# A High Efficiency, Modular Pre-combustion Capture System for 21st Century Power Plant Polygeneration Process

## primary project goal

The overall project goal is to develop a novel, modular pre-combustion carbon capture technology platform that integrates the water-gas-shift (WGS) reaction with a physical adsorbent to eliminate carbon dioxide ($CO_2$) emissions, coupled with a sulfur removal process, for a coal-based polygeneration system (i.e., co-production of power and chemicals) with increased efficiency and lower cost.

## technical goals

- Achieve WGS/$CO_2$ sorbent bed $CO_2$ capacity of 4 wt.% to enable an overall carbon monoxide (CO) conversion greater than 98%.
- Develop and build a test unit for integrated WGS and $CO_2$ adsorption with a capacity of 10 standard cubic feet per minute (SCFM) of raw syngas from coal gasification.
- Capture $CO_2$ at 90+% with $CO_2$ purified via an integrated purification subsystem to 95+%.
- Enable desulfurization via a sulfur sorbent with stable working capacity in excess of 3 wt.% hydrogen sulfide ($H_2S$) and not more than 10% reduction in capacity over 200 cycles, assuming syngas with inlet sulfur in the 500–1,000 parts per million (ppm) range.
- Develop a techno-economic analysis (TEA) showing that the polygeneration system can capture $CO_2$ at $35/tonne or lower while meeting the above $CO_2$ purity and capture targets.

## technical content

Syngas produced by gasification contains mostly hydrogen ($H_2$), CO, and $CO_2$. In order to affect a high degree of carbon capture, it is necessary to add steam to the syngas and react it with the CO via WGS to convert the CO to more $H_2$ and $CO_2$. Carbon dioxide is extracted from the shifted syngas, leaving mostly $H_2$, useful for multiple applications, including decarbonized power generation, transportation fuel, chemical synthesis (e.g., ammonia), and fuels synthesis. Conventionally, a multistage WGS process with interstage cooling is required to attain substantial syngas conversion because WGS is an equilibrium-limited, exothermic reaction. The conventional multistage WGS process scheme is depicted in Figure 1. Although such WGS units can completely shift the CO to $CO_2$, they incur significant capital equipment and process cost, including a significant excess steam demand to suppress carbon formation on the WGS catalyst and help drive the WGS reaction to completion.

program area:
Point Source Carbon Capture

ending scale:
Small Pilot

application:
Pre-Combustion Power Generation PSC

key technology:
Sorbents

project focus:
Integrated PSA-WGS with Coal Syngas

participant:
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predecessor projects:
N/A

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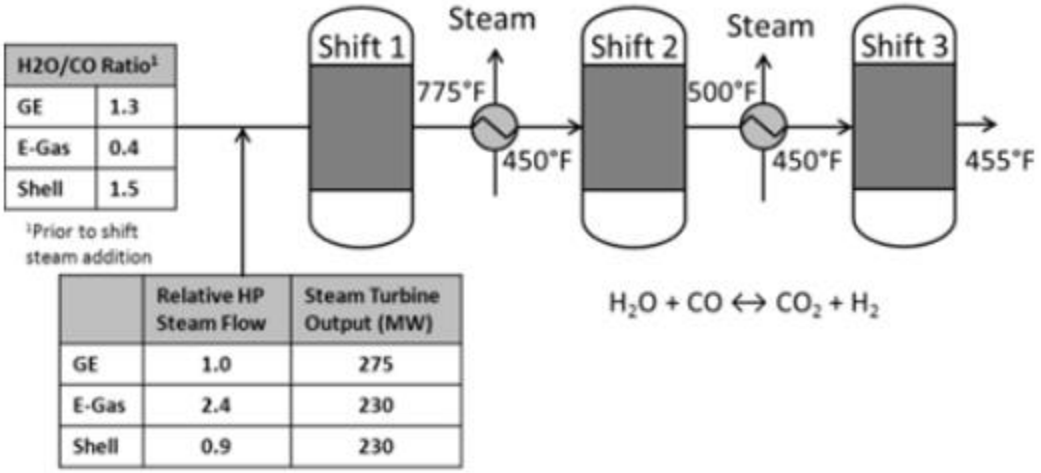

| H2O/CO Ratio[1] | |
|---|---|
| GE | 1.3 |
| E-Gas | 0.4 |
| Shell | 1.5 |

[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 |

Figure 1: Three-stage, conventional WGS unit.

