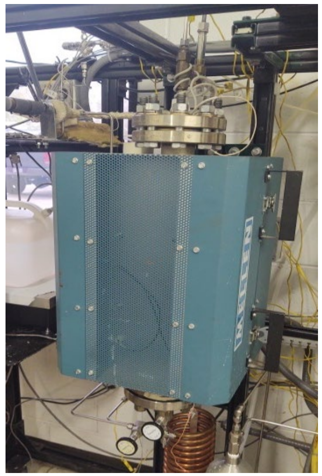


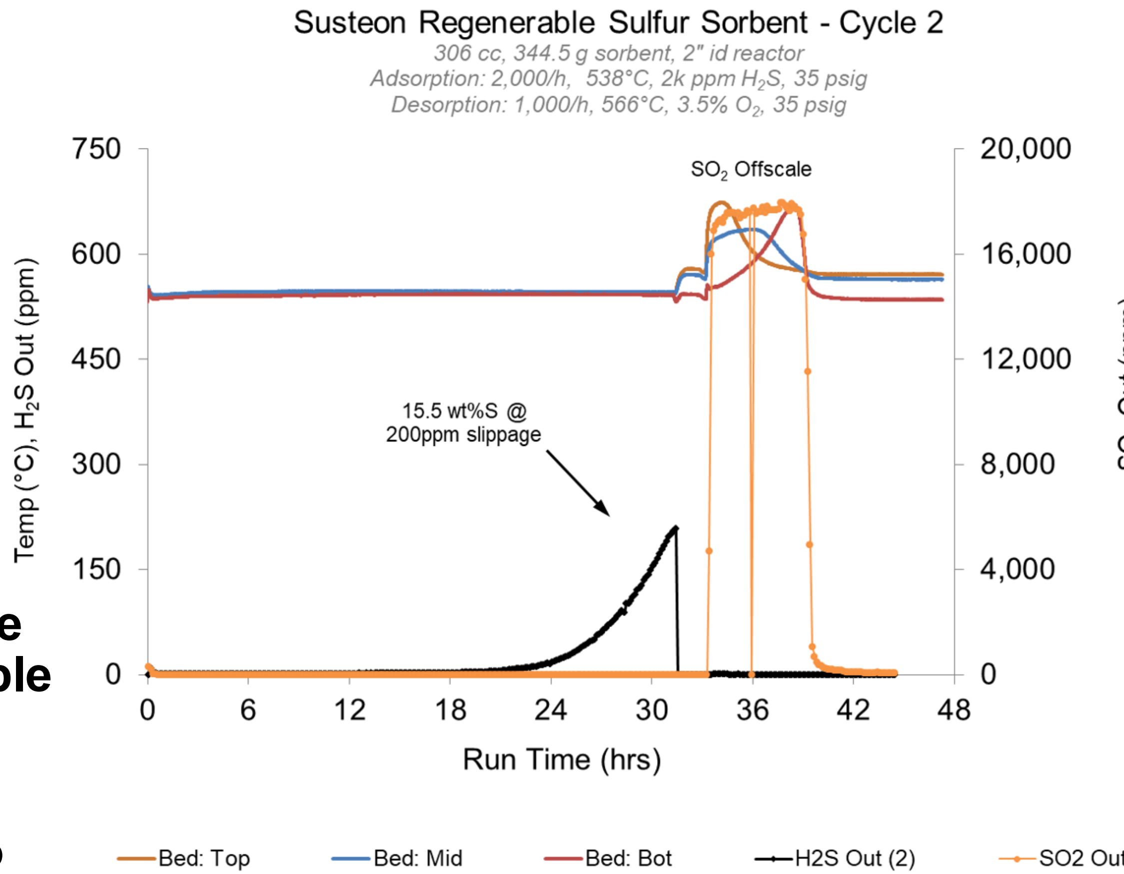


- At 500 psi, WGS/CO_2 sorbent bed achieved 6.2% wt. CO_2 capacity and 99% CO conversion (far exceeding our Milestone M1.1 4% wt. CO_2 capacity at 500 psi)
- 700 cycles with no signs of degradation

