II.A.6 Water-Gas Shift Membrane Reactor Studies

Richard Killmeyer (Primary Contact), Bret Howard, Michael Ciocco, Bryan Morreale, Robert Enick, Felipe Bustamante
National Energy Technology Laboratory
P.O. Box 10940
Pittsburgh, PA 15236
Phone: (412) 386-6409; Fax: (412) 386-5920; E-mail: richard.killmeyer@netl.doe.gov

DOE Technology Development Manager: Arlene Anderson
Phone: (202) 586-3818; Fax: (202) 586-9811; E-mail: Arlene.Anderson@ee.doe.gov

Objectives

- Evaluate water-gas shift (WGS) reaction kinetics and membrane flux using industrial gas mixtures and conditions.
- Test the feasibility of enhancing the WGS at high temperature without added catalysts by using a membrane reactor.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- A. Fuel Processor Capital Costs
- G. Efficiency of Gasification, Pyrolysis, and Reforming Technology
- AB. Hydrogen Separation and Purification

Approach

- Conduct baseline testing of the forward WGS (fWGS) reaction at high pressure with no catalyst in the 300-900°C range in the prototype Pd and Pd-Cu membrane reactors.
- Re-design the membrane reactor to maximize membrane area and minimize thickness in order to enhance conversions of CO and H_2O to H_2 and CO_2.
- Determine H_2 permeance of Pd-Cu in the presence of major gasifier components, such as CO, H_2O, CO_2.

Accomplishments

- Completed fWGS kinetics study.
- Determined catalytic effect of membrane and reactor shell materials.
- Evaluated effect of CO and H_2O on H_2 permeability.
- Fabricated three types of Pd membrane reactors for trials.
- Incorporated WGS kinetics results into membrane reactor model.

Future Directions

- Determine "best" membrane reactor configuration: Coil, Exchanger, or Disk.
- Determine and model the effects of temperature, pressure, feed composition and sweep flow rate on WGS membrane reactor performance.

- Study the effect of H_2S on the catalytic activity of the membrane reactor materials.
- Fabricate and test membrane reactors employing contaminate-resistant membrane materials, such as Pd-Cu.

Introduction

The use of coal as a transition feedstock for a hydrogen economy is likely to be accomplished via gasification, i.e., the conversion of solid coal into a gaseous mixture of CO, CO_2, H_2O, and H_2. The hydrogen yield of such gasifier effluent may be increased by reacting the CO with additional amounts of water using the so-called water-gas shift (WGS) reaction. Although the WGS is customarily used in industry, the reaction has not been explored at the conditions (temperature, pressure) envisioned in the gasification process, primarily due to non-favorable thermodynamics at those conditions. However, the high temperature and high pressure provide a unique scenario to increase the hydrogen yield without the need for an external catalyst, while favoring the overall heat-efficiency of the coal gasification plant. Moreover, the adverse thermodynamics may be overcome by the use of a membrane reactor, which will allow for continual removal of pure hydrogen through the walls of the reactor (Figure 1). The final products of such a reactor would be a high-pressure, pure CO_2 stream and a pure H_2 stream. This project deals with the study of the membrane reactor in conditions similar to those of a gasifier stream.

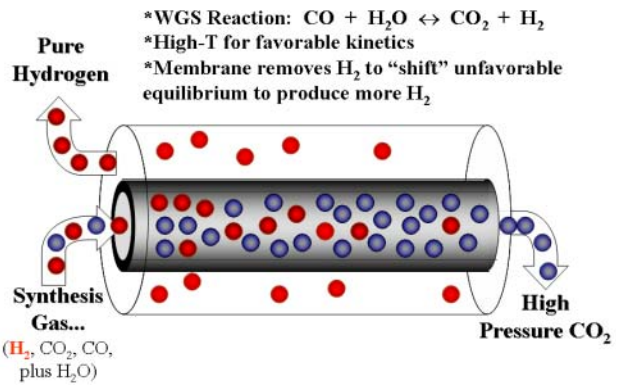

Figure 1. H_2 Membrane Reactor Concept

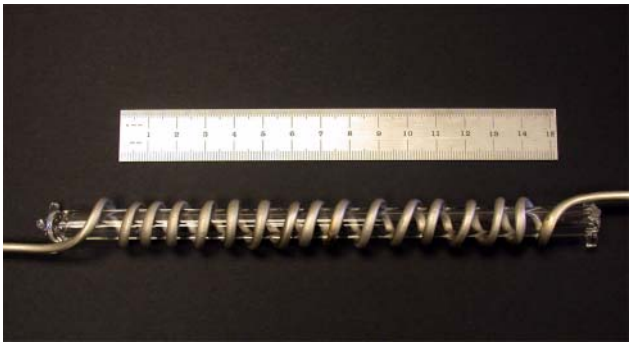

Figure 2. WGS Membrane Reactor Prototype

Approach

Task 1—Conduct baseline testing of the fWGS reaction at high pressure with no catalyst in the 300-900°C range in the prototype Pd-Cu membrane reactor. The feasibility of obtaining a large shift in the otherwise limited equilibrium conversions of the WGS will be determined with contaminant-free gas streams. A broad range of temperatures and operating conditions will be tested to assess the integration of the membrane reactor concept with current technologies, e.g., a lower operating temperature may be required to accommodate existing sulfur-cleaning technologies. This assessment will focus on the increased H_2 yield obtained with the membrane reactor.

Task 2—Determine H_2 permeance of Pd-Cu with major gasifier components such as (H_2 + CO), (H_2 + H_2O), (H_2 + CO_2), and (CO + H_2O + H_2). There are large concentrations of CO, CO_2 and H_2O present in gasifier streams, and most previous studies on membrane reactors have neglected the effect of these components on the permeance of hydrogen, which is the crucial step in the operation of the reactor, or have dealt with it under non-realistic conditions. An understanding of the changes in permeance and selectivity due to the large concentrations of these components is required to optimize the design and operation of the membrane reactor.

Results

Testing the feasibility of enhancing the WGS at high temperature without added catalyst particles by using a membrane reactor was done with the reactor prototype shown in Figure 2. It was a 1/8-inch diameter by 2-foot long piece of Pd tubing with a 125-micron wall thickness that was coiled to fit into

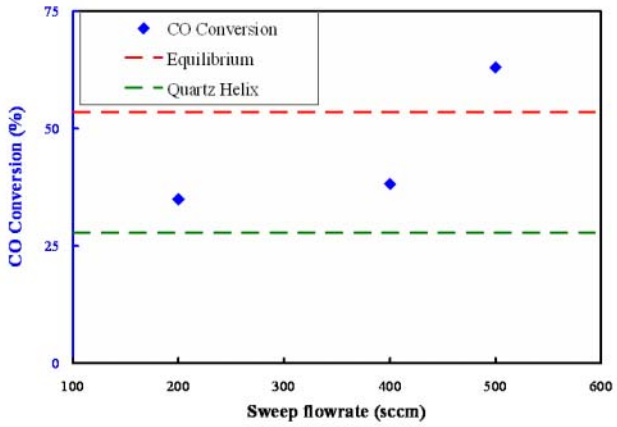

Figure 3. Pd Helix Membrane Reactor Initial Results

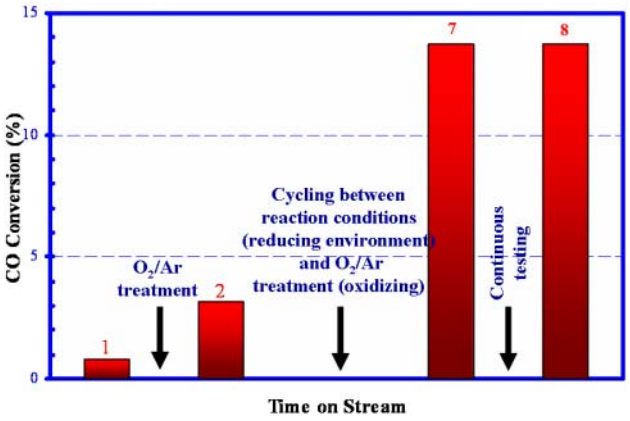

Figure 4. Effect of Pd Packing on WGS Reaction

our 6-inch reactor. The feed gases, CO and H_2O, were fed into the tube, and the H_2 produced from the WGS reaction permeated through the tube and was removed, thus shifting the equilibrium. These tests demonstrated the viability of the water-gas shift with a Pd membrane reactor concept for the increased production of hydrogen. As shown in Figure 3, the CO conversion surpassed the equilibrium conversions when the argon gas sweep rate for removing hydrogen from the permeate side of the membrane was high enough (500 sccm).

To determine the catalytic effect of membrane surfaces (e.g., Pd and Pd-Cu alloy) on the WGS reaction, a quartz reactor filled with Pd particles was utilized. The results in Figure 4 demonstrate that the catalytic effect of Pd and 80/20 Pd-Cu enhances

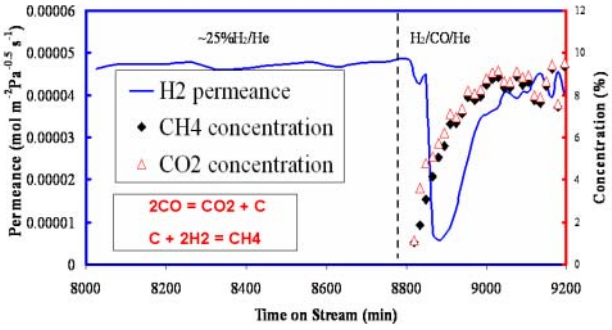

Figure 5. Effect of CO on Hydrogen Permeation Through a Pd Membrane

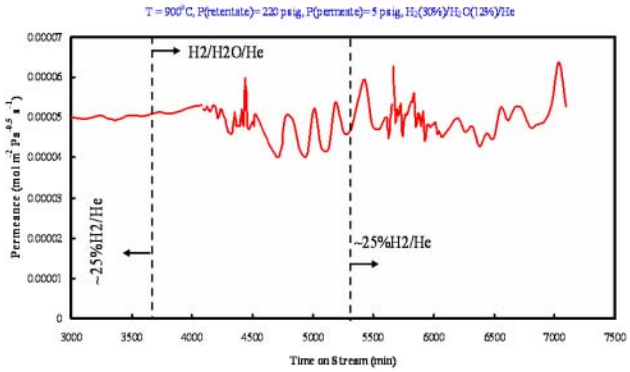

Figure 6. Effect of H_2O on H_2 Permeation Through Pd

WGS conversion, as indicated by the Day #1 bar. This shows a CO conversion of about 1% compared to a conversion of about 0.3% in just a quartz reactor. The subsequent bars show the effect of overnight oxygen treatment on the Pd. This was done to remove any carbon deposition that may have occurred during the WGS run as a result of the Boudouard reaction. This etched the surface of the Pd, increasing the surface area, which increased the CO conversion even more.

The same quartz reactor was used to determine the effect of gasification gases, CO and H_2O, on the permeability of Pd and Pd-Cu alloy membranes. Figures 5 and 6 show that CO and H_2O, two of the major components present in a post-gasifier stream, do not inhibit Pd and Pd-Cu membranes with regard to the permeation of hydrogen at the very high temperature of this study.

Conclusions

- Results for the high-temperature, high-pressure water-gas shift reaction carried out in a membrane reactor demonstrate the viability of the water-gas shift membrane reactor concept for the increased production of hydrogen.
- Pd and Pd-Cu alloy were found to exhibit a significant catalytic effect on WGS reaction. This effect was related to the formation of a porous structure on the surface of the packing.
- CO and H_2O, two of the major components present in a post-gasifier stream, do not inhibit the Pd membrane with regard to the permeation of hydrogen at the very high temperature of this study.

FY 2004 Publications/Presentations

1. F. Bustamante et al., "Hi-Temperature, Hi-Pressure WGS Reaction in a Membrane Reactor," presentation only—AIChE Meeting, San Francisco, CA, 11/03.

2. F. Bustamante et al., "Kinetics of the Uncatalyzed Reverse WGS Reaction at Elevated Temperature and Pressure", AIChE Journal, Vol. 50, No. 4, 04/04.

3. F. Bustamante et al., "Conducting the Hi-Temperature, Hi-Pressure WGSR in a Pd Membrane Reactor," Int'l Technical Conference on Coal Utilization and Fuel Systems, Clearwater, FL, 04/04.

4. R. Enick et al., "Conducting the Homogeneous WGSR in a Pd-Cu Alloy Membrane Reactor at High Temperature & Pressure," National Hydrogen Association Conference, Los Angeles, CA, 04/04.

5. F. Bustamante et al., "Kinetics of the Hi-Temperature Forward WGS Reaction in an Empty Quartz Reactor and Quartz Reactors Packed with Inconel, Pd or Pd-Cu," submitted to AIChE Journal, 05/04.