OPTIMAL DESIGN CONDITIONS FOR DEHYDROGENATION OF CYCLOHEXANE IN A MEMBRANE REACTOR

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Abstract – The design variables of a membrane reactor, such as the permeation rate through the membrane and catalyst loading in the membrane, have received little attention in comparison with the operating conditions. A non-dimensionalized model for a membrane reactor was developed to account for the effects of permeation rate and catalyst loading. The increased permeation rate did not always increase the exit conversion and there existed a maximum point of exit conversion. At isothermal conditions, the exit conversion was saturated as catalyst loading was increased; however, when the reactor was under non-isothermal condition along the axial direction, there existed an optimum catalyst loading at which the exit conversion was maximum. With this model, the optimal configuration of permeation rate and catalyst loading could be determined.

Key words: Membrane Reactor, Dehydrogenation of Cyclohexane, Inorganic Membrane, Membrane Catalysis

INTRODUCTION

A membrane reactor is a unit in which both the chemical reaction and separation take place simultaneously. It can be applied to overcome the thermodynamic equilibrium in reactions such as the dehydrogenation of liquid hydrides in energy conversion and the dehydrogenation process for producing styrene and butadiene, which are the starting materials for styrene-butadiene rubber (SBR). Since Gryaznov first presented the concept of a membrane reactor [Gryaznov, 1964], many researchers have been working on developing a high performance membrane reactor. To be used in dehydrogenation reactions, the membrane should be made to have a high permeation rate of hydrogen. Pore modification of the porous support has been studied to achieve membranes of high permeation rate, but generally, there is trade-off between high permeation rate and high selectivity [Lee et al., 1995].

There have been efforts to model and simulate a membrane reactor to understand how the design and operating variables affect the conversion of the reactor [Itoh and Govind, 1989; Shu et al., 1991; Bernstein and Lund, 1993]. The design variables include gas permeability through the membrane, catalyst loading, and length and diameter of the reactor. The operating variables include the flow rates of both sweeping and carrier gas, initial concentration of the reactant in feed stream, temperature, and pressure difference through the membrane. The overall performance of a membrane reactor is optimized by proper selection of these operating and design variables.

The effect of operating conditions on membrane reactor performance has been exhaustively studied [Mohan and Govind,

1988; Champagnie et al., 1992; Sun and Khang, 1988]. Depending on the operating conditions and types of reaction, it was reported that the flow arrangement of retentate and permeate flow could be either countercurrent or cocurrent for optimum performance [Mohan and Govind, 1988]. The conversion increased with increased sweeping gas flow rate and decreased with carrier gas [Champagnie et al., 1992; Sun and Khang, 1988]. Design variables such as the permeability of gases through the membrane and the catalyst loading, however, have not received much attention. Only the effect of the ratio of the permeation rate of the products to the reaction rate has been investigated [Itoh et al., 1985; Mohan and Govind, 1986]. One study [Itoh et al., 1985] reported that the maximum conversion depended on the relative rates of permeation and reaction. Most of the work reported in the literature has approached from the viewpoint of changing the permeation rate only, which could be achieved experimentally by using different membranes such as Vycor glass and Pd-Al membranes or thinning the thickness of the membrane on the support.

In contrast, the reaction rate or catalyst loading has received little attention up to now. Recently, one publication addressed the effect of catalyst loading in the dehydrogenation of methylcyclohexane [Ali and Rippin, 1994]. The shell side contains catalyst for the dehydrogenation reaction and inert packing materials. The term 'catalyst loading' refers to the amount of catalyst relative to the inert packing. In general, a low permeation rate requires low loading of catalyst because the dehydrogenation reaction quickly reaches a thermodynamic equilibrium. In a membrane reactor, reaction occurs only on the catalysts that are packed in the shell side, and the membrane remains as an inert wall. The rate of reaction per volume of the reaction zone can be changed by diluting the catalysts with inert packing materials.

In this paper, the effects of permeation rate and reaction

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rate or catalyst loading on the exit conversion are investigated by using two dimensionless groups. Complicated phenomena caused by the non-isothermal condition along the axial direction are discussed. The dehydrogenation of cyclohexane was chosen as our model reaction system, and the reaction rate equation from the literature was used [Itoh et al., 1988].

MODEL DEVELOPMENT

The following assumptions were made to develop a model of the membrane reactor.

(1) Steady state, isothermal operation.

(2) Uniform flow in both shell and tube, so no radial distribution of components exists.

