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Catalytic Membranes for Facilitating the Water-Gas Shift Reaction

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Catalytic Membranes for Facilitating the Water-Gas Shift Reaction

CONTRACT INFORMATION

Contract Number DE-FG03-91ER81229

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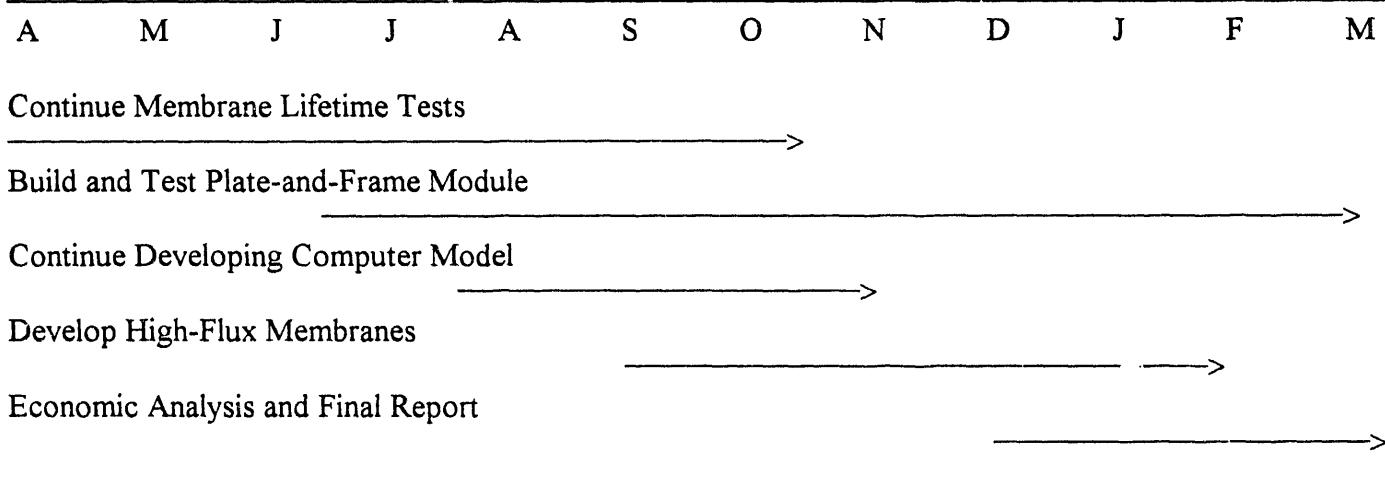
Principal Investigators David J. Edlund

METC Project Manager Venkat Venkataraman

Period of Performance March 31, 1992 to March 31, 1994

Schedule and Milestones

FY93 Program Schedule



OBJECTIVES

This program is directed at furthering the development of a metal-membrane-based process for economically producing pure hydrogen from the raw gasifier stream. A related program is directed

at developing a metal-membrane-based process for cleanly and efficiently removing hydrogen sulfide from the hot gas stream. Both of these processes would be accomplished at 500°C to 800°C and are based on a novel hydrogen-permeable composite-metal membrane. Specific program objectives

include 1) design, fabrication, and demonstration of pre-prototype membrane modules; 2) improving the membrane composition to increase the hydrogen flux; 3) evaluating membrane lifetime; and 4) conducting engineering and economic analyses of the processes.

BACKGROUND INFORMATION

Currently, the gasification of coal incorporates conventional low-temperature unit processes for the production of hydrogen and the elimination of gas-stream impurities such as hydrogen sulfide (Figure 1). The cost of the conventional gas-processing technology (i.e., medium- and low-temperature water-gas-shift (WGS) reactors, heat exchangers, acid-gas scrubbers, and Claus furnace) has given rise to research directed at developing more efficient processes.

PROJECT DESCRIPTION

The Proposed Membrane-Based Processes

Bend Research has proposed the development of two processes that are expected to simplify the overall gasification process and lower the cost of producing hydrogen from coal (Figure 1). These processes are based on a novel hydrogen-permeable composite-metal membrane (Figure 2). This membrane has exhibited stable flux operating at 500°C to 700°C (100 psig hydrogen feed stream) in laboratory tests.

The first of these processes—a membrane reactor for producing pure hydrogen from the WGS reaction at high temperature—would replace the conventional WGS reactors, associated acid-gas scrubbers, and associated heat exchangers (Edlund, 1992a). The second of the two processes under development—a membrane reactor for