TDA's process approach seeks to achieve high CO conversion at low steam-to-CO ratios by combining, in the same bed, the WGS catalyst with a $CO_2$ sorbent capable of withstanding the temperatures experienced in a low-temperature WGS reactor as it selectively removes $CO_2$ from the syngas above the dew point of the gas. The proprietary sorbent consists of a mesoporous carbon grafted with surface functional groups that remove $CO_2$ via an acid-base interaction. The combination of the WGS and $CO_2$ removal improves the overall power cycle efficiency by reducing the amount of water needed for the WGS. TDA's overall process is depicted in Figure 2. Note that a high-temperature WGS reactor is followed by a single integrated low-temperature shift and $CO_2$ removal unit with the combined WGS catalyst and sorbent. Essentially, the conventional three-stage WGS with downstream $CO_2$ capture (four steps) is replaced with a two-stage WGS, with the second stage adding integrated $CO_2$ capture. This represents a significant degree of process intensification by reducing WGS stages and combining $CO_2$ capture in one of those stages.

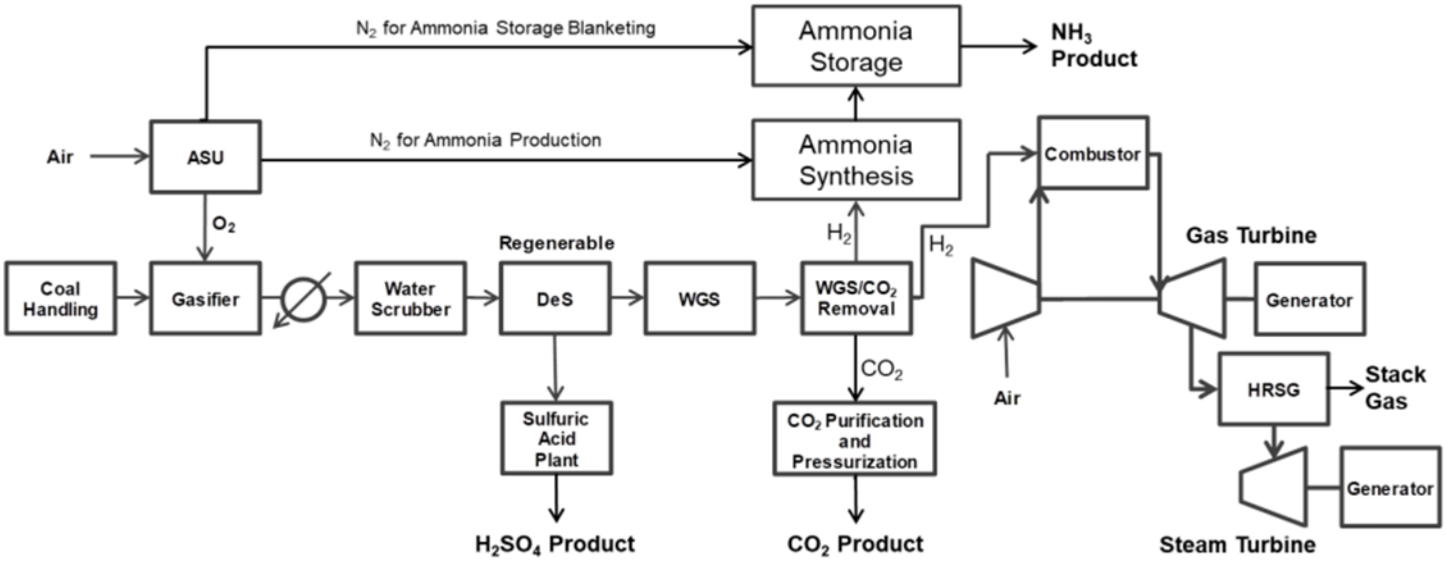

Figure 2: TDA polygeneration process concept.

