Integrated Water-Gas-Shift Pre-Combustion Carbon Capture Process (Contract No. DE-FE0023684)

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2020 Gasification Systems Project Review

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Project Objectives

• The project objective is to demonstrate techno-economic viability of an integrated WGS catalyst/CO₂ removal system for IGCC power plants and CTL plants
  • A high temperature PSA adsorbent is used for CO₂ removal above the dew point of the synthesis gas
  • A commercial low temperature catalyst is used for water-gas-shift
  • An effective heat management system is developed

• Project Tasks
  • Design a fully-equipped slipstream test unit with 10 SCFM raw synthesis gas treatment capacity
  • Design and fabricate CFD optimized reactors capable of managing the WGS exotherm while maintaining energy efficiency
  • Demonstrate critical design parameters including sorbent capacity, CO₂ removal efficiency, extent of WGS conversion as well as H₂ recovery using coal synthesis gas
  • Complete a high fidelity process design and economic analysis
Project Partners

Project Duration
- Start Date = October 1, 2014
- End Date = September 30, 2021

Budget
- Project Cost = $5,632,619
- DOE Share = $4,506,719
- TDA and its partners = $1,125,900
TDA’s Approach

• Conventional IGCC plants use multi-stage WGS with inter-stage cooling
  • 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

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 at low steam:carbon ratios
• Reduced water addition increases process efficiency
TDA’s Sorbent

- TDA’s uses a mesoporous carbon with surface functional groups that remove 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
  - Pore size is tuned to 10 to 100 Å
  - Mesopores eliminates diffusion limitations

US Pat. Appl. 61790193, Alptekin, Jayaraman, Copeland “Pre-combustion CO$_2$ Capture System Using a Regenerable Sorbent"
Operating Conditions

- CO₂ is recovered via combined pressure & concentration swing
  - CO₂ recovery at ~150 psia reduces energy need for CO₂ compression
  - Small steam purge ensures high product purity
- Isothermal operation eliminates heat/cool transitions
  - Rapid cycles reduces cycle time and increases sorbent utilization
- Similar PSA systems are used in commercial H₂ plants and air separation plants
- The WGS catalyst was subjected to the same cycle

Source: Honeywell/UOP
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

**Sorbent’s point of view:**
• Less dilution with water increases CO$_2$ partial pressure and in turn improves sorbent’s working capacity
Application of the Technology to CTL
Sorbent Development Work

- 0.1 MW<sub>e</sub> test in a world class IGCC plant to demonstrate full benefits of the technology
  - Field Test #1 at NCCC
  - Field Test #2 at Sinopec Yangtzi Petro-chemical Plant, Nanjing, Jiangsu Province, China
- Full operation scheme
  - 8 reactors and all accumulators
  - Utilize product/inert gas purges
  - H<sub>2</sub> recovery/CO<sub>2</sub> purity
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
Technology Status/R&D Needs

- Sorbent is developed under a separate DOE project (DE-FE0000469)
- WGS catalyst is commercially available mature technology
- Early-stage concept demonstration has already been completed (DE-FE0007966 and DE-FE0012048)
  - Integrated sorbent/catalyst operation
  - Pointed out the need to incorporate effective heat management
  - Implemented the heat management scheme in a 4-bed PSA system using coal derived synthesis gas at 1 kg/hr CO₂ removal
- Key R&D need is the design/development of a high fidelity prototype to fully demonstrate the concept using actual coal-derived synthesis gas
  - Reactor design to address the heat management needs
  - A 10 kg/hr CO₂ removal is being developed
  - Testing of the high fidelity system will be carried out at Praxair
• Heat generated during adsorption is removed during regeneration
  • Near isothermal operation through the cycle
Heat Wave WGS & CO₂ Capture

- Integrated WGS & CO₂ capture results in higher $\Delta T$
- Not ideal for CO₂ capture (the WGS heat accumulates in the beds)
Conventional Heat Management Options

10 kg/hr CO₂ Removal Pilot Test System – 6” reactors

- Cooling Jacket
- Immersed Tube (1)
- Immersed Tubes (3)
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)
- 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
Bench-Scale Evaluations

- 8L reactors were modified with water injectors
- Successful proof-of-concept demonstrations have been completed
- $\Delta T < 10^\circ$C was maintained over extended cycling (much lower than those in early field tests)
We completed 32,000 cycles showing stable performance for the WGS catalyst and CO₂ sorbent.

