APPENDIX B: CARBON DIOXIDE CAPTURE TECHNOLOGY SHEETS

PRE-COMBUSTION SORBENTS

EVALUATION OF DRY SORBENT TECHNOLOGY FOR PRE-COMBUSTION CO_2 CAPTURE

Primary Project Goals

URS Group is developing dry carbon dioxide (CO_2) sorbent materials, through the coupling of thermodynamic, molecular simulation, and process simulation modeling with novel synthesis methods, that possess superior adsorption and regeneration properties at conditions applicable to water gas shift (WGS) systems. If successful, this project will demonstrate that one or more sorbent materials are able to remove greater than 90% of the CO_2 from a simulated synthesis gas (syngas) at conditions applicable to a WGS reactor, thus meeting a key DOE program objective. Furthermore, a successful project will demonstrate through a detailed techno-economic analysis that DOE COE cost objectives can be met with sorption-enhanced WGS (SEWGS) technology through the development of effective sorbents with superior adsorption-regeneration properties, appropriate reactor design and integration, resulting process enhancements to the WGS reaction (associated with lower steam requirements), and expected future process improvements to integrated gasification combined capture (IGCC) technology. Successful demonstration of DOE performance and cost objectives will validate the feasibility of subsequent scale-up prototype testing of the SEWGS technology.

Technical Goals

This program meets the programmatic objectives established by DOE by targeting novel sorbents that will achieve greater than 90% CO_2 removal from simulated syngas at conditions applicable to WGS reactors. A novel approach will integrate the use of multiple computational models with sorbent synthesis and characterization activities to develop sorbents with optimal CO_2 removal properties at high temperatures and pressures applicable to WGS applications. Tests will be performed in alignment with DOE experimental objectives, where sorbent performance is evaluated in simulated WGS gas mixtures at commercially relevant conditions. Appropriate data reduction and analysis will be conducted in order to provide suitable data that will provide the basis for a techno-economic analysis to evaluate the feasibility and scale-up potential of the SEWGS technology.

Specific technical objectives of this project include:

- Determination of optimal CO_2 sorbent properties and operating conditions for CO_2 removal and regeneration and carbon monoxide (CO) conversion in simulated syngas using a combination of computational and experimental methods.
- Development of one or more sorbents that recover high-quality heat during CO_2 adsorption, regenerate at elevated pressure, have minimal deactivation over multiple cycles, have high selectivity at high temperatures, have high adsorption capacity, and have acceptable thermal stability and mechanical integrity. This will result in sorbents capable of 90% CO_2 removal with high loading capacities and able to operate at the high temperatures and pressures typically encountered upstream of a WGS reactor. If successful, the sorbents developed in this program will augment or replace the CO conversion catalysts currently used in WGS reactors and improve overall WGS thermal efficiency.
- Determine the techno-economic feasibility of the SEWGS process for removing CO_2.

Project objectives will be achieved through the execution of five primary tasks: Project Management and Planning; Sorbent Engineering Analysis and Selection; Sorbent Preparation; Sorbent Evaluation Testing; and Engineering Feasibility Study.

Technology Maturity:

Bench-scale using simulated syngas

Project Focus:

Sorbent-Enhanced Water Gas Shift

Participant:

URS Group

Project Number:

FE0000465

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Partners:

Illinois Clean Coal Institute
University of Illinois at Urbana-Champaign (UIUC)

Performance Period:

1/1/10 – 3/31/13

Technical Content

URS Group, Inc. is leading an investigative effort for the development of a dry sorbent process configured to combine the WGS reaction with CO_2 removal for coal gasification systems. The result will be a SEWGS technology.

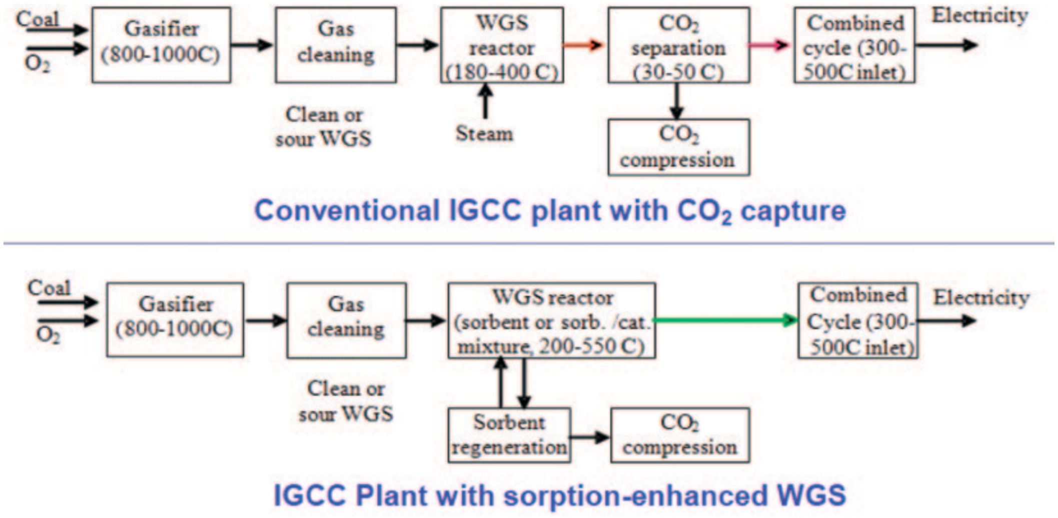

Figure 1: IGCC with SEWGS vs. Conventional IGCC

The University of Illinois at Urbana-Champaign (UIUC) will perform process simulation modeling and sorbent molecular and thermodynamic analyses. These analyses will allow prediction of optimal sorbent properties and identification of optimal operating temperature and pressure windows to maximize the energy efficiency of the combined WGS and CO_2 capture processes. The thermodynamic study will include developing phase equilibrium diagrams for potential sorbents, identifying optimum operating conditions for CO_2 capture, understanding impacts of syngas impurities, and identifying promising sorbents. Molecular simulation will predict isotherms and properties, predict kinetics and dynamics, and identify sorbents with desired properties using quantum chemistry/mechanics, force field-based Monte Carlo (MC), Kinetic Monte Carlo (KMC), Molecular Dynamics (MD), and reactive dynamics (RD) simulations. Process simulation analysis will analyze various process scenarios for heat integration between SEWGS and IGCC and process energy performance for individual sorbents.

Concurrently, UIUC will perform sorbent development. Sorbents will be synthesized with desired pore structure, surface functionality, and composition guided by the first phase testing and modeling effort. Sorbents will be synthesized using various precursors including calcium, magnesium, and other metal oxides, zirconates, titanates, silicates, aluminates, and adsorbent-shift catalyst hybrid. Sorbent down-selection will proceed according to the decision tree shown in Figure 2.

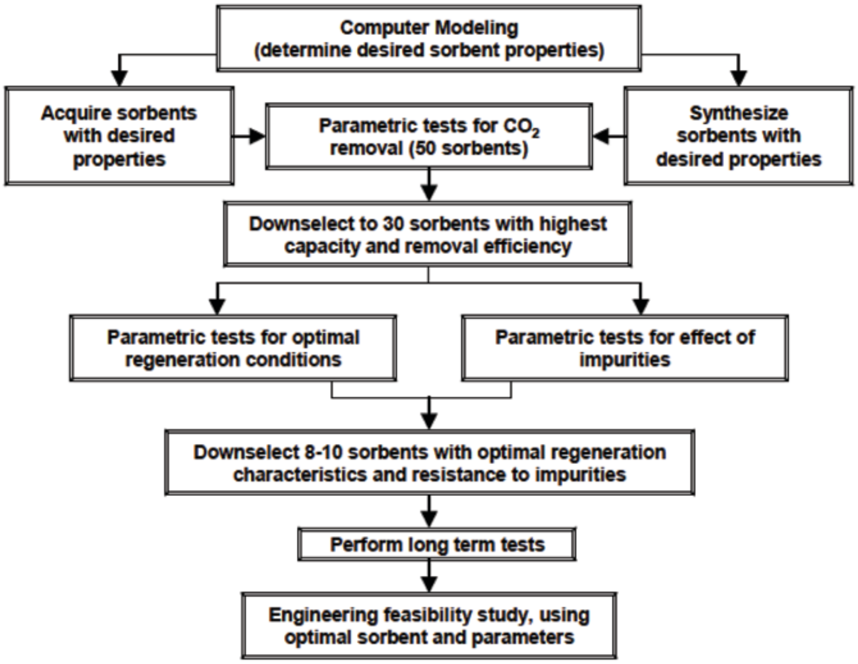

Figure 2: Sorbent Development and Analysis Decision Tree

UIUC will use a high-pressure thermogravimetric analyzer (PTGA) and a high temperature and pressure reactor (HTPR) system capable of 300 pounds per square inch gauge (psig) and 950 °C for screening sorbents for CO_2 removal. Also, URS will construct an HTPR to evaluate sorbent adsorption performance in presence of syngas impurities and regeneration performance. Thirty down-selected sorbents will also be tested for sorbent resistance to syngas impurities and determine optimal regeneration parameters. Eight to 10 sorbents will be further down-selected and will be tested on a longer-term basis.