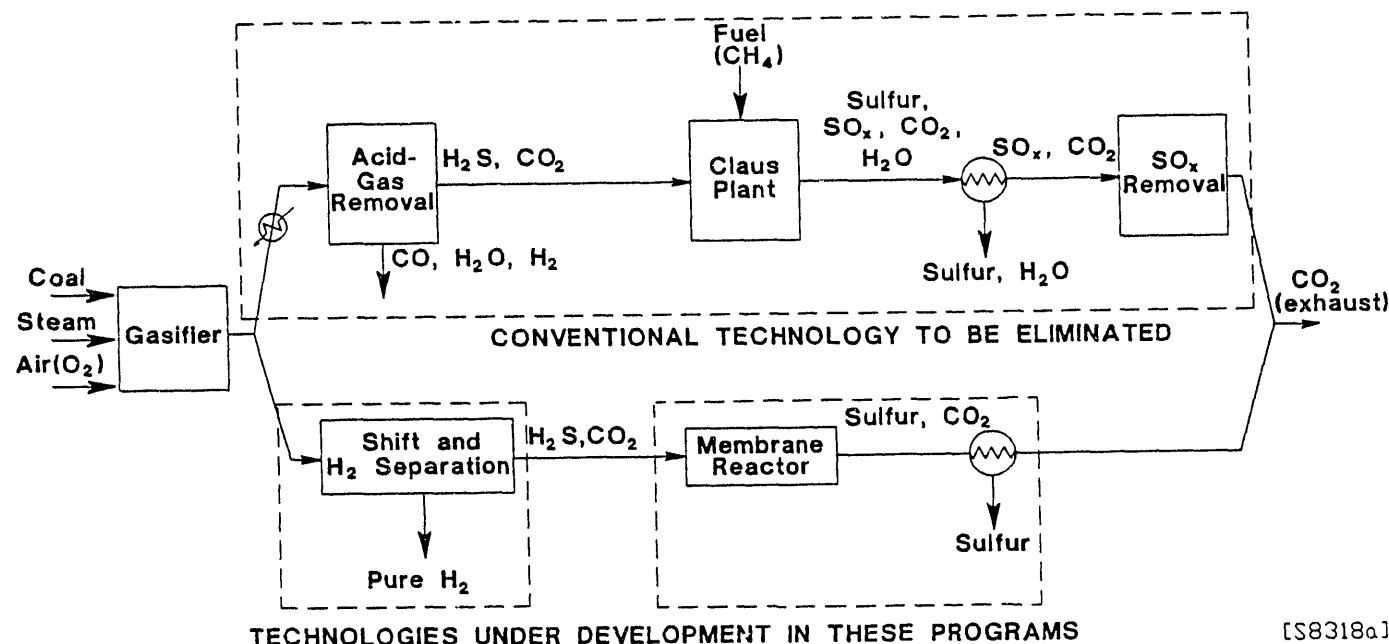
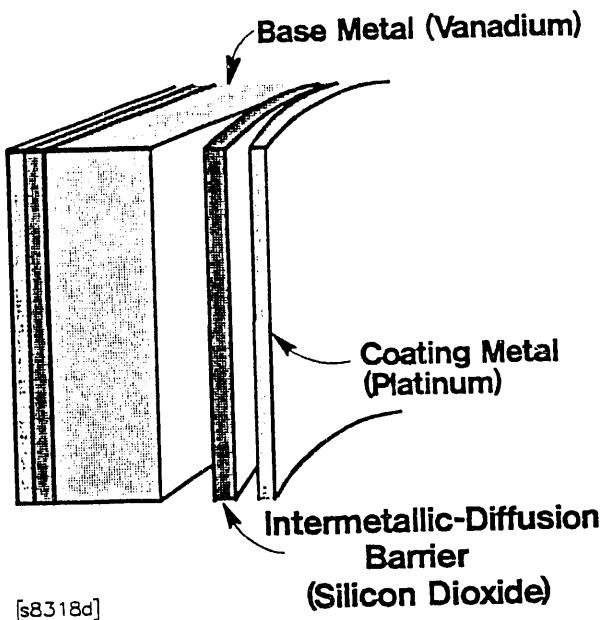


Figure 1. Comparison of Existing and Proposed Technologies for the Production of Pure Hydrogen and the Separation and Decomposition of H_2S From Coal Gas, Showing Conventional Unit Processes to be Eliminated

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[s8318d]

Figure 2. Key Elements of the BRI Composite-Metal Membrane

efficiently thermolyzing hydrogen sulfide in a non-oxidizing atmosphere—would replace acid-gas scrubbers, associated heat exchangers, and the Claus furnace (Edlund, 1992b; Edlund and Pledger, 1993). Furthermore, since these membrane-based processes completely reject nitrogen (while passing only pure hydrogen), the gasifier may be air-blown, rather than oxygen-blown, without suffering a decrease in hydrogen purity.

Hydrogen Production in a Membrane Reactor

The WGS reaction will be driven toward completion within a membrane reactor by removal of hydrogen from the feed side of the membrane. The rate at which hydrogen is transported across the membrane (i.e., the hydrogen flux), as well as the rate of the WGS reaction, will increase with increasing temperature and pressure. Figure 3 shows the effect of increasing pressure on the rate and degree of conversion for the WGS reaction within a laboratory-scale membrane reactor.

At sufficiently long residence times, conversion will approach an equilibrium value defined by the temperature, the feed composition ($H_2O:CO$ ratio), and the partial pressure of hydrogen remaining at the feed side of the membrane. As Figure 3 shows, conversion in excess of 90% was achieved using a 2:1 $H_2O:CO$ feed stream at 235 psia and 700°C, in agreement with the theoretical conversion. By using a staged membrane process and/or a condensable sweep stream (such as steam) at the permeate side of the membrane, it should be possible to recover pure hydrogen at moderate pressure (several atmospheres) and retain high yield ($\geq 95\%$ recovery of hydrogen).