(3) Permeation through the membrane is proportional to the difference of partial pressures in shell and tube.

(4) Membrane is inert to the reaction and the dehydrogenation reaction takes place only on the catalysts packed in the shell side.

(5) The catalysts and packing materials that are used to dilute the catalyst bed have the same size and shape.

(6) A pseudo homogeneous model is assumed in the catalyst bed.

Fig. 1 shows a schematic diagram of a membrane reactor model, which has a simple shell-and-tube geometry. The inner tube corresponds to the membrane on the support. The radius of the inner tube is calculated as an arithmetic mean of the inner radius of the support and outer radius of the membrane. At the entrance of the reactor, only nitrogen, which acts as a sweeping gas, is fed through an inner tube. Cyclohexane and nitrogen are fed through the shell side. The dehydrogenation of cyclohexane, which occurs along the shell; produces benzene and hydrogen.

The mass balance equation for each component was originally developed by Itoh et al. [1985]. For the convenience of the parametric study, the balance equations are nondimensionalized and written as follows:

Shell side (catalyst bed)

$$\frac{dy_i^O}{d\xi} = -\alpha_i D_1 \left(\frac{y_i^O}{\sum y_i^O} - \frac{y_i^I}{\sum y_i^I} \right) + v_i D_2 \eta \tag{1}$$

$$y_i^O = y_{i,0}^O \quad \text{at} \quad \xi = 0 \tag{2}$$
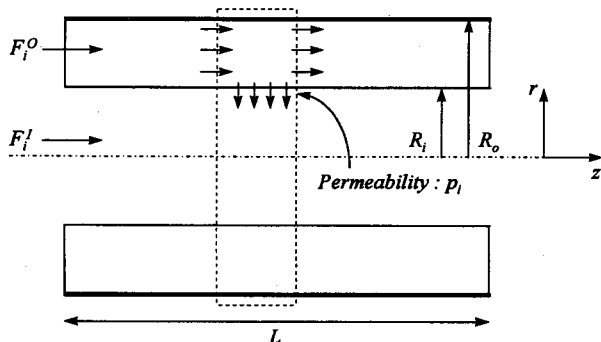

Fig. 1. Schematic diagram of a membrane reactor.

Tube side

$$\frac{dy_i^I}{d\xi} = \alpha_i D_1 \left(\frac{y_i^O}{\sum y_i^O} - \frac{y_i^I}{\sum y_i^I} \right) \tag{3}$$

$$y_i^I = y_{i,0}^I \quad \text{at} \quad \xi = 0 \tag{4}$$

The dimensionless numbers, D_1 and D_2, which contain terms corresponding to the permeation rate and the catalyst loading, respectively, are defined as follows.

$$D_1 = \frac{2\pi R_i L p_H P_T^O}{F_{C,0}^O} \tag{5a}$$

$$D_2 = \frac{\pi(R_o^2 - R_i^2) L \psi k P_T^O}{F_{C,0}^O} \tag{5b}$$

The catalyst loading (ψ) which is defined as the amount of catalyst relative to the inert packing in the shell side, has a value between 0 and 1.

The nondimensionalized rate equation for the dehydrogenation reaction is given as follows:

$$\eta = \frac{\left(K_1 \frac{y_C^O}{\sum y_i^O} - \frac{y_B^O(y_H^O)^3}{(\sum y_i^O)^4} \right)}{\frac{(y_H^O)^3}{(\sum y_i^O)^3} + K_2 \frac{y_C^O}{\sum y_i^O}} \tag{6}$$

Other variables are defined in the nomenclature section. The conversion is defined as the ratio of the mole flow rates of cyclohexane at the exits of both shell and tube side to the mole flow rates of cyclohexane at the entrances of both the shell and tube side. Thus, it is calculated by Eq. (7)