The process is also integrated with a simplified fixed-bed temperature swing adsorption-based warm gas desulfurization system upstream of the WGS (using a desulfurization sorbent previously developed with the assistance of U.S. Department of Energy [DOE] funding) and contaminant removal technologies (for hydrogen cyanide [HCN] and trace metals such as silver [As], mercury [Hg], and selenium [Se]). This will ensure robust protection of the catalysts used in downstream chemical synthesis processes while maintaining the water content of the gas to achieve high efficiency in polygeneration schemes. In the present process concept, ammonia synthesis from hydrogen produced is assumed as a polygeneration pair to decarbonized power generation using the hydrogen, here consisting of a typical combined cycle with gas turbine topping and steam turbine bottoming cycle. The process also includes a catalytic $CO_2$ purification process essential to attain $CO_2$ product purity requirements (residual CO and oxygen [$O_2$] in the $CO_2$ product must be reduced to very low levels for utilization in enhanced oil recovery [EOR] application).

Figure 3 depicts the combined WGS and $CO_2$ adsorber reactor column that has been demonstrated at bench scale. The basic engineering deployed in the column is diagrammed.

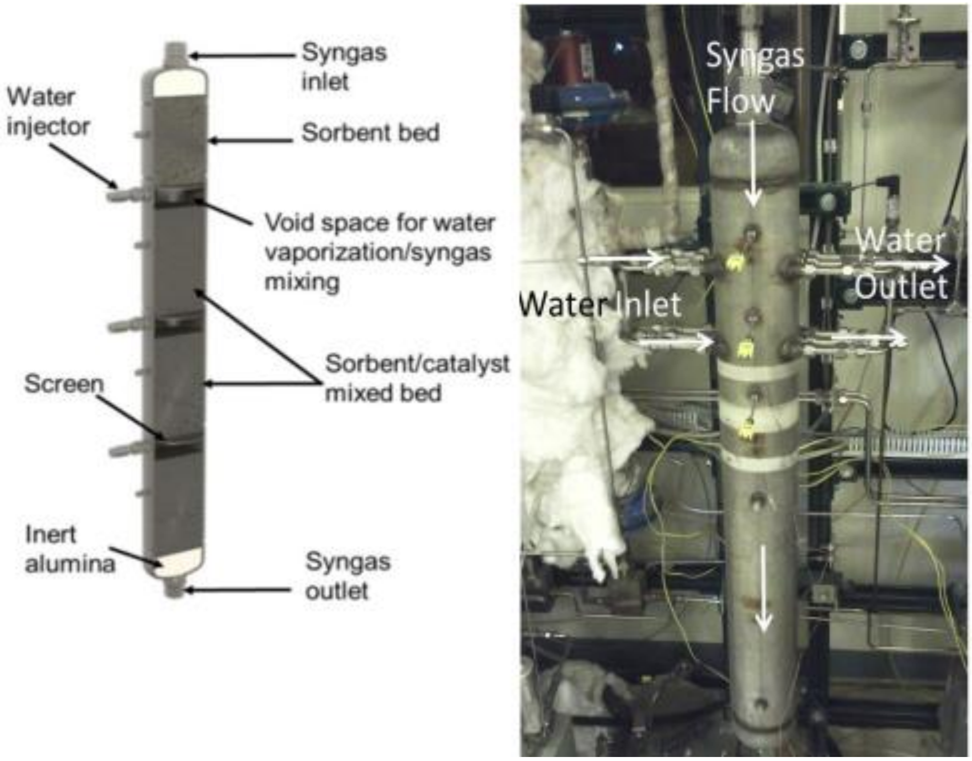

Figure 3: Bench-scale WGS and $CO_2$ adsorption column.

Combining WGS catalyst and $CO_2$ sorbent in the same column creates challenges in the form of proper heat management and temperature control. Uniform temperature without hot or cold spots is required for both optimal WGS conversion of the CO in the syngas and $CO_2$ removal from the syngas. TDA found that advanced heat management based on direct water injection greatly improves temperature control, and that optimal temperature rise occurs when the WGS catalyst is distributed into two layers with water injections before each layer. This is depicted in Figure 4; the top image of Figure 4 shows large, unfavorable temperature variations in a reactor column not employing water injection, while the bottom image of the figure shows excellent temperature uniformity and control attained with staged water injection and two-layer WGS catalyst distribution.

