Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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

A. M. Mondal[a]; S. Ilias[a]
[a] Chemical Engineering Department, North Carolina A&T State University, Greensboro, North Carolina, U.S.A.

To cite this Article Mondal, A. M. and Ilias, S.(2001) 'DEHYDROGENATION OF CYCLOHEXANE IN A PALLADIUM-CERAMIC MEMBRANE REACTOR BY EQUILIBRIUM SHIFT', Separation Science and Technology, 36: 5, 1101 — 1116
To link to this Article: DOI: 10.1081/SS-100103639
URL: http://dx.doi.org/10.1081/SS-100103639

SEPARATION SCIENCE AND TECHNOLOGY, 36(5&6), 1101–1116 (2001)

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

A. M. Mondal and S. Ilias*

Chemical Engineering Department, North Carolina A&T
State University, Greensboro, North Carolina 27411

ABSTRACT

With the advances in new inorganic materials and processing techniques, there has been renewed interest in exploiting the benefits of membranes in many industrial applications. 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 a palladium-ceramic composite membrane in a membrane reactor-separator configuration, we investigated the dehydrogenation of cyclohexane by equilibrium shift. A two-dimensional pseudo-homogeneous reactor model was developed to study the dehydrogenation of cyclohexane by equilibrium shift in a tubular membrane reactor. Radial diffusion was considered to account for the concentration gradient in the radial direction due to permeation through the membrane. For a dehydrogenation reaction, the feed stream to the reaction side contained cyclohexane and argon, while the separation side used argon as the sweep gas. Equilibrium conversion for

---

*Corresponding author.

www.dekker.com

dehydrogenation of cyclohexane is 18.7%. The present study showed that 100% conversion could 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, over 98% conversion could be readily 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. 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 takes 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 makes 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 a 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 the 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 this study, we considered a tubular membrane reactor for the dehydrogenation reaction. Pt-Al_2O_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 paper, 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_2O_3 catalyst pellets are assumed inside the membrane tube, i.e. reaction side. The dehydrogenation of cyclohexane on supported Pt/Al_2O_3 catalyst is a reversible reaction, which can be expressed as:

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

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 expressions that are more practical to ones based on fundamentals. In Table 1, a summary of rate expressions is given that are pertinent to this work [6-8]. In all cases, the dehydrogenation reaction is considered to be catalytic and Pt/Al_2O_3 is used as the catalyst.

The rate expression used by Itoh [8] is essentially based on some minor modifications of the Langmuir-Hinshelwood-Hougen-Watson mechanisms. In his

Table 1. Rate Expressions for Dehydrogenation of Cyclohexane Proposed by Different Investigators

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

work, Itoh [8] used this expression in the analysis of membrane reactor using palladium. The expressions for the constants are:

$$K_B = 2.03 \times 10^{-10} \exp\left(\frac{6270}{T}\right), \text{Pa}^{-1} \tag{2}$$

$$K_p = 4.89 \times 10^{35} \exp\left(\frac{3190}{T}\right), \text{Pa}^3 \tag{3}$$

$$k = 0.211 \exp\left(-\frac{4270}{T}\right), \text{mol/m}^3\cdot\text{Pa}\cdot\text{s} \tag{4}$$

Here K_p is the pressure equilibrium constant, K_B is the adsorption equilibrium constant of benzene, and k is rate constant.

Transport Mechanism through Palladium-Ceramic Membrane

The Pd-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:

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

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 of 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 Sievert's law [10]. The result is expressed as:

$$N_H = \frac{Q_H}{t}\,(P_H^{0.5} - p_H^{0.5}) \tag{6}$$

A value of n equaling 1 implies a slow, rate determining surface reaction of hydrogen with palladium. The transport of hydrogen through a Pd-ceramic membrane does not follow the Sievert's law because the value of n is different from 0.5 [2,3,11]. Thus, it is necessary to develop a generalized model for all values of n, $0.5 \leq n \leq 1$.

