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



Ambal Jayaraman, PhD Gokhan Alptekin, PhD Michael Bonnema

TDA Research, Inc.

Prepared for NETL Annual Review Meeting

Pittsburgh, PA

August 7, 2024

TDA Research Inc. • Golden, CO • www.tda.com

Project Objectives













CLARIANT



Project Duration

Start Date = October 1, 2020

End Date = September 30, 2025

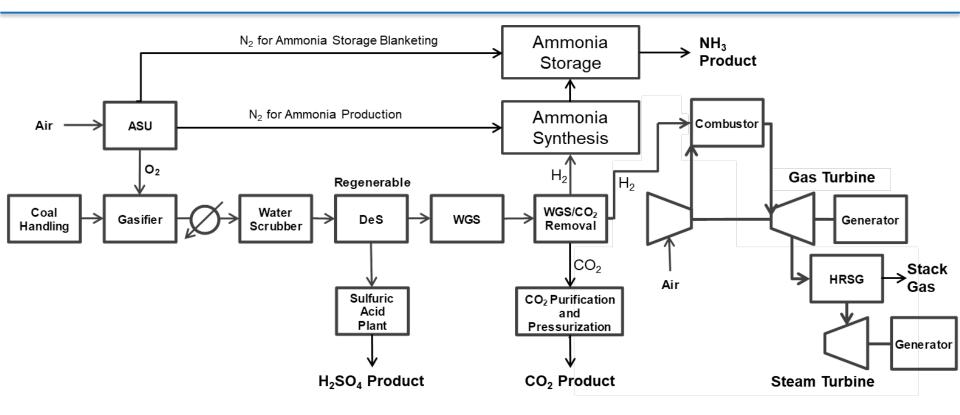
	DOE Share	Cost Share	Total
BP 1	\$886,187	\$221,547	\$1,107,734
BP 2	\$792,419	\$198,105	\$990,524
BP 3	\$1,321,394	\$330,348	\$1651,742
Total	\$3,000,000	\$750,000	\$3,750,000

- The objective is to demonstrate technoeconomic viability of a modular coal-toenergy-and-chemicals process with a focus on syngas treatment and processing
 - A high temperature PSA adsorbent/WGS process is used for CO₂ removal
 - A fixed-bed TSA based sulfur removal system will be used to remove H₂S
 - High temperature contaminant removal process to remove any contaminants

Project Tasks

- Design a fully-equipped slipstream test unit with 10 SCFM treatment capacity
- Demonstrate the operation of the integrated system in achieving high CO₂ and contaminant removal efficiency
- Detailed design of the integrated system
- High fidelity process design and economic analysis

Process Schematic

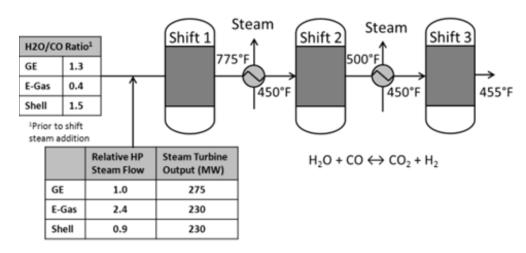


- Warm gas removal of CO₂, sulfur and contaminants improve efficiency
- Reducing the use of excess steam improves power cycle efficiency
 - Lower energy consumption to raise the steam
- Process intensification could potentially reduce the number of hardware components and cost

3

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 CO₂
- Excess water is also used to suppress carbon formation



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

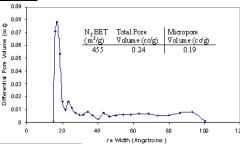
- In our process, the WGS catalyst is combined with a high temperature CO₂ adsorbent to achieve high CO conversion <u>at low steam:carbon ratios</u>
- Reduced water addition increases process efficiency

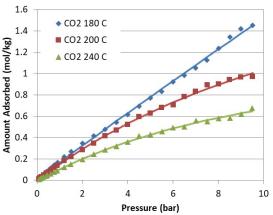


TDA's Sorbent

- TDA uses a mesoporous carbon with surface functional groups that remove CO₂ via strong physical adsorption
 - CO₂-surface interaction is strong enough to allow operation at elevated temperatures
 - Because CO₂ is not bonded via a covalent bond, energy input for regeneration is low
- Heat of CO₂ 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 CO₂ capture
- Favorable material properties
 - Pore size is tuned to 10 to 100 A
 - Mesopores eliminates 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 "Precombustion CO₂ 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 (2017)
 - Field Test #2 at Sinopec Yangtzi Petrochemical Plant, Nanjing, Jiangsu Province, China (2019)
- Full operation scheme
 - 8 reactors and all accumulators
 - Utilize product/inert gas purges
 - H₂ recovery/CO₂ purity



