DEHYDROGENATION OF CYCLOHEXANE IN A PALLADIUM-CERAMIC MEMBRANE REACTOR BY EQUILIBRIUM SHIFT

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ABSTRACT

Using electroless deposition of palladium thin-films on a microporous ceramic substrate, we developed a hydrogen-selective palladium-ceramic composite membrane. The new membrane has significantly higher permeability and selectivity for hydrogen than many of the commercially available dense-metallic membrane. The hydrogen permeability of the new membrane increases with increasing temperature. These properties make it an ideal candidate for use in membrane-reactors to study dehydrogenation reactions by equilibrium shift. To investigate the usefulness of the new membrane in membrane reactor-separator configuration, a model for studying dehydrogenation of cyclohexane by equilibrium in a membrane reactor is developed. Radial diffusion is considered to account for the concentration gradient in the radial direction due to permeation through the membrane. The model is investigated with and without the reaction. In the non-reaction case, a mixture of argon, benzene, cyclohexane, and hydrogen is used in the reaction side and argon is used in the separation side. In the case of dehydrogenation reaction, the feed stream to the reaction side contained hydrogen and argon while in the separation side argon is used as sweep gas. Equilibrium conversion for dehydrogenation of cyclohexane is 18.7%. Present study shows that 100% conversion can be achieved by equilibrium shift using Pd-Ceramic membrane reactor. For a feed containing cyclohexane and argon of 1.64×10^{-6} and 1.0×10^{-3} mol / s, 98% conversion is achieved.
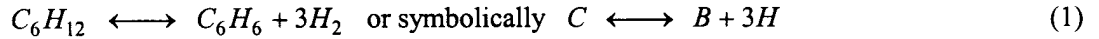
INTRODUCTION

In recent years, there has been increased interest in developing inorganic and composite membranes for in-situ separation of hydrogen to achieve equilibrium shift in catalytic membrane reactors. Many investigators have recognized the potential application of inorganic membranes in high temperature gas separation and reactor technology. With the advances in new inorganic materials and processing techniques, there has been a renewed interest in exploiting the benefits of membranes in many industrial applications. One of the most attractive applications is in membrane-reactors where chemical reaction and product purification by selective separation take place in the same device. Selective separation of one or more reaction products through the membrane wall shifts the equilibrium considerably in the forward direction and results in higher conversion [1,2]. In our laboratory we developed a hydrogen-selective palladium-ceramic composite membrane by electroless deposition of a thin palladium film on a microporous ceramic substrate. Laboratory study has demonstrated that the new membrane has significantly higher hydrogen perm-selectivity than many of the commercially available dense-metallic membrane [3]. The hydrogen permeability of the new membrane increases with increasing temperature which make it an excellent candidate for use in membrane-reactors to study equilibrium-limited hydrogenation and dehydrogenation reactions for enhanced productivity.

We are currently studying the palladium-ceramic membrane in membrane reactor for separation and recovery of hydrogen from a dehydrogenation reaction by equilibrium shift. The dehydrogenation of hydrocarbons is a class of reactions that have been studied extensively in the past. Itoh et al. [4,5] studied the dehydrogenation of cyclohexane in a membrane reactor using thick palladium foil as membrane and developed mathematical models using: (a) a well-mixed (ideal) model in both the reaction and the permeation sides, and (b) a radial mixing model in the reaction side with plug-flow profile in the permeation side. These models could not explain the experimental result. It is believed that both convective and diffusive transport of the species in the reactor side may play an important role in the overall transport process and conversion.

In our study, we considered a tubular membrane reactor for dehydrogenation reaction. Pt-Al$_2$O$_3$ catalyst pellets are loaded inside the palladium-ceramic tube. Hydrogen produced by the reaction 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 permeated hydrogen. Concentration of hydrogen near the membrane wall is depleted due to permeation. As a result, a concentration gradient is developed in the radial direction. A two-dimensional pseudo-homogeneous model was developed to describe the transport mechanism through the catalyst bed. In this presentation, we present our modeling work.

