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Jawad K. Ali[a]; D. W. T. Rippin[a]
[a] CHEMICAL ENGINEERING DEPARTMENT, SWISS FEDERAL INSTITUTE OF TECHNOLOGY, UNIVERSITÄTSTR. 6, CH-8092 ZÜRICH, SWITZERLAND,

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Effect of Reaction and Permeation Rates on the Performance of a Catalytic Membrane Reactor for Methylcyclohexane Dehydrogenation

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JAWAD K. ALI and D. W. T. RIPPIN*
CHEMICAL ENGINEERING DEPARTMENT
SWISS FEDERAL INSTITUTE OF TECHNOLOGY
UNIVERSITÄTSTR. 6, CH-8092 ZÜRICH, SWITZERLAND
TELEPHONE: (+41-1) 632-6873; FAX: (+41-1) 632-1222

ABSTRACT

The effect of the relative rates of reaction and H_2 permeation through palladium–silver (Pd–Ag) membranes upon the performance of a catalytic membrane reactor (CMR) for methylcyclohexane dehydrogenation has been investigated. Mathematical models have been used to identify the conditions at which a membrane reactor gives yields of toluene (TOL) and H_2 significantly in excess of equilibrium values at throughputs of industrial interest. The simulation shows that a catalyst with no product TOL inhibition performs exceptionally well in a CMR, giving conversions considerably above the equilibrium values at favorable operating conditions. Using a membrane unit between two conventional packed-bed reactors to separate the H_2 ex-situ gives significant improvement in performance over the shell-and-tube type CMR, resulting in conversions substantially higher than equilibrium at 633 K, 1.5 MPa, and liquid hourly space velocities of 3–10 volume feed/h/catalyst volume.

Key Words. Pd–Ag membrane; Hydrogen permeation; Methylcyclohexane; Pt–Re/alumina

INTRODUCTION

The performance of a catalytic membrane reactor (CMR) depends profoundly on the relative rates of H_2 generation by the catalyst and H_2

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* Deceased June 26, 1994.

permeation through the membrane (1). Pd and Pd–alloy H_2 diffusion membranes in the form of tubes, foils, and as thin films on porous ceramic supports in conjunction with a packed catalyst bed are being increasingly investigated in the general area of equilibrium-limited reactions as means of exceeding equilibrium conversions. These H_2 permselective membranes are most suited for dehydrogenation reactions (2–4) in which the removal of H_2 through the membrane displaces the equilibrium toward the products side, resulting in conversions higher than equilibrium. Pd–23% Ag membranes, which have long been commercialized as a result of their proven high H_2 permeabilities relative to other Pd-based alloys (5), seemed to be appropriate for our study. However, they are hampered by their low permeabilities compared to porous ceramic membranes (1). To achieve higher permeation fluxes, recent research activities have been directed toward the preparation of thin Pd and Pd–alloy films supported on porous metallic (6, 7) and porous ceramic (8, 9) supports.

Our objective was to study: 1) how higher permeation fluxes achieved with thinner membranes in relation to different catalytic activities affect the conversion of methylcyclohexane (MCH) in a CMR and 2) identify favorable operating conditions at which a CMR gives toluene (TOL) and high purity H_2 yields from MCH dehydrogenation substantially in excess of equilibrium values under economically viable throughputs. The various aspects of Pd-based CMRs have been extensively reviewed by Shu et al. (10). MCH, which has been proposed for storing electricity-deploying H_2, is catalytically dehydrogenated to TOL. The latter is hydrogenated in a cyclic loop to MCH, with H_2 produced electrolytically from inexpensive hydroelectric power. The use of H_2 for both moving (11) and stationary (12) applications has been described.

