A MODEL OF A HIGH TEMPERATURE, HIGH PRESSURE WATER-GAS SHIFT TUBULAR MEMBRANE REACTOR

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ABSTRACT

The reversible water-gas shift reaction is characterized by a very low equilibrium constant at elevated temperatures (>800°C). CO conversion at these temperatures is typically less than 40%. Higher conversions of CO can be achieved under these conditions only if one of the products, H_2 or CO_2, is removed from the reactor mixture. Several novel membranes are being developed for rapid H_2 diffusion/permeation and high H_2 selectivity at these high-temperature conditions. Therefore a model of a non-catalyzed tubular membrane reactor has been developed to evaluate the feasibility of achieving high levels of CO conversion at elevated temperatures via removal of H_2 from the reaction-side gas mixture along the length of a plug flow reactor. The model can provide membrane permeability values that must be achieved to attain desired levels of conversion in specified reactor geometry.

INTRODUCTION

The water-gas-shift reaction has been studied extensively as a basis for the production of hydrogen. In many applications, including ammonia synthesis or fuel reforming for fuel cells, the maximum acceptable level of CO in hydrogen is in the parts per million range. The water-gas shift reaction can also take place in other processes where CO and H_2O are present, such as methanol synthesis and supercritical water oxidation of organic compounds.

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \qquad 1$$

This reaction has no change in the number of moles (or the volume) as the reaction proceeds, therefore the equilibrium conversion is not affected by pressure. Side reactions associated with the water-gas-shift reaction are usually not significant. The equilibrium constant for this exothermic reaction (K, which can be expressed in terms of the concentrations of the reactants and products, Eq. 2) decreases with temperature. For example, the value of K decreases from 4523 at 366.5 K (93.3°C, 200°F) to 0.47 at 1366.5 K (1093.3°C, 2000°F).

$$K = ([CO_2][H_2])/([CO][H_2O]) \qquad 2$$

Therefore, conversion of CO to CO_2 (low concentrations of CO and H_2O, high concentrations of CO_2 and H_2, high values of K) is favored at low temperature[1]. Most heterogeneous catalysis studies of the water-gas shift reaction have been conducted at temperatures less than 450°C. Examples of commercial water-gas shift catalysts include Fe_3O_4-Cr_2O_3 and $CuZnO/Al_2O_3$[2]. The kinetics associated with these catalysts can be adequately described with pseudo-first order or power law kinetics[2]. Another study of the stationary and transient kinetics of this reaction[3] indicates that various mechanisms and kinetic expressions have been proposed for the water-gas shift, and that Langmuir-Hinshelwood and power-law kinetic models are adequate. The water-gas shift reaction also occurs in some processes that do not employ catalysts. For example, the supercritical water oxidation of organic wastes (typically conducted at 400-550°C, 200-300 bar) typically does not employ a catalyst because of the rapid destruction rates that are achieved. The very high rate of the water-gas shift reaction observed in this system[4,5,6] is attributed to the formation of "cages" of water about the reactants under supercritical conditions and very high water concentrations.

There is relatively little information on the kinetics of the water-gas shift reaction at elevated temperatures (>600°C). This can be primarily attributed to the diminished value of K, which would limit CO conversion to unacceptably low levels. Catalysts are typically not used at elevated temperatures because of the rapid rate of the non-catalyzed reaction and the difficulty of identifying a catalyst that would be stable at these extreme conditions. A study of the opposing reactions of the water-gas shift reaction was conducted at extremely high temperatures and low pressure[7] (800-1100°C, 1 bar). No catalyst was employed. Power-law kinetic expressions

developed for the forward and reverse reactions were substantially in agreement with a homogeneous chain mechanism. Despite the rapid attainment of equilibrium conversions without a catalyst, the ability to convert high temperature (800-1000° C) CO-rich combustion gases into hydrogen fuel via the water-gas shift reaction is limited by the low equilibrium conversions of CO.