Manufacturing and Qualification of the Regenerable Sulfur Sorbent

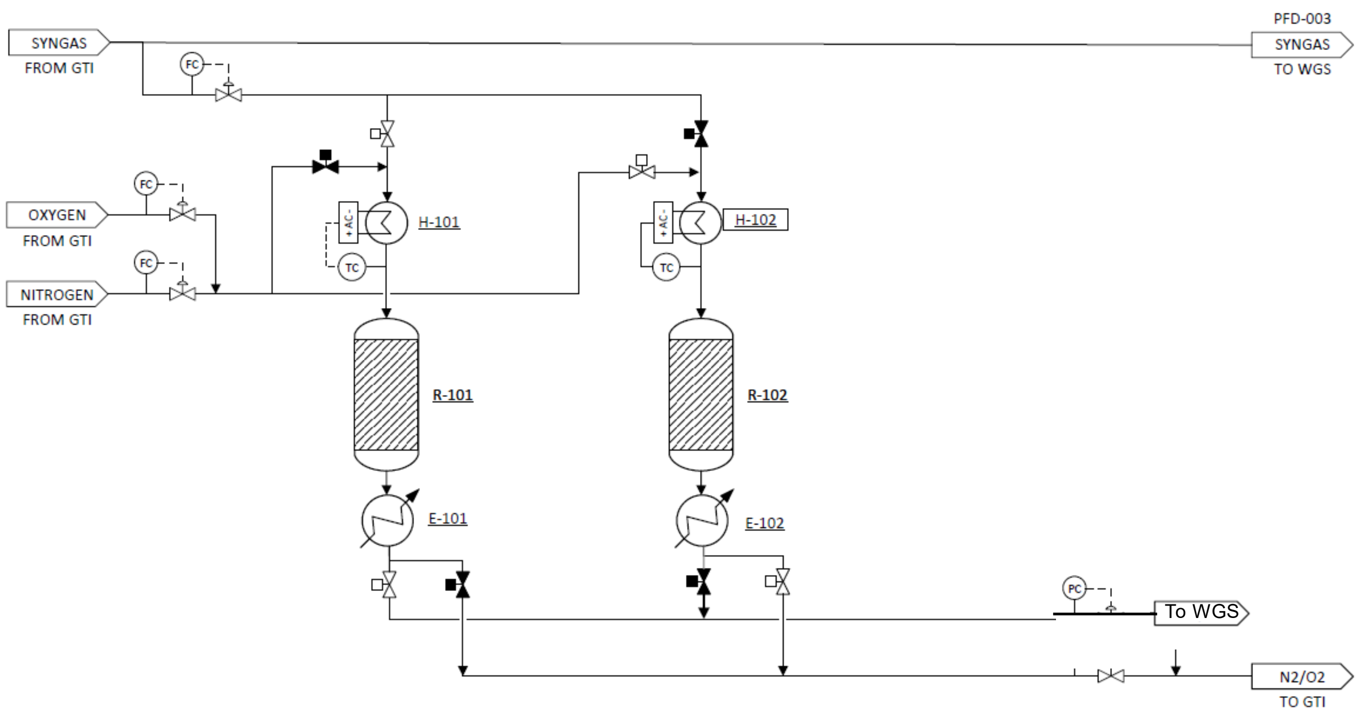






- **Susteon has Clariant produce a large batch of its regenerable sulfur sorbent**
- **Multiple cycling of sorbent is underway (at bench-scale) to assess the long-term stability of the sorbent**
- **Optimize regeneration conditions**

Design of Regenerable Desulfurization System



- Design of the slipstream test skid to be used in the demonstration of the high-temperature sulfur removal was completed
- Design was approved by GTI
- Electric heaters on inlet gas to achieve the required temperatures
- Air-cooled exchangers to cool the outlet gas