METHOD

MCH dehydrogenation to TOL is strongly equilibrium limited, and CMRs have been proposed to overcome such equilibrium restrictions.

$$C_7H_{14} \rightleftharpoons C_7H_8 + 3H_2$$

To show the potential of CMR concepts and identify conditions at which CMRs outperform the conventional packed-bed reactor, a simulation study, i.e., modeling of CMRs, was made. Models may not be reliable without experimental verification. Fortunately, membrane reactors have been successfully modeled (3, 13, 14) where the validity of the assumptions were experimentally confirmed. For the study reported here, the membrane reactor was of a shell-and-tube type with the reactants and the permeate H_2 flowing downward through the annular catalyst bed and inside the membrane tube, respectively, as shown in Fig. 1.

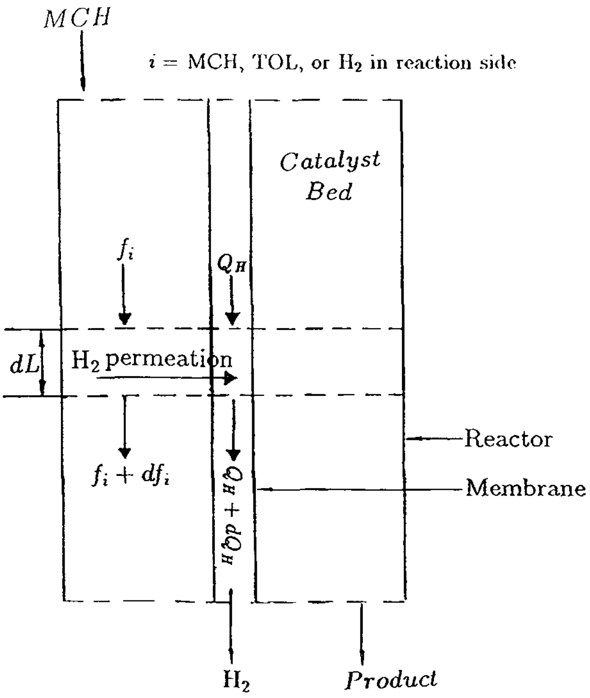

FIG. 1 Flow model of reaction and H_2 permeation in the catalytic membrane reactor.

The following commonly used assumptions in modeling membrane reactors were made.

1. Steady-state isothermal operation. In practice, the reactor operation is non-isothermal because the reaction is highly enothermic. Nevertheless, isothermal simulation, practiced by many (15–19) on analogous system, sets the upper limits of attainable conversions relative to which the performance of the non-isothermal reactor can be assessed.
2. Plug flow, no radial concentration gradients in the catalyst bed.
3. Transport through the membrane is diffusion controlled and obeys the square-root relationship of Sievert's law (20).
4. The fluid flowing through the reactor experiences a negligible pressure drop.
5. Negligible resistance due to pore diffusion under the conditions studied.
6. H_2 pressure (P_m) in the downstream side of the membrane is constant and equal to 100 kPa.

The membrane reactor for the dehydrogenation of MCH to TOL was simulated using the kinetic parameters determined by Rimensberger et al. (21) who employed a commercial Pt–Re/alumina catalyst and the experimentally determined H_2 permeation equation for the Pd–23% Ag membranes (22).

The reaction rate equation is (21)

$$\vartheta = \frac{k_1 P_{\mathrm{mch}} \rho_{\mathrm{b}}}{D_{\mathrm{r}}(1 + k_2 P_{\mathrm{tol}})} \left(1 - \frac{P_{\mathrm{tol}} P_{\mathrm{H}}^3}{K_{\mathrm{eq}} P_{\mathrm{mch}}}\right) \tag{1}$$

with the following Arrhenius constants:

$$k_1 = A_1 \exp\left[\frac{-E_1}{R}\left(\frac{1}{T} - \frac{1}{650}\right)\right] \tag{2}$$

$$k_2 = A_2 \exp\left[\frac{-E_2}{R}\left(\frac{1}{T} - \frac{1}{650}\right)\right] \tag{3}$$

$$K_{\mathrm{eq}} = 4.61(10^9) \exp\left[\frac{-\Delta H_{\mathrm{r}}}{R}\left(\frac{1}{T} - \frac{1}{650}\right)\right] \tag{4}$$

E_1, E_2, ΔH_r = 115,600, −25,200, and 216,350 J·mol^{-1}, respectively.