Lab results will be used in a preliminary engineering study of process feasibility for adsorbing and removing CO_2 as part of the WGS process with the comparison made to base WGS operation and other CO_2 removal strategies. Parameters include cost of >90% removal [cost of electricity (COE), operation and maintenance (O&M)], sorbent costs, anticipated lifetime (i.e., replacement rate), estimated future market costs of precursor materials, handling equipment, sorbent regeneration costs, heat/energy integration, compression costs with SEWGS, unit footprint, and capital costs and scalability.

Table 1: Solid Sorbent Parameters

	Parameter	Current R&D Value	Target R&D Value
Sorbent Properties	Type of sorbent	(1) Calcium based smart sorbents; (2) calcium and magnesium oxide mixture sorbents; (3) zirconate, titanate, silicate, aluminate sorbents; (4) WGS/sorbent hybrid; (5) others	Program is designed to determine optimal sorbent type(s)
	Heat of adsorption, kJ/mole CO_2	100–200	TBD
	CO_2 loading/working capacity, wt%	N/A	Optimal loading properties will be impacted by regeneration properties (TBD in program)
	Surface area, m^2/g	40–75	>40
	Particle density, cm^3/g	N/A	TBD
	Particle size, nm	Nano (20–50 nm) or micro meter (0.5–10 µm) level; particles can be pelletized if needed	TBD
	Heat capacity, kJ/K/kg	N/A	TBD
	Thermal stability, °C	N/A	TBD
	Hydrothermal stability, °C	Inert to water vapor at operating temperatures	TBD
Process Configuration	Attrition rate (fluidized bed), %/year	N/A	Values will be impacted by costs of optimal sorbent type(s)
	Cycle time (fixed bed), minutes	Not applicable to fluidized bed or moving bed configuration	N/A
	Pressure drop (fixed bed), psia	Depending on sorbent properties, to be determined during the project	TBD
Operating Conditions	Adsorption temperature, °C	200–550	550
	Adsorption pressure, atm	30–40	40
	CO_2 capture efficiency, %	90%	>90%
	Regeneration method	Temperature swing	Temperature swing.
	Regeneration temperature, °C	Depends on individual sorbent and highest regeneration pressure achievable	TBD; optimization based on minimal energy input
	Regeneration pressure, atm	Up to 30 atm	Highest possible pressure up to 30 atm
Heat Integration	Required regeneration steam temperature, °C	Steam may not be used; if a steam is used, steam temperature <1,000 °F	TBD
Miscellaneous	Sorbent make-up rate, kg/kg CO_2	N/A	TBD
Product Quality	CO_2 purity, %	>99%	>99%
	N_2 concentration, %	0	0
	Other contaminants, %	Moisture <600 ppm	N/A
Process Performance	Electricity requirement, kJ/kg CO_2	N/A	TBD
	Heat requirement, kJ/kg CO_2	N/A	TBD
	Total energy (electricity equivalent), kJ/kg CO_2	N/A	0.1 kWh/kg CO_2 (360 kJ/kg)

This is a research and development (R&D) program involving fairly immature technology. As such, many target R&D values will be determined during execution of the test program and will be impacted by a number of key process parameters including sorbent type and cost, sorbent performance and loading capacity, sorbent lifetime, regeneration conditions and cycling parameters, and complexity of integration of optimal adsorption and regeneration processing steps.

Sorbent Heating/Cooling Method: For sorbent regeneration, the sorbent is heated in a fluidized bed or moving bed configuration with heat supplied by either hydrogen (H_2) (or syngas) oxy-combustion or steam extracted from the gasification plant steam cycle. Before entering the adsorption bed, the regenerated sorbent is cooled by exchanging heat with inlet regeneration H_2/oxygen (O_2) or syngas. In the adsorption bed, a heat exchanger (such as a boiler tube bundle used in the fluidized bed boiler) is used for recovering heat generated from CO_2 adsorption.

Heat of Adsorption Handling: Adsorption heat is recovered during CO_2 adsorption by using a heat exchanger to generate steam, which is combined into the gasification plant's steam cycle for electricity generation.

Heat Supply Method for Regeneration: Two methods will be considered. One is to burn a small amount of the H_2 or syngas using O_2 to supply heat directly. Another approach is to use the steam from the gasification plant's steam cycle if the regeneration temperature is far below 1,000 °F.

Contamination Resistance: This program will evaluate the impact of various syngas impurities on the adsorption and regeneration performance of promising CO_2 sorbents. Sorbents may not be resistant to sulfur species [hydrogen sulfide (H_2S), carbon disulfide (CS_2), etc].

Flue Gas Pretreatment Requirements: The pretreatment of H_2S/CS_2 is needed for sorbents with no sulfur resistance. If it is determined that the performance of identified sorbents is inhibited by sulfur species present in the syngas, additional work will focus on the development of sorbents materials that are resistant to sulfur; the objective will be to avoid the need for syngas pretreatment associated with this technology.

Waste Streams Generated: Desulfurization byproducts.

Successful completion of this project will demonstrate the feasibility of the SEWGS concept for removing CO_2 from syngas. The separation of CO_2 across a WGS reactor with dry sorbents would reduce or eliminate the need for WGS catalysts and would eliminate the need for a separate downstream CO_2 control process. It would result in a purified CO_2 stream at an appreciably higher temperature and pressure than obtained with existing capture processes, thus reducing the energy requirement for CO_2 compression for subsequent pipeline transport. Specific benefits of a successful SEWGS process would include:

- 50–80% decrease in compression costs relative to existing CO_2 capture processes (such as Selexol).
- Decreased steam requirements associated with syngas cooling/reheating (for downstream CO_2 capture).
- Elimination of capital and operation and maintenance costs associated with downstream CO_2 capture.

It is acknowledged that capital costs associated with the WGS process will increase as a result of this technology due to the additional vessels and mechanical equipment associated with the dry sorbents. The extent of this increase will be impacted by the properties and performance of the developed sorbents and is expected to be considerably lower than the potential cost reductions described above. Sorbent optimization is an objective of this program and subsequent impacts on WGS capital and O&M costs will be a focus of the techno-economic evaluation.

R&D Challenges

- Sorbent pores may be plugged during adsorption causing capacity and activity loss.
- Long-term capacity and activity stability after multiple cycles.
- Selectivity at high temperature.

Results To Date/Accomplishments

Activities conducted to date have included computational modeling (thermodynamic, process, and molecular modeling) to identify key physical and chemical properties for optimal sorbent performance at operating conditions applicable to a WGS process.

The model-derived information has been used to identify a number of promising sorbent materials for subsequent evaluation. Sorbent synthesis methods have been developed or refined and a number of sorbent samples have been prepared and characterized. Preliminary laboratory screening tests have been conducted to compare the CO_2 adsorption ability of the prepared sorbents. Additional activities have included mobilization of an HTPR and design of the integrated reactor for adsorption-regeneration testing. A summary of key project findings is provided below.

The project has achieved milestones associated with thermodynamic and process simulation modeling, as well as sorbent preparation. Thermodynamic modeling activities included screening analyses of a number of different metal oxides and zirconates, silicates, and titanates under various operating conditions. A group of 18 sorbents were further modeled and subsequently down-selected to seven candidates [magnesium oxide (MgO), calcium oxide (CaO), lithium zirconate (Li_2ZrO_3), calcium zirconium oxide ($CaZrO_3$), barium zirconate ($BaZrO_3$), barium titanate ($BaTiO_3$), and barium silicate ($BaSiO_3$)] for further development. Process simulations were performed for a baseline IGCC plant with WGS and a Selexol process and compared to an IGCC with SEWGS. These showed a 0.5–2.4% increase in net thermal efficiency for the simulated plant with SEWGS. The exact value depended on the nature of each of the seven sorbents. It should be noted, however, that these simulations were performed at common operating conditions and the efficiency increase is expected to increase as process conditions are optimized for each of the individual sorbents. Initial molecular simulation efforts have involved simulation of a single CO_2 molecule and how its interaction varied based on the solid sorbent material, crystallographic surface, and local environment.

A series of CaO spheres were synthesized using an ultrasonic spray pyrolysis (USP) procedure that is applicable to the synthesis of other materials of interest. Efforts were made to create hollow spheres with high BET surface areas ranging between 40 and 75 m^2/g, comparing very favorably to commercially available lime products (1–3 m^2/g) and other products reported in the literature (9-36 m^2/g). Water was initially used as the solvent but was replaced with ethanol, resulting in better hollow sphere particles yield; the addition of water to ethanol resulted in further yield improvement. The hollow structure made the materials more robust to extreme volume changes associated with carbonation and calcination, but USP-derived CaO sorbents showed morphological deterioration as well as loss of capacity (19% capacity reduction over 10 cycles) when undergoing multiple CO_2 adsorption/desorption cycles. The sorbent showed a strong affinity for CO_2 in air, adsorbing 31% of its maximum CO_2 capacity in 60 minutes under ambient conditions.

A highly energetic ball mill was used to synthesize new sorbents from commercially available materials using a molecular alloying (MA) process. X-ray diffraction (XRD) of produced particles revealed a decrease in crystallite size from 61 to 20 nm after milling CaO for 1.5 hours and TGA tests showed a 3% increase in capacity over the virgin material. An MgO/CaO alloy was synthesized and displayed a 6% improvement in CO_2 adsorption over a physically mixed sample. The results indicate that fundamental phase and/or structural changes occur to a material, at the nanometer scale, during ball milling. A series of sorbents with varying CaO:MgO ratios were synthesized and it was found that the CaO utilization actually increased over pure CaO when the MgO content was between 30 and 80%.

