Task 6.5 - Gas Separation and Hot-Gas Cleanup

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GAS SEPARATION AND HOT-GAS CLEANUP

1.0 BACKGROUND

Catalytic gasification of coal to produce H_2 - and CH_4 -rich gases for consumption in molten carbonate fuel cells is currently under development; however, to optimize the fuel cell performance and extend its operating life, it is necessary to separate as much of the inerts (i.e., CO_2 and N_2) and impurities (i.e., H_2S and NH_3) as possible from the fuel gas before entering the fuel cell. In addition, the economics of the integrated gasification combined cycle (IGCC) can be improved by separating as much of the hydrogen as possible from the fuel, since hydrogen is a high-value product. One method currently under development for accomplishing this gas separation and hot-gas cleanup is gas separation membranes. These membranes are operated at temperatures as high as $800^\circ C$ and pressures up to 300 psig. These membranes can have very small pores (30–50 Å) that separate relatively inefficiently the undesired gases by operating in the Knudsen diffusion region of mass transport or pore sizes ($< 5\text{Å}$), which operates in the molecular sieving region of mass transport phenomena. Dissolution of atomic hydrogen into metallic membranes made of platinum and palladium alloys is also being developed.

Technological and economic barriers that must be resolved before gas separation membranes are commercially viable include improved gas separation efficiency, membrane optimization, sealing of membranes in pressure vessels, high burst strength of the ceramic material, pore thermal stability, and material chemical stability. Hydrogen separation is dependent on the temperature, pressure, pressure ratio across the membrane, and ratio of permeate flow to total flow. For gas separation under Knudsen diffusion, increasing feed pressure and pressure ratio across the membrane should increase the gas permeability, while decreasing the temperature and the permeate-to-total flow ratio should also increase the gas permeability. In the molecular sieving regime of mass transport, the inlet pressure and pressure ratio should have no effect on gas permeability, while increasing temperature should increase permeability.

2.0 OBJECTIVES

The objective of this task is to develop and test superior gas separation membranes. Several methods will be tested to prepare new membrane materials, including physical vapor deposition via electron beam evaporation. Other ceramic filter materials used in hot-gas particulate filters will be obtained from selected suppliers for use as substrates to develop a thin-film membrane selective to hydrogen permeation. This thin-film membrane will be modified via an EERC proprietary process. The base filter materials will already have been characterized for hydrothermal and chemical stability and pore size. The selectivity of these membrane materials for separating undesired gases will be determined. Selectivity will be measured by mixing bottled gases in a manifold, feeding the gases to the membrane, and sampling the inlet, permeate, and raffinate streams for gas composition and volumetric flow rate.

Specific questions to be answered include the following:

- What are the effects of ceramic membrane properties (i.e., surface area, pore size, and coating thickness) on permeability and selectivity of the desired gases?

- What are the effects of operating conditions (i.e., temperature, pressure, and flow rate) on permeability and selectivity?

3.0 ACCOMPLISHMENTS

A detailed literature search was conducted concerning different methods for preparing a thin-film membrane material. This membrane material would be highly selective to hydrogen permeation, while insensitive to contaminant gases such as hydrogen sulfide and carbonyl sulfide. The literature search will verify that the proposed methods for manufacturing these membrane materials are not duplicative of other research efforts already under way. The literature search will complete Task 3.1 – Gas Separations and Hot-Gas Cleanup and begin the program for Task 6.5 – Materials for Gas Separation and Hot-Gas Cleanup. Formal reporting of this literature review will occur at a later date. A delay in compiling the results of the literature search and in developing the thin-film membrane has resulted from the departure of a key investigator. The EERC is in the process of hiring a material scientist/ceramicist to fill this position.

Once a viable gas separation membrane has been manufactured, the EERC bench-scale CFBR will be used to test the membrane, with bottled and actual coal-derived fuel gases. Figure 1 shows the 4-lb/hr CFBR used for gasification tests with various coals. The unit was originally designed as a pyrolysis unit for a U.S. Department of Energy mild gasification program, but has been used for gasification, pyrolysis, and combustion on a variety of projects. Although predominantly operated as a fluid bed, the unit, which was designed to be flexible, has been operated as a fixed bed by using lower gas flow rates or larger particle sizes in the bed.