The rate of H_2 permeation through Pd–23% Ag membranes is (22)

$$Q_{\mathrm{H}} = \frac{1.209(10^{-9})}{t_{\mathrm{m}}} \exp\left(-\frac{261}{T}\right) (\sqrt{P_{\mathrm{H}}} - \sqrt{P_{\mathrm{m}}}) \tag{5}$$

The following mole balance set of ordinary differential equations was solved numerically by SIMUSOLV (23) using the Runge–Kutta fourth-order algorithm.

$$\frac{df_{\mathrm{mch}}}{dL} = -\pi\vartheta[(R_{\mathrm{r}})^2 - (r_{\mathrm{m}})^2] \tag{6}$$

$$\frac{df_{\mathrm{tol}}}{dL} = \pi\vartheta[(R_{\mathrm{r}})^2 - (r_{\mathrm{m}})^2] \tag{7}$$

$$\frac{df_{\mathrm{H}}}{dL} = 3\pi\vartheta[(R_{\mathrm{r}})^2 - (r_{\mathrm{m}})^2] - 2\pi r_{\mathrm{lm}} Q_{\mathrm{H}} \tag{8}$$

where

$$r_{\mathrm{lm}} = \frac{r_{\mathrm{m}} - r_{\mathrm{im}}}{\ln\left(\dfrac{r_{\mathrm{m}}}{r_{\mathrm{im}}}\right)} \tag{9}$$

The feed was pure MCH, and this is reflected in the initial boundary conditions:

$$L = 0\text{: } f_{\text{mcho}} = \text{initial MCH feed rate, } f_{\text{tolo}} = 0.0\text{, and } f_{\text{H0}} = 0.0$$

The simulations were explicitly expressed in terms of the following operating conditions:

Temperature: 573–673 K
Pressure: 1–2 MPa
LHSV: 2–10 h^{-1}
Membrane thicknesses: 10–200 μm
Catalyst dilution ratio: 1–10
Membrane: Pd–23% Ag; o.d. and length: 3.1 and 250 mm
Reactor i.d. and length: 15.75 and 250 mm

The side reactions are negligibly small due to the very high selectivity of commercially available MCH dehydrogenation catalysts (24). Three cases were considered as shown in Table 1.

Our purpose was to investigate the effect of the relative rates of permeation and reaction upon the performance of a CMR by varying the membrane thickness and the values of the reaction rate. The latter is estimated by Eq. (1) and is not related to what the real kinetic parameters of the modified Catalysts C2 and C3 would be.

RESULTS AND DISCUSSION

Figures 2 and 3 show the membrane reactor MCH conversion to TOL on Catalyst C1 as a function of 1) liquid hourly space velocity (LHSV) at 573–673 K, 1–2 MPa, and a Pd–23% Ag membrane with 100 μm wall thickness; and 2) membrane thickness at 633 K and 1.5 MPa, respectively.

The equilibrium conversion values are those based on the work of Rimensberger et al. (21). As can be noticed from Fig. 2, the equilibrium conversion is exceeded to small extents only at low LHSVs and higher pressures. Decreasing the thickness of the membrane should allow more

TABLE 1
Catalysts Properties Studied

Catalyst	Property	A_1 (kmol·s^{-1}·kgCat^{-1}·kPa^{-1})	A_2 (kPa^{-1})
C1	Rimensberger's catalyst (21)	14.15×10^{-7}	0.0964
C2	TOL inhibition neglected	14.15×10^{-7}	0.0
C3	Activity increased	14.15×10^{-6}	0.0964

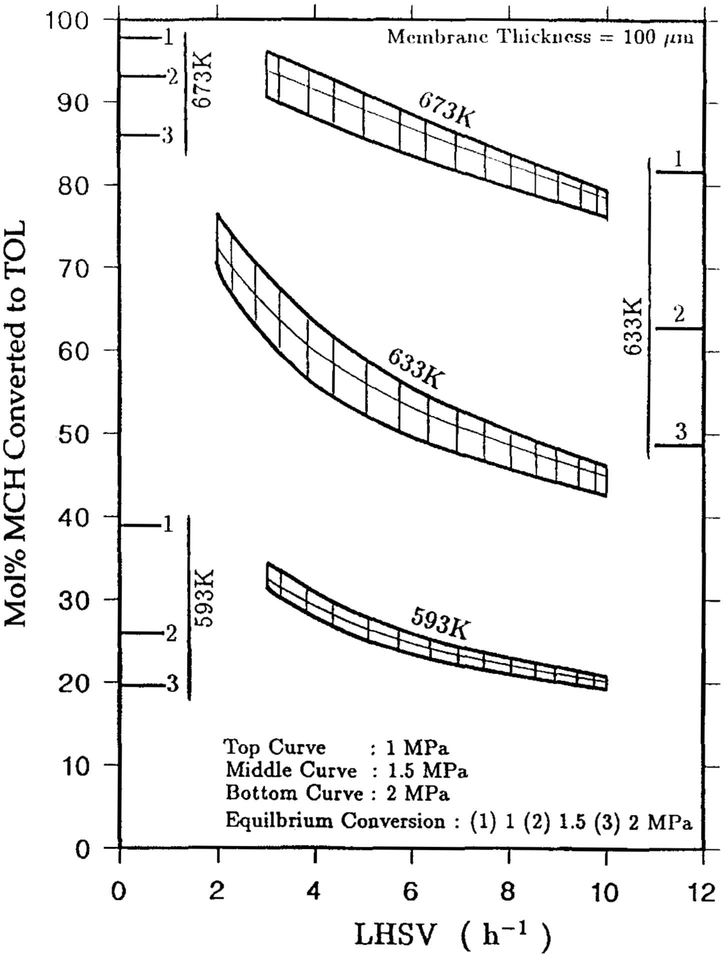

FIG. 2 Effects of temperature, pressure, and LHSV upon membrane reactor performance, Catalyst C1 undiluted.

H_2 to permeate (Eq. 5), but as Fig. 3 shows, a twenty times decrease in the membrane thickness resulted in no significant increase in conversion. This indicates that the process is controlled by the rate of reaction, i.e., rate of H_2 generation and better catalysts should improve conversions. The rate of reaction on Catalyst C1 is strongly inhibited by TOL as normally encountered with Pt–Re/alumina catalysts (21, 25), and this is clear by the presence of the k_2P_{tol} term in the rate equation (Eq. 1). Improved catalysts could be postulated by neglecting the TOL adsorption term, i.e.,