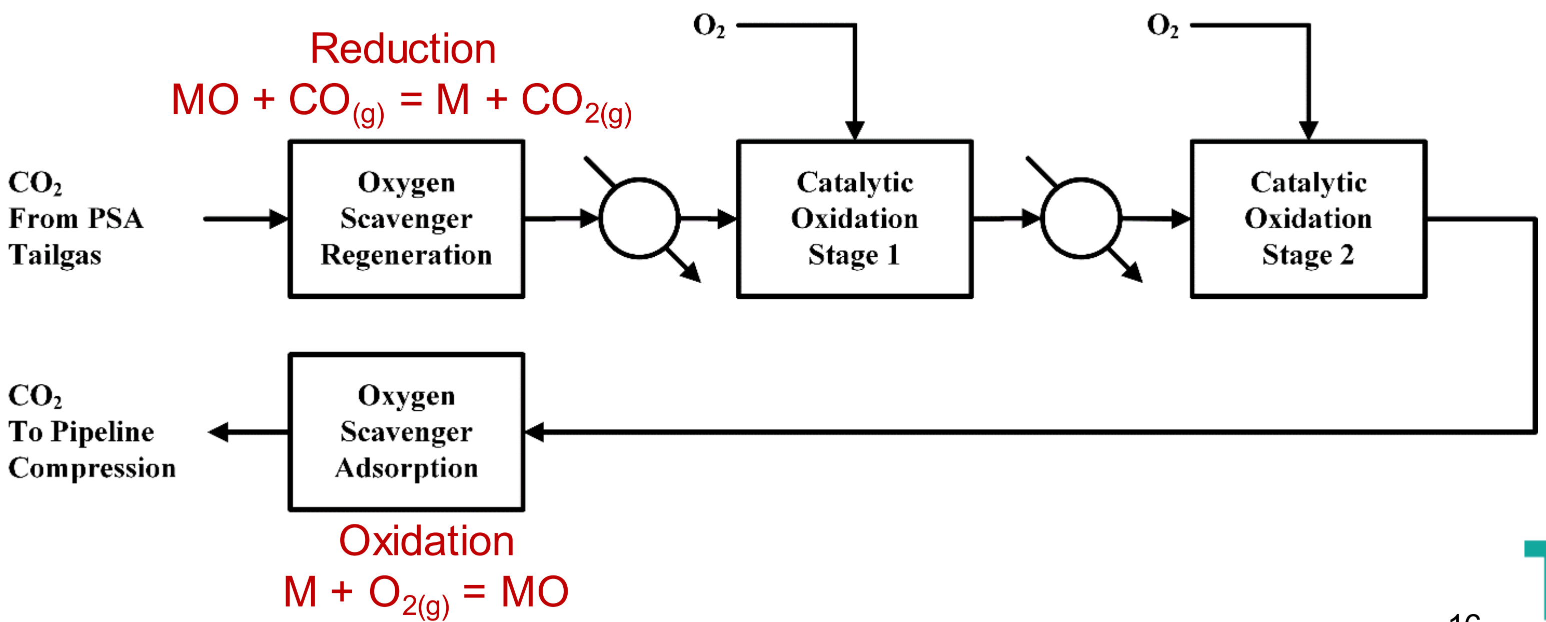
CO_2 Purification Requirement

Component	Unit	Carbon Steel Pipeline	Venting Concerns
	Max	Recommended	
CO_2	vol% (min)	95	IDLH 40,000 ppmv
H_2O	ppmv	500	
N_2	vol%	4	
O_2	vol%	0.001	
Ar	vol%	4	
CH_4	vol%	4	Asphyxiate, Explosive
H_2	vol%	4	Asphyxiate, Explosive
CO	ppmv	35	IDLH 1,200 ppmv
H_2S	ppmv	4	
SO_2	ppmv	100	IDLH 100 ppmv
NO_X	ppmv	100	IDLH NO-100 ppmv, NO_2 -200 ppmv
NH_3	ppmv	50	IDLH 300 ppmv
COS	ppmv	trace	Lethal @ High Conc. (>1,000 ppmv)
C_2H_6	vol%	1	Asphyxiant, Explosive
C3+	vol%	<1	
Part.	ppmv	1	
HCl	ppmv	N.I.*	IDLH 50 ppmv
HF	ppmv	N.I.*	IDLH 30 ppmv
HCN	ppmv	trace	IDLH 50 ppmv
Hg	ppmv	N.I.*	IDLH 2 mg/m3 (organo)
Glycol	ppbv	46	
MEA	ppmv	N.I.*	MSDS limits, 3 ppmv
Selexol	ppmv	N.I.*	

- **CO_2 transmission specifications are stringent**
  - < 1% total HC
  - < 4 ppm H_2S
  - < 35 ppm CO
  - < 10 ppm O_2
- **All separation systems (sorbents, membranes and solvents) need to include impurity removal options to meet the pipeline CO_2 spec**
- **For post-combustion and oxy-combustions systems O_2 requirement is the most stringent**
- **For syngas, there is also the need to remove CO**