MODEL FOR A MEMBRANE REACTOR

In order to develop a model for a membrane reactor, one needs to consider the reaction kinetics and the transport mechanisms through the membrane as well as through the catalyst bed. In the present work, a palladium-ceramic membrane reactor is studied numerically for the dehydrogenation of cyclohexane to benzene and hydrogen. Pt/Al$_2$O$_3$ catalyst pellets are assumed inside the membrane tube, i.e. reaction side. The model is also investigated without reaction. In this case, a mixture of argon, benzene, cyclohexane, and hydrogen is considered in reaction side. The dehydrogenation of cyclohexane on supported Pt/Al$_2$O$_3$ catalyst is reversible reaction, which can be expressed as:

$$C_6H_{12} \longleftrightarrow C_6H_6 + 3H_2 \quad \text{or symbolically} \quad C \longleftrightarrow B + 3H \tag{1}$$

A number of rate expressions have appeared in the literature to describe the dehydrogenation of cyclohexane to benzene and hydrogen. Published expressions vary from empirical expression to that of more practical ones based on fundamentals. In Table 1, a summary of rate expressions is given that are pertinent to this work. In all cases, dehydrogenation reaction is considered to be catalytic and Pt/Al$_2$O$_3$ is used as the catalyst.

TABLE 1. Rate expressions for dehydrogenation of cyclohexane proposed by different investigators

Investigators (Year)	Rate Equation	Remarks
Shinji et al. 1982 [6]	$r_B = k\left(P_C - \dfrac{P_{H,e}^2}{K_P}P_B P_H\right)$	Homogeneous Reaction, empirical expression
Itoh et al. 1985 [7]	$r_C = -k_o e^{-E/RT}\left(P_C - \dfrac{P_B P_H^3}{K_P}\right)$	Improved from the previous expression
Itoh, 1987 [8]	$r_C = -\dfrac{k\left(K_P K_C / P_H^3 - P_B\right)}{1 + K_B K_P P_C / P_H^3}$	More realistic model, adsorption phenomena considered

The rate expression used by Itoh [8] is essentially based on some minor modifications of the Langmuir-Hinshelwood-Hougen-Watson mechanisms. In his work, Itoh [8] used this expression in the analysis of membrane reactor using palladium. The expressions for the constants are:

$$K_B = 2.03 \times 10^{-10} \exp(6270/T) \text{ Pa}^{-1}; \quad K_p = 4.89 \times 10^{35} \exp(3190/T) \text{ Pa}^3$$
$$k = 0.211 \exp(-4270/T) \text{ mol}/\text{m}^3 \cdot \text{Pa} \cdot \text{s} \tag{2}$$

Transport Mechanism through Palladium-Ceramic Membrane

Palladium-ceramic membrane is nonporous. No pore space is available for diffusion. The transport of gases through nonporous membranes occurs by a solution-diffusion mechanism. The gas molecules dissolve in the membrane surface on the high-pressure side of the membranes. The gas molecules then diffuse through the membrane phase and desorb at the low-pressure side. Different investigators have studied the mechanism of hydrogen transport through the palladium membrane [9,10] and palladium-ceramic membrane [1,11]. The hydrogen flux was given by:

$$N_H = \frac{Q_H}{t}\left(P_H^n - p_H^n\right)$$
(3)

where P_H and p_H are the hydrogen partial pressures of feed side and separation side, Q_H is the permeability and t 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. The hydrogen concentration is proportional to the square root of hydrogen pressure, which is known as Sivert's law [10]. The result is expressed as:

$$N_H = \frac{Q_H}{t}\left(P_H^{0.5} - p_H^{0.5}\right)$$
(4)

A value of n equaling 1 implies a slow, rate determining surface reaction of hydrogen with palladium. According to Fan [11], hydrogen transport through palladium-ceramic membrane does not follow the Sivert's law because the value of n is different from 0.5. Thus, it is necessary to develop a generalized model for all values of n, $0.5 \le n \le 1$.

