Report Title: **Enhancement of Equilibriumshift in Dehydrogenation Reactions Using a Novel Membrane Reactor**

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DISCLIMER

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.

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EXECUTIVE SUMMARY

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. In this work, we are currently studying the use of palladium-ceramic membrane in membrane reactor for separation and recovery of hydrogen from a dehydrogenation reaction. In our previous report, we presented a mathematical model to describe the dehydrogenation of cyclohexane in palladium-ceramic composite membrane reactor. The model includes radial diffusion to account for the concentration gradient in the radial direction due to H_2-permeation through the membrane. In this report we present the simulation results. Present study shows that nearly 100% conversion of cyclohexane is possible by equilibrium shift using Pd-Ceramic membrane reactor.

INTRODUCTION

The overall objective of this project is to develop inorganic and composite membranes for in-situ separation of hydrogen and equilibrium shift in catalytic membrane reactors. The specific objectives of this research are to:

1. Design and fabrication of catalytic membrane reactor using thin film palladium-composite membrane for dehydrogenation of cyclohexane to benzene
2. Conduct dehydrogenation reaction experiments to study the equilibrium shifts and hydrogen permeation characteristics
3. Develop a theoretical foundation for equilibrium shifts and hydrogen transport in the membrane reactor

Mathematical Model for a Membrane Reactor: Numerical Solution

In our previous report, we presented the mathematical model that describes the dehydrogenation of cyclohexane in palladium-ceramic composite membrane reactor. The model includes radial diffusion to account for the concentration gradient in the radial direction due to H_2-permeation through the membrane. The model equations are solved developing a suitable finite-difference scheme. In this report, we summarize the important simulation results.

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:

<u>Reactor Dimensions:</u>

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

<u>Dimensions of cylindrical catalyst-pellet:</u>

Outer diameter = 3.3 mm
Height = 3.6 mm

Permeation parameters:

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

In numerical solution, predicted results should be stable and also needs to be grid independent. Figure 1 shows the effect of grid spacing on numerical solution-stability. This analysis was done for two-component system $(\mathrm{argon} = 1.348 \times 10^{-4};\ \mathrm{hydrogen} = 7.248 \times 10^{-4}\ \mathrm{mol / s})$. From stability analysis [1], 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 $N = 700,\ 800 \text{ and } 900$ 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.

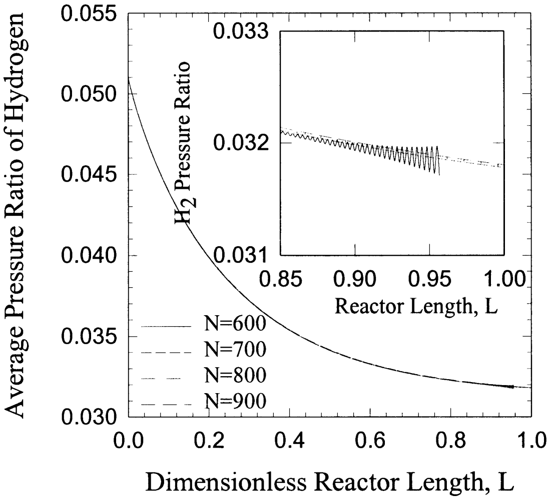


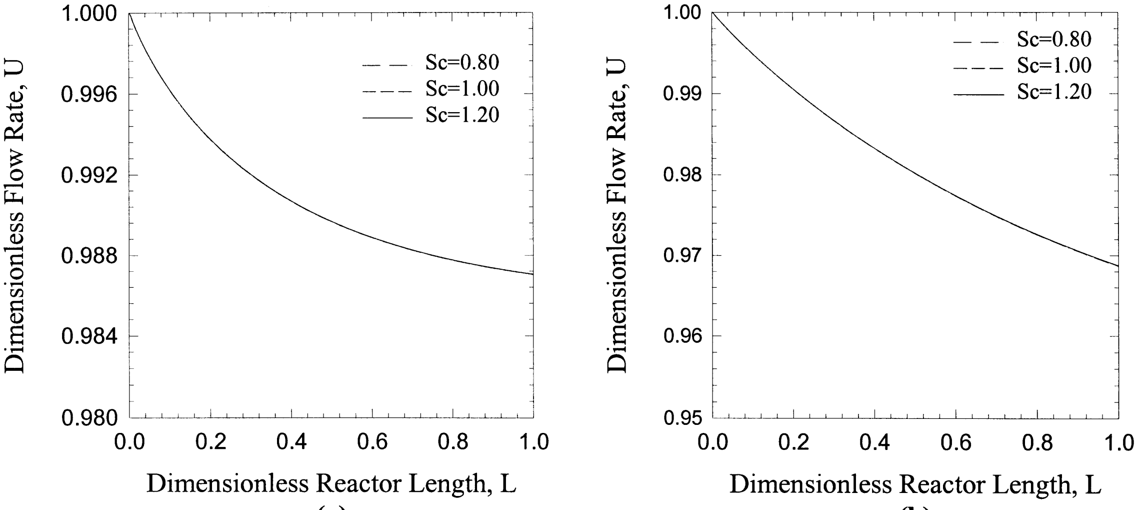
Figure 1. Effect of grid spacings on numerical stability of reactor model.

