DEVELOPMENT OF BIOMIMETIC MEMBRANES FOR NEAR-ZERO PC POWER PLANT EMISSIONS

primary project goals

Carbozyme set out to develop an enzyme-based, contained liquid membrane (CLM) to extract carbon dioxide (CO_2) from coal and natural gas combustion flue gas. Carbozyme also set out to evaluate a state-of-the-art electrodialytic (EDI) method for CO_2 capture, comparing its performance with that of the CLM.

technical goals

- Scale-up the enzyme-catalyzed, CLM permeator design (4 to 400 m^2) to include multiple units organized as a skid (3×40 m^2) for testing with various coal ranks and natural gas.
- Implement a pretreatment conditioner to ensure that the flue gas constituents will not adversely impact the CLM permeator.
- Validate technology to cost-effectively produce carbonic anhydrase (CA) enzymes for the CLM.
- Test and analyze three different EDI test cells: a controlled pH resin wafer, a hollow fiber fed bipolar membrane (BPM), and an ion exchange membrane-resin wafer (IEM-RW).
- Conduct a commercialization study for both the CLM and EDI technologies.

technical content

The enzyme-based CA CLM membrane process mimics the natural process for removing CO_2 from an organism. An organism's blood stream is used to transport oxygen (O_2) and CO_2 to and from its cells, respectively. CA is an enzyme in the blood that captures the CO_2 from the cells and converts it to bicarbonate (HCO_3^-). The enzyme reverses this reaction in the lungs, allowing the CO_2 to be exhaled. Figure 1 shows the configuration for the enzyme-based CA CLM membrane process Carbozyme set out to develop. The CA CLM membrane is able to incorporate the absorption and stripping processes into a single unit. A membrane module consists of two groups of hollow fibers – one group contains the incoming CO_2 lean flue gas, and the second group contains the CO_2 rich permeate stream. The CA enzyme is contained in a thin-film liquid between the two groups of fibers. The CA helps catalyze the CO_2 to HCO_3^- to pro-

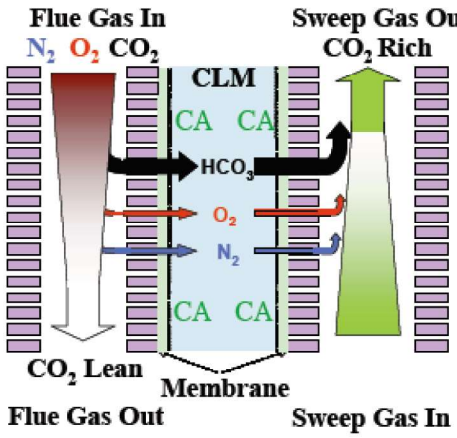

Figure 1: Configuration for Carbozyme-Developed, Enzyme-Based Carbonic Anhydrase Contained Liquid Membrane

technology maturity:

Laboratory/Bench-Scale, Using Simulated Flue Gas

project focus:

Biomimetic Membrane

participant:

Carbozyme

project number:

FC26-07NT43084
FG26-06NT42824

NETL project manager:

José Figueroa
jose.figueroa@netl.doe.gov

principal investigator:

Michael Trachtenberg
Carbozyme, Inc.
mct@cz-na.com

partners:

Argonne National Laboratory
EERC
Electrostep
Kansas State University
Siemens
SRI
Visage Energy

performance period:

3/28/07 – 7/31/09

mote permeation across the CO_2 lean membrane and reverses the process, promoting permeation across the CO_2-rich membrane. CA is one of the fastest acting enzymes with a turnover rate of 600,000 katals (catalyzes the hydration of 600,000 molecules of CO_2 per second per molecule of CA).

Figure 2 shows a process schematic for the CA CLM. Pretreated combustion flue gas from the boiler enters the membrane. A vacuum system is used to provide the driving force across the membrane. After the CO_2 is separated from the flue gas, it goes through a knockback condenser for water removal prior to compression. The resulting product is a 95 percent pure CO_2 stream. The remaining flue gas is sent to the plant stack.

The concentrated ammoniated solution is used to capture CO_2 and hydrogen sulfide (H_2S) from synthesis gas (syngas) at high pressure. This technique reduces the size of the CO_2 stripper and operates at high pressure, reducing CO_2 compression needs; both reduce electric power consumption. AC has high net CO_2 loading, is a low-cost and readily available reagent, and requires little solvent makeup; the solubility of hydrogen (H_2), carbon monoxide (CO), and methane (CH_4) in absorber solution is extremely low.

The project, in its first phase, constructed a bench-scale batch reactor unit to test the technology at SRI's facility in California. Testing was performed to validate the concept and to determine the optimum operating conditions.

Absorber testing was conducted to first determine the solubility of shifted-gas components (H_2, CO, nitrogen [N_2], argon [Ar]), then to determine the reactivity of CO_2 and H_2S; mixed-gas testing was performed to determine the relative reaction kinetics.

Regenerator testing was conducted to determine CO_2 and H_2S release characteristics, as well as the relative kinetics of CO_2 and H_2S release. Optimal operating conditions derived in bench-scale testing will be used at the pilot-scale test.