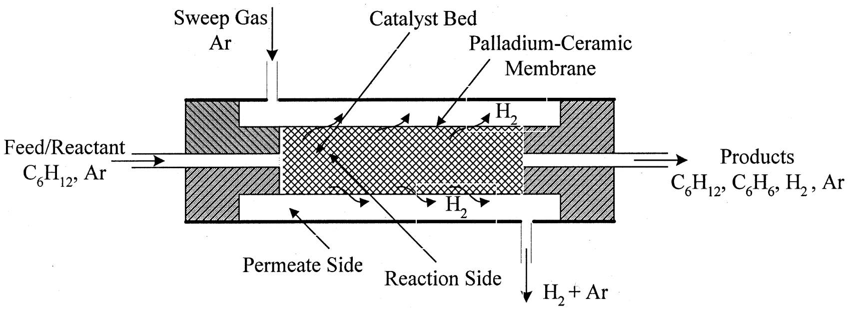


Figure 1. Pd-Ceramic membrane reactor.

Two-Dimensional Pseudo-Homogeneous Membrane Reactor Model

Figure 1 shows the schematic of the membrane reactor. Pellets of Pt-Al_2O_3 catalyst 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. The 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.

A two-dimensional heterogeneous model requires the knowledge of an effectiveness factor. For a first-order reaction it can be evaluated easily. However, dehydrogenation of cyclohexane is a complex reaction and defining the effectiveness factor is complicated. In order to avoid this complexity, a two-dimensional pseudo-homogeneous model is assumed to describe the transport mechanism through the catalyst bed. In developing the mathematical model for a membrane-reactor for the dehydrogenation reaction, the following simplifying assumptions are made:

- 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
- A flat concentration profile is assumed on the separation side

- A 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, N_H, can be expressed by Eqn. (5), where n is different from one-half, i.e. $0.5 < n < 1.0$ [11]. Based on these assumptions, the governing equations (continuity equations) for different components in dimensionless form may be expressed as:

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

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

$$\frac{\partial(U\Phi_C)}{\partial Z} = \frac{d_p l_0}{(Pe_r)_C \mathrm{r}_1^2}\left(\frac{1}{\mathrm{R}}\frac{\partial \Phi_C}{\partial R} + \frac{\partial^2 \Phi_C}{\partial R^2}\right) - \varphi \tag{9}$$

$$\frac{\partial(U\Phi_H)}{\partial Z} = \frac{d_p l_0}{(Pe_r)_H r_1^2}\left(\frac{1}{R}\frac{\partial \Phi_H}{\partial R} + \frac{\partial^2 \Phi_H}{\partial R^2}\right) + 3\varphi \tag{10}$$

where Z and R are the dimensional axial and radial coordinates, respectively. The component dimensionless partial pressures on the reaction and separation side are given by Φ_i and ϕ_i, respectively.

The dimensionless variables are defined as:

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

$$\Phi_i = \frac{P_i}{P_0} = \frac{X_i}{\Sigma X_i}\frac{P_r}{P_0}; \qquad \phi_i = \frac{p_i}{P_0} = \frac{x_i}{\Sigma\, x_i}\frac{p_s}{P_0}; \qquad \Sigma\,\Phi_i = 1; \text{ and } \Sigma\,\phi_i = 1$$

where r and z are the radial and axial directions, respectively. The variables l_0 is the length of the membrane reactor, r_i is the inner radius of membrane tube, u is the interstitial velocity of gas on reaction side, and u_0 is the gas velocity at the inlet on reaction side. The pressure terms are defined as follows: P_i is the partial pressure of component i on the reaction side, P_0 is the reference pressure, p_i is the partial pressure of component i on the separation side, and P_r & p_s are total pressures on the reaction and separation sides, respectively. The component molar flow rates on the reaction and separation sides are given by X_i and x_i, respectively.

The dimensionless source term and Peclet numbers ($(Pe_r)_i$) are defined as:

$$\phi = \frac{R_g T l_0}{u_0 P_0}\,\frac{k(K_p\Phi_C - P_0^3\Phi_H^3\Phi_B)}{P_0^2\Phi_H^3 + K_B K_p \Phi_C}; \qquad (Pe_r)_A = \frac{u_0 d_p}{(D_{er})_A}$$

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

where $(D_{er})_i$ is the effective radial diffusion coefficient of component i, and d_p is the sphere-equivalent diameter of catalyst pellets, and R_g is the universal gas constant.

Boundary conditions in dimensionless form are given as:

$$\text{at R} = 0, 0 \leq \text{Z} \leq 1: \begin{cases} \dfrac{\partial \Phi_A}{\partial r} = 0 & \dfrac{\partial \Phi_B}{\partial r} = 0 \\ \dfrac{\partial \Phi_C}{\partial r} = 0 & \dfrac{\partial \Phi_H}{\partial r} = 0 \end{cases} \tag{11}$$

$$\text{at R} = 1, 0 \leq \text{Z} \leq 1: \begin{cases} \dfrac{\partial \Phi_A}{\partial r} = 0 & \dfrac{\partial \Phi_B}{\partial r} = 0 \\ \dfrac{\partial \Phi_C}{\partial r} = 0 & \dfrac{\partial \Phi_H}{\partial r} = \beta(P_H^n - p_H^n) \end{cases} \tag{12}$$

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

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

$$\text{at Z} = 0, 0 \leq \text{R} \leq 1 \begin{cases} \Phi_A = \Phi_A^0 & \Phi_B = 0 \\ \Phi_C = \Phi_C^0 & \Phi_H = 0 \end{cases} \tag{13}$$

$$\text{at Z} = 0, \text{ for any position} \begin{cases} \Phi_A = \Phi_A^0 \\ \Phi_H = 0 \end{cases} \tag{14}$$

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

Numerical Solution

The Eqns. (7)-(10) are subject to initial and boundary conditions, Eqns. (11)-(14) can not be solved analytically. A Finite Difference method is used to solve these equations. Forward finite difference approximations for axial derivatives and central finite difference approximations for radial derivatives are used in discretization of the governing equations, Eqns. (7)-(10). The second term of the right hand side of the differential equations, except the equation for argon, is the reaction term and this is a source term. This term is highly non-linear and complex in form. It is not possible to linearlize this term. It has been treated as a constant and evaluated at a previous grid point. The source term is given as:

$$\varphi = \varphi\left((\varphi_B)_{i,j}, (\varphi_C)_{i,j}, (\varphi_H)_{i,j}\right) = \varphi_{i,j} \tag{15}$$

The finite difference approximations of the Eqns. (5)-(8) are:

$$\begin{aligned}(U\Phi_A)_{i,j+1} = (U\Phi_A)_{i,j} + M_A\Biggl(\biggl(1 + \frac{1}{2i}\biggr) \\ \times\ (\Phi_A)_{i+1j} - 2(\Phi_A)_{ij} + \biggl(1 - \frac{1}{2i}\biggr)(\Phi_A)_{i-1j}\biggr)\end{aligned} \tag{16}$$

$$\begin{aligned}(U\Phi_B)_{i,j+1} = (U\Phi_B)_{i,j} + M_B\Biggl(\biggl(1 + \frac{1}{2i}\biggr)(\Phi_B)_{i+1j} \\ - 2(\Phi_{\mathrm{B}})_{ij}\biggr) + M_B\Biggl(\biggl(1 - \frac{1}{2i}\biggr)(\Phi_{\mathrm{B}})_{i-1j}\biggr) + \varphi_{i,j}\Delta Z\end{aligned} \tag{17}$$

$$\begin{aligned}(U\Phi_C)_{i,j+1} = (U\Phi_C)_{i,j} + M_C\Biggl(\biggl(1 + \frac{1}{2i}\biggr)(\Phi_C)_{i+1j} - 2(\Phi_C)_{ij}\biggr) \\ + M_C\Biggl(\biggl(1 - \frac{1}{2i}\biggr)(\Phi_C)_{i-1j}\biggr) + \varphi_{i,j}\Delta Z\end{aligned} \tag{18}$$

$$\begin{aligned}(U\Phi_H)_{i,j+1} = (U\Phi_H)_{i,j} + M_H\Biggl(\biggl(1 + \frac{1}{2i}\biggr) \\ \times\ (\Phi_H)_{i+1j} - 2(\Phi_H)_{ij}\biggr) + M_H\Biggl(\biggl(1 - \frac{1}{2i}\biggr)(\Phi_H)_{i-1j}\biggr) + 3\varphi_{i,j}\Delta Z\end{aligned} \tag{19}$$

where,

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

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

Here M_A, M_B M_C and M_H are dimensionless modulus including Peclet numbers for argon, benzene, cyclohexane and hydrogen, respectively. These finite difference equations are written for *i*th radial and *j*th axial grid points where ΔR and ΔZ are the radial and axial increments, respectively. They are indexed as $i = 0, 1, 2,\ldots, I$ $(= 1 / \Delta R)$ and $j = 0, 1, 2,\ldots, J\ (= 1 / \Delta Z)$. 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 used in solving is as follows:

1. Calculate Re_p, Sc and Pe_r using appropriate correlations
2. Solve the finite difference equations to determine $(\mathrm{U}\Phi)_{i,j+1}$
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

8. If $\left| \dfrac{0.5\,((N_H)_j + (N_H)_{j+1}) - ((U_j - U_{j-1})^* \, XTO + G)}{(U_j - U_{j-1})^* \, XTO + G} \right| \leq \varepsilon_1$, 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 the 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
Length	= 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 solutions, 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 a two-component system argon (=1.348 x 10^{-4}; hyrdrogen = 7.248 x 10^{-4} mol/s). From the stability analysis, the number of grid in the axial direction is $N = 577$ when the number of grid in the 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 to be 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 obtained by setting $N = 700$, 800 or 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 for effective diffusivity in the radial direction is required. For a binary sys-

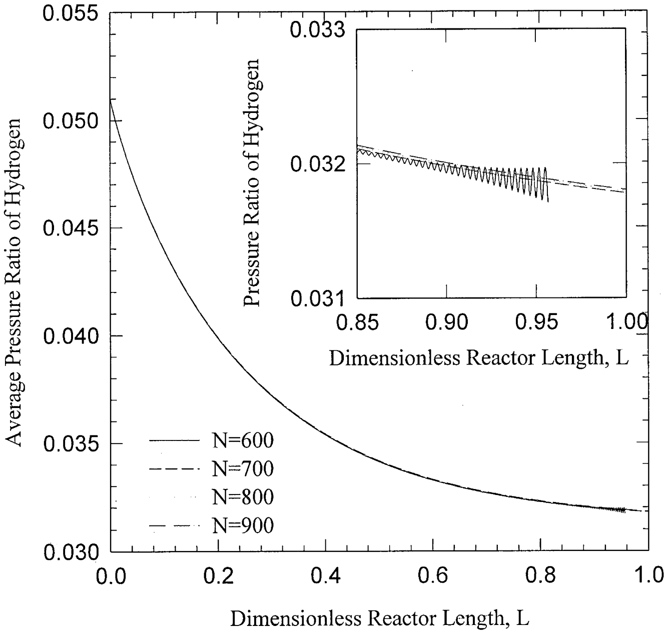


Figure 2. Effect of grid spacings on numerical stability of reactor model.

tem, few data are available and these are related to the Reynolds number (Re_p) and Schmidt number (Sc) by the following correlation [13]:

$$\frac{1}{Pe_r} = \frac{0.4}{(Re_p Sc)^{0.8}} + \frac{0.09}{1 + \dfrac{10}{Re_p Sc}} \qquad \text{for } 11090.4\, Re_p < 500,\ 0.77 < Sc < 12 \tag{20}$$

No such relation is available for three or four component systems. To analyze the radial diffusion of hydrogen in four component systems, Wen and Fan's equation (Eqn. (20)) which is applicable to binary systems, is used. For non-reactive four component systems, the effect of Sc number on the dimensionless flow rate was investigated to determine an acceptable Sc number for calculation of effective radial diffusivity. The results are shown in Figures 3(a,b) and 4(a,b). It is clear from Figure 3(a,b) that the Sc numbers has no effect on the flow rate at high Reynolds number. Figure 4(a,b) reveal that the Sc number has little effect on flow rate at small Reynolds number, and essentially remains unchanged at some distance away from the inlet position.

Based on the above results, it was concluded that the effect of Schmidt number, Sc, on the numerical prediction for gas permeation is minimal. Thus, $Sc = 1.0$ was used in the study of dehydrogenation reaction by equilibrium shift in the

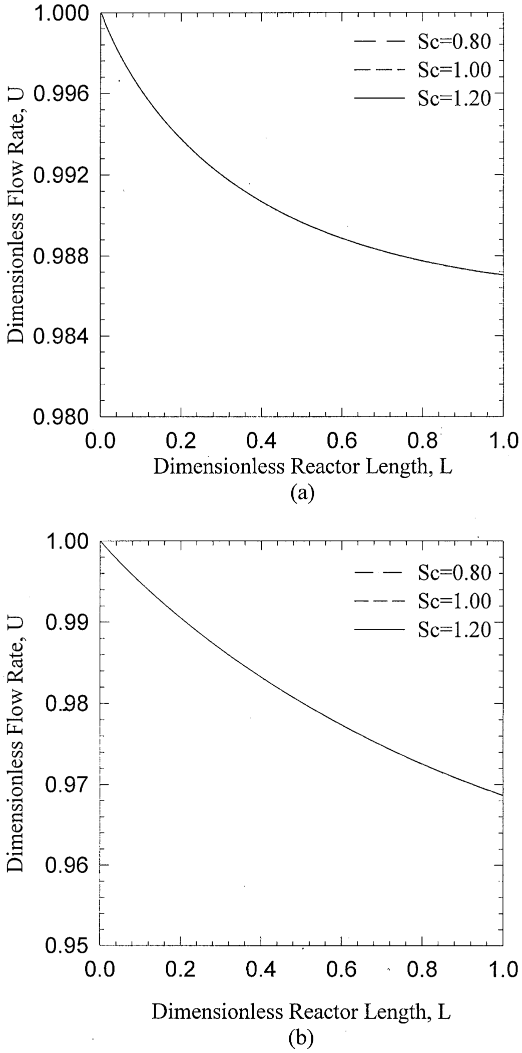
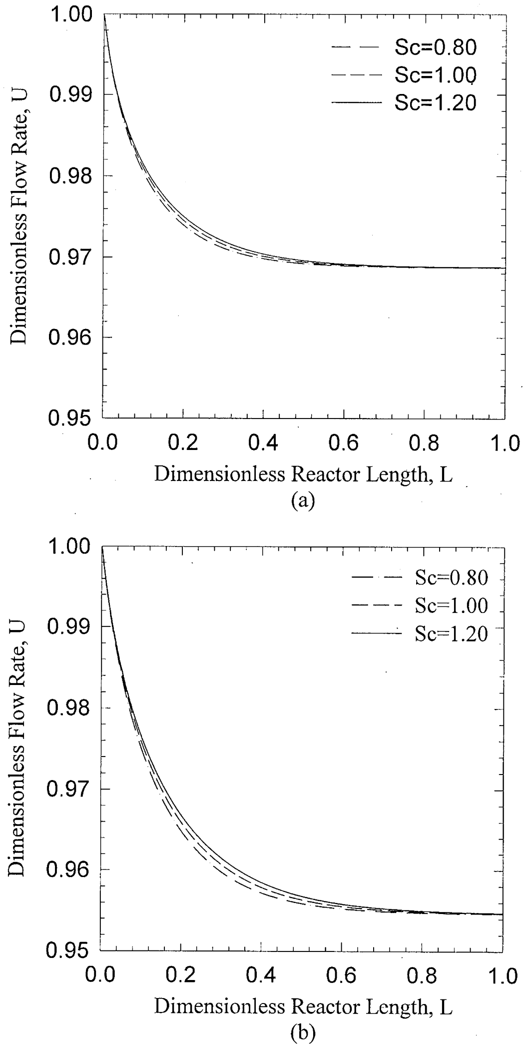


Figure 3. Effect of Schmidt number on flow rate. (a) $Re_p = 27.06$; Sweep = 4.0E-04 mol/s; and (b) $Re_p = 27.06$; Sweep = 1.60E-03 mol/s.

membrane reactor. Two sets of feed compositions were used in the analysis. Feed compositions and their corresponding dimensionless numbers are given in Table 2.

Figures 5(a,b) show the pressure profile of benzene, cyclohexane, and hydrogen along the reactor length for Feed-2 at two sweep rates. The average pres-



(a)

(b)

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

Table 2. Feed Flow Rate and Corresponding Re_p and Pe_r

Feed	Cyclohexane (mol/s)	Argon (mol/s)	Rep	Per
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

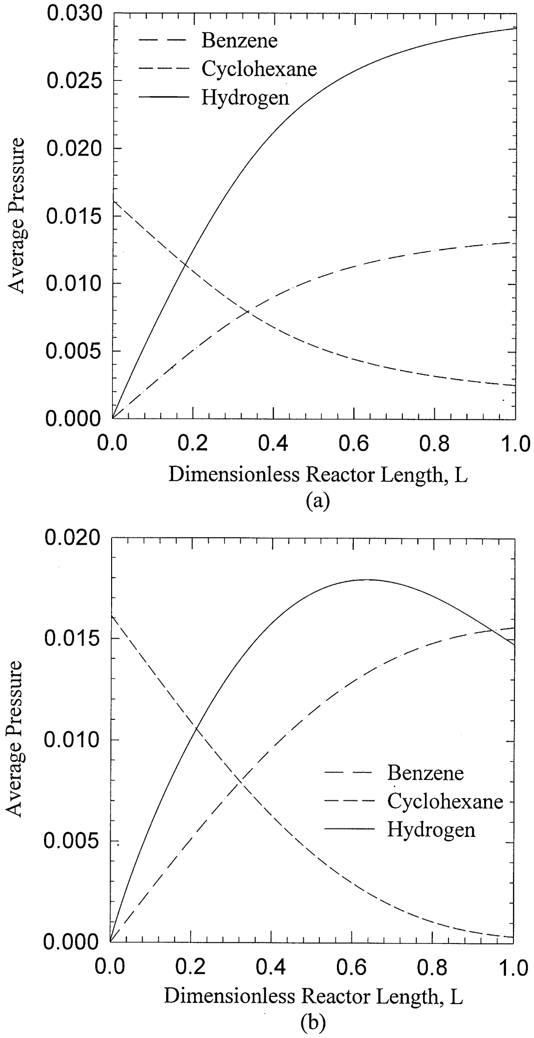


Figure 5. Pressure profile of reactive components. (a) $Re_p = 2.01$; Sweep = 1.0E-04 mol/s; and (b) $Re_p = 2.01$; Sweep = 1.0E-03 mol/s.