Yangtzi Petro-chemical Plant



Integrated WGS/CO₂ Capture System

100%

95%

90%

85%

Conversion

Temperature



Operating

Temperature

Equilibrium CO Conversion at

 $H_2O:CO = 2.0$

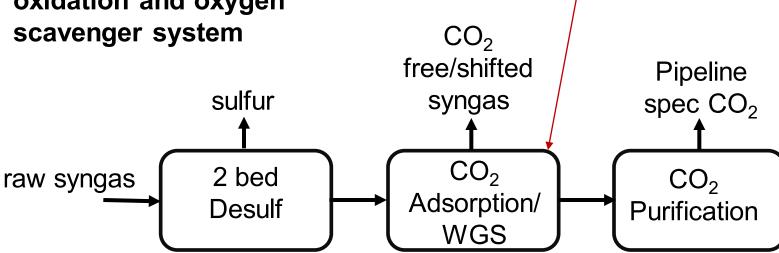
- Following repurposing of the Wabash
 River IGCC plant and decommissioning of
 PSDF at NCCC, we identified Praxair R&D
 Center (Tonawanda, NY) as a test site
 - Integrated with OTM on natural gas
- Two test campaigns were completed at Praxair

- An overall CO conversion >98% was achieved
- By coupling the WGS with the CO₂ 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

Integrated WGS/CO₂ Field Test System

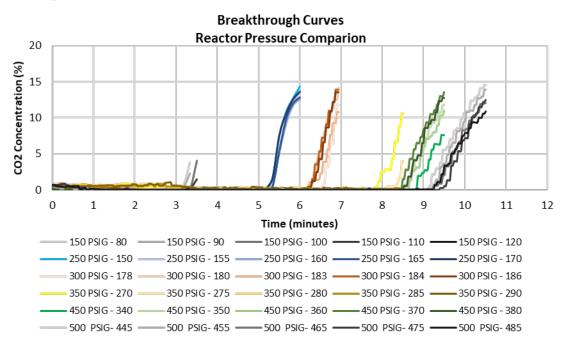
- Regenerable sulfur sorbent skid will be upstream of the other two skids to desulfurize the syngas
- CO₂ PSA will shift the CO and selectively remove CO₂
- CO₂ from the PSA will be purified using TDA's catalytic oxidation and oxygen scavenger system

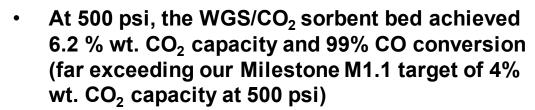




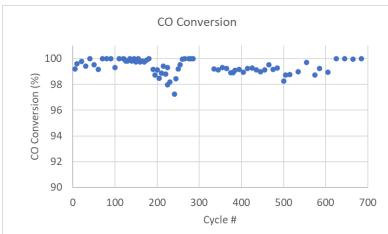


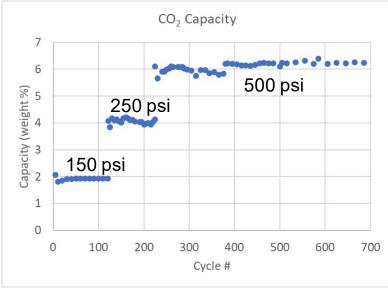
CO₂ Sorbent/WGS Catalyst Multiple Cycle Tests





- We completed over 700 adsorption/ desorption cycles with the integrated WGS/CO₂ capture bed
- Previously we had demonstrated life over 32,000 cycles with stable performance







