

## Water-Gas Shift Membrane Reactor Studies

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### Objectives

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

### Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- L. Hydrogen Purification/Carbon Monoxide Cleanup
- M. Fuel Processor System Integration and Efficiency
- N. Cost

### Approach

- Complete reverse kinetics and Computational Fluid Dynamics (CFD) modeling to optimize reactor geometry for forward reactions
- Measure forward kinetics in quartz & Inconel reactors to determine reactor wall catalysis
- Measure forward kinetics in reactor packed with membrane material to determine catalytic activity
- Measure membrane H<sub>2</sub> permeability in presence of clean syngas components
- Conduct forward water-gas shift using a membrane reactor at favorable conditions

### Accomplishments

- Conducted first-ever high temperature and high pressure reverse WGS reaction kinetics study
- Determined catalytic effect of reactor shell material on WGS reaction
- Conducted CFD simulations to determine effect of reactor geometry on kinetics
- Completed intrinsic kinetics testing of the forward WGS reaction
- Designed and constructed a new hydrogen membrane testing unit with enhanced features for membrane reactor testing

### Future Directions

- Evaluate forward WGS reaction kinetics and the catalytic effect of membrane materials
- Design, construct, and test a Pd-Cu alloy membrane reactor to enhance the WGS

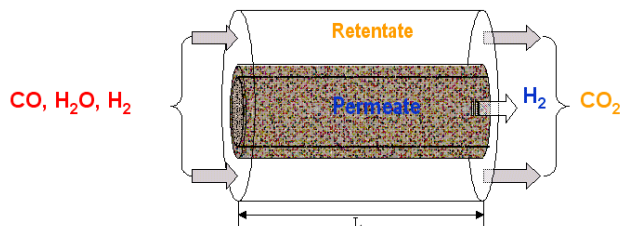
- Determine the effect of sulfur poisoning on catalytic reactor materials, membrane materials, and heterogeneous catalyst particles
- Incorporate reaction kinetics results and permeability results into a high temperature, high pressure WGS membrane reactor model

## **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<sub>2</sub>, H<sub>2</sub>O, and H<sub>2</sub>. 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 reaction 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, 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 thermodynamics may be enhanced 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<sub>2</sub> stream and a pure H<sub>2</sub> stream. This project deals with the study of the membrane reactor in conditions similar to those of a gasifier stream.

## **Approach**

The success of a membrane reactor in increasing the yield of hydrogen will ultimately depend both on a high production rate of hydrogen inside the reactor



**Figure 1.** Schematic of a Membrane Reactor for the WGS Reaction

(fast *kinetics*) and a high rate of flow of hydrogen through the membrane (fast *permeation rate*). The knowledge of the reaction kinetics and membrane permeation is then required to evaluate the suitability of the membrane reactor.

The reaction kinetics of both the *reverse* and *forward* WGS reactions were studied in an inert environment (non-membrane, quartz reactor) to determine the intrinsic kinetics. The effects of high pressure and high temperature were addressed. The influence of the reactor walls was investigated for a high-performance alloy (e.g., Inconel 600<sup>®</sup>); this is important in order to model the behavior of the reaction in an actual industrial setting.

Pd-Cu alloys, known for their sulfur tolerance (sulfur being one of the main contaminants in the gasifier stream), their good mechanical performance, and their infinite selectivity towards hydrogen, were selected as membrane materials. The membranes were characterized in regard to hydrogen permeance both with sulfur-free and sulfur-laden gases. Current research efforts are focused on the performance of the high-temperature, high-pressure water-gas shift reaction in a Pd-Cu membrane reactor.

## **Results**

The high-pressure, high-temperature *reverse* WGS reaction can be described using an expression of the form

$$r = k_r [H_2]^{1/2} [CO_2]$$

where [H<sub>2</sub>] and [CO<sub>2</sub>] are the concentrations of hydrogen and carbon dioxide respectively. This suggests that the reaction behaves in a similar way as the low-pressure gas-phase reaction. However, the values for the rate constant ( $k_r$ ), Figure 2, are somewhat larger for the high-pressure reaction. Figure 2 also presents the experimental and simulation results for the low-pressure reaction. The

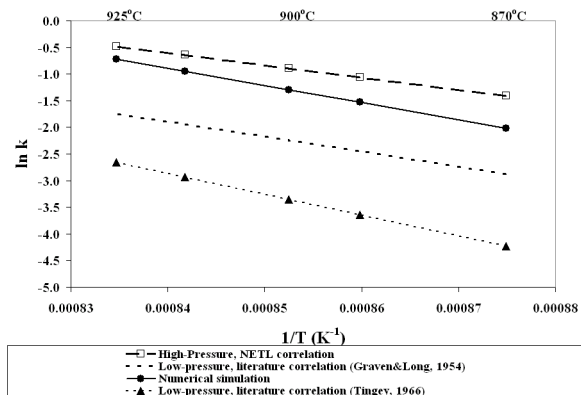
differences can be explained by considering the chemistry of the reaction, which requires an initial induction period before reaching steady state.