sure of cyclohexane (reactant) decreases with reactor length and the average pressure of hydrogen and benzene (products) increases. The increase in hydrogen pressure would be three times the pressure of benzene if the membrane were not used. Hydrogen pressure at the reactor outlet is less than the three times of benzene pressure, Figure 5(a). It may be even less than the benzene pressure, when

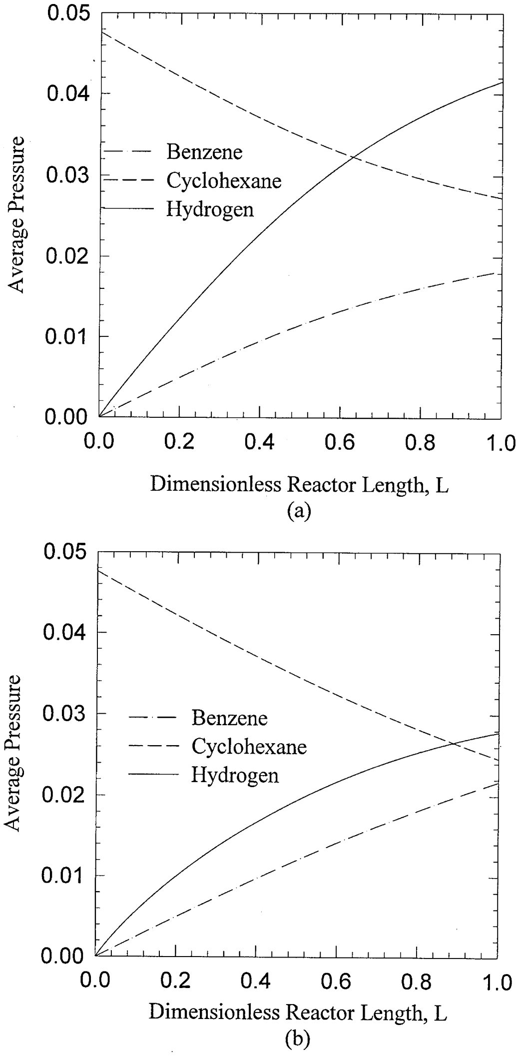


Figure 6. Pressure profile of reactive components. (a) $\mathrm{Re}_p = 2.28$; Sweep = 1.0E-04 mol/s; and (b) $\mathrm{Re}_p = 2.28$; Sweep = 1.0E-03 mol/s.

conversion is high, as shown in Figure 5(b). At high conversion of cyclohexane, one may observe a hydrogen peak. As shown in Figure 5(b), at 98% conversion a peak is observed in the hydrogen pressure profile.

Figure 6(a,b) shows a similar behavior for Feed-1. No peak in hydrogen pressure was observed, as the conversions were significantly lower. Conversions

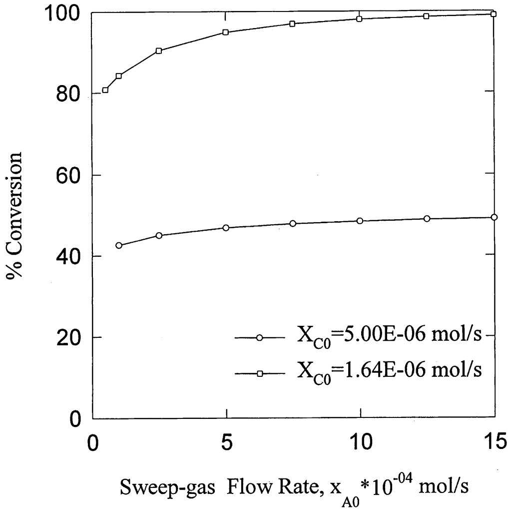


Figure 7. Effect of sweep-gas flow rate on conversion.

achieved are 42.6% and 48.4% at sweep rate 1.0 x 10^{-4} and 1.0 x 10^{-3} mol/s, respectively.

