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A CATALYTIC MEMBRANE REACTOR FOR FACILITATING THE WATER-GAS SHIFT REACTION AT HIGH TEMPERATURE

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9b.2 A Catalytic Membrane Reactor for Facilitating the Water-Gas Shift Reaction at High Temperature

CONTRACT INFORMATION

Contract Number	DE-FG03-91ER81229
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Period of Performance	March 31, 1992 to March 30, 1995

Schedule and Milestones

FY94 Program Schedule

J J A S O N D J F M A M

Conduct Parametric Tests

Conduct Slip-Stream Tests

Construct Computer Model of Process

Evaluate Process Economics

Prepare Final Report

OBJECTIVES

This program is directed toward the development of a metal-membrane-based process for the economical production of hydrogen at elevated temperature by the reaction of carbon monoxide with steam—i.e., the water-gas shift (WGS) reaction. Key to achieving this objective is the development of an inexpensive and durable metal-membrane module. The specific program objectives include the following:

- design, fabrication, and demonstration of prototype membrane modules;
- improving the membrane composition to increase the hydrogen flux;
- demonstrating that membrane lifetime ≥2 years is likely to be achieved; and
- conducting engineering and economic analyses of the process.

BACKGROUND INFORMATION

Currently, the gasification of coal incorporates conventional high- and low-temperature WGS reactors for the production of hydrogen, valued as a chemical feedstock (Figure 1). The cost and complexity of the conventional gas-processing technology, with associated heat exchangers and acid-gas scrubbers, has given rise to research directed at developing a more-efficient and less-expensive process.

PROJECT DESCRIPTION

The Proposed Membrane-Based Process

The proposed membrane-reactor process for producing hydrogen via the WGS reaction at elevated temperature is shown in Figure 2. This process is based on the principle that an equilibrium-limited reaction can be driven toward complete conversion of reactants to products if one of the products is removed from the reactor as it is formed. This operating characteristic of membrane reactors has led to numerous investigations of membrane reactors for a wide range of applications, in addition to facilitating the WGS reaction (Hsieh, 1991; Shu et al., 1991; Armor, 1989)

Essential to the successful development of this process is an affordable, durable, highly-selective membrane. A composite-metal membrane under development at Bend Research promises to meet these requirements. The composite-metal membrane (Figure 3) utilizes a coating-metal layer that is permselective for hydrogen, rejecting all other feed-stream components. The mechanical-support layer prevents the membrane from rupturing under high transmembrane pressures, and the intermediate-oxide layer prevents intermetallic diffusion between the coating-metal layer and the mechanical-support layer. Intermetallic diffusion between these layers leads to rapid flux decline and shortened membrane lifetime.

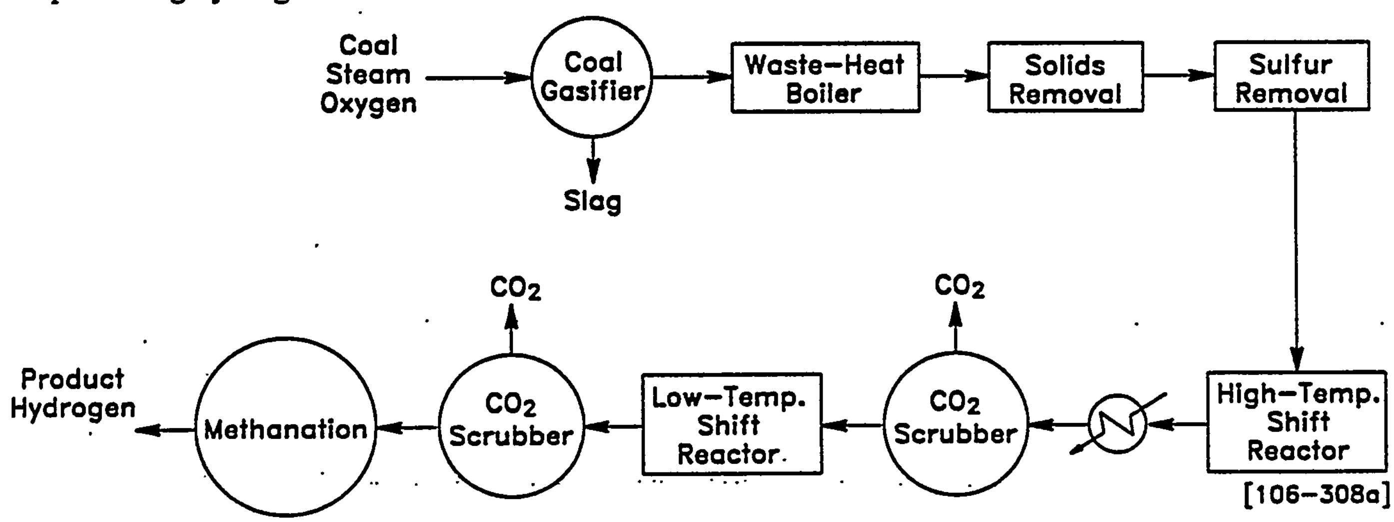

Figure 1. Conventional Process Scheme for the Production of Hydrogen

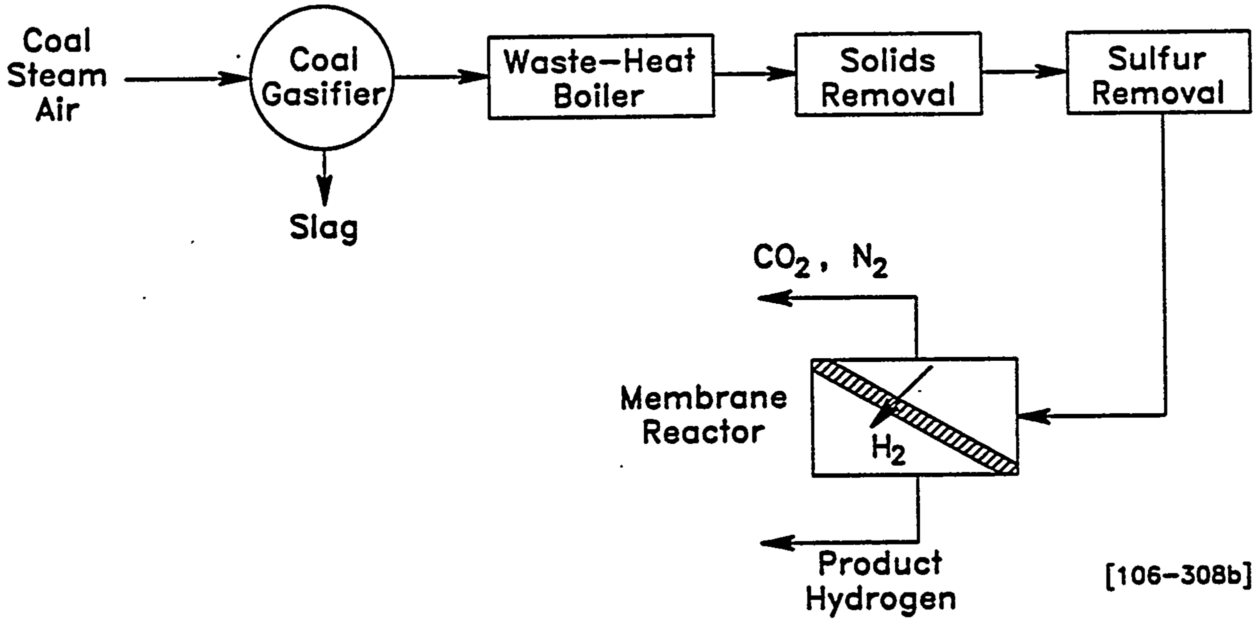

Figure 2. Proposed Membrane-Reactor Process For The Production Of Hydrogen

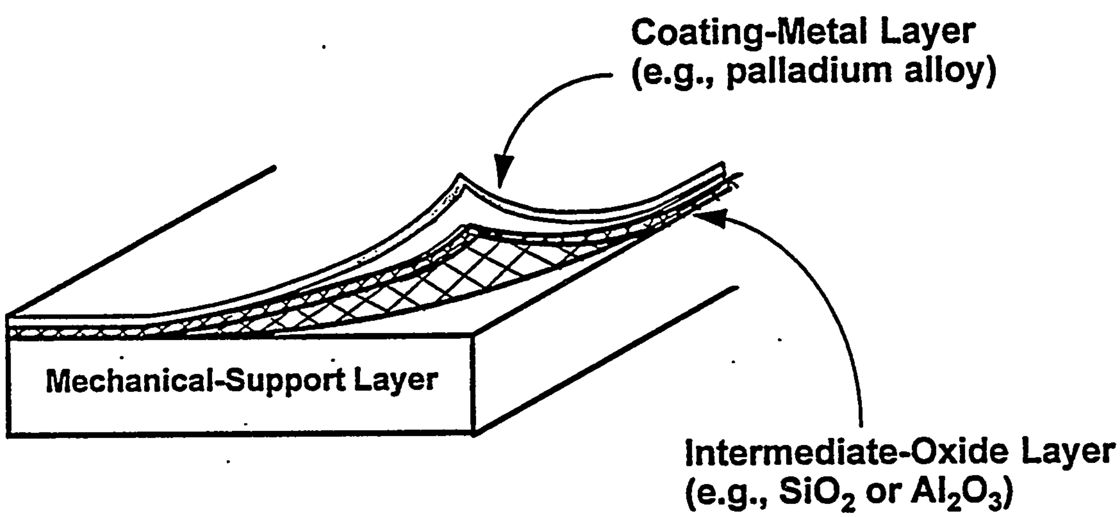

Figure 3. Key Elements Of The Bend Research Composite-Metal Membrane

The membrane composition shown in Figure 3 is sensitive to poisoning by sulfur compounds. Therefore, an absorbent bed prior to the membrane reactor will be necessary to remove sulfur compounds from the feed stream. However, since the membrane only permeates hydrogen, the gasifier can be air-blown without adversely affecting the hydrogen purity.