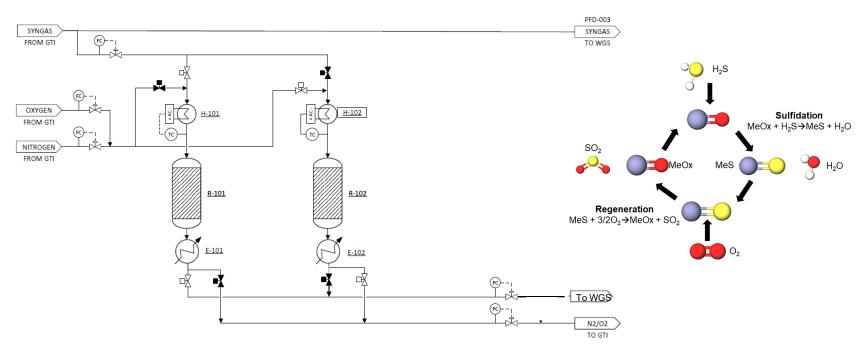
CO₂ Sorbent/WGS Catalyst Test System

- We replaced the sorbent/WGS catalyst in all 8 beds
- Utilized a new sorbent/spring retention system to help stabilize the sorbent and prevent movement

 System was powered up and ready for testing



Design of Regenerable Sulfur Sorbent System



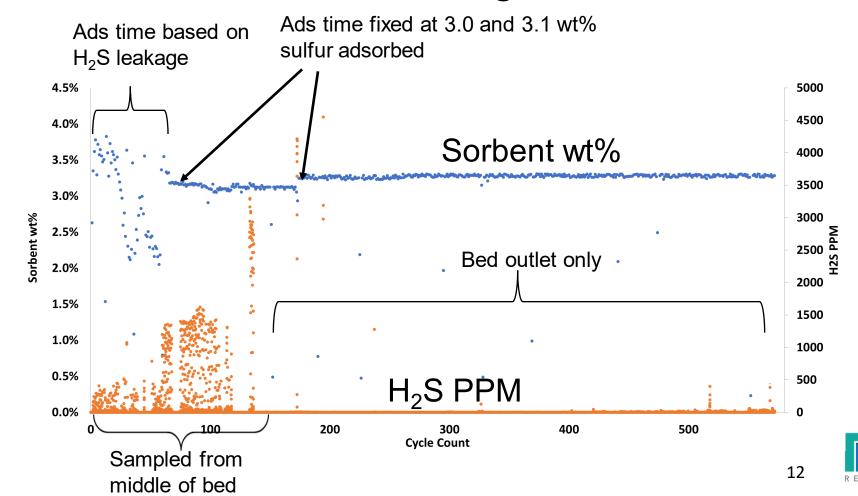
2 bed system

- One is adsorbing while the other is regenerating
- H₂S is removed during adsorption by reacting with metal oxides to form metal sulfides
- Regeneration occurs by reacting O₂ with metal sulfides to form SO₂
- Electric heaters on inlet gas to achieve required adsorption and regeneration operating temperatures
- Deliver a constant stream of desulfurized syngas to the integrated CO₂/WGS system



Manufacturing and Qualification of the Regenerable Sulfur Sorbent

- Completed over 500 adsorption/regeneration cycles
- 3.0 wt% was maintained throughout the test



Regenerable Sulfur Sorbent Test System

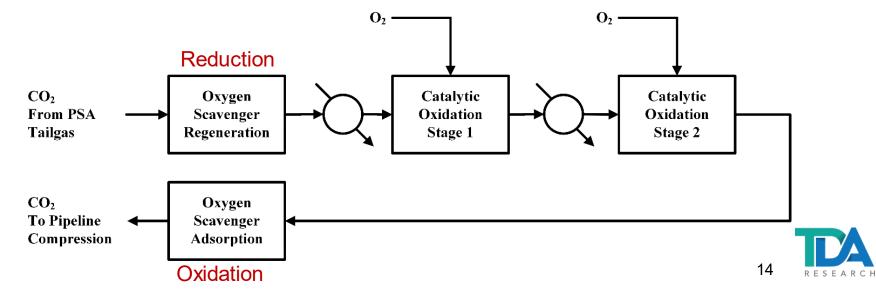
- Dual bed regenerable sulfur sorbent system is currently being lab tested as part of FAT
- Sulfur removal will be measured using a lead acetate tape analyzer