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, the feed rate of cyclohexane is less. So the residence time is high for lower feed flow rate, thus giving higher conversion. For each case, conversion increases with increasing sweep rate. More of hydrogen permeates with higher sweep rates. As a result, the reaction is moving into the forward direction and giving the higher conversion by equilibrium shift.

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 a membrane reactor. Equilibrium conversion for dehydrogenation of cyclohexane is 18.7%. The present study shows that 100% conversion can be achieved by the proper selection of parameters. For a feed containing cyclohexane and argon of 1.64 x 10^{-6} mol/s and 1.0 x 10^{-3} mol/s, respectively, 98% conversion is possible.

ACKNOWLEDGMENTS

The authors would like to acknowledge the funding from the US DOE, National Energy Technology Laboratory, Pittsburgh, Grant No. DE-FG22-96PC9622. The authors would like to thank Dr. Carl Udovich, BP Amoco, R&D center, Naperville, for his support and encouragement of this work.

REFERENCES

1. Shu, J., Grandjean, B. P. A., Van Neste, A., and Kaliaguine, S., "*Catalytic Palladium-based Membrane Reactors:* A Review," **Can. J. Chem. Eng., 69,** 1036 (1991).
2. Collins, J. P. and Way, J. D., *" Preparation and Characterization of a Composite Palladium-Ceramic Membrane,"* **Ind. Eng. Chem. Res., 32,** 3006 (1993).
3. Ilias, S., Su, N., Udo-Aka, U. I., and King, F. G., "*Application of Electroless Deposited Thin-Film Palladium Composite Membrane in Hydrogen Separation,*" **Sep. Sci. Technol.**, **32**, 487 (1997).
4. Itoh, N., Xu, W. C., and Haraya, K.,"*Basic Experimental Study on Palladium Membrane Reactors,*" **J. Membr. Sci., 66**, 149 (1992).
5. Itoh, N., Xu, W. C., and Haraya, K., "*Radial Mixing Diffusion of Hydrogen in a Packed-Bed Type of Palladium Membrane Reactor,*" **Ind. Eng. Chem. Res., 33**, 197 (1994).
6. Shinji, O., Misono, M., and Yoneda, Y., "*The Dehydrogenation of Cyclohexane by the Use of a Porous-Glass Reactor,*" **Bull. Chem. Soc. Japan, 55**, 2760 (1982).
7. Itoh, N., Tanabe, H., Shindo, Y., and Hakuta, T., "*Kinetic Analysis of Cyclohexane Dehydrogenation over Platinum Catalyst,*" **Sekiyu Gakkaishi, 28**, 323 (1985b).
8. Itoh, N., "*A Membrane Reactor Using Palladium,*" **AIChE. J., 33**, 1576 (1987).
9. Hulbert, R. C. and Konecny, J. O., *"Diffusion of Hydrogen through Palladium,"* **J. Chem. Phys., 34**, 655 (1961).
10. Sieverts, A., and Danz, W., *"Solubility of D_2 and H_2 in Palladium,"* **Z. Physik. Chem., 34(B)**, 158 (1936).
11. Fan, T., "*Perm-selectivity of Hydrogen Through Electroless Deposited Thin-Film Palladium-Ceramic Composite Membrane,*" **M. S. Thesis**, North Carolina A&T State University, 1996.
12. Mondal, A.M., *"Stability in Single-Stage gas Permeation and Dehydrogenation of cyclohexane in Pd-Ceramic Membrane Reactor,"* **M. S. Thesis**, North Carolina A&T State University, 1998.
13. Wen, C. Y., and Fan, L. T., Models for Flow Systems and Chemical Reactors, Dekker, New York, 1975.

Downloaded At: 10:49 25 January 2011

Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/Reprints Here" link below and follow the instructions. Visit the U.S. Copyright Office for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on Fair Use in the Classroom.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our Website User Agreement for more details.

Order now!

Reprints of this article can also be ordered at

http://www.dekker.com/servlet/product/DOI/101081SS100103639