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 [2]:

$$\frac{1}{Pe_r} = \frac{0.4}{\left(Re_p Sc\right)^{0.8}} + \frac{0.09}{1 + \dfrac{10}{Re_p Sc}} \tag{1}$$

$$\text{for } 0.4 < Re_p < 500,\quad 0.77 < Sc < 12$$

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. (1) 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. 2(a,b) and 3(a,b). It is clear from Figs. 2(a,b) that the *Sc* numbers has no effect on flow rate at high Reynolds number. Figures 3(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.



(a) **(b)**

Figure 2(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.

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 1.

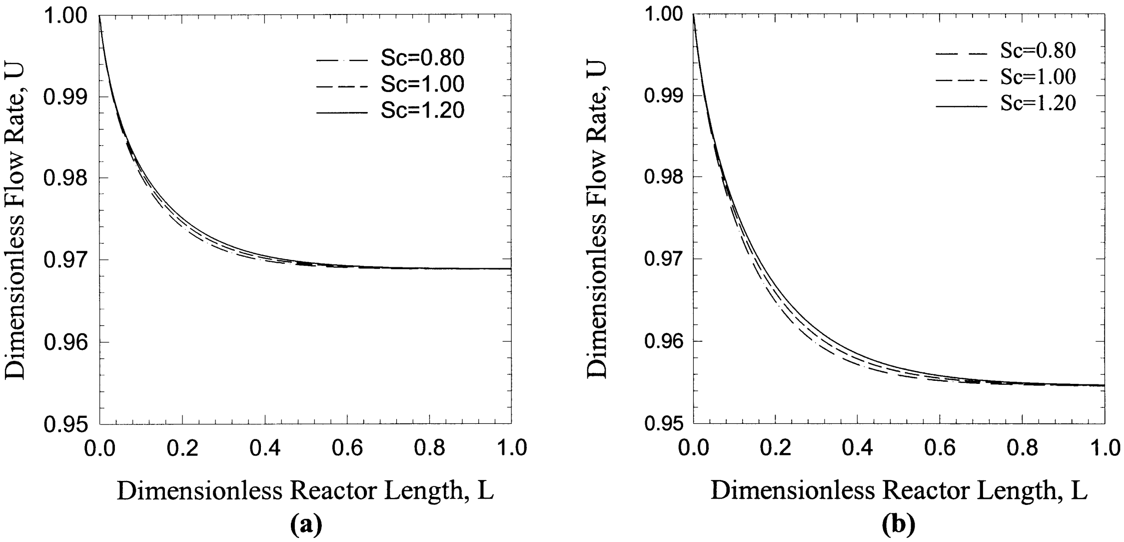


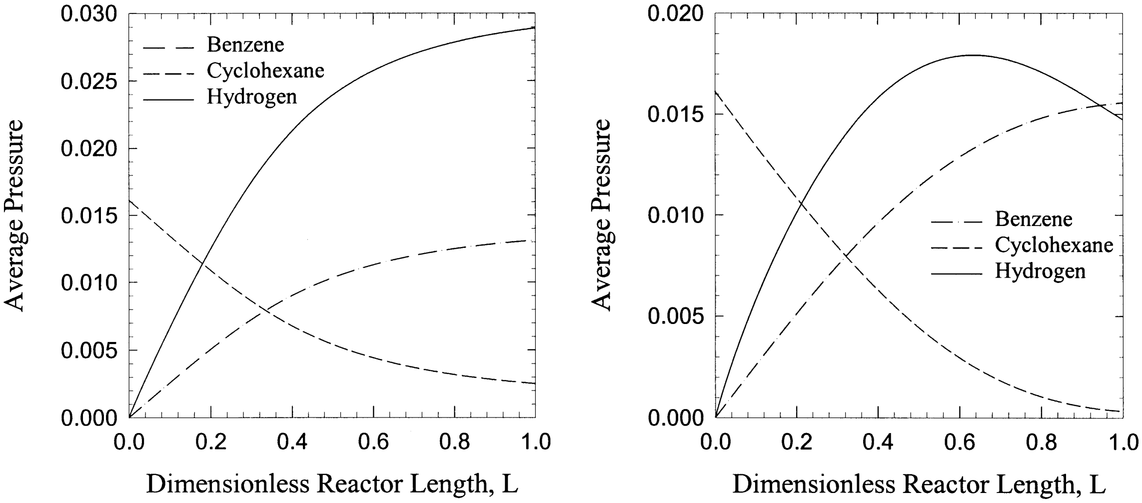
Figure 3(a,b). Effect of Schmidt number on flow rate. (a) Re_p=2.706; Sweep=1.60E-04 mol/s, and (b) Re_p=2.706; Sweep=6.40E-04 mol/s.