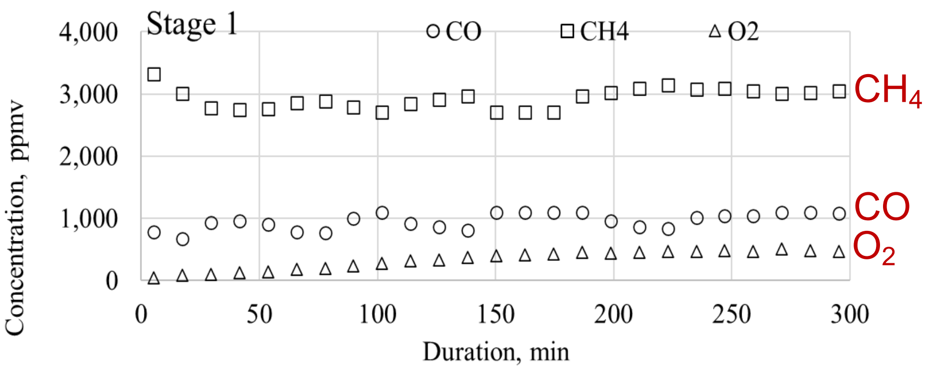
CO_2 Purification Technology

- **A hybrid process is developed that combines catalytic oxidizer and a REDOX based oxygen scavenging sorbent**
- **Catalytic oxidation removes hydrocarbons/combustibles (e.g., CO, CH_4, H_2)**
  - Operates with slight excess of oxygen
  - Adiabatic, multi-staged design with intercoolers for heat management
- **Oxygen Scavenging System polishes excess O_2 to <10 ppm**
  - Regenerable mixed metal oxide based chemical looping process
  - Oxidation step captures O_2; Reduction with inlet gas regenerates the sorbent

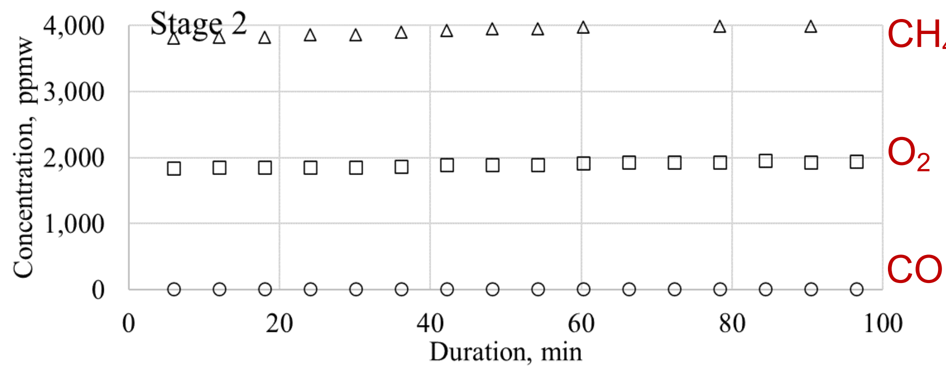


Evaluation of the Oxidation Catalyst

O_2:(CO+CH_4) molar ratio = 4.25
Sub-stoichiometric



O_2:(CO+CH_4) molar ratio = 5
Stoichiometric



Stage 1

- Operates w/ sub-stochiometric O_2 (fuel rich)
- Inlet – 2% vol. CO and 2% vol. CH_4 in CO_2

Stage 2

- Operates with excess O_2 (fuel lean)

- **Outlet gas meets spec for HC < 1% vol, CO < 35 ppmv**

	Stage 1	Stage 2
Inlet Temp (°C)	160	300
Outlet Temp (°C)	453	456
HC Percentage Inlet (total)	4	4
O_2 Percentage	4.25	4.25
O_2 Out (ppm)	7.31	4026
CH_4 Out (%)	0.43	**0.19**
CO Out (ppm)	813	**10.2**
Steam (%)	46	46
Pressure	150	150