Two-Dimensional Pseudo-Homogeneous Membrane Reactor Model

Figure 1 shows the schematic of the membrane reactor. Pt-Al$_2$O$_3$ catalyst pellets are assumed inside the palladium-ceramic membrane tube. Hydrogen produced by the reaction 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. There are two types of models to describe the transport mechanism through the catalyst bed: pseudo-homogeneous and heterogeneous. Pseudo-homogeneous models do not account explicitly for the presence of catalyst, in contrast with heterogeneous models, which lead to separate conservation equations for fluid and catalyst. From the discussion of different reactor models, it can be concluded that a two-dimensional model is suitable to describe the transport mechanism through the catalyst bed.
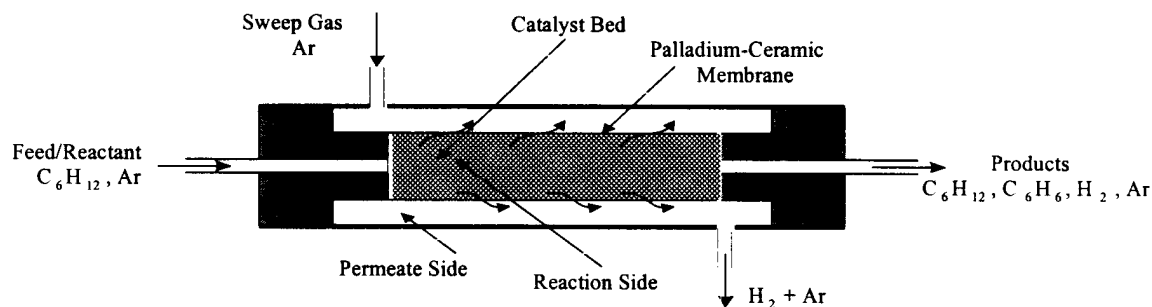

Figure 1. Pd-Ceramic Membrane Reactor

Two-dimensional heterogeneous model requires the knowledge of effectiveness factor. For a first-order reaction it can be evaluated easily. Dehydrogenation of cyclohexane 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.

Model Assumptions:

- Isothermal, isobaric and steady state flow through the whole reactor (both the packed-bed and separation sides) and axial diffusion is negligible.
- Plug flow is assumed through the shell side or separation side and 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.
- The amount of dehydrogenation taking place on the palladium-ceramic tube is negligibly small compared to that on the catalyst pellet surface.

The permeation rate of hydrogen gas through the palladium-ceramic membrane [11], N_H, can be expressed as

$$N_H = \frac{Q_H}{t}\left(P_H^n - p_H^n\right) \tag{5}$$

where n is different from one-half, i.e. $0.5 < n < 1.0$

Based on these assumptions, the governing equations (continuity equations) for different components in dimensionless form may be expressed as:

$$\frac{\partial(U\Phi_A)}{\partial Z} = \frac{d_p l_0}{(Pe_r)_A r_1^2}\left(\frac{1}{R}\frac{\partial \Phi_A}{\partial R} + \frac{\partial^2 \Phi_A}{\partial R^2}\right) \tag{6}$$

$$\frac{\partial(U\Phi_B)}{\partial Z} = \frac{d_p l_0}{(Pe_r)_B r_1^2}\left(\frac{1}{R}\frac{\partial \Phi_B}{\partial R} + \frac{\partial^2 \Phi_B}{\partial R^2}\right) + \varphi \tag{7}$$

$$\frac{\partial(U\Phi_C)}{\partial Z} = \frac{d_p l_0}{(Pe_r)_C r_1^2}\left(\frac{1}{R}\frac{\partial \Phi_C}{\partial R} + \frac{\partial^2 \Phi_C}{\partial R^2}\right) - \varphi \tag{8}$$

$$\frac{\partial(U\Phi_H)}{\partial Z} = \frac{d_p l_0}{(Pe_r)_H r_1^2}\left(\frac{1}{R}\frac{\partial \Phi_H}{\partial R} + \frac{\partial^2 \Phi_H}{\partial R^2}\right) + 3\varphi \tag{9}$$

where,

$$Z = \frac{z}{l_0}; \quad U = \frac{u}{u_0}; \quad R = \frac{r}{r_1}; \quad C_i = \frac{P_i}{R_g T} \quad \text{with } i = A, B, C, \text{and } H$$

$$\Phi_i = \frac{P_i}{P_0} = \frac{X_i}{\sum X_i}\frac{P_r}{P_0}; \quad \phi_i = \frac{p_i}{P_0} = \frac{x_i}{\sum x_i}\frac{p_s}{P_0}; \quad \sum \Phi_i = 1; \quad \text{and } \sum \phi_i = 1$$

$$\varphi = \frac{R_g T l_0}{u_0 P_0}\frac{k\left(K_P \Phi_C - P_0^3 \Phi_H^3 \Phi_B\right)}{P_0^2 \Phi_H^3 + K_B K_P \Phi_C}; \quad (Pe_r)_A = \frac{u_0 d_p}{(D_{er})_A}$$

$$(Pe_r)_B = \frac{u_0 d_p}{(D_{er})_B}; \quad (Pe_r)_C = \frac{u_0 d_p}{(D_{er})_C}; \quad (Pe_r)_H = \frac{u_0 d_p}{(D_{er})_H}$$