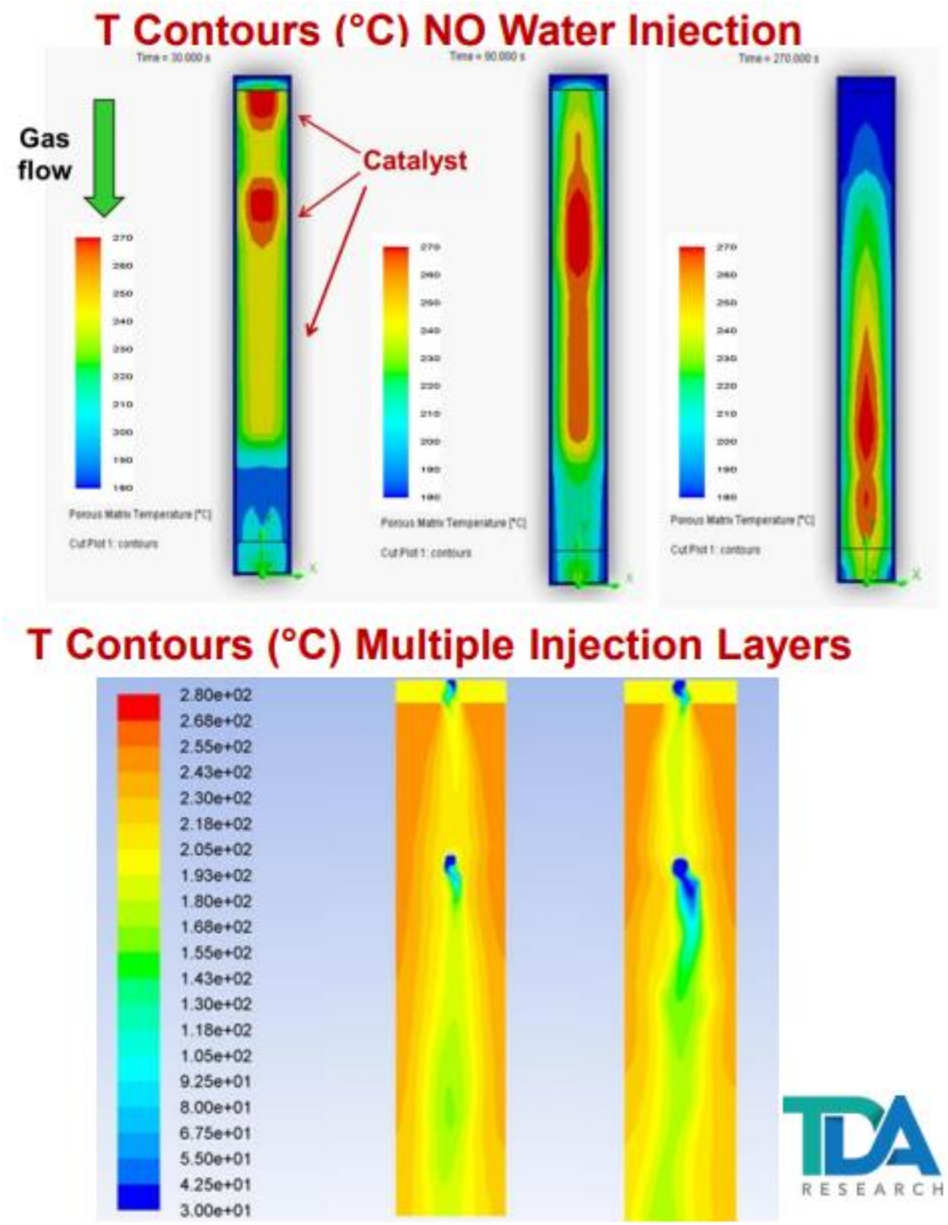

Figure 4: Heat-integrated WGS and $CO_2$ capture.

The integrated WGS and $CO_2$ capture system uses multiple columns that switch operating modes between adsorption and regeneration of the $CO_2$ sorbent. Pressure is high for adsorption (up to 500 pounds per square inch gauge [psig]) and low for regeneration (50–65 psig), constituting the $CO_2$ removal as a pressure swing adsorption (PSA) cycle. The alternating modes are obviously required for operation of the $CO_2$ sorbent, not the WGS catalyst, which raises the question of whether the pressure cycling has any adverse effect on the WGS catalyst. TDA completed 32,000 cycles of the combined WGS catalyst and sorbent and determined that catalytic activity of the WGS catalyst was unaffected. Temperature is relatively isothermal (200–215°C), which is ideal for sorbent performance. In quantifying sorbent performance, TDA determined heat of adsorption at 5–7 kcal/mol and measured $CO_2$ capacities as a function of pressure, as shown in Figure 5. TDA's target for capacity was 4 wt.% $CO_2$ at 500 psi; this was well exceeded with 6.2 wt.% achieved at that pressure.