Hydrogen Production in a Membrane Reactor

We have previously demonstrated that the WGS reaction is driven toward completion in a small, laboratory-scale membrane reactor incorporating the Bend Research composite-metal membrane (Edlund, 1991). Greater than 90% conversion to hydrogen was achieved in these initial experiments using a 2:1 steam:carbon monoxide ratio at 235 psia and 700°C (Figure 4).

As expected, the overall rate of conversion decreases with decreasing pressure (Figure 4) since both the chemical-reaction rate and the rate of hydrogen transport across the membrane are decreased at lower feed pressures.

The reaction time required to achieve maximum conversion shown in Figure 4 are relatively long, as no shift catalyst was used in these experiments (the rate of the non-catalyzed gas-phase WGS reaction is relatively slow even at 700°C). Incorporating a commercial shift catalyst (e.g., Haldor Topsoe SK-201) at the feed side of the membrane is expected to increase the overall rate of conversion significantly. Additional improvements in the process design might include multiple membrane stages and/or a condensable sweep stream (such as steam) over the permeate side of the membrane to achieve ≥95% hydrogen recovery while maintaining moderate permeate pressure (several atmospheres).

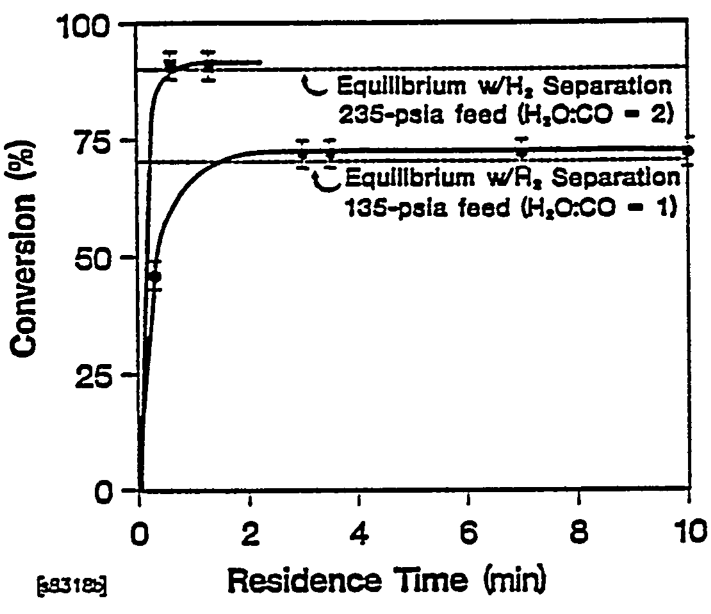

Figure 4. Conversion Versus Residence Time at 700°C in a Laboratory-Scale Membrane Reactor

RESULTS

Work in this program has focused on the first three program objectives listed above. Specifically, the following primary results have been obtained:

- Prototype plate-and-frame membrane modules containing up to 0.4 ft^2 of membrane have been designed, fabricated, and operated for up to 3 weeks. This represents a scale-up factor of about 100-fold relative to the laboratory-scale membrane samples that had been the focus of our testing. A patent application on the module design is being filed. The projected selling price of membrane modules is expected to be about $275/$ft^2$.
- The membrane composition has been improved, resulting in a several-fold increase in hydrogen flux versus that obtained using earlier-generation membranes, while the overall cost of membrane materials has decreased seven-fold. Thus, the current-generation membrane delivers a hydrogen flux of 150 SCFH/ft^2 at 400°C and 100-psig hydrogen feed pressure, and 210 SCFH/ft^2 at 400°C and 100-psig hydrogen feed pressure.
- Small, laboratory-scale membranes have been operated for 6 months at 500°C without showing any flux decline, indicating that operational lifetimes of ≥2 years are likely to be achieved.

In addition, we have begun a collaboration with Teledyne Wah Chang (Albany, OR) to develop and market metal-membrane modules for a wide range of applications. It is anticipated that Teledyne Wah Chang will become the exclusive manufacturer of the membrane modules.

FUTURE WORK

We expect that the relatively high flux and low cost of the composite-metal membrane modules will lead to favorable process economics for producing hydrogen from coal. During the next year we will work toward completing an economic analysis of the membrane-reactor process. Parametric studies of conducting the WGS reaction within the membrane reactor will be completed. In these studies the prototype plate-and-frame modules will be used and a commercial shift catalyst will be placed within the reactor at the feed side of the membrane to ensure rapid chemical kinetics.

The parametric studies will be designed to determine the overall rate of conversion of reactants to hydrogen and carbon dioxide over a range of operating conditions. Furthermore, we will determine whether the catalyzed reaction kinetics or the rate of hydrogen removal from the feed side of the reactor is rate-limiting (the rate-limiting factor may vary with changing operating conditions). This information will serve as the basis for the design and optimization of the process.

Concurrent with the parametric studies, we plan to conduct a field test on a research-gasifier slip-stream in collaboration with the University of North Dakota Energy & Environmental Research Center.

REFERENCES

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