Boundary conditions in dimensionless form are given as:

$$\text{at } R = 0,\ 0 \le Z \le 1:\ \begin{cases} \frac{\partial \Phi_A}{\partial r} = 0 & \frac{\partial \Phi_B}{\partial r} = 0 \\ \frac{\partial \Phi_C}{\partial r} = 0 & \frac{\partial \Phi_H}{\partial r} = 0 \end{cases} \quad \text{at } R = 1,\ 0 \le Z \le 1:\ \begin{cases} \frac{\partial \Phi_A}{\partial r} = 0 & \frac{\partial \Phi_B}{\partial r} = 0 \\ \frac{\partial \Phi_C}{\partial r} = 0 & \frac{\partial \Phi_H}{\partial r} = \beta\left(P_H^n - p_H^n\right) \end{cases} \tag{10,11}$$

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where, $\beta = \dfrac{r_1}{r_2 - r_1} \dfrac{R_g T Q_H}{P_0^{1-n} (D_{er})_H}$

Initial conditions in dimensionless variables on the reaction and separation sides are then given as:

$$\text{at } Z = 0, \quad 0 \le R \le 1 \quad \begin{cases} \Phi_A = \Phi_A^0 & \Phi_B = 0 \\ \Phi_C = \Phi_C^0 & \Phi_H = 0 \end{cases} \qquad \text{at } Z = 0, \quad \text{for any position} \quad \begin{cases} \Phi_A = \Phi_A^0 \\ \Phi_H = 0 \end{cases} \qquad (12,13)$$

The details of the derivation of above system of equations are reported elsewhere [12].

NUMERICAL SOLUTION

The Eqns. (6)-(9) subject to initial and boundary conditions, Eqns. (10)-(13) can not be solved analytically. Finite difference method is used to solve these equations. The finite difference approximations of the Eqns. (6)-(9) are:

$$(U\Phi_A)_{i,j+1} = (U\Phi_A)_{i,j} + M_A\left(\left(1 + \frac{1}{2i}\right)(\Phi_A)_{i+1,j} - 2(\Phi_A)_{i,j} + \left(1 - \frac{1}{2i}\right)(\Phi_A)_{i-1,j}\right) \qquad (14)$$

$$(U\Phi_B)_{i,j+1} = (U\Phi_B)_{i,j} + M_B\left(\left(1 + \frac{1}{2i}\right)(\Phi_B)_{i+1,j} - 2(\Phi_B)_{i,j} + \left(1 - \frac{1}{2i}\right)(\Phi_B)_{i-1,j}\right) + \varphi_{i,j}\Delta Z \qquad (15)$$

$$(U\Phi_C)_{i,j+1} = (U\Phi_C)_{i,j} + M_C\left(\left(1 + \frac{1}{2i}\right)(\Phi_C)_{i+1,j} - 2(\Phi_C)_{i,j} + \left(1 - \frac{1}{2i}\right)(\Phi_C)_{i-1,j}\right) - \varphi_{i,j}\Delta Z \qquad (16)$$

$$(U\Phi_H)_{i,j+1} = (U\Phi_H)_{i,j} + M_H\left(\left(1 + \frac{1}{2i}\right)(\Phi_H)_{i+1,j} - 2(\Phi_H)_{i,j} + \left(1 - \frac{1}{2i}\right)(\Phi_H)_{i-1,j}\right) + 3\varphi_{i,j}\Delta Z \qquad (17)$$

where,

$$M_A = \frac{d_p l_o}{(Pe_r)_A r_1^2} \frac{\Delta Z}{(\Delta R)^2}; \quad M_B = \frac{d_p l_o}{(Pe_r)_B r_1^2} \frac{\Delta Z}{(\Delta R)^2}$$

$$M_C = \frac{d_p l_o}{(Pe_r)_C r_1^2} \frac{\Delta Z}{(\Delta R)^2}; \quad \text{and } M_H = \frac{d_p l_o}{(Pe_r)_H r_1^2} \frac{\Delta Z}{(\Delta R)^2}$$