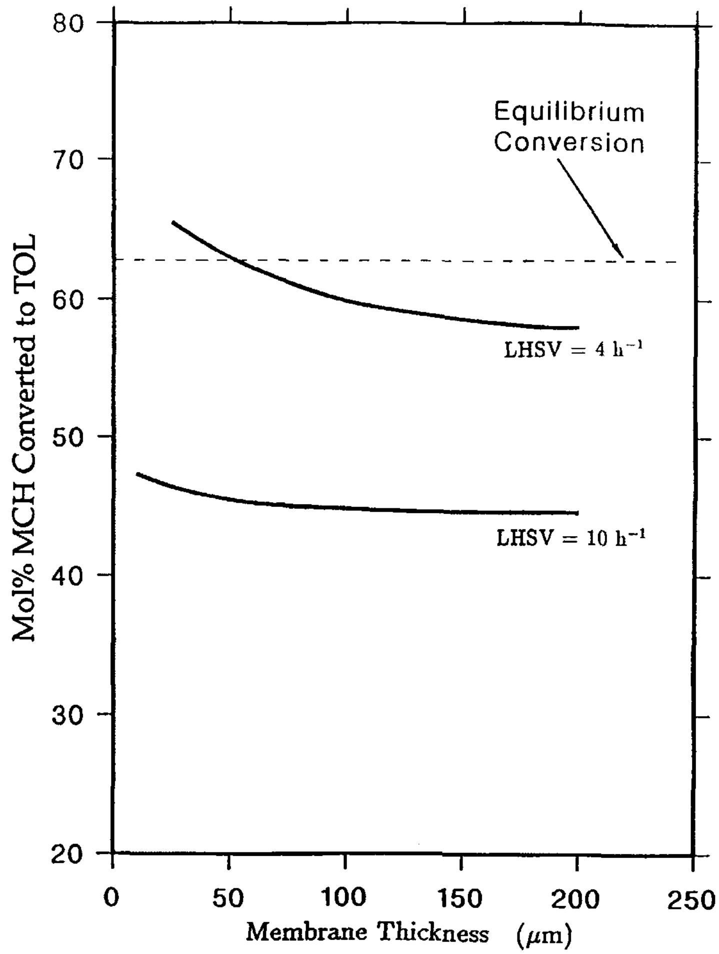

FIG. 3 Effect of the membrane thickness upon membrane reactor performance at 633 K and 1.5 MPa, Catalyst C1 undiluted.

by assuming $A_2 = 0.0$ and subsequently k_2 becomes zero (Catalyst C2, Table 1) or simply increasing the kinetic parameter k_1 ten times by setting A_1 ten times higher (Catalyst C3, Table 1). Neglecting TOL inhibition is not an unrealistic assumption since it is known that the rate of MCH dehydrogenation on monometallic noble metal catalysts is not inhibited by the TOL product (25, 26). Figure 4 shows MCH conversions to TOL as a function of membrane thickness for the Catalysts C1, C2, and C3 at 633 K, 1.5 MPa, and LHSV = 4 h^{-1}.

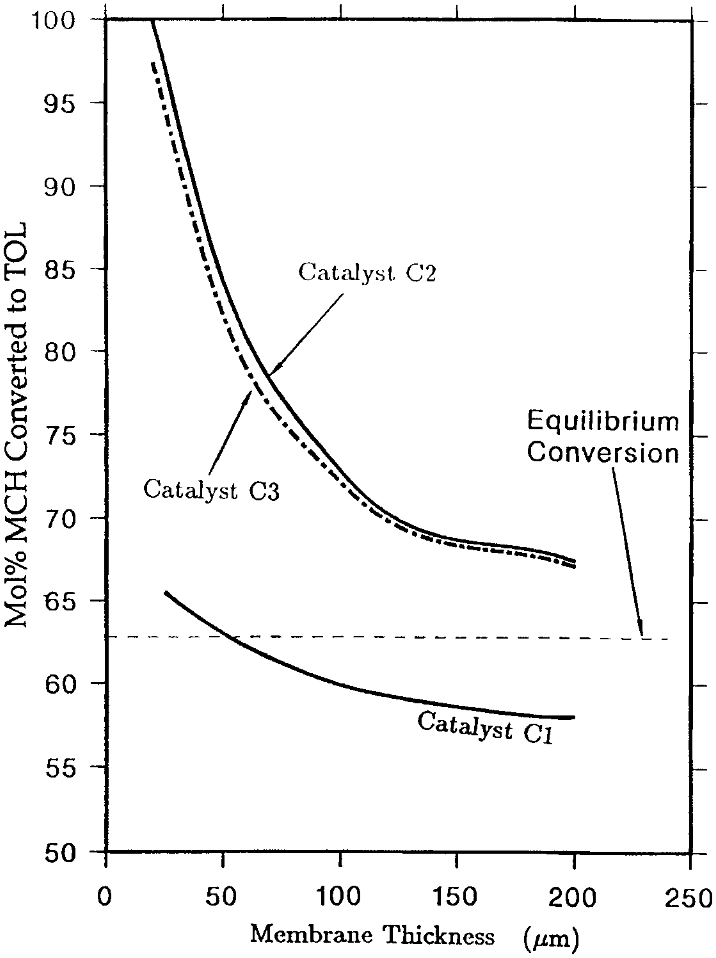

FIG. 4 Effect of the membrane thickness upon membrane reactor performance for the undiluted Catalysts C1, C2, and C3 at 633 K, 1.5 MPa, and LHSV = 4 h^{-1}.

