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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. We designed and built a membrane reactor to study the reforming reaction. A two-dimensional pseudo-homogeneous reactor model was developed to study the performance of the membrane reactor parametrically. The important results are presented in this report.

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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 recovery 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. Parametrically we studied the performance of the reactor and the simulation results show that under appropriate operating conditions, the membrane reactor outperforms the conventional packed-bed reactor.

## 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.

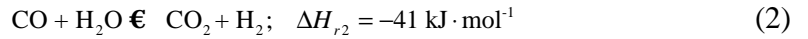
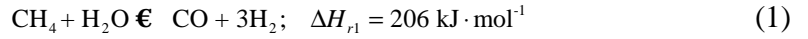
## STEAM REFORMING OF METHANE IN MEMBRANE REACTOR

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.

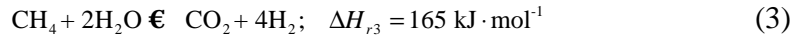
In order to develop a model for a membrane reactor, one needs to consider the reaction kinetics and the transport mechanism through the membrane as well as through the catalyst bed. The present work is to study a palladium-ceramic or palladium-stainless steel membrane reactor for methane-steam reforming reaction. Nickel catalyst pellets are assumed inside the membrane tube, i.e. tube side is the reaction side.

### Kinetic Parameters

The three major reactions in steam reforming of methane are:



The over all reaction is given as:



A number of kinetic rate expressions have appeared in the literature to describe the steam reforming of methane. These rate expressions vary from empirical expressions to ones based on fundamentals. In this work, kinetic parameters are taken from work of Xu et al. (1989) where they studied steam reforming of methane in a tubular reactor without membrane. The steam reforming of methane was carried out using nickel catalyst supported on magnesium pellets. The reaction rate equations for three main reactions are given as:

$$r_1 = \frac{\frac{k_1}{p_H^{2.5}} \left( p_M p_S - \frac{p_H^3 p_C}{K_1} \right)}{k^2} \quad (4)$$

$$r_2 = \frac{\frac{k_2}{p_H} \left( p_C p_H - \frac{p_H p_D}{K_2} \right)}{k^2} \quad (5)$$

$$r_3 = \frac{\frac{k_3}{p_H^{3.5}} \left( p_M p_H^2 - \frac{p_H^4 p_D}{K_3} \right)}{k^2} \quad (6)$$

where

$$k = 1 + K_C p_C + K_H p_H + K_M p_M + K_S \frac{p_S}{p_H} \quad (7)$$

Here  $k_1$ ,  $k_2$  and  $k_3$  are the rate constants for three reactions and corresponding equilibrium constants are denoted by  $K_1$ ,  $K_2$  and  $K_3$ , respectively. The adsorption equilibrium constants of the species are denoted as  $K_i$ , where the subscript  $i = M$  for methane,  $S$  for steam,  $C$  for carbon monoxide,  $D$  for carbon dioxide, and  $H$  for hydrogen. The numerical values of the rate constants,

equilibrium constants and adsorption equilibrium constants were taken from Xu et al. (1989). We write the rate of production or depletion of the species ( $i = M, S, C, D, H$ ) as:

$$\begin{aligned} r_M &= r_1 + r_3 \\ r_S &= r_1 + r_2 + r_3 \\ r_C &= r_1 - r_2 \\ r_D &= r_2 + r_3 \\ r_H &= 3r_1 + r_2 + 4r_3 \end{aligned} \quad (8-12)$$

### Hydrogen Transport through Membranes

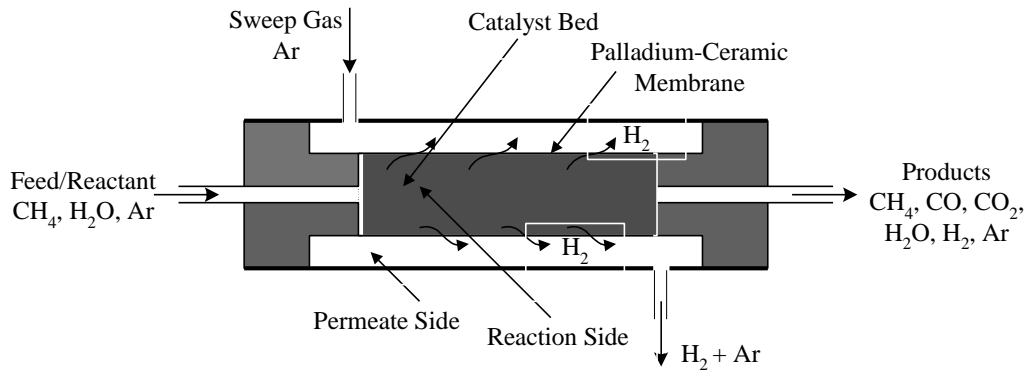
Palladium-ceramic/SS membrane is nonporous. No pore space is available for diffusion. The transport of gases through nonporous membranes occurs by an activated solution-diffusion mechanism. The permeation of hydrogen through the membrane can be described by Siebert's law as:

$$N_H = \frac{Q_H}{h} (P_H^n - p_H^n) \quad (13)$$

where  $P_H$  and  $p_H$  are the hydrogen partial pressures of feed side and separation side,  $Q_H$  is the permeability and  $h$  is the membrane thickness. The values for  $n$  range from 0.5 to 1. The value of 0.5 implies that the transport of hydrogen through the bulk of metal is rate determining and that equilibrium is established at the surface, i.e. an equilibrium between hydrogen molecules in gas phase and hydrogen atoms dissolved in the metal.

### Membrane Reactor Model

The membrane reactor shown schematically in Figure 1 is a packed-bed catalytic tubular reactor. Catalyst pellets are inside the palladium-ceramic membrane tube. Hydrogen produced by the steam reforming of methane permeates through the membrane into the shell side. Argon is used as the carrier gas in the feed side and as sweep gas in the shell side to remove the permeated hydrogen. Concentration of hydrogen near the membrane wall is depleted due to permeation. Hence, a concentration gradient occurs in the radial direction. A two-dimensional model is suitable to describe the transport mechanism through the catalyst bed.



**Figure 1:** Pd-ceramic/stainless steel membrane reactor



Two-dimensional heterogeneous model requires the knowledge of effectiveness factor. For a first-order reaction, it can be evaluated easily. Steam methane reforming is a complex reaction and defining the effectiveness factor is complicated. In order to avoid this complexity, two-dimensional pseudo-homogeneous model is assumed to describe the transport mechanism through the catalyst bed. Based on some simplifying assumptions, the continuity equation for each of the components, argon (A), methane (M), hydrogen (H), carbon monoxide (C), carbon dioxide (D) and steam (S) can be written as:

$$u \frac{\partial C_i}{\partial Z} = (D_{er})_i \frac{1}{R} \frac{\partial}{\partial R} \left( R \frac{\partial C_i}{\partial R} \right) + r_i \quad (14-19)$$

where  $i = A, M, H, C, D, S$  and since argon is non-reactive,  $r_A = 0$ . The boundary conditions are given as:

BC 1: at  $R = 0$  and  $0 \leq Z \leq L_o$ ,

$$\frac{\partial C_i}{\partial R} = 0; \quad i = A, M, H, C, D, S \quad (20)$$

BC 2: at  $R = R_1$  and  $0 \leq Z \leq L_o$ ,

$$\begin{aligned} \frac{\partial C_i}{\partial R} &= 0; \quad i = A, M, C, D, S \\ (D_{er})_H \frac{\partial C_H}{\partial R} &= \frac{Q_H}{h} (P_H^n - p_H^n) \end{aligned} \quad (21)$$

The inlet conditions on the reaction and permeation sides are:

IC 1: at  $Z = 0$  and  $0 \leq Z \leq L_o$ ,

$$C_i = C_i^o; \quad i = A, M, S \quad \text{and} \quad C_i = 0; \quad i = H, C, D \quad (22)$$

IC 2: at  $Z = 0$  and  $R_2 \leq R \leq R_3$  for cocurrent and at  $Z = L_o$  and  $R_2 \leq R \leq R_3$  for countercurrent flow configurations,

$$c_A = c_A^o, \quad c_H = 0 \quad (23)$$

Expressing the concentration of the species in partial pressures, the governing equations, Eqns. (14-19) and the boundary conditions, Eqns. (20-23) were normalized for numerical solution. The equations were solved by finite difference method. An iterative scheme was used to get converged solution. The details are reported elsewhere (Khan, 2001).

## RESULTS AND DISCUSSIONS

Membrane reactor model was investigated in a tubular reactor with following dimensions:

Total reactor length,	$L_0 = 0.10 \text{ m}$
Inner radius of inner tube,	$R_1 = 5.350 \times 10^{-3} \text{ m}$
Outer radius of inner tube,	$R_2 = 5.36 \times 10^{-3} \text{ m}$
Inner radius of shell,	$R_3 = 6.00 \times 10^{-3} \text{ m}$

#### Catalyst Properties:

Radius = 0.11 mm.  
Composition of Ni in the catalyst = 15.2%  
BET surface area = 58 m<sup>2</sup>.  
Catalyst surface area = 9.3 m<sup>2</sup>/gm<sub>cat</sub> (fresh catalyst).  
Void fraction = 0.528

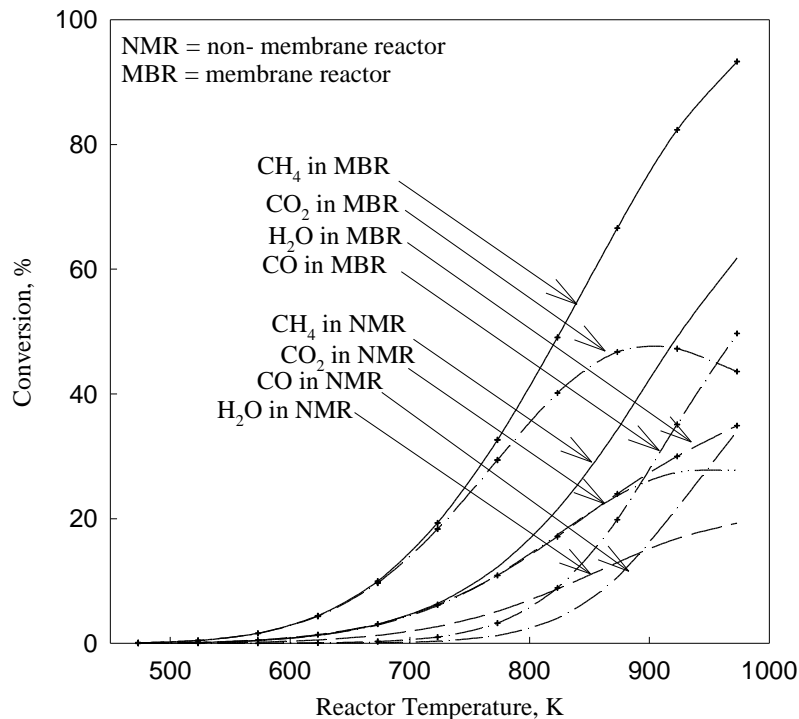
Permeation parameters used in this investigation were:

Power index,  $n = 0.5$   
Permeability,  $Q_H = 1.618 \times 10^{-08}$  (mol/m.Pa<sup>n</sup>.s)  
Permeation constant,  $a = 1.824 \times 10^{-08}$  (mol/s)

Some important results are presented here to compare the performance of the membrane reactor with that of a non-membrane reactor.

#### Effect of Temperature on Conversions

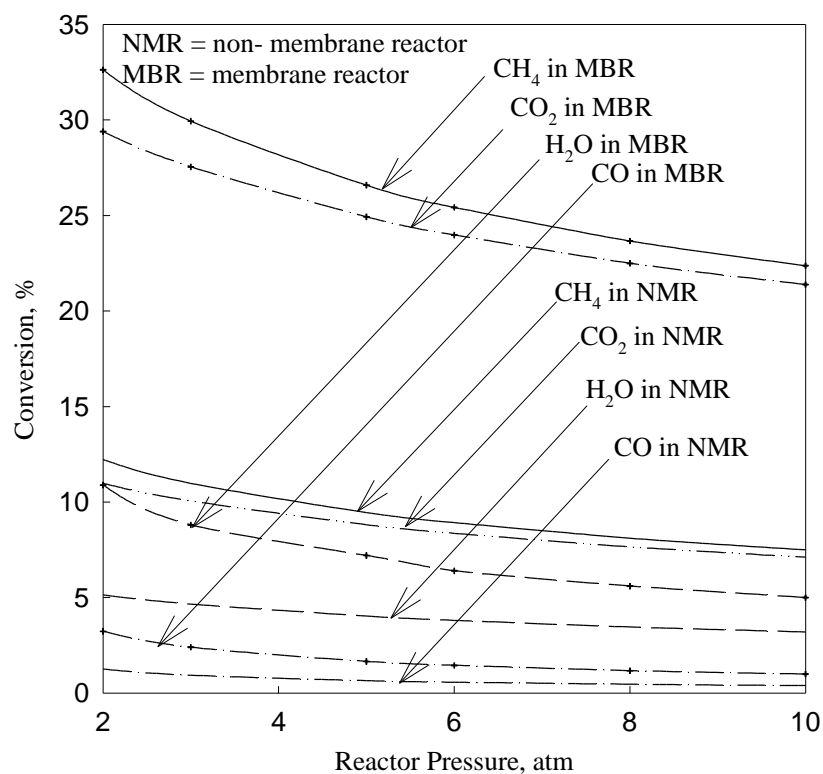
Temperature plays a great role in the conversions of methane-steam reforming reactions. Figure 2 shows the influence of temperature on conversion of methane, conversion of methane into carbon monoxide and carbon dioxide. The conversion patterns are similar for both membrane reactor and non-membrane reactor. Conversion of methane increases exponentially with temperature. Methane conversion into carbon monoxide also increases exponentially at higher temperatures (above 700 K). Conversion of methane into carbon dioxide has a decreasing trend at higher temperatures. The results show that membrane reactor out performs the conventional reactor in conversions.