Here M_A, M_B, M_C and M_H are dimensionless modulus including Peclet numbers for argon, benzene, cyclohexane and hydrogen, respectively. The details of the finite difference formulation of the problem, stability analysis of the finite difference scheme and solution methodology are given elsewhere [12]. The solution algorithm is as follows:

1. Calculate Re_p, Sc and Pe_r using appropriate correlations

2. Solve the finite difference equations to determine $(U\Phi)_{i,j+1}$

3. Assume U_{j+1}

4. Determine $\Phi_{i,j+1}$ from $(U\Phi)_{i,j+1} / U_{i,j+1}$

5. Calculate hydrogen permeation rate, $(N_H)_{j+1}$

6. Calculate generation of moles G within the grids j and $j + 1$

7. Compare the averaged permeation rate, $\{0.5((N_H)_j + (N_H)_{j+1})\}$ with $\{(U_j - U_{j-1}) * XTO + G\}$ where XTO is the total mole flow rate at the feed inlet

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8. If $\left|\left(\left\{0.5\left((N_H)_j + (N_H)_{j+1}\right)\right\} - \left\{(U_j - U_{j-1}) * XTO + G\right\}\right)\middle/\left\{(U_j - U_{j-1}) * XTO + G\right\}\right| \le \varepsilon_1$, then

go to the next grid $j + 2$. Otherwise assume new U_{j+1} and repeat steps 4-8.

RESULTS AND DISCUSSIONS

A two-dimensional pseudo-homogenous reactor model is presented to describe the dehydrogenation of cyclohexane to benzene in a membrane-reactor. To have a better understanding of the performance of a membrane reactor, we investigated the dehydrogenation of cyclohexane in a tubular reactor. The physical parameters used in numerical simulation are:

Reactor Dimensions:

Total reactor length, $l_0 = 0.140$ m
Inner radius of inner tube, $r_1 = 8.50 \times 10^{-3}$ m
Outer radius of inner tube, $r_2 = 8.70 \times 10^{-3}$ m
Inner radius of shell, $r_3 = 14.00 \times 10^{-3}$ m

Dimensions of cylindrical catalyst-pellet:

Outer diameter   = 3.3 mm
Height   = 3.6 mm

Permeation parameters:

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

In numerical solution, predicted results should be stable and also needs to be grid independent. Figure 2 shows the effect of grid spacing on numerical solution-stability. This analysis was done for two-component system (argon $= 1.348 \times 10^{-4}$; hydrogen $= 7.248 \times 10^{-4}$ mol/s). From stability analysis, the number of grid in axial direction is $N = 577$ when the number of grid in radial direction is 10. Results with $N = 600$ show oscillation with increasing amplitude. But for $N = 700$ or more, results are stable. In stability analysis, the dimensionless flow rate (U) is assumed unity. But the value of U decreases due to permeation of hydrogen through the membrane. As a result, larger N is required for stable operation. Variation in results with $N = 700$, 800 and 900 is minimal. A value of $N = 900$ is about 50% more than the calculated grid numbers (577) for stability. In all work reported here, we used 50% more grids than that obtained by stability analysis.

To solve the model equation for gas permeation using radial diffusion, the value of effective diffusivity in radial direction is required. For binary system few data are available and these are related to Reynolds number and Schmidt number by the following correlation [13]:
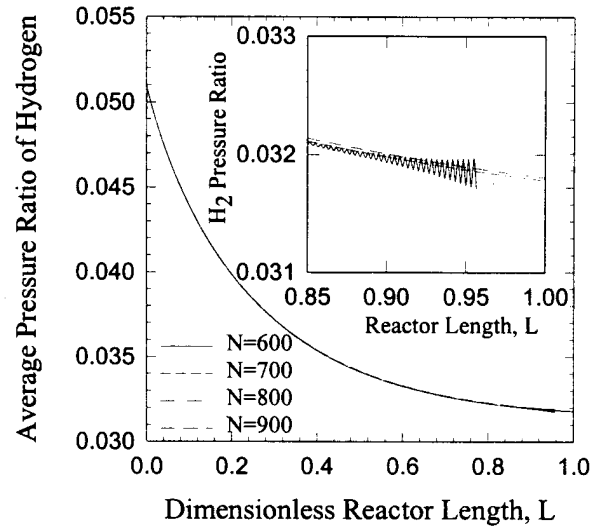

Figure 2. Effect of grid spacings on numerical stability of reactor model.