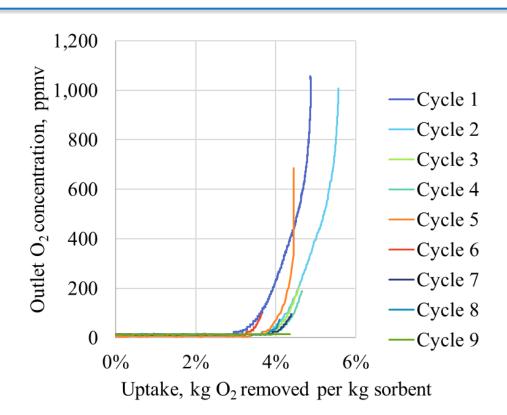
Design of CO₂ Purification System

- CO₂ purification skid includes a catalytic oxidizer with a REDOX based oxygen scavenger to meet the CO₂ purity requirements
- Catalytic Oxidation removes hydrocarbons and other combustibles (e.g., CO, CH₄, H₂)
 - Operates at slightest excess stoichiometric amounts of oxygen
 - Adiabatic, multi-staged design with intercoolers for heat management
- Oxygen Scavenging system polishes excess O₂ to < 10 ppm
 - Regenerable mixed metal oxide based chemical looping process
 - Oxidation step captures O₂; Reduction with inlet gas regenerates the sorbent
 - Oxygen sorbent will be regenerated using the H₂ in incoming CO₂



TDA's O₂ Scavenger Sorbent

- The oxygen scavenger was tested for nine cycles verifying consistent breakthrough capacity at <10 ppmv O₂ in the outlet
- Tested the effect of regen temperature, residence time, inlet oxygen concentration, presence of CO
- Uptake is 3.8%-w O₂ with a breakthrough time of 6.2 hours



Oxygen Sorbent Design Conditions				
GHSV, 1/hr	3,000 - 6,300			
Inlet O ₂ , ppmv	1,000 – 4,000			
Inlet Temp, deg C	400 - 450			
Bed L/D	2.7			



CO₂ Purification Test System

- System is currently being lab tested before shipment to GTI
- Trace O₂ in the CO2 product stream will be measured using an electrochemical analyzer





Testing Schedule

 We will be shipping the test systems in mid August to GTI is Des Plaines IL for testing using biomass derived syngas



 Testing is scheduled to start the beginning of September



Process Design and System Analysis with Poly-generation Options

DOE Baseline Rev. 4 Study Basis

\$2018 basis

				Mean over
Operating Scenario	Max Power	Mid Power	Min Power	24 hr day
Operating Scenario as Fraction of 24 hr day	0.25	0.5	0.25	
Power Block Power as Fraction of Max Power	1.00	0.80	0.65	
Increase in CC Heat Rate over Max Power Scenario, Factor	0	0.04	0.1	
GROSS POWER GENERATED (AT GENERATOR TERMINALS),				
GAS TURBINE POWER	88,000	70,400	57,200	71,500
STEAM TURBINE POWER	66,657	53,326	43,327	54,159
SYNGAS EXPANDER POWER	1,644	1,315	1,069	1,336
CO2 VENT EXPANDER	-	-	-	-
TOTAL POWER	156,301	125,041	101,596	126,995
AUXILIARY LOAD SUMMARY, kWe				
TOTAL AUXIIARIES	73,763	75,520	76,693	75,374
NET POWER, kWe	82,538	49,521	24,903	51,621
COPRODUCT (NH ₃)				
ST/D	959	1,096	1,191	1,085
TONNE/D	869	994	1,080	984
TOTAL (ELECTRIC + COPRODUCT) ENERGY, kW	308,866	308,214	306,135	307,857
ELECTRICITY / COPRODUCT ENERGY RATIO	0.365	0.191	0.089	0.201
NET PLANT EFFICACY, % HHV	47	47	47	47
THERMAL INPUT, kWt HHV	652,542	652,542	652,542	652,542
CARBON CAPTURED, %	95.8	95.8	95.8	95.8

Electricity Credit	\$/MWh	64.5	71.7	78.9	107.2	152.3
NH3 RSP with CO ₂ T&S	\$/ST	884	870	855	798	708



Acknowledgements

- NETL, Project Managers, Andrew Jones, Dr. Elliot Roth, Dr. Nicole Shamitko-Klingensmith (current)
- Zach El Zahab, GTI
- Dr. Ashok Rao

Disclaimer: "This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof."