EVALUATION OF DRY SORBENT TECHNOLOGY FOR PRE- COMBUSTION CO_2 CAPTURE

primary project goals

URS Group and the University of Illinois at Urbana-Champaign (UIUC) are developing dry carbon dioxide (CO_2) sorbent materials, through the coupling of thermodynamic, molecular simulation, as well as 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 percent of the CO_2 from a simulated synthesis gas (syngas) at conditions applicable to a WGS reactor, thus meeting a key U.S. Department of Energy (DOE) program objective.

technical goals

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 conversion in a 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 percent 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 carbon monoxide conversion catalysts currently used in WGS reactors and improve overall WGS thermal efficiency.
- Determine the techno-economic feasibility of the sorption-enhanced WGS (SEWGS) process for removing CO_2.

technical content

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

A novel approach integrates 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 evaluate sorbent performance in simulated WGS gas mixtures at commercially relevant conditions. Appropriate data reduction and analysis provides suitable data for a techno-economic analysis to evaluate the feasibility and scaleup potential of the SEWGS technology.

technology maturity:
Bench-Scale Using Simulated Syngas

project focus:
Sorbent Development for WGS

participant:
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project number:
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performance period:
1/1/10 – 9/30/13

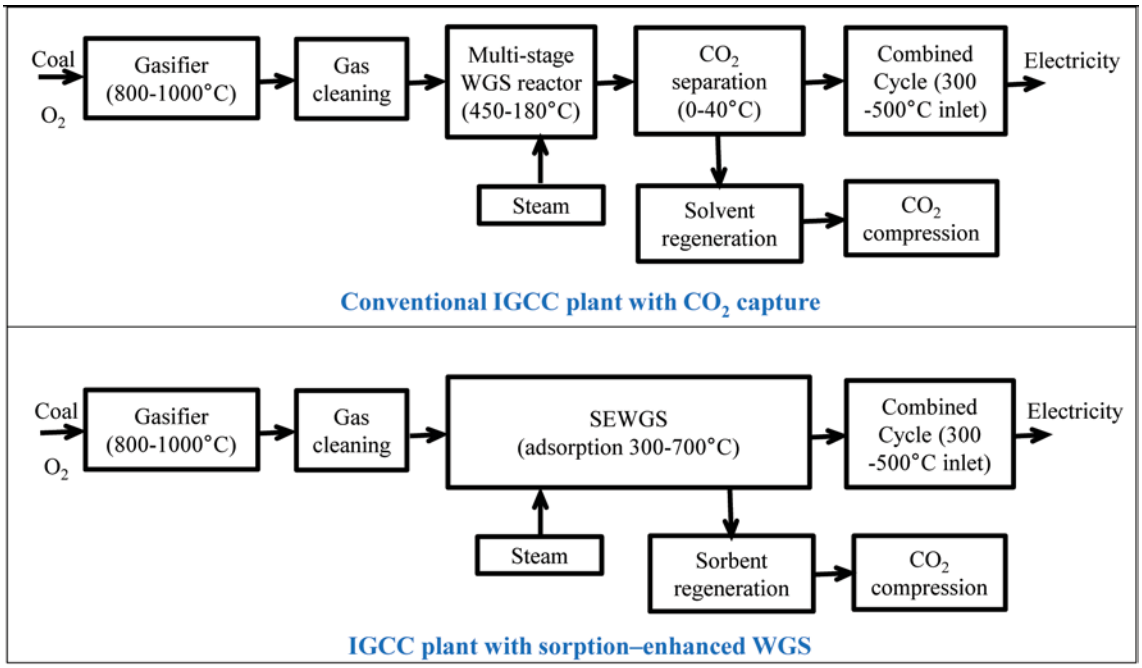

Figure 1: IGCC with SEWGS vs. Conventional IGCC

Process simulation modeling and sorbent molecular and thermodynamic analyses by UIUC 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 includes 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 predicts isotherms and properties, kinetics, and dynamics, and identifies sorbents with desired properties using quantum chemistry/mechanics, force field-based molecular dynamics (MD), and reactive dynamics (RD) simulations. Process simulation analyzes various process scenarios for heat integration between SEWGS and integrated gasification combined cycle (IGCC) and process energy performance for individual sorbents.

The first phase testing and modeling efforts guide the synthesis of sorbents with desired pore structure and composition. Synthesis includes use of various precursors, including calcium, magnesium, and other metal oxides, as well as zirconates, titanates, silicates, aluminates, and adsorbent-shift catalyst hybrid. The sorbent down-selection process is guided by the decision tree shown in Figure 2.

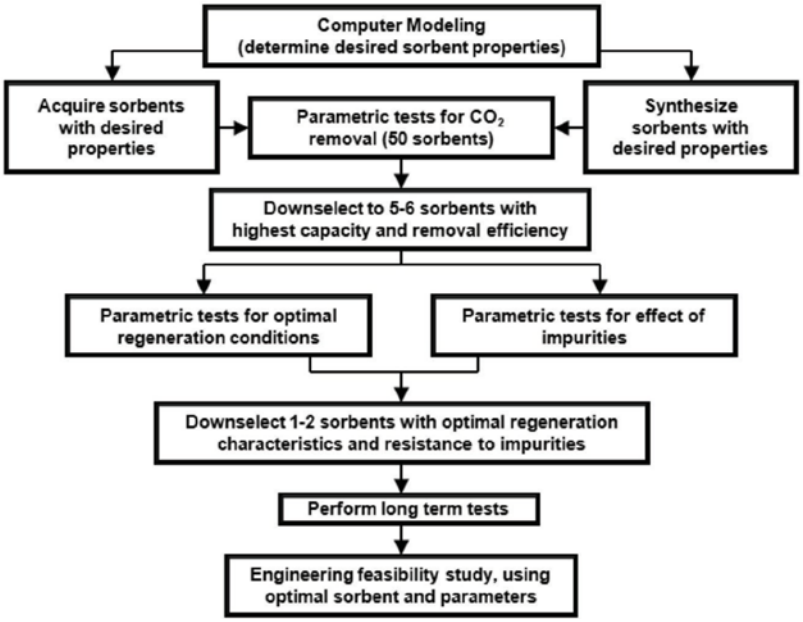

Figure 2: Sorbent Development and Analysis Decision Tree

An atmospheric-pressure thermogravimetric analyzer (TGA) and high temperature and pressure reactor (HTPR) system, capable of 300 pounds per square inch gauge (psig) and 950 °C, are UIUC's primary tools for screening sorbents for CO_2 removal. A URS HTPR provides the capability to evaluate five to seven down-selected sorbents' adsorption performance in the presence of syngas impurities and regeneration performance. Long-term testing is limited to a down-selection of one to two sorbents.

A preliminary engineering study of process feasibility for adsorbing and removing CO_2 as part of the WGS process, and comparison to base WGS operation and other CO_2 removal strategies, is informed by the preceding laboratory test results. Parameters under evaluation include costs of >90 percent 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

	Units	Current R&D Value	Target R&D Value
Sorbent			
True Density at STP	kg/m^3		TBD
Bulk Density	kg/m^3		TBD
Average Particle Diameter	mm	nano (20–70 nm) or micro meter (0.5–10 µm) level; particles can be pelletized if needed	TBD based on the reactor design analysis
Particle Void Fraction	m^3/m^3		
Packing Density	m^2/m^3		
Solid Heat Capacity at STP	kJ/kg-K	<1	<1
Crush Strength	kg_f		
Manufacturing Cost for Solvent	$/kg		
Absorption			
Pressure	bar	30–40	40
Temperature	°C	300–700	550–650
Equilibrium CO_2 Loading	g mol CO_2/kg		
Heat of Absorption	kJ/mol CO_2	100–200	TBD

Desorption			
Pressure	bar	up to 30	highest possible up to 30
Temperature	°C	depends on individual sorbent and highest regeneration pressure achievable	TBD; optimization based on minimal energy limit
Equilibrium CO_2 Loading	mol/mol		
Heat of Desorption	kJ/mol CO_2		
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	temperature swing	temperature swing
Flue Gas Flowrate	kg/hr		
CO_2 Recovery, Purity, and Pressure	%/%/bar	90 percent, 99 percent	
Adsorber Pressure Drop	bar	depending on sorbent properties, to be determined during project	TBD

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. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40 °C; however, measured data at other conditions are preferable to estimated data.

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. Note that for a typical PC power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2 percent. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

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.

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 are 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 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).

Syngas 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.

technology advantages

- High carbon monoxide conversion with reduced stream addition.
- No or limited WGS catalyst use.
- High-quality adsorption heat usable for generation of high-quality steam.
- Limited gas cooling/reheating requirement downstream.
- No separate CO_2 capture unit required.
- Reduced energy requirement for CO_2 compression.

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.
- System/reactor issues, such as material transport and handling at high temperature and pressure.

results to date/accomplishments

- More than 40 sorbents were 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 percentage point increase in net thermal efficiency for the simulated plant with SEWGS.
- Molecular simulation studies included quantum chemical (QC) calculations and MD simulations with reactive field force
- (ReaxFF). Molecular simulation was successfully applied to assess carbonation and calcination reactions (CaO).
- The impacts of sorbent structure and the sintering of calcium oxide particles with and without CO_2 chemisorption, and the role of a dopant in reducing the sintering of CaO particles, were also determined.
- More than 60 SEWGS sorbents were synthesized using mechanical alloying (MA), ultrasonic spray pyrolysis (USP), and flame spray pyrolysis (FSP) techniques.
- CaO sorbents prepared by dry and wet ball-milled MA methods exhibited improved CO_2 adsorption capacities and stabilities over commercial $CaCO_3$ materials. The performance of $CaCO_3$ sorbents was improved by doping with inert MgO.
- Hollow, porous $CaCO_3$ sorbents synthesized using the USP method were spheres of ≈1 μm with a shell thickness of 50–100 nm. The CaO generated upon calcination of the $CaCO_3$ exhibited a high surface area (up to 75 m^2/g).

- A 75:25 w/w CaO:$Ca_{12}Al_{14}O_{33}$ (mayenite) sorbent retained 91 percent of its initial CO_2 capacity after 15 cycles and 79 percent after 50 cycles, while a USP CaO only retained 43 percent after 15 cycles.
- The surface area of nano-sized (<70 nm) CaO, ZrO_2-doped CaO, MgO, MgO-doped CaO, and ZrO_2-doped MgO sorbents synthesized using the FSP method ranged between 21 and 54 m^2/g. ZrO_2 was found to be an effective dopant to improve the stability of CaO-based sorbents. A ZrO_2-CaO (Zr:Ca=0.2:1) sorbent maintained its capacity at 0.5 g CO_2/g sorbent over 15 adsorption-desorption cycles.
- An HTPR tube reactor with quarter-inch ID and 1-foot length was also used to test sorbents at UIUC. These tests were performed at 650 °C and CO_2 partial pressures up to 4 bar adsorption conditions.
- Results from the HTPR testing showed sorbents with as high as 0.4 grams of CO_2 per grams of sorbent capacity with the ability to initially shift the WGS completely toward CO_2/H_2.
- A longer term experiment with a simple syngas matrix and N_2/steam regeneration stream showed a USP sorbent (#199) to be stable through 50 adsorption-regeneration cycles, though the sorbent tested had a somewhat diminished initial capacity.

next steps

This project ended on September 30, 2013.

available reports/technical papers/presentations

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Hong Lu, Yongqi Lu, Massoud Rostam-Abadi, "CO_2 Sorbents for a Sorption-Enhanced Water-Gas-Shift Process in IGCC plants: A Thermodynamic Analysis and Process Simulation Study," International Journal of Hydrogen Energy, Volume 38, Issue 16, 30 May 2013, Pages 6663-6672. *http://www.sciencedirect.com/science/article/pii/S0360319913006770*.

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