$$X = 1 - \frac{(y_C^I + y_C^O)}{(y_{C,0}^I + y_{C,0}^O)} \tag{7}$$

Table 1. Parameters for simulation

Inner radius of the membrane	3.5×10^{-3} (m)
Outer radius of the membrane	5×10^{-3} (m)
Radius of the shell (R_o)	1×10^{-2} (m)
Length of the reactor (L)	0.3 (m)
Flow rate of the cyclohexane at the entrance of shell side ($F_{C,0}^O$)	1.92×10^{-6} (mol s^{-1})
Flow rate of the cyclohexane at the entrance of tube side ($F_{C,0}^I$)	0
Flow rate of the nitrogen at the entrance of shell side ($F_{N,0}^O$)	1.09×10^{-5} (mol s^{-1})
Flow rate of the nitrogen at the entrance of tube side ($F_{N,0}^O$)	5.42×10^{-5} (mol s^{-1})
Reaction rate constant (k)	$0.221 \times \exp(-4.27 \times 10^3/T)$ (mol m^{-3} s^{-1})
Permeability of hydrogen (p_H)	3.03×10^{-6} (mol m^{-2} s^{-1} Pa^{-1})
Permeability of cyclohexane (p_C)	4.68×10^{-7} (mol m^{-2} s^{-1} Pa^{-1})
Permeability of benzene (p_B)	4.85×10^{-7} (mol m^{-2} s^{-1} Pa^{-1})
Permeability of nitrogen (p_N)	8.10×10^{-7} (mol m^{-2} s^{-1} Pa^{-1})
Reactor pressure (P_T)	1.013×10^5 (Pa)
K_P	$4.89 \times 10^{35} \exp(-2.649 \times 10^4/T)$ (Pa^3)
K_B	$2.03 \times 10^{-10} \exp(6.27 \times 10^3/T)$ (Pa^{-1})

These eight equations with eight initial conditions were solved simultaneously by the 4th order Runge-Kutta method. The calculation proceeded when the consistency criterion [Eq. (8)] was satisfied within 0.1%.

$$\Sigma(y_i^f + y_i^p) = y_{\ell,0}^\ell (1 + 3X) \tag{8}$$

The values for each parameters used in this simulation are summarized in Table 1.

RESULTS AND DISCUSSION

Since the dehydrogenation of cyclohexane is an endothermic reaction, the exit conversion is expected to increase with temperature. Fig. 2 shows that the conversion in the membrane reactor exceeds the equilibrium conversion, but the merit of the membrane reactor diminishes as the temperature is increased owing to the enhanced equilibrium conversion.

The exit conversion for an isothermal membrane reactor is shown in Fig. 3(a) and (b). The conversion is increased as D_2 increases and finally reaches a steady value. But, as D_1 increases at a fixed value of D_2, the conversion goes up to the maximum point. The geometry of the membrane reactor and flow rate of gas stream are the common part of parameters D_1 and D_2 as defined in Eq. (5a) and (5b). With those values fixed, the parameter D_1 represents the permeability of hydrogen, and D_2, the catalyst loading. The dependency of conversion on D_2 can be explained by the fact that although higher loading of catalyst increases the exit conversion owing to the enhanced reaction rate, the reaction cannot proceed because of the equilibrium restriction unless hydrogen permeability is further increased. However, the exit conversion goes through the maximum point as D_1 increases as shown in Fig. 3(b). It is obvious that as D_1 increases to 40, the selective removal of hydrogen helps to drive the exit conversion to reach a maximum. But when the permeation rate increased, selective removal of hydrogen works no longer, since the reactant as well as product species can flow out of the shell through the membrane and be carried away by the sweeping gas. As a result, the exit conversion decreased. Therefore, the optimum permeability and catalyst loading should be determined around $D_1=40$ and $D_2=256$.
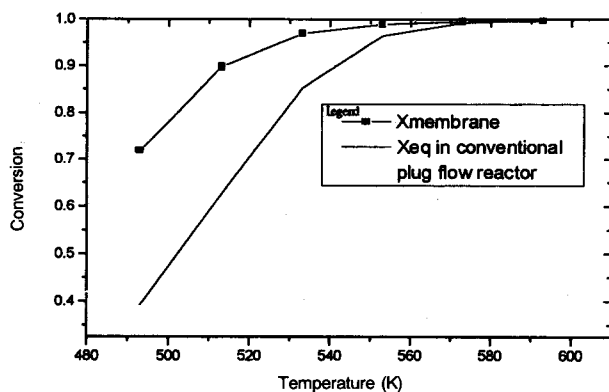
In a lab-scale membrane reactor, the isothermal condition can hardly be achieved when the end cap of the membrane reactor is cooled to protect the sealing. Understanding the behavior of a non-isothermal membrane reactor is important from the practical point of view. The exit conversion for a non-isothermal membrane reactor as a function of D_1 and D_2 is shown in Fig. 4(a) and (b). The temperature profile along the axis was assumed to be parabolic and symmetric around the center of the reactor. Fig. 4(b) shows that the exit conversion varies as a function of D_1 in the same way as at isothermal conditions. The dependency on D_2 in Fig. 4(a) shows, however, a different behavior compared with the results for the isothermal case. In Fig. 4(a), when the permeability (D_1) is 0.1, there exists an optimum loading of catalyst at which the exit conversion is maximum. As the catalyst loading (D_2) increases, the exit conversion is obviously increased when D_2 is lower than 8. However, with low permeation rate, the products, such as hydrogen and benzene, are not effectively removed from the tube side. The remaining product gases react to produce cyclohexane again as they pass the rest of the reactor, resulting in low exit conversion. As D_1 increased, the peak in conversion with D_2 disappeared and the trend of the exit conversion became the same as for an isothermal reactor.