Shakedown and preliminary tests of the PTGA were performed so that sorbents can be screened at conditions more closely reflected those that will be experienced during an SEWGS. The effect on weight change due to CO_2 adsorption of both sample buoyancy and drag force were quantified and data sets generated with this unit will be adjusted accordingly.

Next Steps

- Complete molecular simulation analysis.
- Continue to refine sorbent preparation activities to achieve high activity and multi-cycle stability.
- Sorbent evaluation testing.
    - PTGA and high temperature and pressure reactor sorbent screening testing.
    - Syngas simulation tests.
    - Regeneration tests.
- Engineering feasibility study.

Available Reports/Technical Papers/Presentations

Evaluation of Dry Sorbent Technology; Presentation at the 2010 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, September 13–17, 2010.

"Evaluation of Dry Sorbent Technology for Pre-Combustion CO_2 Capture," **Pre-Combustion CO_2 Capture Kick-off Meetings**, Pittsburgh, PA, November 12–13, 2009. http://www.netl.doe.gov/publications/proceedings/09/CO2capture/7-URS Dry Sorbent Kickoff Presentatin-111309.pdf

A LOW-COST, HIGH-CAPACITY REGENERABLE SORBENT FOR PRE-COMBUSTION CO_2 CAPTURE

Primary Project Goals

TDA Research is further developing a low-cost, high-capacity regenerable carbon dioxide (CO_2) sorbent technology, demonstrating its technical and economic viability for pre-combustion CO_2 capture from coal-derived synthesis gas (syngas) fueling integrated gasification combined cycle (IGCC) power plants.

Technical Goals

- Optimize chemical and physical properties of an existing sorbent.
- Modify the sorbent to improve capacity and stability.
- Scale up sorbent production using commercially adoptable equipment.
- Demonstrate long-term sorbent performance at bench-scale in the presence of contaminants.
- Design and build a prototype unit to support slipstream demonstration tests using actual syngas.
- Detailed process design and cost analysis to evaluate sorbent's ability to remove CO_2 at a lower cost than current technologies.

Technical Content

TDA is developing a new pre-combustion CO_2 capture technology that uses a TDA proprietary sorbent modified to remove CO_2 from shifted syngas. The CO_2 capture system uses two (or more) beds that switch positions between adsorption and regeneration. In addition to the conventional pressure and temperature swing operation, the sorbent can be regenerated under near isothermal and isobaric conditions while the driving force for separation is provided by a swing in CO_2 concentration. The sorbent consists of a carbon support modified with surface functional groups that remove CO_2 via strong physical adsorption. The CO_2 surface interaction is strong enough to allow operation at elevated temperatures. Because the CO_2 is not bonded via a covalent bond, the energy input to the regeneration is low—only 4.9 kcal/mole of CO_2 removed (comparable to Selexol). This energy requirement is much lower than that of the chemical absorbents [e.g., sodium carbonate (Na_2CO_3) requires 29.9 kcal/mol] and amine solvents (~14 kcal/mol). The energy output loss of the IGCC plant is expected to be similar to that of Selexol's; however, a higher overall IGCC efficiency can be achieved due to higher temperature CO_2 capture.

Initially, the researchers will be optimizing the chemical, mechanical, and physical properties of the sorbent to optimize the active material content; assess the impact of key synthesis parameters on surface area, pore volume, and pore size distribution; and determine crush strength and attrition resistance. Cost will be kept to a minimum by evaluating low-cost raw materials and optimizing the production process. Sorbents will be evaluated under simulated syngas, water gas shift (WGS), and simulated contaminant conditions using two TGAs and a 1-, 3-, and 6-inch bench-scale flow reactor. TDA and the University of California Irvine (UCI) will carry out process design and modeling. Based on that information, UCI will carry out multiple design options and the best option will be selected for detailed simulation.

Technology Maturity:

Pilot-scale slipstream using actual syngas

Project Focus:

High Capacity Regenerable Sorbent

Participant:

TDA Research, Inc.

Project Number:

FE0000469

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Partners:

ConocoPhillips
KBR
MeadWestvaco
Southern Company
University of California Irvine

Performance Period:

10/1/09 – 9/30/11

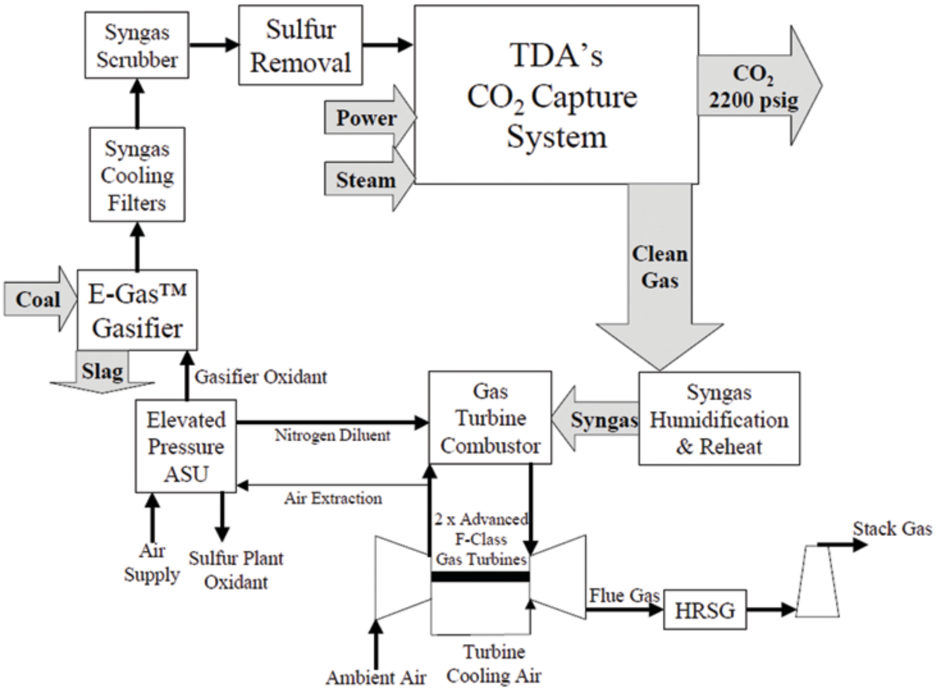

Figure 1: IGCC Integrated CO_2 Removal System

The next objective is to scale up sorbent production by a factor of 10 at the end of Year 1 using commercially adoptable equipment. Scale up will explore the use of continuous or semi-continuous preparation approaches, and reduce or optimize the number of processing steps via intensification (co-synthesis, co-firing, etc.). A preparation recipe will be developed in cooperation with MeadWestvaco, who will carry out a detailed analysis to estimate the cost of the sorbent. Long-term tests will be performed to ensure that the sorbent does maintain its CO_2 capacity over many cycles. A minimum of 2,000 cycles are planned in Year 1.

Year 2 of the project focuses on designing, building, and testing a prototype unit using slipstream syngas and analyzing the results. TDA will work with KBR to carry out a detailed design and sizing of sorbent reactors for each of the two gasifier types that will be used for pilot testing.

TDA and UCI will continue to optimize the process design and modeling. The focus of system analysis in Year 2 will be on the integration of the CO_2 capture system with the IGCC plant. TDA will fabricate the test module, which will have a control rack using Labview programming to control, monitor, and log key process parameters. The test module will also have an analyzer rack for continuous analysis of carbon monoxide (CO), CO_2, methane (CH_4), hydrogen (H_2), and water (H_2O) on the adsorption and regeneration sides, and hydrogen sulfide (H_2S) analysis on the adsorption side. TDA will perform all shakedowns and troubleshooting before shipping the test system. Field tests will be performed at ConocoPhillips' Wabash River IGCC Plant with the oxygen (O_2)-blown E-Gas gasifier in Terre Haute and in collaboration with the Southern Company at the National Carbon Capture Center (NCCC) using the syngas generated by an air-blown gasifier at Wilsonville, AL. Two, three-week long (500 hours) test campaigns are scheduled with 24 hr/day continuous operation. A majority of testing will be performed under optimum conditions and limited scope testing to assess the impact of operating parameters.

Table 1: Solid Sorbent Parameters

	Parameter	Current R&D Value	Target R&D Value
Sorbent Properties	Type of sorbent	Physical adsorbent	Physical adsorbent
	Heat of adsorption (kJ/mole CO_2)	20.5	Less than 30
	CO_2 loading/working capacity, wt%	7	TBD
	Surface area, m^2/g	350–450	TBD
	Particle density, cm^3/g	0.6–0.7	TBD
	Packing density, cm^3/g	0.40–0.45	TBD
	Particle size (mm)	3.2	TBD
	Heat capacity (kJ/K/kg)	TBD	TBD
	Thermal stability, °C	1,100	Greater than 400
	Hydrothermal stability, °C	600	Greater than 400
Process Configuration	Attrition rate (fluidized bed), %/year	TBD	Less than 1%
	Cycle time (fixed bed), minutes	TBD	TBD
	Pressure drop (fixed bed), psia	TBD	TBD
Operating Conditions	Adsorption temperature, °C	20–320	200–300
	Adsorption pressure, atm	1–60	50
	CO_2 capture efficiency, %	98+	90+
	Regeneration method	TBD	TBD
	Regeneration temperature, °C	TBD	TBD
	Regeneration pressure, atm	TBD	TBD
Heat Integration	Required regeneration steam temperature, °C	TBD	TBD
Miscellaneous	Sorbent make-up rate, kg/kg CO_2	TBD	TBD
Product Quality	CO_2 purity, %	TBD	Pipeline spec
	N_2 concentration, %	TBD	Pipeline spec
	Other contaminants, %	TBD	Pipeline spec
Process Performance	Electricity requirement, kJ/kg CO_2	TBD	TBD
	Heat requirement, kJ/kg CO_2	TBD	TBD
	Total energy (electricity equivalent), kJ/kg CO_2	TBD	TBD

Sorbent Heating/Cooling Method: Isothermal operation is planned.

Heat of Adsorption Handing: The small heat of adsorption will be removed by convective losses (i.e., warming the syngas) and by increasing the sensible heat of the sorbent pellets.

Heat Supply Method for Regeneration: The stored heat in the sorbent pellets and the convective heat input.

Contaminant Resistance: The sorbent will be resistant to syngas contaminants.

Fuel Gas Pretreatment Requirements: Particulate removal, bulk desulfurization, and WGS.

Waste Streams Generated: The spent sorbent will be replaced periodically.

Technology Advantages

- Carbon dioxide recovered at pressure reduces compression costs for sequestration.
- A weak CO_2 surface interaction allows fast regenerations at low temperature with the minimal or no heat input.
- Short adsorption/regeneration cycles reduce bed size and weight.

R&D Challenges

- Demonstration to the resistance of syngas contaminants.
- Reducing the use of purge gas during regeneration.

Results To Date/Accomplishments

- Completed sorbent optimization.
    - Identified an optimum chemical composition.
    - Production scale-up.
- Demonstrated high CO_2 capacity in bench-scale experiments.
    - Saturation capacity approaching 20 wt% CO_2.
    - 6–8 wt% working capacity.
- Long-term durability was demonstrated through 6,000 cycles.
- System simulation indicates that TDA's CO_2 technology will provide higher net plant efficiency than that of IGCC-Selexol.

Next Steps

- Complete 10,000 cycles to demonstrate sorbent life.
- Complete the process design and optimization.
    - Estimate the cost of capital equipment.
    - Economic analysis.
- Complete the fabrication of a skid-mounted unit for field evaluations.
- Carry out field demonstrations.

Available Reports/Technical Papers/Presentations

Low Cost, High Capacity Regenerable Sorbent; Presentation at the 2010 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, September 13–17, 2010. http://www.netl.doe.gov/publications/proceedings/10/co2capture/presentations/friday/Gokhan Alptekin - FE0000469.pdf

"A New Sorbent-Based Pre-Combustion CO_2 Capture System," presented at the International Conference of Energy and Power Generation Systems, Costa Mesa, CA, 2010.

HYDROGEN PRODUCTION AND PURIFICATION FROM COAL AND OTHER HEAVY FEEDSTOCKS

Primary Project Goals

The University of North Dakota Energy and Environmental Research Center (UNDEERC) is evaluating the ability of various conventional and high-temperature carbon dioxide (CO_2) sorbents to resist the deleterious effects of hydrogen sulfide (H_2S)-containing (sour) synthesis gas (syngas).

Technical Goals

- Assess the performance of high-temperature and conventional CO_2 sorbents in simulated and real syngas.
- Evaluate the effect of H_2S on solid sorbents when operating in a fixed bed under simulated and real syngas conditions.
- Analyze CO_2 sorbents after exposure to real and simulated syngas.

Technical Content

Gasification of coal and other heavy feedstocks is becoming an attractive approach for power and chemical production. The solid fuels are transformed into a sour syngas which must be further processed to yield the desired final products [e.g., high-purity hydrogen (H_2) or H_2-rich fuel and a CO_2-rich byproduct]. Air Products is interested in two types of syngas treatment processes: a high-temperature process (400 °C) and an ambient-temperature process. Both require information on the impact of sour gas species on the solid adsorbents and the ability of these adsorbents to reversibly adsorb H_2S and CO_2.

UNDEERC has conducted two major sets of experiments in this program. In Phase 1 of the program, a 10-bed exposure unit was built and operated, and the impact of a synthetic sour syngas on various high- and low-temperature CO_2 adsorbents was determined. Most of the adsorbents showed an increase in sulfur content and subsequent decrease in surface area and CO_2 adsorption capacity with exposure. Two materials were able to maintain their CO_2 capacity at ambient temperature.

Figure 1: Fixed-Bed Reactor Skid

In the next phase of work, these two materials were tested in a fixed-bed skid (Figure 1). The unit consisted of two packed beds, with the necessary valves and heating equipment to permit regeneration by pressure swing adsorption (PSA) or temperature swing adsorption (TSA) cycles.

Breakthrough experiments were conducted with 2% H_2S in H_2 feed gas to determine the H_2S adsorption capacity and mass transfer coefficients for the two materials. Hydrogen sulfide adsorption was shown to be reversible and rapid.

Technology Maturity:

Laboratory- and pilot-scale

Project Focus:

Evaluation of Sorbents

Participant:

UNDEERC

Project Number:

NT42465-1.4

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Partners:

Air Products and Chemicals, Inc.

Performance Period:

6/23/05 – 5/31/11

The fixed-bed unit was then connected to UNDEERC's existing lab-scale circulating fluidized-bed gasifier. The gasifier processed Powder River Basin (PRB) sub-bituminous coal spiked with elemental sulfur (S) to generate a syngas with an elevated H_2S concentration. The syngas was continuously fed to the fixed-bed unit (operating in PSA mode) for more than 1,000 cycles. The adsorbent beds were capable of reducing H_2S in the product stream to less than 50 parts per million (ppm). The H_2S capacity of the adsorbent decreased with initial syngas exposure (first couple of hundred cycles), but then remained stable. Post-mortem analysis of the adsorbent showed some deposition of S and chlorine (Cl) species at the front of the bed and capture of organic tar species.

UNDEERC operated the entrained-flow gasifier under oxygen-blown conditions with petcoke feed to generate a second sour syngas feed to the fixed-bed unit. The system was operated under various conditions (temperature and process flow rates) to determine the impact on separation performance. At the end of the testing, the adsorbent was systematically removed and analyzed to monitor changes in capacity/integrity. UNDEERC also modified the exposure unit to allow injection of low levels of iron carbonyl, carbonyl sulfide, and hydrogen fluoride. Impact of exposure was determined for the most promising adsorbent to date.

Technology Advantages

High-temperature acid gas (H_2S and CO_2) removal from integrated gasification combined cycle (IGCC) syngas streams has the potential to increase the net power system efficiency by maintaining a high- temperature, high-moisture feed stream to the combustion turbine power cycle. These advantages also hold for applications that utilize the syngas for coproducing hydrogen, fuels, or chemicals. Energy losses through syngas cooling and re-heating resulting from cool acid gas removal (such as Rectisol® or Selexol™) are prevented with high-temperature separation.

An ambient-temperature acid gas separation process based on adsorption would also be attractive relative to typical liquid absorption-based processes because of reductions in steam consumption and capital cost.

R&D Challenges

The physical/chemical stability of the adsorbents in a sour syngas environment remains a concern, as does the ultimate fate of trace components (mercury, Cl, particulate matter) and the reversibility of heavy component (tars) adsorption.

Results To Date/Accomplishments

- Identified two promising ambient-temperature adsorbents that exhibited very little CO_2 capacity loss after sour syngas exposure.
- Conducted H_2S breakthrough experiments, both with and without CO_2, which showed that the most promising adsorbent is selective for H_2S over CO_2, the mass transfer rate of H_2S is described by macropore diffusion, and H_2S adsorption is reversible.
- Operated the fixed-bed test unit in PSA mode with coal-based syngas produced in a circulating fluidized-bed gasifier. Demonstrated that H_2S and CO_2 can be effectively rejected from the sour syngas. Completed roughly 1,500 adsorption/regeneration cycles. Showed that the H_2S capacity initially dropped but then leveled off at about 80% of the fresh capacity.
- Conducted postmortem analysis of adsorbent to determine progression of Cl, S, and organics into bed. Chlorine and sulfur were limited to the first few inches of the bed. Organics were found to penetrate deeper, and are thought to be responsible for the initial drop in H_2S capacity.
- Operated a second batch of adsorbent in the fixed-bed unit with syngas generated from petroleum coke in an entrained-flow gasifier. Observed negligible levels of organics in the syngas. Completed more than 1,000 adsorption/regeneration cycles with no indication of H_2S capacity loss.

Next Steps

Experimental work is complete. Final test results will be included in the project report scheduled to be available by May 31, 2011. This task is being continued under a new cooperative agreement, DE-FE0003466—Activity 1.4, Add-On Task.

Available Reports/Technical Papers/Presentations

"Hydrogen Production and Purification from Coal and Other Heavy Feedstocks—Final Topical Report" will be available May 31, 2011.

An abstract will be submitted for presentation of results at the 28th Annual International Pittsburgh Coal Conference (September 2011).

HIGH-DENSITY ACTIVATED CARBON FOR HIGH-PRESSURE HYDROGEN PURIFICATION

Primary Project Goals

The University of North Dakota Energy and Environmental Research Center (UNDEERC) is developing high-density, electrically conductive monolithic-activated carbon for use in a high-pressure swing adsorber to produce hydrogen (H_2) and sequestration-ready carbon dioxide (CO_2) from gasification synthesis gas (syngas).

Technical Goals

- Prepare a high-density, electrically conductive monolithic-activated carbon sorbent for H_2/CO_2 separation.
- Measure adsorptivity, pressure drop, and electrical conductivity (for regeneration) of monolith.
- Determine the feasibility of using activated carbons as CO_2 sorbents in gasification syngas.

Technical Content

UNDEERC worked with SGL Carbon to produce a monolithic, high-density activated carbon sorbent for use in high-pressure swing adsorbers to separate H_2 and CO_2 in a high-pressure syngas stream, while maintaining the pressure of the H_2 near that of the incoming syngas. By producing and purifying the H_2 from liquid feedstocks at high pressure, the associated cost of compressing the H_2 is reduced. This process, if employed at an integrated gasification combined cycle (IGCC) power plant, could potentially be used to produce high-purity CO_2 for storage.

As syngas passes through the activated carbon adsorbers, CO_2 is adsorbed onto the surface of the material, leaving relatively pure H_2 to pass through. Once saturated, the adsorbers can possibly be regenerated by passing an electrical current through it at constant pressure. Oak Ridge National Laboratory (ORNL) has been developing such a process and has produced a continuous, low-density, porous, fiber-reinforced activated carbon. By being continuous, it can conduct electricity at low voltage and can be sealed in a horizontal container that will not allow gas bypass. However, when used at high pressures, the high pore volume requires significant H_2 for backflushing. UNDEERC is attempting to significantly increase the density of the carbon monolith in order to reduce the amount of clean H_2 required for backflushing at high pressures and decrease the regeneration interval.

During this project, UNDEERC attempted to activate four different formulations of high-density carbon fiber/carbon matrix composites. Activation methods included heating to 450 °C in static, high-pressure steam or oxygen and the use of chemical activation. However, only butane adsorptivities of 2–3% were able to be obtained for the activated carbon produced from the monolithic carbon fiber composite, whereas commercial granulated activated carbons have butane adsorptivities of up to 18%. In follow-on work, the focus was on pressing mixtures of granular and powdered activated carbon and binder. These results were successful in making conductive monoliths with twice the density of granular beds, or approximately 40% of the theoretical skeletal carbon density. In addition, a method of treatment of the activated carbon granules were developed to

Technology Maturity:

Laboratory-scale

Project Focus:

High-Density Activated Carbon

Participant:

UNDEERC

Project Number:

NT42465-3.1

NETL Project Manager

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Partners:

SGL Carbon

Performance Period:

6/23/05 – 6/22/07

reduce the resistivity of the monoliths by a factor of 10 relative to those made from the commercially available granular activated carbon.

Figure 1 shows how well the monolith separates different components from a simulated reformer gas stream. The figure is a plot of gas breakthrough curves for a monolith tested at 200 pounds per square inch gauge (psig) with a simulated reformer gas stream. The horizontal dashed lines show the concentrations of the different gases in the incoming gas stream. The light blue curve on the lower left is oxygen coming out of the monolith that was originally saturated with air. The difference between the sums of the curves and 100% is due to nitrogen, which was not directly detected. The monoliths are being tested at higher pressures in a follow-on U.S. Department of Defense (DoD) project and will be tested for their ability to be regenerated by passing an electric current through the monolith, possibly to disrupt the Vander Waals forces holding the gas molecules to the activated carbon surface or to resistively heat the monolith in a thermal swing adsorption process.

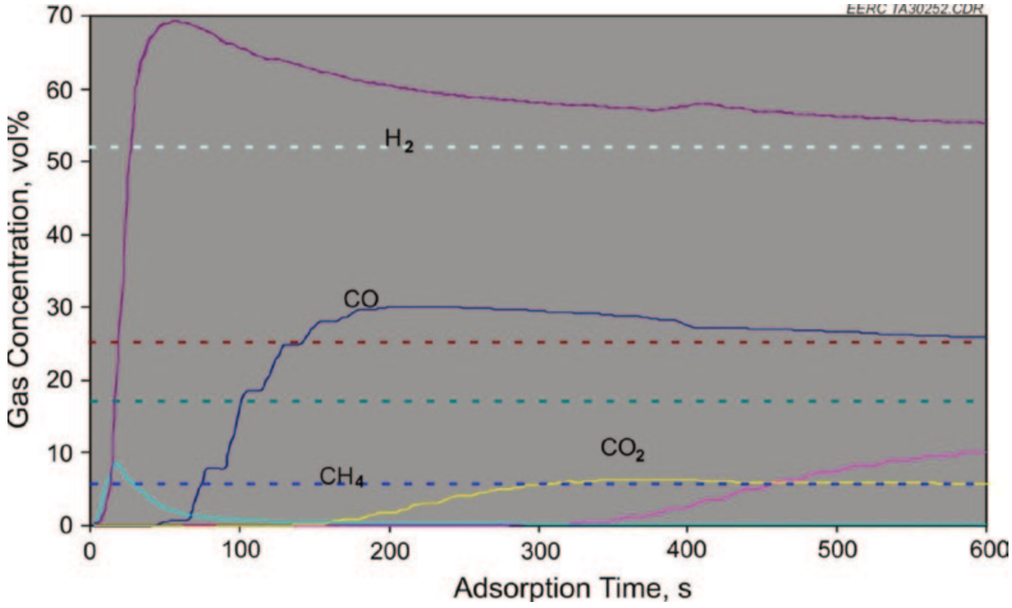

Figure 1: Gas Breakthrough Curves for a Monolith Tested at 200 psig

The following solid sorbent parameter table (Table 1) was completed by the Principal Investigator (PI) with best available data. "N/A" has been used for data that are not available. Data entered in the "Current R&D Value" column are based on test results achieved to date. As this project has ended, there are no further test results to enter in the "Target R&D Value" column.

Table 1: Solid Sorbent Parameters

	Parameter	Current R&D Value	Target R&D Value
Sorbent Properties	Type of sorbent	Activated carbon	—
	Heat of adsorption (kJ/mole CO_2)	N/A	—
	CO_2 loading/working capacity, wt%	9	—
	Surface area, m^2/g	1,200	—
	Particle density, g/cm^3	N/A	—
	Packing density, g/cm^3	0.85	—
	Particle size (mm)	Monolith	—
	Heat capacity (kJ/K/kg)	N/A	—
	Thermal stability, °C	75 °C	—
	Hydrothermal stability, °C	N/A	—
Process Configuration	Attrition rate (fluidized bed), %/year	Near 0	—
	Cycle time (fixed bed), minutes	N/A	—
	Pressure drop (fixed bed), psia	N/A	—

Table 1: Solid Sorbent Parameters

	Parameter	Current R&D Value	Target R&D Value
Operating Conditions	Adsorption temperature, °C	N/A	—
	Adsorption pressure, atm	N/A	—
	CO_2 capture efficiency, %	N/A	—
	Regeneration method	Electrical/thermal	—
	Regeneration temperature, °C	N/A	—
	Regeneration pressure, atm	N/A	—
Heat Integration	Required regeneration steam temperature, °C	N/A	—
Miscellaneous	Sorbent make-up rate, kg/kg CO_2	N/A	—
Product Quality	CO_2 purity, %	N/A	—
	N_2 concentration, %	N/A	—
	Other contaminants, %	N/A	—
Process Performance	Electricity requirement, kJ/kg CO_2	N/A	—
	Heat requirement, kJ/kg CO_2	N/A	—
	Total energy (electricity equivalent), kJ/kg CO_2	N/A	—

Technology Advantages

High-pressure H_2/CO_2 separation, coupled with isobaric sorbent regeneration using an electrical current, will increase plant efficiency by reducing the parasitic load associated with gas compression. Also, because of the high density of the monolith, the gas adsorption per unit volume is nearly doubled, and the amount of H_2 necessary to flush the intergranular spaces is cut by 25%.

R&D Challenges

The project team discovered that the carbon sorbents require a long adsorption/desorption cycle time and no activation occurred during exposure to steam for 24 hours, while attempts to activate the material by reaction with an oxidizing gas showed limited results. Further, the introduction of reactive metals had a nominal effect on surface area creation.

Results To Date/Accomplishments

- Prepared high-density, monolithic-activated carbons for high-pressure H_2/CO_2 separation.
- Measured the surface area, pressure drop, and electrical conductivity of the activated carbon sorbents.

Next Steps

Development activities for this technology are no longer part of the DOE/NETL portfolio, but work is continuing under a DoD program.

Available Reports/Technical Papers/Presentations

Hurley, J.P. *High-Density Activated Carbon for High-Pressure Hydrogen Purification*; Final Report; U.S. DOE, April 2008.

INTEGRATED WARM GAS MULTI-CONTAMINANT CLEANUP TECHNOLOGIES FOR COAL-DERIVED SYNGAS

Primary Project Goals

Research Triangle Institute (RTI) is developing a modular warm, multi-contaminant synthesis gas (syngas) cleaning system that can be adapted to meet the specifications for both power and chemical/fuels production.

Technical Goals

- Develop a modular high-temperature (150–370 °C or 300–700 °F) and high-pressure [up to 83 atm or 1,200 pounds per square inch gauge (psig)] cleanup process that produces an effluent syngas suitable for chemical/fuels production by controlling trace contaminants to the levels shown in Table 1.

Table 1: Targeted Control Levels for Syngas Contaminants

Contaminant	Control Level
Sulfur (S)	<50 ppbw
Ammonia (NH_3)	10 ppm
Chlorine (Cl)	10 ppb
Mercury (Hg)	5 ppbw
Selenium (Se)	0.2 ppm
Arsenic (As)	5 ppb
Phosphorus (P)	<20 ppbw

- Utilize a transport reactor and regenerable sorbents to control bulk syngas contaminants, such as hydrogen sulfide (H_2S), carbonyl sulfide (COS), ammonia (NH_3), and hydrogen chloride (HCl).
- Evaluate the performance of high-temperature carbon dioxide (CO_2) sorbents and promoters.

Technical Content

In this project, RTI is developing a sequential process where high-temperature syngas is cleaned using a transport reactor and a multi-functional fixed-bed system. The system is designed to operate at syngas feed conditions [150–370 °C (300–700 °F)] and 28–83 atm (400–1,200 psig), which will improve plant efficiency by eliminating the need for syngas cooling and re-heating. RTI's novel warm syngas cleaning technology could represent a significant improvement for chemical/fuels production applications due to reduced capital and operating costs; however, development and optimization for trace contaminant removal and warm CO_2 capture is needed to achieve the target syngas specifications for both power [integrated gasification combined cycle (IGCC) applications] and chemical/fuels production.

The bulk contaminant removal system consists of a transport reactor containing regenerable sorbents that target H_2S, COS, NH_3, and HCl. RTI investigated three sorbents: (1) RTI-3 for sulfur; (2) CBV-712 for NH_3; and (3) a sodium carbonate-based sorbent for chlorine. Syngas

Technology Maturity:
Bench-scale

Project Focus:
Warm Gas Cleanup with Sorbents

Participant:
RTI International

Project Number:
NT42459

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Partners:
Nexant

Performance Period:
6/1/05 – 9/30/10

leaving the transport reactor is routed to a multi-functional, fixed sorbent bed that reduces contaminants to parts per billion by volume (ppbv) levels.

Figure 1: Modified TGA for CO_2 Sorbent Testing

RTI employed the modified, high-pressure thermal gravimetric analyzer (TGA) shown in Figure 1 and a microreactor system to evaluate the performance of high-temperature CO_2 sorbents. The bench-scale CO_2 sorbent testing campaign included experiments with lithium orthosilicate (Li_4SiO_4) and magnesium oxide (MgO) sorbents, as well as several promoters and support structures. RTI's Li_4SiO_4 sorbent exhibited a CO_2 adsorption capacity of about 35 wt% at high temperatures, but a technical-economic analysis concluded that the regeneration stage is prohibitively expensive.

Meanwhile, a promoted MgO sorbent has demonstrated a CO_2 capacity of nearly 60 wt% and the ability to be regenerated at a CO_2 partial pressure of about 150 psig. RTI developed a knowledge base for the promoted MgO sorbent and focused research on fundamental issues, including sorbent preparation procedures, sorbent support structures and binders, and syngas pretreatment requirements.

Table 2: CO_2 Solid Sorbent Parameters

	Parameter	Current R&D Value	Target R&D Value
Sorbent Properties	Type of sorbent	Promoted MgO	—
	Heat of adsorption (kJ/mole CO_2)	95–100	~98
	CO_2 loading/working capacity, wt%	10–60	30–40
	Surface area, m^2/g	N/A	—
	Particle density, cm^3/g	N/A	—
	Packing density, cm^3/g	N/A	—
	Particle size (mm)	N/A	—
	Heat capacity (kJ/K/kg)	N/A	—
	Thermal stability, °C	N/A	—
	Hydrothermal stability, °C	N/A	—
Process Configuration	Attrition rate (fluidized bed), %/year	N/A	—
	Cycle time (fixed bed), minutes	N/A	—
	Pressure drop (fixed bed), psia	N/A	—
Operating Conditions	Adsorption temperature, °C	350–450	350–450
	Adsorption pressure, atm	~24	40
	CO_2 capture efficiency, %	>85	90
	Regeneration method	Thermal	Investigating
	Regeneration temperature, °C	500–550	Investigating
	Regeneration pressure, atm	~24	Investigating
Heat Integration	Required regeneration steam temperature, °C	N/A	Investigating
Miscellaneous	Sorbent make-up rate, kg/kg CO_2	N/A	—
Product Quality	CO_2 purity, %	N/A	—
	N_2 concentration, %	N/A	—
	Other contaminants, %	N/A	—
Process Performance	Electricity requirement, kJ/kg CO_2	N/A	Investigating
	Heat requirement, kJ/kg CO_2	N/A	Investigating
	Total energy (electricity equivalent), kJ/kg CO_2	N/A	Investigating

In parallel with this experimental program, RTI investigated potential process configurations and operating conditions to exploit the attributes of the promoted MgO sorbent. Research was geared toward developing a suitable fluidized version of the sorbent to facilitate sorbent transport between the adsorption and stripping columns, while also improving the heat transfer coefficient of the sorbent bed. RTI also worked to identify the temperature window between adsorption and regeneration that maximizes the sorbent's CO_2 working capacity, while minimizing the sensible heating requirement. In addition, RTI explored techniques to reuse the high-quality heat generated during the high-temperature CO_2 adsorption process, (e.g., transferring the high-quality heat to the steam cycle to generate additional power, or replacing a portion of the steam generated in the radiant syngas cooler).

Technology Advantages

Warm syngas cleanup will increase IGCC net power plant efficiency by eliminating the need for syngas cooling and re-heating, while also producing an effluent syngas suitable for chemical/fuels production and high-purity CO_2 for storage.

R&D Challenges

Integration and scale up of the bench-scale transport reactor and multi-functional fixed-bed system, as well as startup and standby options for the warm syngas cleanup technologies.

Results To Date/Accomplishments

- Technical support provided to DOE/NETL researchers has resulted in a computational fluid dynamics (CFD) model that predicts temperature and differential pressure profiles similar to actual pilot plant results.
- Demonstrated that combustion products [CO_2, steam, and carbon monoxide (CO)] do not adversely affect the desulfurization performance of RTI-3.
- Adapted existing bench-scale testing system to support phosphine (in addition to arsine and hydrogen selenide) testing.
- Developing a coconut-based charcoal as a quality control cartridge for supporting mass balance determination during phosphine testing.
- Identified a family of promoters that increased the CO_2 capacity of the MgO sorbent from <2 wt% to 40–60 wt%.
- Completed a technical-economic analysis of warm CO_2 capture using RTI's Li_4SiO_4 sorbent, which concluded that the regeneration stage is prohibitively expensive.
- Independent system analysis by both Nexant and Noblis indicate that RTI's warm syngas cleaning system can yield a three to four point increase in the net HHV thermal efficiency and a 10–15% reduction in capital costs, compared to an IGCC plant equipped with Selexol™ for acid gas removal.
- Identified a new process configuration/operating cycle that demonstrates technical and economic promise and achieves 82–87% CO_2 capture with warm MgO-based sorbent CO_2 capture.
- Demonstrated that the operational cycle (higher adsorption temperature than regeneration temperature) is valid.
- Demonstrated the potential to achieve low effluent CO_2 concentrations (~100 ppmv) with MgO-based sorbents at pressures from 150 to 325 psig.
- Completion of preliminary techno-economic evaluations by RTI and Noblis for multiple warm CO_2 capture processes with RTI's promoted MgO sorbents demonstrating a slight thermal efficiency advantage.

Next Steps

Development activities for this CO_2 capture technology are no longer part of the DOE/NETL portfolio.

In a follow-on DOE/NETL project (DE-FE0000489), RTI is designing, building, and testing a pre-commercial scale [30–50 megawatt electric equivalent (MWe)] warm gas cleanup system, integrated with CCS at Tampa Electric Company's Polk Power Station.

Available Reports/Technical Papers/Presentations

Final report not yet available.

"Integrated Warm Gas Multicontaminant Cleanup Technologies for Coal-Derived Syngas" fact sheet, http://www.netl.doe.gov/publications/factsheets/project/Proj395.pdf

Scaleup and Commercialization of Warm Syngas Cleanup Technology with Carbon Capture and Storage, presented at the 2010 Gasification Technologies Conference, Washington, DC, October 31 to November 3, 2010. http://www.gasification.org/uploads/downloads/Conferences/2010/38GUPTA.pdf

RTI/Eastman Warm Syngas Clean-up Technology: Integration with Carbon Capture, presented at the 2009 Gasification Technologies Conference, Colorado Springs, CO, October 4–7, 2009. http://www.gasification.org/uploads/downloads/Conferences/2009/37GUPTA.pdf

"Warm Syngas Cleanup for Chemical Applications using Regenerable CO_2 Sorbents," presented at the 26th International Pittsburgh Coal Conference, Pittsburgh, PA, September 20–23, 2009.

"High Temperature CO_2 Capture from Syngas for Gasification Applications," Eighth Annual Carbon Capture and Sequestration Conference, (May 2009).

"Development of a Warm Gas Cleanup Technology Platform for Power and Chemicals Production," Pittsburgh Coal Conference, (September 2008).