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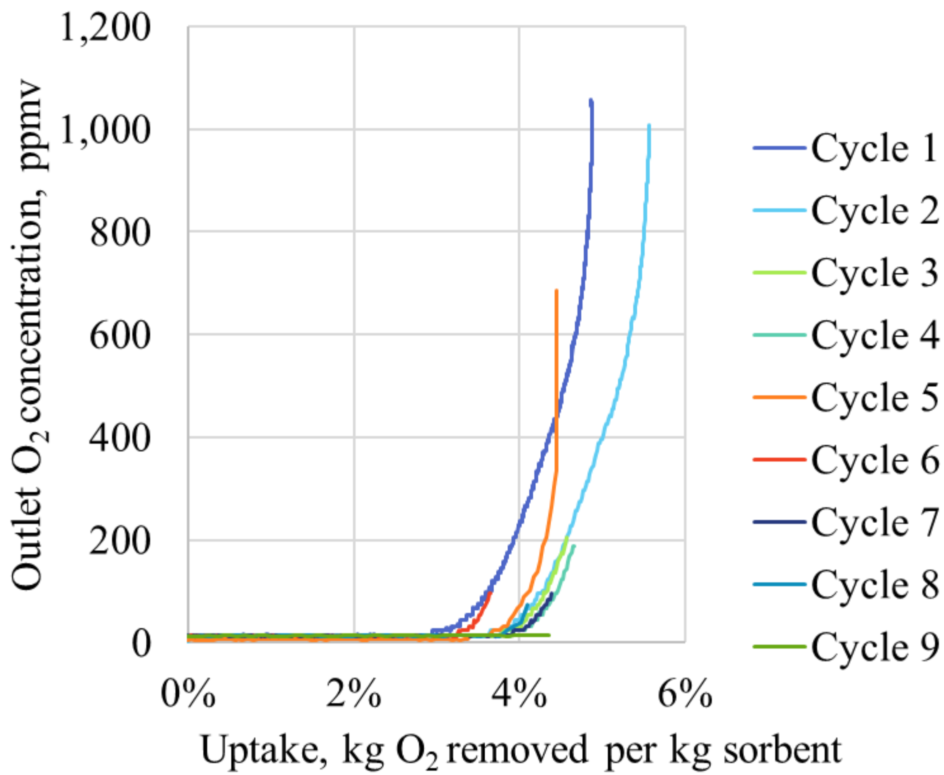
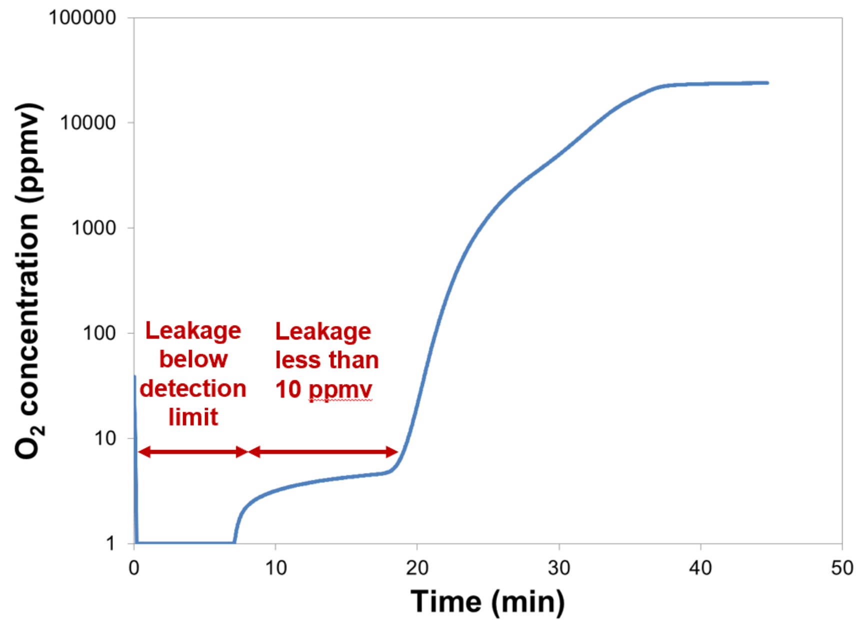
TDA's O_2 Scavenger Sorbent

