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Separation of Hydrogen and Carbon Dioxide Using a Novel Membrane
Reactor in Advanced Fossil Energy Conversion Process

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ABSTRACT

Inorganic membrane reactors offer the possibility of combining reaction and separation in a single operation at high temperatures to overcome the equilibrium limitations experienced in conventional reactor configurations. Such attractive features can be advantageously utilized in a number of potential commercial opportunities, which include dehydrogenation, hydrogenation, oxidative dehydrogenation, oxidation and catalytic decomposition reactions. However, to be cost effective, significant technological advances and improvements will be required to solve several key issues which include: (a) permselective thin solid film, (b) thermal, chemical and mechanical stability of the film at high temperatures, and (c) reactor engineering and module development in relation to the development of effective seals at high temperature and high pressure.

In this project, we are working on the development and application of palladium and palladium-silver alloy thin-film composite membranes in membrane reactor-separator configuration for simultaneous production and separation of hydrogen and carbon dioxide at high temperature. From our research on Pd-composite membrane, we have demonstrated that the new membrane has significantly higher hydrogen flux with very high perm-selectivity than any of the membranes commercially available. The steam reforming of methane by equilibrium shift in Pd-composite membrane reactor is being studied to demonstrate the potential application this new development. To have better understanding of the membrane reactor, during this reporting period, we developed a two-dimensional pseudo-homogeneous reactor model for steam reforming of methane by equilibrium shift in a tubular membrane reactor. In numerical solution of the reactor model equations, numerical difficulties were encountered and we seeking alternative solution techniques to overcome the problem.

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EXECUTIVE SUMMARY

Inorganic and composite membranes are being considered as potential candidates for use in membrane-reactor configuration for effectively increasing reaction rate, selectivity and yield of equilibrium limited reactions. To investigate the usefulness of palladium-ceramic and palladium-stainless steel composite membrane in membrane-reactor configuration, we are investigating the steam reforming of methane by equilibrium shift for simultaneous separation and concentration of hydrogen and carbon dioxide. To have a better understanding of the membrane reactor, we developed a two-dimensional pseudo-homogeneous reactor model for steam reforming of methane by equilibrium shift in a tubular membrane reactor. Some preliminary simulation results are reported here.

INTRODUCTION

Inorganic membrane reactors allow simultaneous reaction and separation, and therefore offer the possibility of combining reaction and separation in a single operation at high temperatures to overcome the equilibrium limitations experienced in conventional reactor configurations. Such attractive features can be advantageously utilized in a number of potential commercial opportunities, which include dehydrogenation, hydrogenation, oxidative dehydrogenation, oxidation and catalytic decomposition reactions. However, to be cost effective, significant technological advances and improvements will be required to solve several key issues which include: (a) permselective thin solid film, (b) thermal, chemical and mechanical stability of the film at high temperatures, and (c) reactor engineering and module development in relation to the development of effective seals at high temperature and high pressure.

In our laboratory, we developed a new class of palladium-ceramic composite membranes by depositing thin-film palladium on microporous ceramic substrate. Laboratory tests at elevated temperature and pressure indicated that the new membrane has both high permeability and selectivity for hydrogen [1]. We believe this new membrane will be an excellent candidate for hydrogen separation and applicable in membrane-reactor configuration for separation of hydrogen by equilibrium shift when the reaction product (H_2) thermodynamically limits the equilibrium conversion. In IGCC application, the clean syngas or natural gas can be steam reformed to produce H_2 and CO_2 in an H_2 -selective membrane reactor. Since, these reactions are thermodynamically equilibrium-limited, the membrane reactor offers an opportunity for H_2 separation and CO_2 capture in a single unit. This method will have several technological advantages over other hydrogen-purification methods, including the following:

- Reforming reaction is not limited by chemical equilibrium. As soon as product hydrogen is formed, hydrogen is transported across the membrane.
- Reforming and separation will be carried out in a single unit, thereby eliminating the need of hydrogen separation and recovery units.
- The membrane reactor-separator is modular and compact in size.

We propose to use our newly developed membrane to study the water gas shift reaction and/or steam reforming of methane in a membrane reactor-separator for concentration and recovery of H_2 and CO_2 simultaneously.

RESEARCH OBJECTIVES

The objectives of this research are to:

1. Design and fabrication of membrane reactor using thin film Pd-Ag alloy composite membrane in tubular configuration.
2. Conduct water-gas shift reaction and/or steam reforming of methane experiments to study the equilibrium shifts and permeation characteristics.
3. Model the membrane reactor for water-gas shift reaction and steam reforming of methane by equilibrium shift and validate the performance of the reactor.

MEMBRANE REACTOR MODEL: STEAM REFORMING OF METHANE

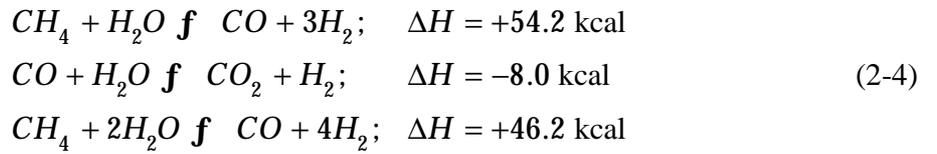
To have a better understanding of the membrane reactor, we developed a two-dimensional pseudo-homogeneous reactor model for steam reforming of methane by equilibrium shift in a tubular membrane reactor. Radial diffusion was taken into account for concentration gradient in

the radial direction due to H_2 -permeation through the membrane. For H_2 -permeation, Sieverts law was used in the solution of the reactor model equations with the index n (dependent on the type and thickness of the membrane film) as a parameter.

$$N_H = \frac{Q_H}{h} (P_H^n - p_H^n) \quad (1)$$

where N_H is the hydrogen flux, Q_H is the permeability coefficient and h is the effective membrane thickness (Pd-film). Hydrogen partial pressures on the feed side and separation side are given by P_H and p_H , respectively.

The steam reforming of methane can be represented by the following equations:



Model Assumptions:

- Isothermal, isobaric and steady state flow through the whole reactor (both the packed-bed and separation sides).
- Plug flow is assumed through the shell side or separation side.
- Ideal gas law is applicable
- Flat concentration profile is assumed in separation side
- Partial pressure gradient of hydrogen in the radial direction, caused by the permeation of hydrogen through the palladium-ceramic membrane, is taken into account.
- Axial diffusion is negligible

Further it is assumed that the reaction is predominantly taking place on the catalyst pellet surface. Rate expressions of three reactions under consideration are [2]:

$$r_1 = \frac{\frac{k_1}{p_{H_2}^{2.5}} \left(p_{CH_4} p_{H_2O} - \frac{p_{H_2}^3 p_{CO}}{K_1} \right)}{DEN^2} \quad (5)$$

$$r_2 = \frac{\frac{k_2}{p_{H_2}} \left(p_{CO} p_{H_2O} - \frac{p_{H_2} p_{CO_2}}{K_2} \right)}{DEN^2} \quad (6)$$

$$r_3 = \frac{\frac{k_3}{p_{H_2}^{3.5}} \left(p_{CH_4} p_{H_2O}^2 - \frac{p_{H_2}^4 p_{CO_2}}{K_3} \right)}{DEN^2} \quad (7)$$

where $DEN = 1 + K_{CO} p_{CO} + K_{H_2} p_{H_2} + K_{CH_4} p_{CH_4} + K_{H_2O} \frac{p_{H_2O}}{p_{H_2}}$

The rate equation for each of the reactants and products (M: methane; S: steam; CO: carbon monoxide; CO₂: carbon dioxide; and H: hydrogen) are:

$$r_M = r_1 + r_3 \quad r_S = r_1 + r_2 + 2r_3 \quad r_{CO} = r_1 - r_2$$

$$r_{CO_2} = r_2 + r_3 \quad r_H = 3r_1 + r_2 + 4r_3$$

The continuity equation for component I can be presented as:

$$u \frac{\partial C_I}{\partial z} = (D_{er})_I \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_I}{\partial r} \right) + R_I \quad (8)$$

where z is axial direction and r is the radial coordinate for tubular reactor. Here effective diffusivity of each of the component, $(D_{er})_I$ in the catalyst packed reactor is used instead of relative diffusivity. Correlations for D_e are available in literature. Component rate expressions consider adsorption characteristics and amount of the catalyst.

RESULTS AND DISCUSSIONS

With appropriate reaction rate expressions, a set of partial differential equations was derived using the continuity equation for the reaction system. These equations were solved by finite difference methods. The solution of the model equations is complicated by the coupled reactions. To overcome the numerical difficulties, several alternative schemes were implemented in the solution algorithm to get converged solution. The solution would be straightforward if only the third reaction (Equation 4) is considered. Since the concentration of carbon monoxide (water-gas shift reaction) may be significant in many operating conditions, and a good model should be able to predict it, one needs to consider the system of reactions as presented.

In Figure 1, the performances of the membrane reactor with that of conventional packed-bed plug flow reactor for steam reforming of methane as a function of catalyst loading is shown. The reactor is simulated at operating temperature and pressure of 873 K and 10 atm, respectively with methane feed rate of $2.77E-03$ mol/s. The results clearly show that with selective removal of hydrogen, membrane reactor out-performs conventional reactor

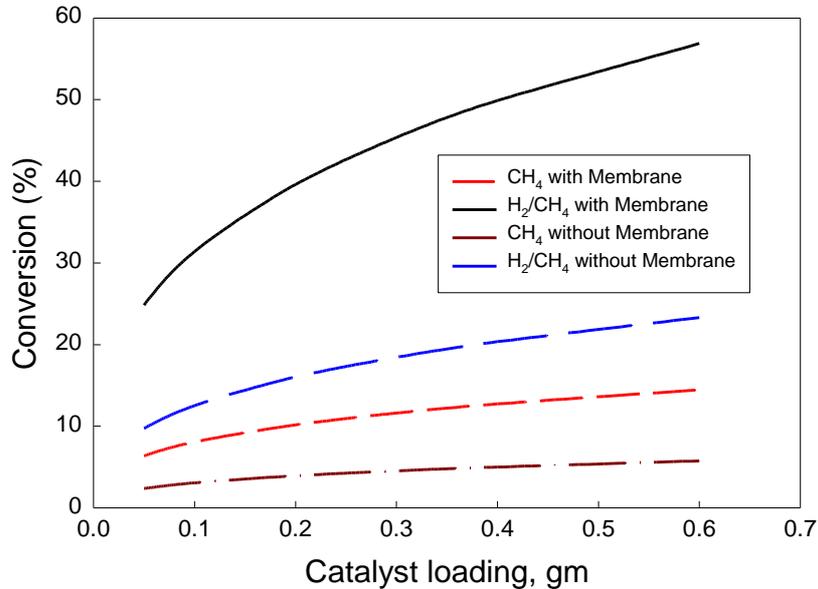


Figure 1: Comparison of conversion of membrane reactor with conventional reactor ($T = 873$ K, $P = 10$ atm, feed rate = $2.77E-03$ mol/s CH_4)

The effect of catalyst loading on conversion of reactants in the membrane reactor is shown in Figure 2. The equilibrium conversion refers to the conversion in conventional reactor. The simulation shows that there is a limit above which increased catalyst loading has no effect on conversion. This information is valuable in deciding upon catalyst loading for a given reactor operation.

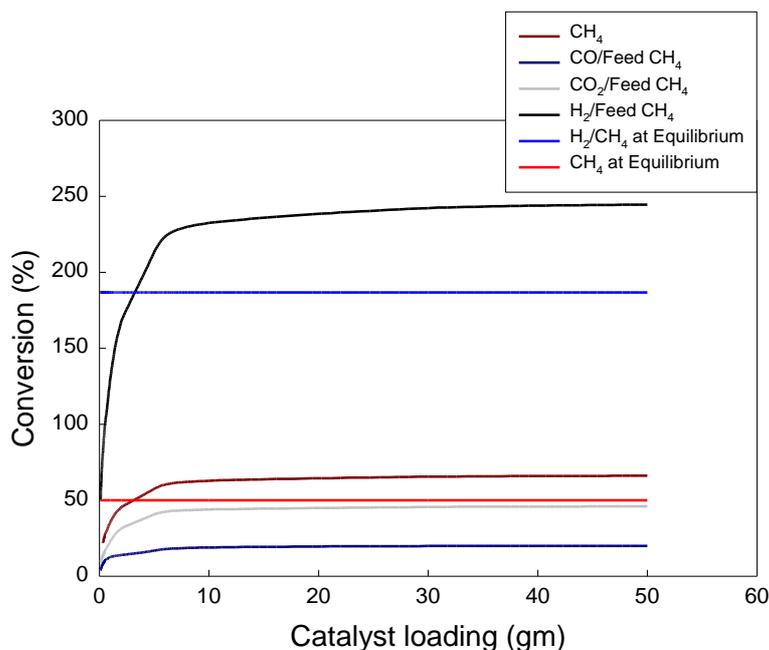


Figure 2: Effect of catalyst loading on conversions (T = 873 K, P = 2 atm, feed rate = $2.77\text{E-}03$ mol/s CH₄, steam/methane mole ratio = 3).

CONCLUSIONS

A mathematical model is developed to study the steam reforming of methane in a hydrogen-selective membrane reactor. The effect of radial diffusion due to selective permeation of hydrogen through the membrane reactor wall is included in the two-dimension pseudo-homogeneous model. The simulation results will be used to set operating parameters in actual steam reforming of methane in the membrane reactor.

NOMENCLATURE

- C_I Molar concentration of I component on reaction side, mol/m³
 $(D_{er})_I$ Effective radial diffusion coefficient of I component in the packed bed,
 K_I Adsorption equilibrium constant of component I
 M_I Dimensionless modulus for i component
 N_I Permeation of I component per unit area, mol/m².s
 P_I Partial pressure of i component on reaction side, Pa
 P_r Reaction-side total pressure, Pa
 P_s Separation-side total pressure, Pa
 P_I Partial pressure of i component on separation side, Pa

p_i^0	Partial pressure of i component on separation-side inlet, Pa
Q_i	Permeability of i component, mol/m.s.Pa, mol/m.s.Pa ⁿ
r	Radial distance from the center of packed bed, m
r_i	Reaction rate of i component, mol/m ³ .s
t	Membrane thickness, m
u	Interstitial velocity of gas on reaction side, m/s
z	Length of palladium membrane, m

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