NOVEL SORPTION ENHANCED REACTION PROCESS FOR SIMULTANEOUS PRODUCTION OF CO_2 AND H_2 FROM SYNTHESIS GAS PRODUCED BY COAL GASIFICATION

Primary Project Goals

Lehigh University has evaluated the feasibility of the novel thermal swing sorption enhanced reaction (TSSER) process to simultaneously separate carbon dioxide (CO_2) and carry out the water gas shift (WGS) reaction as a single-unit operation in a fixed bed reactor.

Technical Goals

While evaluating the feasibility of the TSSER process through experiments and process modeling, develop a sorbent that exhibits:

- High selectivity of CO_2 in the presence of steam at 200–500 °C.
- Adequate CO_2 working capacity at the reaction temperature.
- Low heat of adsorption for reversible CO_2 sorption and desorption.
- Adequately fast kinetics of CO_2 sorption and desorption.
- Thermal stability.

Technical Content

The WGS reaction, which converts most of the synthesis gas (syngas) carbon monoxide (CO) to hydrogen (H_2) and CO_2 by reacting the CO with water over a bed of catalyst, can be utilized to enhance H_2 production at an integrated gasification combined cycle (IGCC) plant. The excess steam serves to drive the shift equilibrium toward the products. The reaction is exothermic and, due to equilibrium constraints, typically consists of two stages: (1) high-temperature shift that benefits from high reaction rates at elevated temperatures; and (2) low-temperature shift that yields more favorable reaction equilibrium.

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H_{rxn} = -41.2 \text{ kJ/mol}$$

The TSSER process (Figure 1), under development by Lehigh University, simultaneously carries out the WGS reaction and the separation of CO_2 as a single-unit operation in a sorber-reactor (Step A). According to this process, the syngas from the coal gasifier (after removal of sulfur impurities) is introduced to a sorber-reactor, which is packed with an admixture of a WGS catalyst and a CO_2 sorbent that can selectively sorb CO_2 in the presence of excess steam. Removal of CO_2 (for geological storage) from the reaction zone drives the reversible reaction to the product side (circumventing equilibrium limits) and enhances the forward reaction rate.

An essentially pure (fuel cell grade) stream of H_2 (dry basis) is produced at feed gas pressure. The sorbed CO_2 is periodically removed (regeneration) by counter-currently purging the reactor with

Technology Maturity:

Laboratory-scale

Project Focus:

Sorbent-Enhanced Water Gas Shift

Participant:

Lehigh University

Project Number:

NT42455

NETL Project Manager:

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Principal Investigator:

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Partners:

None

Performance Period:

5/25/05 – 6/4/10

superheated steam at feed gas and near-ambient pressures, as well as at a temperature higher than that of the feed step. An intermediate step of co-current CO_2 rinse at feed gas pressure prior to the regeneration step produces an essentially pure CO_2 stream at high pressure. This significantly reduces CO_2 compression costs.

Two novel CO_2 sorbents have been identified as candidates for the TSSER concept, and key parameters for the optimal CO_2 sorbent are provided in Table 1.

- Potassium carbonate (K_2CO_3) promoted hydrotalcite (400–550 °C).
- Sodium oxide (Na_2O) promoted alumina (200–550 °C).

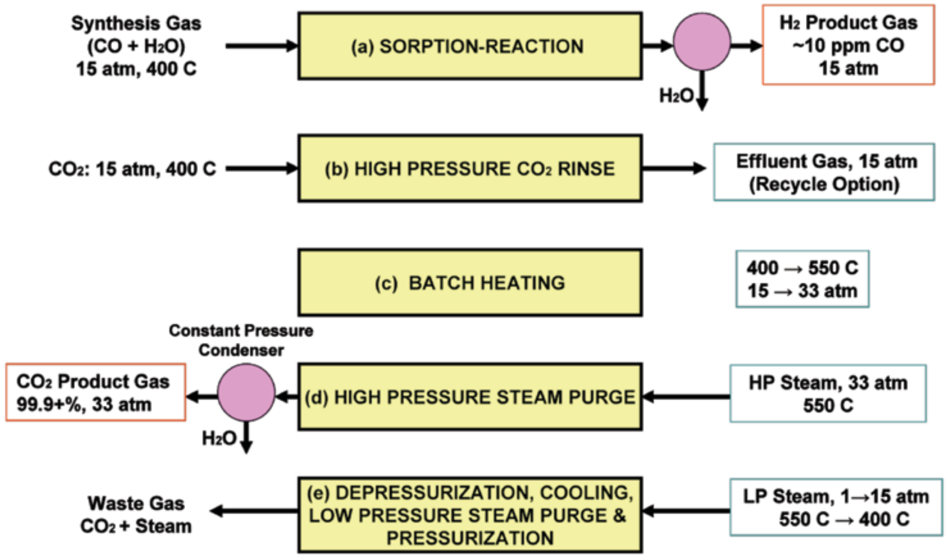

Figure 1: Components of the TSSER Process

This research project includes retrofitting an existing single-column sorption apparatus for measurement of high-pressure CO_2 adsorption characteristics; measurement of high-pressure CO_2 adsorption equilibria, kinetics, and sorption/desorption column dynamic characteristics under the conditions of thermal swing operation of the TSSER process; experimental evaluation of the individual steps of the TSSER process; development of a detailed mathematical model for simulating the performance of the individual steps of the TSSER process for optimization, process scale up, and for guiding future work; simulation and testing of the TSSER concept using a realistic syngas composition; demonstration of the thermal stability of sorbents using a thermogravimetric analysis (TGA) apparatus; and evaluating the effects of sulfur compounds [hydrogen sulfide (H_2S)] present in coal-derived syngas on the CO_2 sorbents.

Table 1: Solid Sorbent Parameters

	Parameter	Current R&D Value	Target R&D Value
Sorbent Properties	Type of sorbent	Na_2O promoted Al_2O_3	New material
	Heat of adsorption (kJ/mole CO_2)	64.9 kJ/mol	Same
	CO_2 loading/working capacity, wt%	0.65 mol/kg	0.5 mol/kg
	Surface area, m^2/g	N/A	N/A
	Particle density, cm^3/g	2.22 g/cm^3	Same
	Packing density, cm^3/g	0.694 g/cm^3	Same
	Particle size (mm)	1.5 mm	Same
	Heat capacity (kJ/K/kg)	1.05	Same
	Thermal stability, °C	Stable to 600 °C	Acceptable
	Hydrothermal stability, °C	Yes to 550 °C	—

Table 1: Solid Sorbent Parameters

	Parameter	Current R&D Value	Target R&D Value
Process Configuration	Attrition rate (fluidized bed), %/year	N/A	Fixed-bed operation
	Cycle time (fixed bed), minutes	20 min	Acceptable
	Pressure drop (fixed bed), psia	<1 psia	<1 psia
Operating Conditions	Adsorption temperature, °C	200–400 °C	Same
	Adsorption pressure, atm	Up to ~25 atm	Same
	CO_2 capture efficiency, %	71%	>50%
	Regeneration method	Thermal Swing	Novel
	Regeneration temperature, °C	550 °C	Same
	Regeneration pressure, atm	Up to 40 atm	N/A
Heat Integration	Required regeneration steam temperature, °C	550 °C	Acceptable
Miscellaneous	Sorbent make-up rate, kg/kg CO_2	N/A	—
Product Quality	CO_2 purity, %	99.9+%	95+%
	N_2 concentration, %	<0.5%	—
	Other contaminants, %	<0.5%	—
Process Performance	Electricity requirement, kJ/kg CO_2	45.2 kJ/kg CO_2 (for CO_2 compression to 140 atm)	<180 KJ/kg
	Heat requirement, kJ/kg CO_2	6,014 kJ/kg CO_2	—
	Total energy (electricity equivalent), kJ/kg CO_2	6,059 kJ/kg CO_2	—

Technology Advantages

The simultaneous removal of CO_2 drives the WGS reaction to completion, which along with operation at feed conditions (high temperature and pressure), will increase plant efficiency. Regeneration via thermal swing with steam maximizes the CO_2 working capacity of the sorbent, while eliminating H_2 losses that occur during system purging with pressure swing adsorption processes. The TSSER process also produces high-purity H_2 and CO_2 streams.

R&D Challenges

- Qualitative results suggest that the chemisorbents cannot be exposed to trace sulfur dioxide (SO_2) or H_2S impurities in the TSSER feed gas, and they must be removed by a conventional method such as selective sorption on zinc oxide (ZnO) employing a pretreatment system.
- A considerable amount of time is required to regenerate the sorbents via thermal swing cycling.

Results To Date/Accomplishments

- Retrofitted and debugged an existing test apparatus for high-pressure operation.
- Characterized the CO_2 sorbents at high pressures, including measurement of isotherms, kinetics, and sorption/desorption column dynamics for CO_2 adsorption from nitrogen (N_2).
- Ascertained the thermal stability of the sorbents.
- Evaluated isothermal and isobaric high-pressure desorption of CO_2 by N_2 purge.
- Developed a CO_2 adsorption isotherm model for use in data analysis and process simulation.

- Developed a process model for data correlation and process simulation.
- Evaluated the performance of each step of the TSSER process.
- Identified Na_2O promoted alumina as the best available CO_2 sorbent for the TSSER process.

Next Steps

Development activities for this technology are no longer part of the DOE/NETL portfolio.