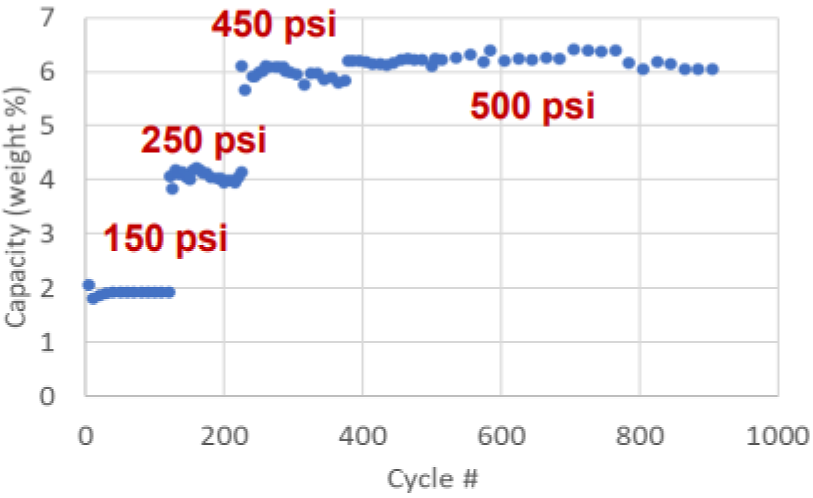

Figure 5: TDA capture sorbent $CO_2$ capacity.

The offgas from regeneration of the combined WGS and $CO_2$ sorbent columns is high in $CO_2$ but does contain $H_2$, methane ($CH_4$), and CO as minor constituents, which must be removed or converted to achieve pipeline quality, consistent with typical use of the product $CO_2$ in EOR. Accordingly, a $CO_2$ purification subsystem is necessary. The subsystem process is depicted in Figure 6. It uses oxygen (sourced from the main air-separation unit [ASU] associated with the gasifier) in a catalytic oxidizer, and excess oxygen downstream of the catalytic oxidation step is dealt with by leveraging trace oxygen removal sorbents previously developed for removing residual oxygen from oxy-combustion processes (refer to National Energy Technology Laboratory [NETL] project FE0029090).

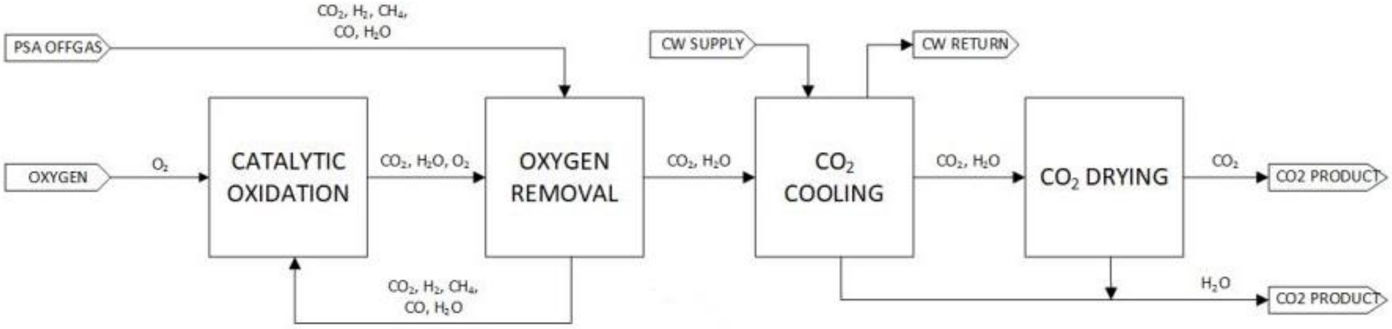

Figure 6: $CO_2$ purification subsystem.

TDA is currently developing a test unit designed to treat 10 SCFM of actual syngas flow. This will deploy eight sorbent beds and two accumulator tanks. The test unit will contain three sub-assemblies/skids: (1) integrated WGS and $CO_2$ separation skid with the new column/reactor design, (2) a regenerable warm gas desulfurization gas processing skid, and (3) a $CO_2$ purification skid. It is planned that testing will occur at partner GTI's pilot gasifier test site, using real syngas generated by either the fluidized bed U-GAS® gasifier or the R-GAS™ gasifier pilots that GTI has onsite.