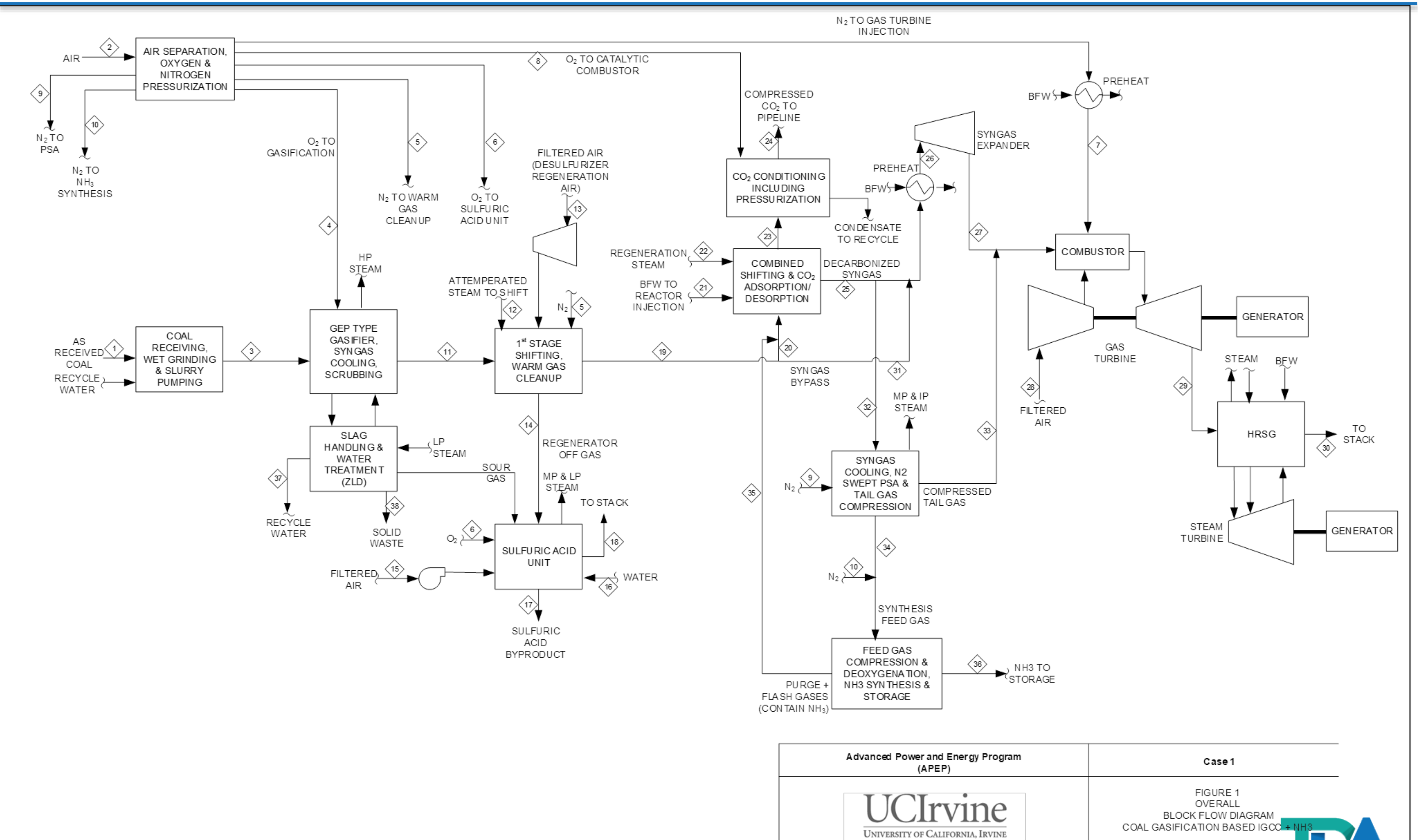
Feed gas: 2.5% vol. O_2 (1,000-4,000 ppmv) in CO_2, T= 400°C, GHSV = 3,500 to 6,000 h^{-1}





- **Oxygen scavenger was tested for nine cycles verifying consistent breakthrough capacity with <10 ppmv O_2 in the outlet**
- **Uptake is 3.8%-w O_2 at <10 ppm O_2 slip**

TEA Poly-generation - BFD



TDA RESEARCH

Process Design and System Analysis

Case	1	2	3	4
Gross Power Generated (At Generator Terminals), kWe				
Gas Turbine Power	208,022	88,000	88,000	88,000
Steam Turbine Power	155,650	68,494	67,442	71,843
Syngas Expander Power	3,824	1,701	1,643	2,034
CO2 Vent Expander	-	-	-	4,363
Total Power	367,496	158,194	157,085	166,241
Auxillary Load Summary, kWe				
Total Auxillaries	166,134	73,399	73,741	65,560
Net Power, kWe	201,362	84,795	83,345	100,681
Coproduct NH3, ST/D	2,310	976	956	1,160
Total (Electric + Coproduct) Energy, kW	746,752	315,236	309,030	374,558
Net Plant Efficacy, %HHV	49.16	47.90	47.39	52.77
Carbon Captured, %	90.0	90.0	95.8	-
Total Plant Cost , $1000	3,109,013	1,579,429	1,584,599	1,618,209
Process Economics, NH3 Production				
1st year Required Sale Price w/o CO2 T&S, $/ST	1,414	1,714	1,759	1,454
1st year Required Sale Price, $/ST	1,457	1,758	1,806	1,454

NH_3 RSP Sensitivity to Sale Price of Electricity for Case 2

Electricity Credit	$/MWh	64.5	**71.7**	78.9	107.2	152.3
NH3 RSP with CO_2 T&S	$/ST	1,773	**1,758**	1,743	1,684	1,590

DOE Baseline Rev. 4 Study Basis $2018 basis

TDA RESEARCH

Acknowledgements

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