**Test Conditions:**
- Adsorb: 45-50% H₂, 30% CO₂, 7% H₂O, 4-6% CO, Balance N₂
- T: 200-215°C, P: 150-300 psig
- Regen: 25% H₂O, Balance N₂
- T: 200-215°C, P: 50-65 psig

Adsorption Pressure
300 psig

Adsorption Pressure
150 psig
• By evaluating continuous 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
Fabrication of the Prototype
Installation at Praxair

• Fabrication of the Prototype unit was completed in 2018 Q2 and installation at Praxair R&D Center (Tonawanda, NY) was completed in 2018 Q3

• First campaign is completed in Q2 2019
Control of Water Injection

- We demonstrated that precise amounts of water can be injected and their individual flow rates can be controlled within tolerances of less than 0.5 g/min between injectors.
Temperature Management via Water Injection

- We observed an increase in bed temperature by increasing the inlet steam:CO from 1 to 2
- Bed temperature was maintained at ~40°C lower when injecting the same amount water directly into the beds
Impact of Water Injection

- An overall CO conversion >98% was achieved
- Cycle times were not yet optimized in this run therefore carbon capture was only at 60% (incoming CO$_2$ + CO$_2$ from shifted CO$_2$)
- Optimization was planned for the test scheduled for the next campaign
Effect on Equilibrium Conversion

- By coupling the WGS with the 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.
Integration with E-Gas™ Gasifier

<table>
<thead>
<tr>
<th>Gasifier Type/Make</th>
<th>E-Gas</th>
<th>E-Gas</th>
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</thead>
<tbody>
<tr>
<td>Case</td>
<td>1</td>
<td>2</td>
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<tr>
<td>CO₂ Capture Technology</td>
<td>Cold Gas Cleanup</td>
<td>Warm Gas Cleanup</td>
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<tr>
<td></td>
<td>Selexol™</td>
<td>TDA's CO₂ Sorbent</td>
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<tr>
<td>CO₂ Capture, %</td>
<td>90</td>
<td>90</td>
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<tr>
<td>Gross Power Generated, kW</td>
<td>710,789</td>
<td>670,056</td>
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<tr>
<td>Gas Turbine Power</td>
<td>464,000</td>
<td>425,605</td>
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<td>Steam Turbine Power</td>
<td>246,789</td>
<td>244,450</td>
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<td>Syngas Expander Power</td>
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<td>Auxiliary Load, kW</td>
<td>194,473</td>
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<tr>
<td>Net Power, kW</td>
<td>516,316</td>
<td>545,917</td>
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<tr>
<td>Net Plant Efficiency, % HHV</td>
<td>31.0</td>
<td>34.1</td>
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<tr>
<td>Coal Feed Rate, kg/h</td>
<td>220,549</td>
<td>212,265</td>
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<td>Raw Water Usage, GPM/MW</td>
<td>10.9</td>
<td>10.3</td>
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<tr>
<td>Total Plant Cost, $/kW</td>
<td>3,464</td>
<td>3,042</td>
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<tr>
<td>COE without CO₂ TS&amp;M, $/MWh</td>
<td>136.8</td>
<td>120.5</td>
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<td>COE with CO₂ TS&amp;M, $/MWh</td>
<td>145.7</td>
<td>128.6</td>
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<tr>
<td>Cost of CO₂ Captured, $/tonne</td>
<td>53.2</td>
<td>37.4</td>
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</tbody>
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- IGCC plant efficiency is estimated as 34.7% with TDA's WGS/CO₂ system
- Cost of CO₂ capture is estimated as less than $26/tonne (including TS&M less than $35.8/tonne)
Integrated WGS with CO₂ capture reduced the required selling price for Naphtha to $100 per bbl compared to $107 per bbl for a CTL plant with Rectisol.

Integrated WGS with CO₂ capture reduced the required selling price for Diesel to $143 per bbl compared to $153 per bbl for a CTL plant with Rectisol.
Acknowledgement

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