The separation factor of this system is defined as the ratio of the permeability of hydrogen to that of the sweeping gas (nitrogen). To investigate the effect of the separation factor on the exit conversion, all the gas species except hydrogen
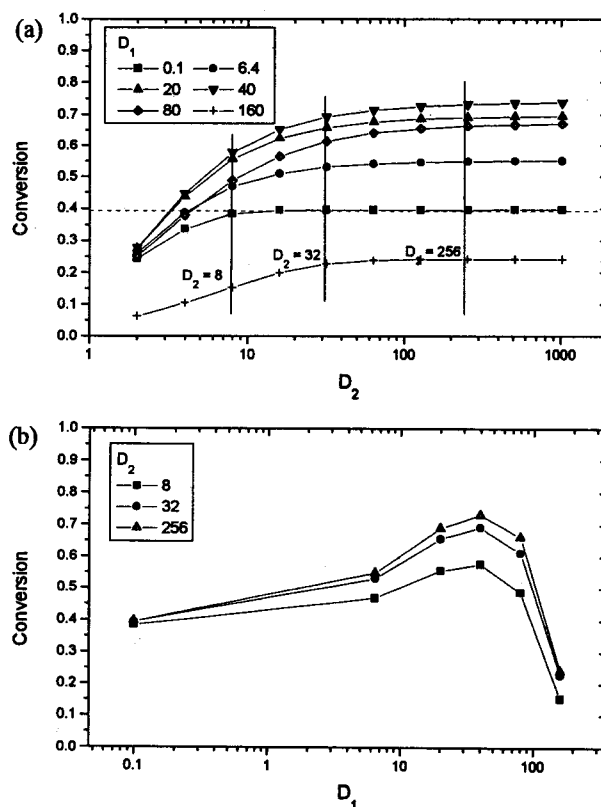
Fig. 3. Change of exit conversion with D_1 and D_2 in an isothermal reactor.
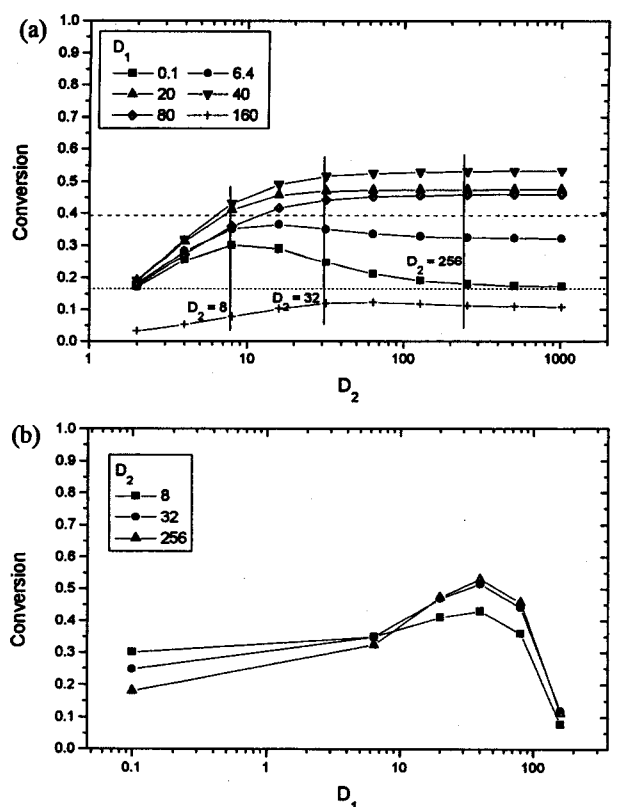(T=493 K, Horizontal line represents the equilibrium conversion)

Fig. 2. Change of exit conversion with reactor temperature in an isothermal reactor.
($D_1=50.1$, $D_2=100$)

Fig. 4. Change of exit conversion with D_1 and D_2 in a non-isothermal reactor.