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$$\frac{1}{Pe_r} = \frac{0.4}{\left(Re_p Sc\right)^{0.8}} + \frac{0.09}{1 + \dfrac{10}{Re_p Sc}} \qquad \text{for } 0.4 < Re_p < 500, \ 0.77 < Sc < 12 \tag{18}$$

No such relation is available for three or four components system. To analyze the radial diffusion of hydrogen in four component systems, Wen and Fan's equation, Eqn. (23) applicable to binary system, is used. For non-reactive four components system, the effect of Sc number on dimensionless flow rate was investigated to determine acceptable Sc number for calculation of effective radial diffusivity. The results are shown in Figs. 3(a,b) and 4(a,b). It is clear from Figs. 3(a,b) that the Sc numbers has no effect on flow rate at high Reynolds number. Figures 4(a,b) reveal that Sc number has little effect on flow rate at small Reynolds number, and essentially remains flat at distance away from the inlet position.
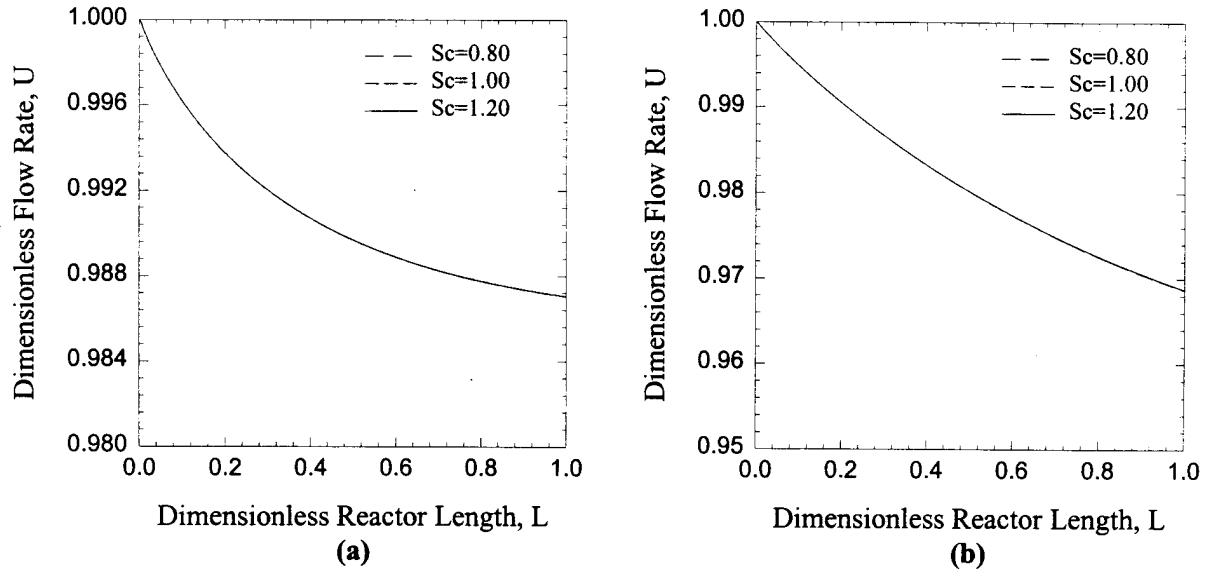