It has long been recognized that high levels of conversion in equilibrium-limited reactions can be achieved only if one or more of the products can be simultaneously extracted during the reaction. (For a given value of K in Eq. 2, if the concentration of either CO_2 or H_2 is reduced, the concentrations of CO and H_2O must also decrease, thereby increasing conversion.) For example, a method for producing H_2 via the water-gas shift reaction with carbon dioxide removal was recently demonstrated[8]. In this study, a calcium-based sorbent was introduced to a non-catalyzed reactor operating in the 500-600°C temperature range. The CO_2 product reacted with the sorbent and formed calcium carbonate, diminishing the gas phase concentration of CO_2 and increasing CO conversion. Several research groups have recently developed hydrogen-permeable membranes that might also he used in a different approach to increasing CO conversion. The use of these membranes in a plug flow reactor would result in the removal of hydrogen from the reaction mixture, leading to an increase in CO conversion. Several types of membranes are now under development. Los Alamos National Laboratory has fabricated composite Pd/Ta membranes using vapor deposition techniques[9]. Measurements in the 300-400°C range indicate that the pressure-dependence of the gas flux is not proportional to $\Delta(P_{H2}^{0.5})$ as in the case with membranes that are rate-limited by bulk diffusion. This implies that surface effects are significant in the determination of hydrogen flux. Argonne National Laboratory is developing proton-conducting ceramic membranes. These dense ceramic membranes are fabricated from mixed protonic/electronic conductors and have been tested at 800°C. Their hydrogen selectivity is very high because they do not have interconnected pores, and the only species that pass through them are those that participate in proton conduction[10] (e.g. hydrogen). Inorganic membranes, composed of ceramics developed by Oak Ridge National Laboratory[12], have interstitial pores with diameters as small as 5 angstroms and act as molecular sieves, have been tested at temperatures less than 600°C. An assessment of a conceptual plant that produces hydrogen from coal using these inorganic membranes[11] was recently completed.

OBJECTIVE

The goal of this investigation is to develop a model of a tubular, plug-flow, non-catalyzed, membrane reactor for the high temperature, high pressure water-gas shift reactor. This model will be used to assess the viability of obtaining a high purity hydrogen product from synthesis gas. Specifically, it will be used to estimate the surface area of the membrane required to achieve a desired level of CO conversion or hydrogen recovery. Alternately, it can be used to provide estimates of the hydrogen permeability a membrane must exhibit to attain a specified CO conversion or H_2 recovery in a reactor with a specified membrane area. This information, in conjunction with cost data for the membranes, can then be used to evaluate the economic feasibility of the process. A model of a reactor with hydrogen-permeable membranes has been previously developed[13] for CO_2 control in IGCC systems using water-gas shift integrated with H_2/CO_2 separation. This system employed microporous ceramic membranes, Fe-Cr and Pt/ZrO_2 catalysts, maximum pressure of 70 bar, maximum pressure drop across the wall of the membrane of 25 bar, and temperatures up to 400°C. Another water-gas shift membrane reactor model was developed for a Fe-Cr catalyzed reactor operating at 400°C and low pressures with a Pd membrane[14]. The model developed in this work will focus on a higher temperature (>800°C), high pressure (25-50 bar), high pressure drop (up to 50 bar), non-catalyzed tubular membrane reactor with either Pd/Ta composite membranes, proton conducting dense ceramic membranes, or microporous ceramic diffusion membranes.

MODEL DESCRIPTION

The basis of the model is a tubular membrane located within a coaxial cylindrical shell. The feed gases are introduced on the shell-side (reaction-side, annular-side, retentate-side, raffinate-side) of the reactor. As the reaction proceeds, hydrogen will permeate the membrane if the concentration of the hydrogen on the reaction-side (shell-side) exceeds the concentration on the tube-side (permeate-side). As the reaction gases proceed down the length of the reactor, hydrogen will continue to permeate the membrane if the partial pressure of hydrogen on the reaction side exceeds the permeate hydrogen partial pressure, increasing the conversion of the CO. The CO_2-rich retentate exits the reactor on the shell-side. A low-pressure, high-purity hydrogen permeate stream is recovered from the tube-side. It is desirable not use a sweep gas to avoid the need to for a subsequent hydrogen-sweep gas separation unit. This will result in a substantial pressure drop across the wall of the membrane, however. The basic design equations for a tubular, plug flow reactor were incorporated into the model[15]. The model predicts the

performance of the reactor under steady-state isothermal or adiabatic conditions. The adiabatic model accounts for the heat of reaction being transferred to the reaction gases and the permeate. The reactants and products are assumed to behave as ideal gases. The pressure drop along the length of the reactor is assumed to be negligible for both the retentate-side and the permeate-side of the reactor. Published correlations for K[1,13] can be used for pseudo-first order or power-law kinetic expressions that may include the equilibrium constant. The low pressure, high temperature (800-1100°C) results of Graven and Long[7] are used to model the reaction kinetics. (During this investigation, more accurate rate expressions for the water-gas shift reaction at elevated temperature *and* pressure will be determined.) The appropriate expressions for the permeation of hydrogen in the dense, proton-conducting ceramic membrane or expressions for permeability of H_2, CO, and CO_2 (i.e. membrane selectivity) in the microporous metal or ceramic membranes[9,12] are incorporated to account for the flow of gases through the membrane. The flux of hydrogen through these membranes, R_{H2}, is proportional to the "permeability" of the membrane, k_{H2} and inversely proportional to the membrane thickness, t_m. The driving force for the hydrogen flux is related to the hydrogen partial pressure or molar concentration of hydrogen, C_{H2}, raised to the exponent n (the units of k are dependent upon the value of n).

$$R_{H2} = A_m k_{H2} (C_{H2,retentate}^{n} - C_{H2,permeate}^{n})/t_m \qquad 3$$

If transport through a membrane with surface reaction and ionic transport is limited by surface reactions, n = 1. If flux through the membrane is diffusion-limited, n = 0.5. Intermediate values of n ($0.5<n<1$) have also been reported[14]. During this investigation, values of n at elevated temperature and pressure will be determined for each membrane.