**Figure 2:** Effect of temperature on conversion at 2 atm. Ni catalyst loading = 4.0 g, feed rate of CH<sub>4</sub> =  $2.777 \times 10^{-3}$  mol/s, steam to CH<sub>4</sub> mole ratio = 3.0, sweep gas flow rate =  $3.0 \times 10^{-3}$  mol/s.

### Effect of Reactor Pressure on Conversions

Pressure also has a great effect on the conversions of methane-steam reforming reactions. As shown in Figures 3, virtually both for membrane reactor and non-membrane reactor conversion of methane, steam, methane to CO, methane to CO<sub>2</sub> decrease with the increase in pressure at a particular temperature.



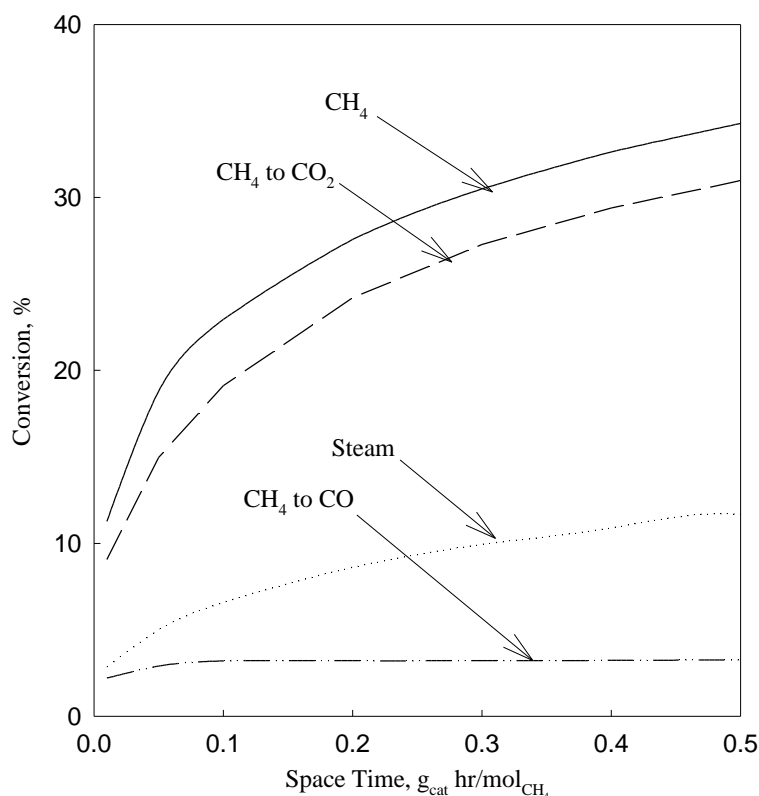
**Figure 3:** Influence of pressure on conversion at 773 K. Ni catalyst loading = 4.0 g, feed rate of CH<sub>4</sub> =  $2.777 \times 10^{-3}$  mol/s, steam to CH<sub>4</sub> mole ratio = 3.0, sweep gas flow rate =  $3.0 \times 10^{-3}$  mol/s.

### Effect of Space Time on Conversions

The rate of reactions is dependent on the amount and adsorption properties of the catalyst. This leads to different definition of the space-time. Here the space-time is defined as the amount of catalyst (in gram) per mol feed of methane per hour.