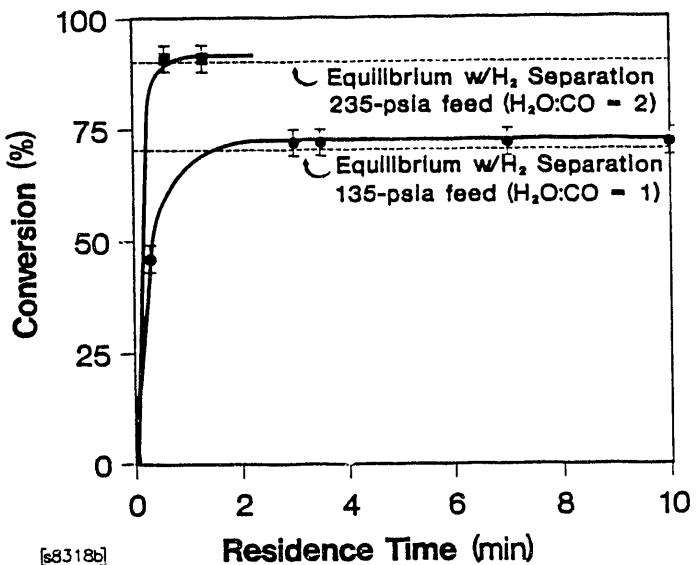


Figure 3. Conversion Versus Residence Time at 700°C Showing the Increase in Conversion and Rate Obtained by Increasing the Feed Pressure

RESULTS

During the past year, the following key results have been obtained:

- The intermetallic-diffusion barrier is key to achieving stable membrane performance. Therefore, several thermodynamically stable oxides have been evaluated for use as this layer. Based on these studies, we have learned that premature membrane failure can occur if the oxide that comprises the intermetallic-diffusion barrier 1) contains residual water or organics, 2) undergoes a partial reduction at operating temperatures (e.g., the Group 3 oxides), or 3) contains substantial cracks or holes that penetrate to the vanadium surface (i.e., to provide a direct route for the Pt coating metal to contact the vanadium surface due to plastic flow under operating conditions).
- Using a model membrane system composed of vanadium as the base metal, Al_2O_3 paper as the intermetallic-diffusion barrier, and Pd as the coating metal, we have demonstrated continuous operation at 500°C and 100 psig H_2 for 21 days without any decline in H_2 flux (see Figure 4). This test is still in progress. A similar membrane is currently being tested at 600°C and has, to date, shown no flux decline after 10 days under 100 psig H_2 .
- Both metal-diffusion bonding and graphite gasketing show promise for making membrane modules. A diffusion-bonded pre-prototype plate-and-frame module containing 21 cm^2 of membrane was constructed and thermally cycled between about 70°C and 700°C five times without suffering any leaks.
- A detailed design and cost analysis has been completed for plate-and-frame and shell-and-tube module designs. The results indicate that the plate-and-frame design will be the least

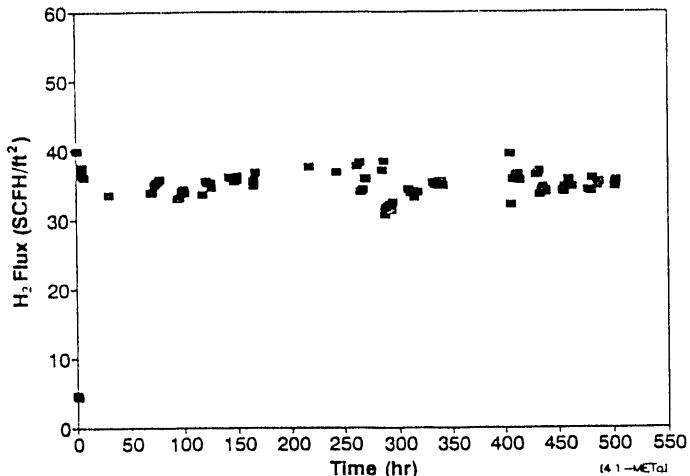


Figure 4. Lifetime Test Results for a Bend Research Composite-Metal Membrane
Test Conditions: 500°C, 100-psig H_2 feed, permeate at ambient pressure

expensive of the two designs, largely as a result of less expensive membrane supports and easier module assembly. The installed price for the plate-and-frame module is estimated to be about \$150/ ft^2 vs. about \$230/ ft^2 for the shell-and-tube design.

FUTURE WORK

During the next year we will work on the following tasks:

- continue lifetime testing to demonstrate membrane lifetime ≥ 1 year;
- work with a third party (a company with expertise in vapor-coating technologies) toward scale-up of membrane fabrication;
- build plate-and-frame membrane modules containing $\geq 1 \text{ ft}^2$ of membrane and evaluate the

module design for reliable operation and ease of fabrication;

- complete and validate computer models for accurately assessing the operating performance of the membrane-based process for producing H₂, and develop high-flux membranes suitable for use in sulfur-bearing feedstreams; and
- complete engineering and economic analyses of the process, and prepare a comprehensive final report.

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