Figure 7: Eight-column integrated WGS and $CO_2$ capture unit.

## TABLE 1: SORBENT PROCESS PARAMETERS

| **Sorbent** | Units | Current R&D Value | Target R&D Value |
|---|---|---|---|
| True Density @ STP | $kg/m^3$ | 1,314 | 1,314 |
| Bulk Density | $kg/m^3$ | 620 | 620 |
| Average Particle Diameter | mm | 0.42–1.68 | 0.42–1.68 |
| Particle Void Fraction | $m^3/m^3$ | 0.368 | 0.368 |
| Packing Density | $m^2/m^3$ | 4.59E+08 | 4.59E+08 |
| Solid Heat Capacity @ STP | kJ/kg-K | 0.93 | 0.93 |
| Crush Strength | $kg_f$ | 3 | 3 |
| Manufacturing Cost for Sorbent | $/kg | 3.88 | 3.88 |
| **Adsorption** | | | |
| Pressure | bar | 33.8 | 33.8 |
| Temperature | °C | 198 | 198 |
| Equilibrium Loading | g mol $CO_2$/kg | 1.04 | 1.04 |
| | g mol $CO_2/m^3$ | 645 | 645 |
| Heat of Desorption | kJ/mol $CO_2$ | -28.5 | -28.5 |
| **Desorption** | | | |
| Pressure | bar | 10 | 10 |
| Temperature | °C | 195.5 | 195.5 |
| Equilibrium $CO_2$ Loading | g mol $CO_2$/kg | 0.005 | 0.005 |
| | g mol $CO_2/m^3$ | 3.22 | 3.22 |
| Heat of Desorption | kJ/mol $CO_2$ | 28.5 | 28.5 |
| **Proposed Module Design** | | *(for equipment developers)* | |
| Flow Arrangement/Operation | — | radial-flow fixed bed/cyclic | |
| Syngas Flowrate | kg/hr | 668,083 | |
| $CO_2$ Recovery, Purity, and Pressure$^+$ | %/%/bar | 90.0% 96.0% 10 | |
| Adsorber Pressure Drop | bar | 1.41 | |
| Estimated Absorber/Stripper Cost of Manufacturing and Installation | $\frac{\$}{kg/hr}$ | 212.8 | |

$^+$ $CO_2$ is recovered at 10 bar from TDA's $CO_2$ capture system, which is further purified and compressed to 152.7 bar with a final $CO_2$ purity of 99.96%.

**Definitions:**

***STP*** – Standard temperature and pressure (15°C, 1 atm).

***Sorbent*** – Adsorbate-free (i.e., $CO_2$-free) and dry material as used in adsorption/desorption cycle.

***Manufacturing Cost for Sorbent*** – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

***Adsorption*** – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column.

***Desorption*** – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process dependent. Measured data at other conditions are preferable to estimated data.

***Pressure*** – The pressure of $CO_2$ in equilibrium with the sorbent. If the vapor phase is pure $CO_2$, this is the total pressure; if it is a mixture of gases, this is the partial pressure of $CO_2$.

***Packing Density*** – Ratio of the active sorbent area to the bulk sorbent volume.

***Loading*** – The basis for $CO_2$ loadings is mass of dry, adsorbate-free sorbent.

***Flow Arrangement/Operation*** – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either continuous, cyclic, or semi-regenerative operation.

***Estimated Cost*** – Basis is kg/hr of $CO_2$ in $CO_2$-rich product gas; assuming targets are met.

**Other Parameter Descriptions:**

***Chemical/Physical Sorbent Mechanism*** – Surface functionalized mesoporous carbon removing $CO_2$ via weak interactions similar to physical adsorption at temperatures above the dew point of the syngas.

***Sorbent Contaminant Resistance*** – The sorbent is highly resistant to contaminants such as $H_2S$, carbonyl sulfide (COS), ammonia ($NH_3$) and trace metals such as mercury (Hg), arsenic (As), etc. If needed, additional functionalities can be incorporated into the sorbent to remove these contaminants simultaneously with $CO_2$. Results of 707-hour-long testing with coal-derived syngas with the 0.1-MWe pilot unit at the NCCC in Wilsonville, Alabama, showed excellent resistance to contaminants that could be present in syngas.