Figure 3(a,b). Effect of Schmidt number on flow rate. (a) Re_p=27.06; Sweep=4.00E-04 mol/s, and (b) Re_p=27.06; Sweep=1.60E-03 mol/s.
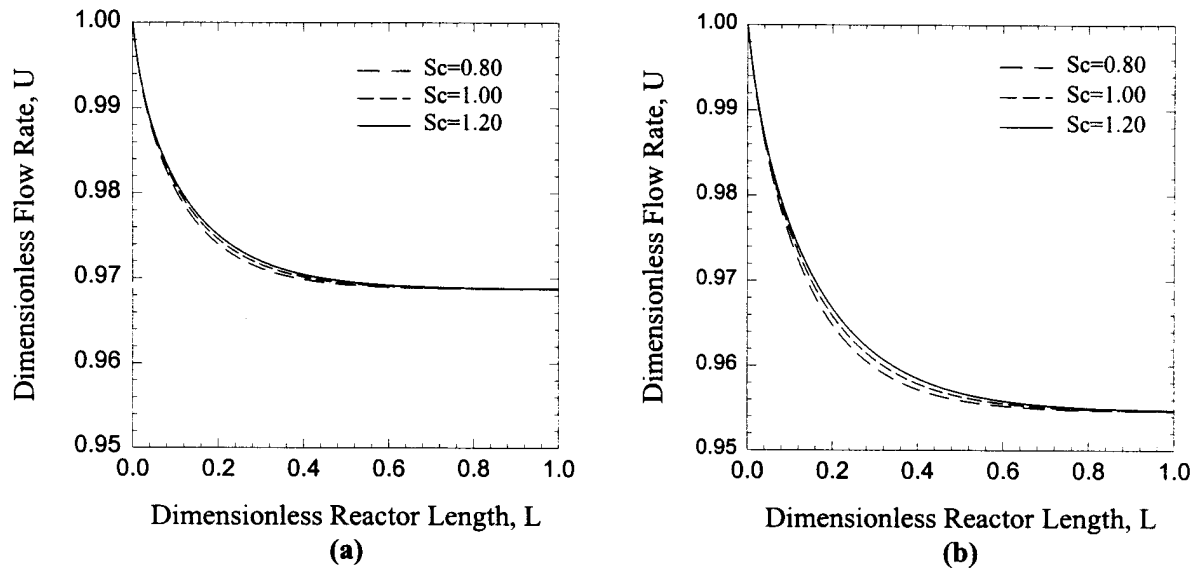

Figure 4(a,b). Effect of Schmidt number on flow rate. (a) Re_p=2.706; Sweep=1.60E-04 mol/s, and (b) Re_p=2.706; Sweep=6.40E-04 mol/s.

Based on above results, it was concluded that the effect of Schmidt number, Sc, on numerical prediction for gas permeation is minimal. Thus $Sc = 1.0$ was used in the study of dehydrogenation reaction by equilibrium shift in the membrane reactor. Two sets of feed compositions were used in the analysis. Feed compositions and corresponding dimensionless numbers are given in Table 6.1.

Table 6.1 Feed flow rate and corresponding Re_p and Pe_r.

Feed	Cyclohexane (mol / s)	Argon (mol / s)	Re_P	Pe_r
1	5.00×10^{-6}	1.00×10^{-4}	2.275	4.466
2	1.64×10^{-6}	5.00×10^{-4}	2.010	4.098

Figures 5(a,b) show the pressure profile of benzene, cyclohexane, and hydrogen along the reactor length for Feed-2 at two sweep rates. Average pressure of cyclohexane (reactant) decreases with the reactor length and the average pressure of hydrogen and benzene (products) increase. Increase in hydrogen pressure would be three times the pressure of benzene if membrane were not used. Hydrogen pressure at the reactor outlet is less than the three times of benzene pressure, Fig. 5(a). It may be even less than the benzene pressure, when conversion is high as shown in Fig 5(b). At high conversion of cyclohexane, one may observe a hydrogen peak. As shown in Fig. 5(b), at 98% conversion a peak is observed in hydrogen pressure profile.

Figures 6(a,b) show the similar behavior for Feed-1. No peak in hydrogen pressure was observed, as the conversions were significantly lower. Conversions achieved are 42.6% and 48.4% at sweep rate 1.0×10^{-4} and 1.0×10^{-3} mol / s.