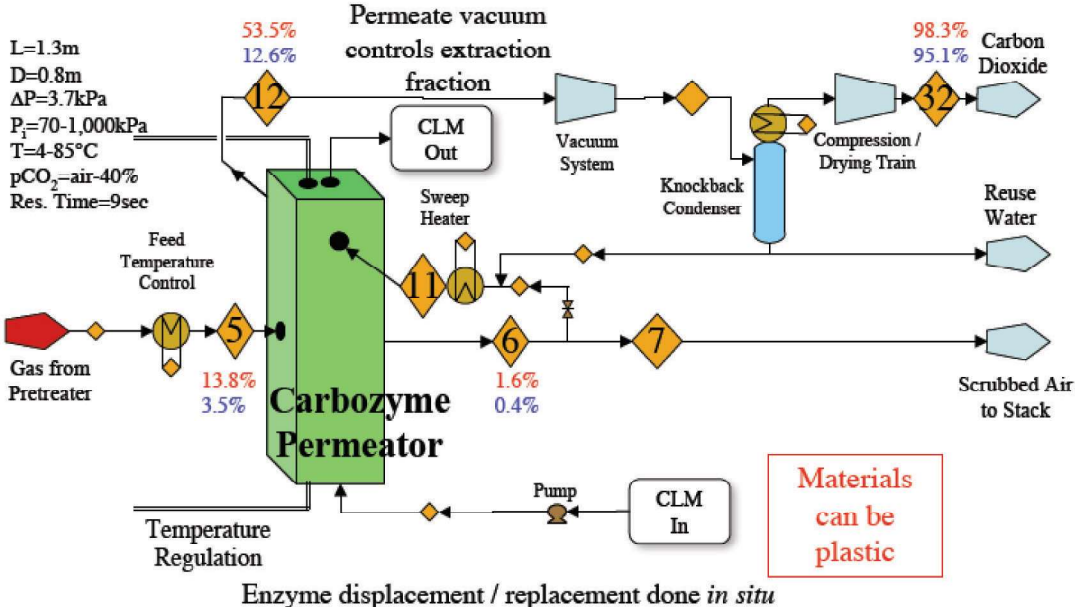

Figure 2: Process Schematic for the Carbonic Anhydrase Contained Liquid Membrane

technology advantages

- The CA enzyme catalyst does not contain any toxic chemicals or byproducts, making it more environmentally friendly than competing technologies.
- The CA enzyme catalyst has a fast CO_2 production rate with low energy requirements and boosts separation and purification due to its low nitrogen (N_2) and O_2 solubility.
- The enzyme catalyst is not vulnerable to oxidation or the formation of stable salts.
- The CA CLM system requires only minimal pumping and no heat exchangers, allowing it to consume 30 to 50 percent less energy compared to competing technologies.
- The CA CLM system recycles nearly all of its water and a portion of its waste heat.
- The modular design of the membrane makes it easy to manufacture, install, and scale up.

R&D challenges

- The cost of the purified CA enzyme remains high and production costs will need to be reduced in order to be considered economically viable.
- Early immobilization of the CA enzyme needs to be addressed.
- Sulfur dioxide (SO_2) acidification of the carbonate carrier fluid needs to be addressed via flue gas pretreatment.
- Ionized mercury in the flue gas could reduce enzyme activity.

results to date/accomplishments

Development progress for the CA CLM process was made in several categories, such as flue gas stream analysis and conditioning, enzyme selection, enzyme immobilization, membrane module construction, and economic analysis.

Specific accomplishments include:

- Developed an immobilized CA enzyme catalyst based on a thermophilic form of CA that can maintain a high activity at elevated temperature (≈50°C). The enzyme was immobilized using a proprietary surface activation method using an ultrathin polyamino acid (PAA) layer that can be removed and replaced, as needed. Enzyme testing indicated up to 80 percent of initial activity was retained over a 60-day period.
- Developed a 0.5-m^2 bench-scale CLM permeator that combines absorption and desorption in a single house through use of dual hollow-fiber, spiral-wound, polymer membranes. In this configuration, CO_2 capture is driven by a combination of pressure, vacuum, and temperature. More than 90 percent CO_2 capture was achieved during testing.
- Developed an alternate process technology based on separate absorption/desorption modules using single hollow-fiber, spiral-wound, polymer membranes.
- Fabricated an 11-m^2 CLM module for scale-up testing.
- Developed and tested a flue gas pre-treatment system for the CLM process.
- Developed computer modeling for CLM process components and integrated systems.
- Developed and tested a second technology based on a resin-wafer EDI system that uses a pH shift to accomplish CO_2 absorption/desorption.

next steps

This project ended on July 31, 2009.

available reports/technical papers/presentations

"Development of Biomimetic Membranes for Near Zero PC Power Plant Emissions," Final Report for Project #43084, March 2011.

"Capture of CO_2 by the Carbozyme Permeator," 8th Annual Conference on Carbon Capture and Sequestration, Pittsburgh, Pennsylvania, May 2009.

"Development of Biomimetic Membranes for Near-Zero Power Plant Emissions," Annual NETL CO_2 Capture Technology for Existing Plants R&D meeting, Pittsburgh, Pennsylvania, March 2009.

"Membrane-based, Enzyme Facilitated, Efficient, Carbon Dioxide Capture," 9th International Conference on Greenhouse Gas Control Technologies, Washington, DC, November 2008.

"Progress on Carbozyme's HFCLM Permeator Technology Scale-up Project," 7th Annual Conference on Carbon Capture and Sequestration, Pittsburgh, Pennsylvania, May 2008.

"Biomimetic Membrane for CO_2 Capture from Flue Gas," Final Report for Project #42824, August 2007.