***Sorbent Attrition and Thermal/Hydrothermal Stability*** – The sorbent has good thermal/hydrothermal stability; it is stable in nitrogen up to 900°C and in steam stable up to 400°C. The attrition index for the sorbent is estimated to be 0.1% loss per 1,000 hours of operation.

***Syngas Pretreatment Requirements*** – Syngas sulfur content needs to be reduced to less than 100 parts per million (ppm) before WGS and $CO_2$ removal.

***Sorbent Make-Up Requirements*** – The expected life of the sorbent is five years. The annualized sorbent make-up requirement is expected to be 261.5 tonnes on the 550-MWe process plant basis.

***Waste Streams Generated*** – Condensate from cooling the raw $CO_2$ stream.

***Process Design Concept*** – See Figure 2.

***Proposed Module Integration*** – TDA's combined WGS and $CO_2$ removal module is located downstream of the syngas desulfurization unit as shown in Figure 2; syngas composition and conditions entering module are as follows:

| | | Composition | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Pressure | Temperature | vol% | | | | | | ppmv |
| psia | °F | $CO_2$ | CO | $CH_4$ | $N_2$ | $H_2$ | $H_2O$ | $H_2S$ |
| 722.2 | 388.4 | 28.30 | 8.16 | 0.10 | 0.54 | 44.76 | 17.46 | <10 |

## TABLE 2: INDUSTRIAL PLANT CARBON CAPTURE ECONOMICS

| Economic Values | Units | Current R&D Value | Target R&D Value |
|---|---|---|---|
| Cost of Carbon Captured | \$/tonne $CO_2$ | 28.1 | 35.0 |
| Cost of Carbon Avoided | \$/tonne $CO_2$ | 69.9 | 70.0 |
| Capital Expenditures | \$/tonne $CO_2$ | 13.7 | 15.0 |
| Operating Expenditures | \$/tonne $CO_2$ | 14.4 | 20.0 |

**Definitions:**

***Cost of Carbon Captured*** – Projected cost of capture per mass of $CO_2$ captured under expected operating conditions.

***Cost of Carbon Avoided*** – Projected cost of capture per mass of $CO_2$ avoided under expected operating conditions.

***Capital Expenditures*** – Projected capital expenditures in dollars per tonne of $CO_2$ captured.

***Operating Expenditures*** – Projected operating expenditures in dollars per tonne of $CO_2$ captured.

***Calculations Basis*** – The TEA numbers provided in the Table for both current and target values are all based on Rev. 2a DOE Baseline Study. Capital expenditures are \$ per tonne $CO_2$ captured, based on the recommended capacity charge factor of 0.124 in Rev. 2a DOE Baseline Study.

***Scale of Validation of Technology Used in TEA*** – The numbers were from modeling data that was validated from pilot-scale testing.

## technology advantages

- Warm gas removal of $CO_2$, sulfur, and contaminants improves process efficiency.
- Reducing the use of excess steam improves power cycle efficiency by lowering parasitic energy requirements for the process.
- Process intensification should reduce the number of hardware components and their cost.

## R&D challenges

- Integrated WGS and $CO_2$ adsorption results in higher temperatures as heat from the exothermic WGS reaction accumulates in the beds—this makes $CO_2$ capture more difficult.
- Achieving more uniform cooling of the WGS and $CO_2$ adsorption bed without having hot or cold spots.
- Need for modular warm gas sulfur removal technologies.

## status

TDA finished detailed design of the integrated WGS and $CO_2$ removal skid, $CO_2$ purification skid, and regenerable sulfur skid, and performed various tests of the $CO_2$ purification catalyst and regenerable sulfur sorbent. The preliminary TEA shows favorable polygeneration plant efficiencies for combined electricity and ammonia production.

## available reports/technical papers/presentations

"A High Efficiency, Modular Pre-combustion Capture System for CoalFIRST Poly-generation Process," Project Kickoff Presentation, November 3, 2020. *https://www.netl.doe.gov/projects/plp-download.aspx?id=11001&filename=A+High+Efficiency%2c+Modular+Pre-combustion+Capture+System+for+CoalFIRST+Poly-generation+Process.pdf*

"A High Efficiency, Modular Pre-Combustion Capture System for CoalFIRST Poly-generation Process," presented by Gokhan Alptekin and Ambalavanan Jayaraman, TDA Research Inc., 2021 NETL Carbon Management Research Project Review Meeting, August 13, 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Alptekin_cap.pdf*