Available Reports/Technical Papers/Presentations

Novel Sorption Enhanced Reaction Process for Simultaneous Production of CO_2 and H_2 from Synthesis Gas Produced by Coal Gasification, (June 2010) Final Report.

Lee, K. B, A. Verdooren, H. S. Caram, and S. Sircar, “Chemisorption of CO_2 on Potassium Carbonate Promoted Hydrotalcite,” ***J. Colloid Interface Sci., 308, 30 (2007)***.

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Lee, K. B, M. G. Beaver, H. S. Caram, and S. Sircar, “Novel Thermal Swing Sorption Enhanced Reaction Process Concept for H_2 Production by Low Temperature Steam-Methane Reforming,” ***Ind. Eng. Chem. Res., 46, 5003 (2007).***

Lee, K. B, M. G. Beaver, H. S. Caram, and S. Sircar, “Performance of Na_2O Promoted Alumina as CO_2 Chemisorbent in Sorption Enhanced Reaction Process for Simultaneous Production of Fuel-Cell Grade H_2 and Compressed CO_2 from Synthesis Gas,” ***J. Power Sources, 176, 312 (2008)***.

Lee, K. B, M. G. Beaver, H. S. Caram, and S. Sircar, “Production of Fuel-Cell Grade H_2 by Thermal Swing Sorption Enhanced Reaction Concept,” ***Int. J. Hydrogen Energy, 33, 781 (2008).***

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HYDROGEN PRODUCTION USING WATER GAS SHIFT CATALYST WITH CO_2 SORBENTS

Primary Project Goals

The University of North Dakota Energy and Environmental Research Center (UNDEERC) is developing a high-temperature carbon dioxide (CO_2) sorbent to enhance the water gas shift (WGS) reaction and produce a synthesis gas (syngas) stream that is at least 90% hydrogen (H_2) on a nitrogen-free basis.

Technical Goals

- Develop hydrotalcite sorbent briquettes and determine the required chemical composition for optimal WGS and CO_2 capture conditions.
- Test a pressure swing absorber on a continuous fluidized-bed reactor (CFBR) gasification system.
- Test lithium silicate and hydrotalcite sorbents in a bench-scale, heated fixed-bed reactor using a slipstream from the CFBR gasification system.
- Determine the optimum high-temperature CO_2 sorbent.

Technical Content

The WGS reaction, which converts most of the syngas carbon monoxide (CO) to H_2 and CO_2 by reacting the CO with steam over a bed of catalyst, can be utilized to enhance H_2 production at an integrated gasification combined cycle (IGCC) plant. The excess steam serves to drive the shift equilibrium toward the products. The reaction is exothermic and, due to equilibrium constraints, typically consists of two stages: high-temperature shift that benefits from high reaction rates at elevated temperatures; and low-temperature shift that yields more favorable reaction equilibrium.

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H_{rxn} = -41.2\ \text{kJ/mol}$$

The sorption-enhanced WGS (SEWGS) process, which combines a high-temperature CO_2 sorbent and a WGS catalyst in a packed-bed reactor that can operate at high temperature and pressure, represents one approach to further promote H_2 production. The SEWGS reactor consists of an initial adsorbent bed to remove inherent CO_2 from the syngas, followed by a second bed wherein the WGS reaction occurs as the CO_2 produced during the reaction is simultaneously captured by the adsorbent bed. Regeneration of the saturated adsorbent bed is accomplished by pressure swing absorption. By incorporating sorbent-based CO_2 removal, not only is a near capture-ready stream of CO_2 produced, but the efficiency of the plant is increased by driving the WGS reaction further to completion.

By routing a slipstream from the CFBR gasification system to the bench-scale, heated fixed-bed reactors shown in Figure 1, UNDEERC evaluated the performance of high-temperature lithium orthosilicate (Li_4SiO_4) and hydrotalcite CO_2 sorbents in the SEWGS process. Hydrotalcites are anionic clays with positively charged brucitelike [$Mg(OH)_2$] layers and inter layers of anions such as carbonates. Although the hydrotalcite sorbent did exhibit some enhanced WGS properties during bench-scale testing, the sorbent is unlikely to be a cost-effective option for IGCC power plants due to the observed low CO_2 adsorption capacity and the long purge cycles required for regeneration.

Technology Maturity:

Bench-scale

Project Focus:

Sorbent-Enhanced Water Gas Shift

Participant:

UNDEERC

Project Number:

FT40320

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Performance Period:

4/1/05 – 3/31/09

UNDEERC also compared the performance of two Li_4SiO_4 sorbents provided by Toshiba and Research Triangle Institute (RTI). Lithium orthosilicate, which reacts with CO_2 via the following reversible reaction, has exhibited a CO_2 adsorption capacity of about 35% (based on sorbent weight) at high temperatures.

$Li_4SiO_4 + CO_2 \leftrightarrow Li_2CO_3 + Li_2SiO_3$ $\Delta H_{rxn} = -142.8$ kJ/mol

As shown in Table 1, the Toshiba sorbent demonstrated superior adsorption at elevated temperatures, whereas the sorbent supplied by RTI showed higher adsorption capacity at relatively lower temperatures. One notable pattern is the sorbent provided by Toshiba demonstrated a reduction in adsorption capacity with decreasing CO_2 concentrations, eventually leading to inferior adsorption at higher temperatures as compared to RTI's sorbent.

Additionally, it was found that RTI's sorbent had slightly better desorption properties with complete desorption taking place at 700 °C, whereas Toshiba's sorbent required temperatures as high as 800 °C to attain complete desorption in a 100% nitrogen atmosphere.

Figure 1: Heated Fixed-Bed Reactors

Table 1: Comparison of Adsorption Properties of Sorbents Provided by Toshiba and RTI

Temperature (°C)	100% CO_2		40% CO_2		20% CO_2	
	Adsorption (wt%)		Adsorption (wt%)		Adsorption (wt%)	
	Toshiba	RTI	Toshiba	RTI	Toshiba	RTI
400	1.32	4.33	0.89	2.48	0.69	1.43
500	19.32	14.10	18.04	12.48	15.89	14.10
600	23.26	15.22	19.87	14.04	18.61	14.39
700	33.32	15.88	31.68	—	2.41	8.97
800	3.46	—	1.45	—	1.31	—

Technology Advantages

The simultaneous removal of CO_2 drives the WGS reaction to completion, which along with operation at feed conditions (high temperature and pressure), will increase IGCC power plant efficiency by maintaining a high-temperature, high-pressure feed gas to the combustion turbine. The Li_4SiO_4 sorbents exhibit high CO_2 adsorption capacity at elevated temperatures and effectiveness across a wide range of CO_2 concentrations.

R&D Challenges

A considerable amount of time is required to regenerate a Li_4SiO_4 sorbent which, when coupled with the large quantity of sorbent required, imposes significant limitations for industrial use.

Results To Date/Accomplishments

- Completed testing of a pressure swing absorber on a continuous fluid-bed gasification system.
- Produced 20 wt% potassium carbonate/80 wt% hydrotalcite briquettes.
- Completed testing of Li_4SiO_4 sorbents in heated fixed-bed reactors using a slipstream from the CFBR gasification system, and determined the physical strength in high-moisture atmospheres and the CO_2 adsorption capacity of the sorbents at various operating conditions.

Next Steps

Project completed March 2009.

Available Reports/Technical Papers/Presentations

Base Research Program—Final Report, August, 2009. http://www.osti.gov/bridge/product.biblio.jsp?query_id=0&page=0&osti_id=984507&Row=1

Baseline testing of the oxy-combustion system will follow similar procedures as the absorption system. The data collected will be used to identify potential challenges concerning this technology. These challenges include effects of mercury (Hg) capture, flame stability, fouling, slagging, and heat-transfer issues.

Once CO_2 capture technologies have been selected, testing will begin. Some of the technologies under consideration include other solvents [monodiethanolamine (MDEA), tailored amines, designer amines, ammonia, and potassium bicarbonate), membranes (metal membranes and carbozyme], and solid sorbents (zeolites, metal-organic frameworks, solid amines, and C-Quest). In addition to testing these technologies, different fuels will be used to evaluate their impact on the performance of the fabricated test units. Factors to be examined will include the effects of SO_x, NO_x, and other gas components; effects of ash deposition along with corrosion of refractory; and alloy components.

UNDEERC has completed the construction of the oxy-combustion system and has begun shakedown testing of the units.UNDEERC has also completed an Aspen model of the solvent absorption and stripping column (SASC) system.

Technology Advantages

UNDEERC will be capable of providing experimental data for a variety of advanced CO_2 capture technologies and oxy-combustion systems. This information will not only provide needed information for further advancement, but will provide a clear comparison of various approaches.

R&D Challenges

Retrieving enough information on existing technologies to make appropriate selections for testing.

Results To Date/Accomplishments

- Completed design and construction of the post-combustion test system.
- Evaluated four solvents in the post-combustion test system: three advanced solvents and MEA
- Completed the oxy-combustion retrofit.
- Conducted two phases of testing with the oxy-combustion system
- Modeled the combustion test facility (CTF) system in Aspen with and without the oxygen-fired retrofit modifications.

Next Steps

- Perform additional experiments on promising technologies.
- Conduct systems engineering analyses to evaluate technology integration opportunities for CO_2 capture systems.

Final test results will not be available until the August 2011 project completion date.

Available Reports/Technical Papers/Presentations

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