RESULTS

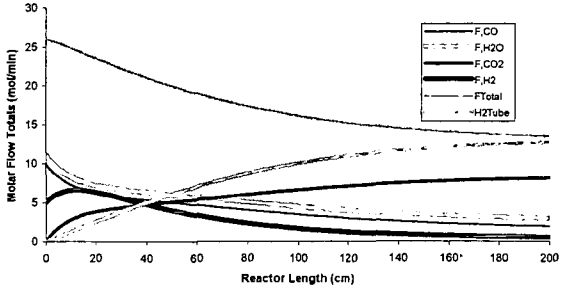
The following conditions are associated with a conceptual coal processing plant for producing hydrogen while recovering carbon dioxide[16]. Because membrane parameters have not yet been established at these conditions, a high value of permeability was selected to clearly illustrate the effect of hydrogen removal on conversion.

Catalyst	No catalyst used at this high temperature
Mode of Operation	Isothermal
Temperature	850°C
Reaction-Side	Annular-side, Shell-side
Pressure on reaction-side	27.572 bar
Pressure on tube-side	0.9869 bar
Reactor length	200 cm
Reactor (shell) diameter	4.0 cm
Tube-side sweep gas	None
Membrane	Proton Transport
Membrane diameter	2.0 cm
Permeable gases	Hydrogen Only
Membrane thickness	0.1 cm (1 mm)
Membrane driving force	$C_{H2,retentate}^{0.5} - C_{H2,permeate}^{0.5}$
Membrane permeability	10 cm^2/min(mol/liter)$^{0.5}$
CO inlet flow rate	10 gmol/min
Steam inlet flow rate	11 gmol/min
Hydrogen inlet flow rate	5.0 gmol/min
Reaction kinetics	Reference 7

Table 1. Model Conditions and Assumptions Used in the Example Problem

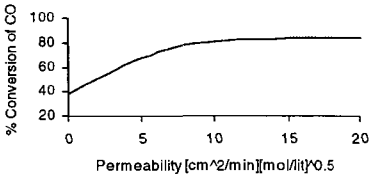
Conversion of CO *in the absence of a membrane* is 38.2% at 850° C, which is 99% of the equilibrium value. The *membrane reactor* profiles of molar flow rates of the components are illustrated in Figure 1. As the CO and H_2O react near the inlet, their molar flow rates decrease as the hydrogen flow rate on the reactor-side increases. The CO and H_2O continue to decrease as the CO_2 concentration increases along the length of the reactor. The hydrogen also begins to permeate the membrane because the concentration on the annular-side is greater than the hydrogen concentration on the tube side. Because the rate of hydrogen generation is initially greater than the rate of permeation, the hydrogen flow rate on the annular-side increases from 5 to 7 mol/min along the length of the reactor between 0 - 15 cm.

Figure 1. Flow Rate Profiles within the Membrane Reactor



After 15 cm, the rate of permeation exceeds the generation due to reaction and the flow rate of hydrogen on the annular-side decreases. As the end of the reactor is approached, the permeate flow rate of hydrogen approaches a limiting value because the concentration of the hydrogen on the annular-side (raffinate), 0.013 mol H_2/liter is approximately equal to the concentration on the tube-side (permeate), 0.011 mol H_2/liter. CO conversion has increased to 81%. The permeability of the membrane has a significant effect on the performance of the reactor. Figure 2 illustrates the conversion of CO that can be achieved in this particular membrane reactor as a function of the membrane permeability. For a permeability of 0 (impermeable membrane), the conversion is 38.5%. As the permeability increases beyond 10 $(cm^2/min)(mol/liter)^{0.5}$, the limiting conversion of 84% is attained. To achieve comparable conversions with membranes of lower permeability, the length of the membrane tube must increase to provide more area for the hydrogen removal, increasing the membrane reactor size and cost.

Figure 2. Effect of Membrane Permeability on CO Conversion



CONCLUSIONS

A model of a tubular, plug flow membrane reactor has been developed for evaluating the effect of hydrogen permeable membranes on the conversion of CO in the water-gas shift reaction. The model has been developed for very high temperature systems (>800°C) that do not employ a catalyst. The model can incorporate hydrogen permeation/diffusion models that are appropriate for novel membranes currently being developed at several national laboratories. This tool will be used to assess the levels of CO conversion, H_2 purity and recovery, and CO_2-rich retentate flow rate and recovery that can be realized in a reactor of specified geometry if these novel membranes are incorporated. The model can also be used to provide "targets" for hydrogen permeability that would be required to make this technology economically feasible.

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