The high-pressure, high-temperature *forward* WGS was then studied. The form of the rate expression, was similar to that predicted from the

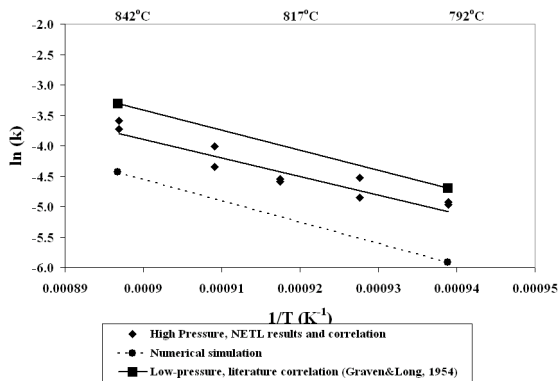
$$r = k_f [CO]^{1/2} [H_2O]$$

low-pressure mechanism. In this case, both the low-pressure and high-pressure values of the rate constant ( $k_f$ ), Figure 3, are in good agreement, as a result of a much shorter induction period.

There is a dramatic increase in the rate of reaction when the reaction is carried out in a metallic



**Figure 2.** Rate Constant as a Function of Temperature for the Reverse WGS Reaction (Experiments were carried out in a quartz reactor)

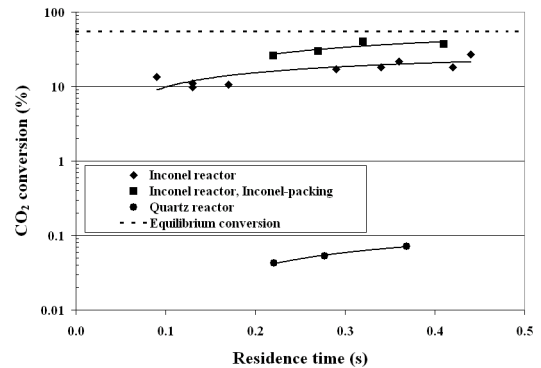


**Figure 3.** Rate Constant as a Function of Temperature for the Forward WGS Reaction (Experiments were carried out in the quartz reactor)

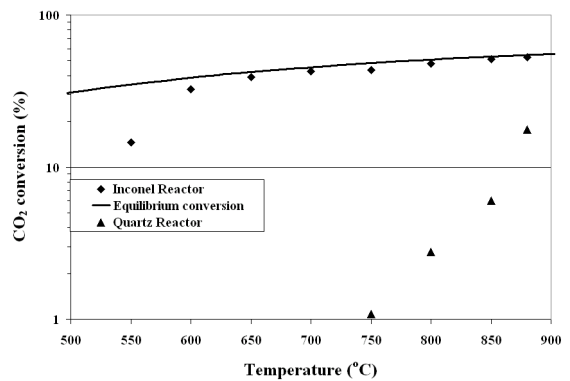
(Inconel 600) reactor. Figure 4 indicates that the reaction is 100-fold faster when it takes place in a metallic reactor. This behavior is valid for the low-pressure (Figure 4) and high-pressure (Figure 5) reactions. As a result, the reaction is fast enough that no external addition of catalyst is needed. Surface analysis of the Inconel 600 showed a change in the chemical composition of the alloy in the surface, confirming the catalytic effect brought about by the reactor walls. A long-term study of the consequences of the stability of Inconel 600 under the reaction conditions is required.

**Conclusions**

- Reaction kinetics of the high-temperature, high-pressure WGS reaction follow the same reaction mechanism as the high-temperature, low-pres-



**Figure 4.** Reactor Wall Effects for the High-Temperature, Low-Pressure Reverse WGS Reaction as a Function of Residence Time



**Figure 5.** Reactor Wall Effects in the High-Temperature, High-Pressure Reverse WGS Reaction as a Function of Temperature

sure reaction. No significant effect of high pressure in the rate constant was observed.

- Inconel 600 is a strong enhancer of the WGS reaction. As a result, the reaction achieves equilibrium conversions at relatively low temperature.

### **FY 2003 Publications/Presentations**

1. F. Bustamante et al., "Reverse WGS Reaction Kinetics at Elevated Temperature and Pressure in Quartz and Inconel Reactors," AIChE Meeting, Indianapolis IN, November 2002.
2. F. Bustamante et al., "Kinetics of the Homogeneous WGS Reverse Reaction at Elevated Temperature," AIChE Journal, in press summer 2003.
3. M. Ciocco et al., "Hydrogen from Coal: WGS Membrane Reactor Studies," International Coal Utilization Conference, Clearwater FL, March 2003.
4. R. Killmeyer et al., "WGS Membrane Reactor Studies," EE HFCIT Annual Merit Review Meeting, Berkeley CA, May 2003.

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1. Graven, W., Long, J. *J. Am. Chem. Soc.* 1954, 76, 2602, 6421.
2. Tingey, J. *J. Phys. Chem.* 1966, 70, 1406.