Figure 4 shows the effect of space-time on conversion of methane, steam, conversion of methane into carbon monoxide and conversion of methane into carbon dioxide at 2 atm. These conversions increase with an increase in space-time. At lower values of the space-time, an increase in space-time causes a significant increase in conversions. As the value of the space-time increases the effect flattens.

This figure indicates that it requires a lower space-time i.e. lower catalyst loading to get a conversion or yield higher than the equilibrium conversion or yield at higher reactor pressures. These figures also clearly show that conversions in a membrane reactor are much higher than that in a non-membrane tubular reactor.



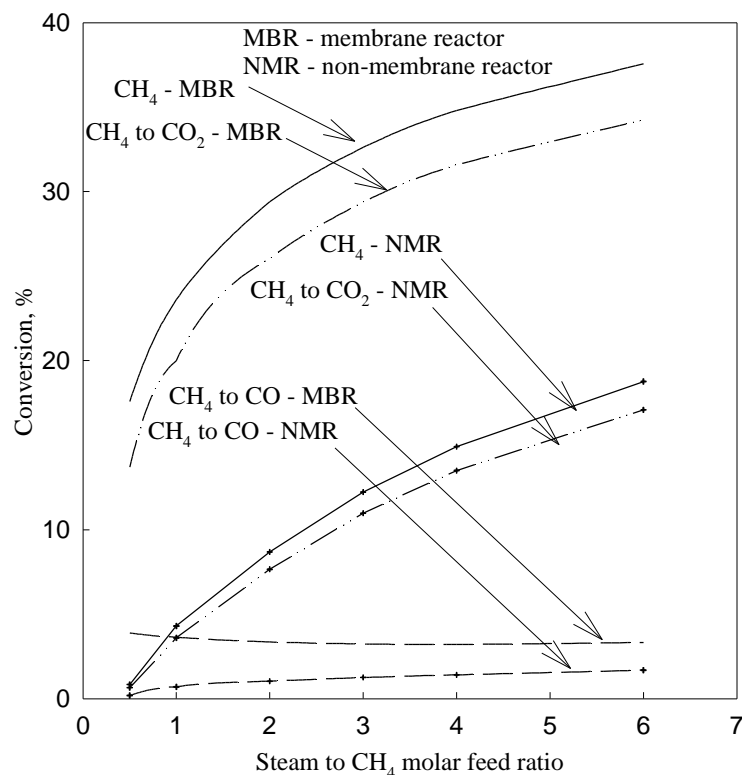
**Figure 4:** Effect of space-time on conversion.  $P = 2$  atm,  $T = 773$  K, steam to  $\text{CH}_4$  mole ratio = 3.0.

#### Effect of Steam/Methane Feed Ratio on Conversions

Figure 5 shows the effect of steam to methane molar feed ratio on conversion of methane, methane into carbon monoxide, and methane into carbon dioxide with respect to feed methane at 2 atm. These conversions increase with an increase in the steam to methane molar feed ratio. At lower values, an increase in the ratio causes a significant increase in conversions. As the value of the ratio increases the effect flattens.

Higher steam to methane feed ratio results in a relatively low carbon monoxide production. At a steam to methane molar feed ratio of 0.5, about 22% of the total converted methane produces carbon monoxide. On the other hand, a steam to methane molar feed ratio of 3.0 the corresponding conversion is about 10%. This is true for both membrane and non-membrane reactor.

The above discussion clarifies that steam to methane molar feed ratio is very important in methane-steam reforming reactions. To reduce the carbon monoxide production at an operating condition, a higher steam to methane ratio can be used. Moreover, a higher steam to methane ratio reduces the coke formation on the catalyst. However, if the ratio is too high, it will reduce the efficiency of the reactor. In laboratories to get a better conversion, a safe carbon monoxide level and to protect the costly catalyst from carbon deposition use of higher steam to methane molar ratio is an excellent idea.



**Figure 5:** Effect of steam to methane molar ratio on conversions.  $P = 2 \text{ atm}$ ,  $T = 773 \text{ K}$ , Ni catalyst loading = 4g,  $\text{CH}_4$  feed rate =  $2.777 \times 10^{-3} \text{ mol/s}$ .

## 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-dimensional pseudo-homogeneous model. The governing equations are solved numerically. Numerical simulation results show that under appropriate operating conditions, the membrane reactor outperforms the conventional packed-bed reactor. These operating conditions will be used in running the actual membrane reactor for steam reforming of methane.

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