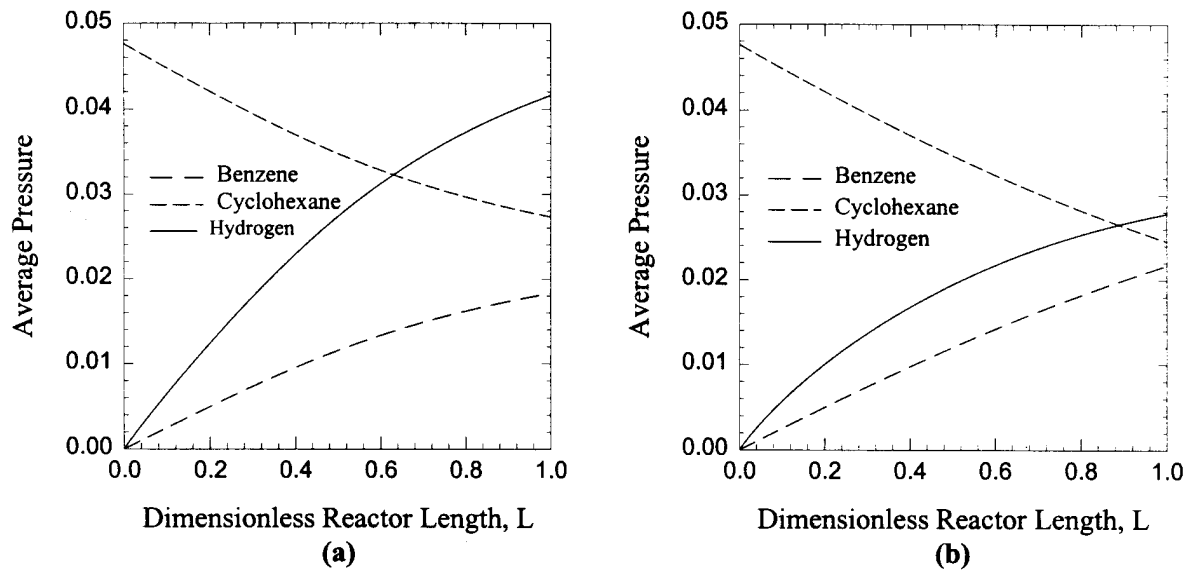Figure 6.(a,b). Pressure profile of reactive components. (a) Re_p=2.28; Sweep=1.0E-04 mol/s, and ReP=2.28; Sweep=1.0E-03 mol/s.

Figure 7 shows the %conversion of cyclohexane as a function of sweep rate for two feed compositions. At a particular sweep rate conversion is higher for Feed-2. In Feed-2, feed rate of cyclohexane is less. So the residence time is high for lower feed flow rate and thus giving the higher conversion. For each case, conversion increases with increasing sweep rate. More amount of hydrogen is permeated with higher

sweep rate. As a result, the reaction is moving into the forward direction and giving the higher conversion.

CONCLUSIONS

A mathematical model is presented to describe the dehydrogenation of cyclohexane to benzene and hydrogen in a membrane-reactor. The model considers the radial diffusion due to selective permeation of hydrogen through the membrane wall. The concentration of the permeable component, hydrogen, near the membrane wall is depleted due to permeation. Hence, consideration of radial diffusion is required in the modeling of membrane reactor. Equilibrium conversion for dehydrogenation of cyclohexane is 18.7%. Present study shows that 100% conversion can be achieved by proper selection of parameters. For a feed containing cyclohexane and argon of 1.64×10^{-6} mol / s and 1.0×10^{-3} mol / s, respectively, 98% conversion is possible.
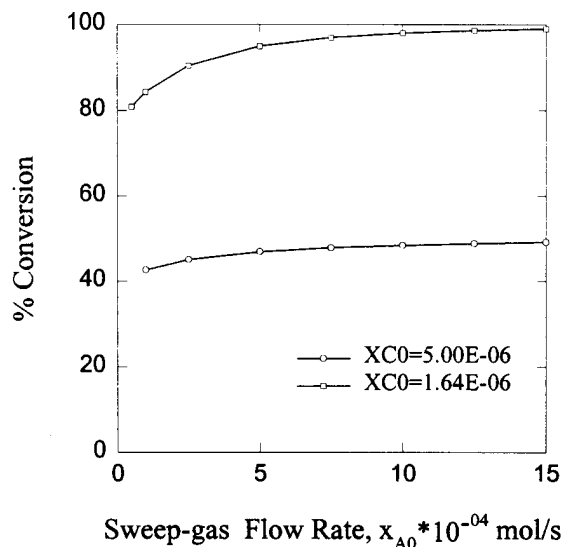

Figure 7. Effect of sweep-gas flow rate on conversion

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