(T_0=463 K, T_{max}=493 K, Upper and lower horizontal lines represent the equilibrium conversion for T_{max} and T_0, respectively)

are assumed to permeate more slowly than the permeation rate of Knudsen diffusion where the separation factor is 3.74. Fig. 5 shows that the exit conversion is increased as the separation factor is increased. However, the exit conversion is saturated at 0.776. Though D_1 was kept constant in the above calculation, the separation factor, in general, is increased at the expense of permeability. This shows that the separation factor and permeability of hydrogen of the membrane should be optimized together for better performance of a membrane
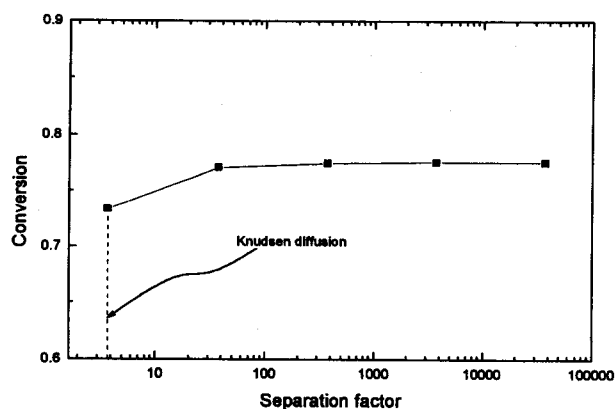

Fig. 5. Change of exit conversion with separation factor.
(D_1=40, D_2=256)

reactor.

CONCLUSION

A membrane reactor for the dehydrogenation of cyclohexane was modeled for isothermal and non-isothermal conditions. The effects of two nondimensional groups D_1 and D_2 on the exit conversion of a membrane reactor were investigated, where D_1 and D_2 represented the nondimensionalized permeability and catalyst loading, respectively.

The changes in exit conversion with D_1 and D_2 showed that there existed an optimum permeability and catalyst loading. When the reactor was under isothermal condition, it was shown that the shell side did not have to be overloaded with catalyst. The catalyst loading corresponding to a D_2 value of 256 was enough to achieve the saturated conversion. Under a non-isothermal condition, however, there existed an optimum catalyst loading when D_1 was under 6.4. The exit conversion dropped to a lower value than the equilibrium one as D_1 was increased to 160. With this model, the optimum configuration of permeability and catalyst loading can be found for a given reactor geometry.

NOMENCLATURE

D_1 : dimensionless group, $\dfrac{2\pi R_i L p_H P_Y^O}{F_{C,o}^O}$ [-]

D_2 : dimensionless group, $\dfrac{\pi(R_O^2 - R_i^2)L\psi k P_T^O}{F_{C,0}^O}$ [-]

F_i^I : flow rate of each species in tube side [mol s^{-1}]

F_i^O : flow rate of each species in shell side [mol s^{-1}]

K_1 : dimensionless equilibrium constant, $\dfrac{K_P}{(P_T^O)^3}$ [-]

K_2 : dimensionless equilibrium constant, $\dfrac{K_B K_P}{(P_T^O)^2}$ [-]

K_B : equilibrium constant [Pa^{-1}]

K_P : equilibrium constant [Pa^3]

k : rate constant [mol m^{-3} s^{-1}Pa^{-1}]

L : total length of reactor [m]

P_T^O : total pressure within the reactor [Pa]

p_i : permeation rate of each species [mol m^{-2} s^{-1} Pa^{-1}]

R_i : radius of tube [m]

R_O : radius of shell [m]

$-r_C$: rate of reaction [mol m^{-3} s^{-1}]

X : conversion [-]

y_i^I : dimensionless flow rate of each species in tube side, $\dfrac{F_i^I}{F_{C,0}^O}$ [-]

y_i^O : dimensionless flow rate of each species in shell side, $\dfrac{F_i^O}{F_{C,0}^O}$ [-]

z : axial position [m]

α_i : separation factor of each species, $\dfrac{p_i}{p_H}$ [-]

η : dimensionless rate of reaction, $\dfrac{-r_C}{k P_T^O}$ [-]

ν_i : stoichiometric coefficient [-]

ξ : dimensionless axial position, $\frac{Z}{L}$ [-]

ψ : catalyst loading [-]

Subscript

C, B, H, N : each represents cyclohexane, benzene, hydrogen and
    nitrogen, respectively

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