Gas used for fluidization is mixed in a gas manifold. Bottled gas, house nitrogen, house air, and any liquid desired (such as steam) are first preheated, then mixed and heated to reaction temperature in a superheater (20' of 3/8" tubing coiled into a 18" ceramic fiber heater). Two bottled gases in combination with either house air or house nitrogen and a liquid can be used at the present time. Using more bottled gases in the feed gas mix would involve additional mass flow controllers.

The reactor was constructed of 316H stainless steel Schedule 80 pipe. The first (bottom) section is made of 3-inch pipe and is 33 inches in length. The next (top) reactor section is made of 4-inch pipe and is 18.75 inches in length. The two sections are connected with a 316H weld reducer. The unit was designed such that the top of the fluid bed lies 33 inches above the coal injection point. A solids offtake leg at the top of the bed is the primary means of solids removal from the reactor. A ball valve facilitates the collection of product while the system is operating.

The reactor currently has two ceramic fiber heaters to maintain the vessel temperature and eliminate hot spots. Using external heaters allows the evaluation of internal and external heating methods for process development and scaleup. The reactor is capable of operation at a maximum of 155 psig and 840°C.

A 3-inch-diameter cyclone is used for solids removal from the gas stream. A ball valve allows the changing of the solids catch pot while the system is operating. The cyclone is heated with a ceramic fiber heater capable of operating at 1650°F (900°C) and 200 psig. An 8-inch-long section of 2-inch 316H stainless steel Schedule 80 pipe is used as a pressure vessel to contain a fixed bed of

Figure 1. Four-lb/hr continuous fluid-bed reactor.

zinc titanate sorbent bed to reduce the H_2S levels to less than 10 ppm and preferably to less than 1 ppm.

Three 4-inch-diameter vessels are used to remove all condensables from the gas stream. Two separate trains were installed: one for mass balance sampling, and the other for heatup, non-steady-state conditions, and cooldown. The first condenser pot is indirectly cooled by water and typically cools the gas stream from 570°F (300°C) to 200°F (9°C). The next two condensers, also indirect, are glycol-cooled. The exit gas temperature is typically 50°F (10°C). A glass wool filter was used to capture aerosols passed through the condenser system. A wet scrubber neutralizes any chlorine still present in the gas stream before sending the gas through a product gas meter.

A Genesis™ software package is used for process control and data acquisition. Pressure drop across the bed is measured by two transmitters, and thermocouples throughout the unit measure temperatures. Temperature and pressure readings are recorded every 30 seconds, and these data are directly transferred to Lotus® spreadsheets.

Mass flow controllers for hydrogen, carbon monoxide, carbon dioxide, and nitrogen for supplying a clean gas stream from bottled gases are available at the EERC. The CFBR will be used as the mixing chamber and heater for the hot-gas source for the initial work. This testing would be accomplished without the presence of coal in the reactor. An on-line Foxboro 931°C gas chromatograph, as well as collecting gas bag samples to be analyzed by a HP 5880 gas chromatograph, will be used for measuring gas compositions in this program. Initial tests will be performed to conduct short-term performance tests using the membrane to separate hydrogen from

the mixed-gas stream. Subsequent tests could then look at the effects of impurities (e.g., H_2S , HCL) on the membrane performance by adding these impurities to the bottled gas mixture or by using actual coal-derived fuel gases from the same CFBR equipment. The gas composition of the coal-derived gas stream may be adjusted by adding some bottled gas to the gas stream entering the reactor.

4.0 FUTURE WORK

The literature review on membrane materials and fabrication methodologies will be completed when new personnel are hired. Procurement of substrate and membrane materials must be accomplished. Testing of thin-film coating technologies needs to be completed. Testing of the best membrane materials must be performed in the bench-scale CFBR.

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