Table 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

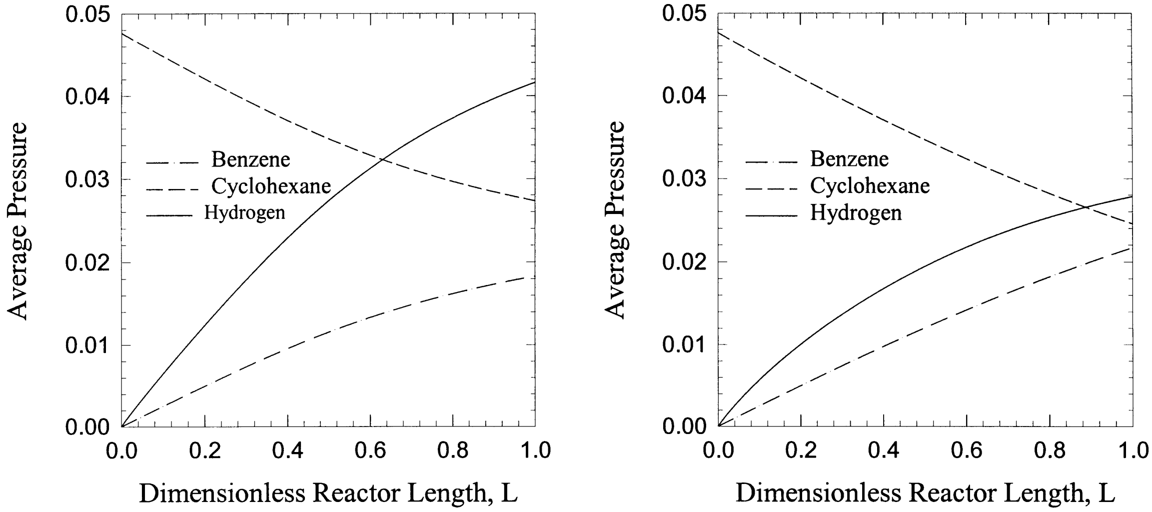
Figures 4(a,b) show the pressure profile of benzene, cyclohexane, and hydrogen along the reactor length for Feed-2 at two sweep rates. Average pressure of cyclohexane (reactant) decreases with the reactor length and the average pressure of hydrogen and benzene (products) increase. Increase in hydrogen 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. 4(a). It may be even less than the benzene pressure, when conversion is high as shown in Fig 4(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 5(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.



(a) **(b)**

Figure 4(a,b). 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.



(a) **(b)**

Figure 5(a,b). Pressure profile of reactive components. (a) Re_p=2.28; Sweep=1.0E-04 mol/s, and Re_p=2.28; Sweep=1.0E-03 mol/s.

Figure 6 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.

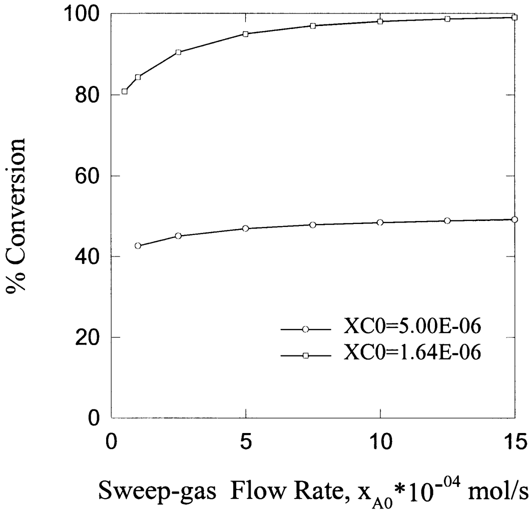


Figure 6. Effect of sweep-gas flow rate on conversion of cyclohexane.

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 that100% 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.

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1. Anderson, D.A., Tannehill, J.C., and Fletcher, R.H., **Computational Fluid Mechanics and Heat Transfer**, Hemisphere Publishing, 1990.

2. Wen, C.Y., and Fan, L.T., **Models for Flow Systems and Chemical Reactors**, Dekker, NY., 1995.