Catalysts C2 and C3 give substantially higher conversions than Catalyst C1 and significantly in excess of the equilibrium values, Catalyst C2 being the best of the three. The outstanding performance of Catalyst C2 is due to the absence of product TOL inhibition since in a membrane reactor the TOL partial pressure increases to high values as the reactants approach the reactor exit as a result of H_2 permeation through the membrane, thus impeding the reaction. Catalyst C3 with a rate constant k_1 is increased tenfold over that of Catalyst C1 but, having the same TOL inhibition effect, performs nearly as well as Catalyst C2. However, the availability of such catalysts is less likely than that of Catalyst C2. It is also clear from Fig. 4 that the process becomes permeation controlled for Catalysts C2 and C3 since there is a sharp increase in conversion below a membrane thickness of 50 μm. This means that the development of Pd–alloy-based membranes <50 μm thick should be a goal for future work. Now, focusing on Catalyst C2, Fig. 5 shows that as the membrane thickness decreases, conversion approaches 100% over the temperature range of 613 to 673 K. Nearly equal conversions are attained at 633 and 673 K with a membrane thickness of ~30 μm, resulting in a potential saving in energy.

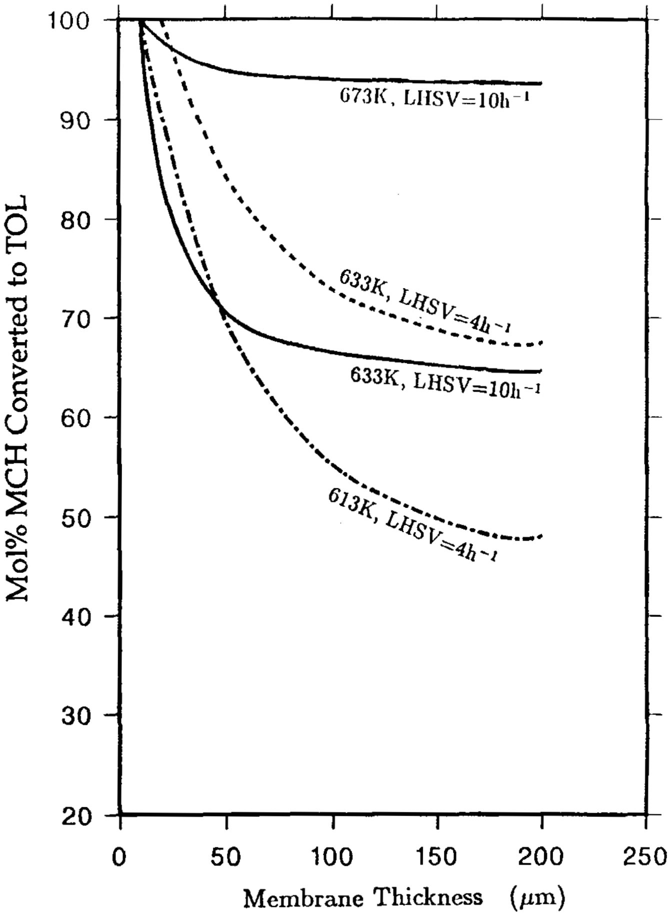

FIG. 5 Effect of the membrane thickness upon membrane reactor performance at 613–673 K and 1.5 MPa, Catalyst C2 undiluted.

Unlike conventional packed-bed reactors, MCH conversion to TOL in a CMR increases significantly above the equilibrium values with catalyst dilution as shown in Fig. 6.

Catalyst dilution ratio (D_r) is defined as the volume of the catalyst and inert particles divided by the catalyst volume. Diluting the catalyst is analogous in effect to thinning the membrane. For instance, it can be deduced from Fig. 6 that the same conversion is obtained at equal LHSVs with a 200-μm thick membrane, catalyst dilution of 10 and a 20-μm thick

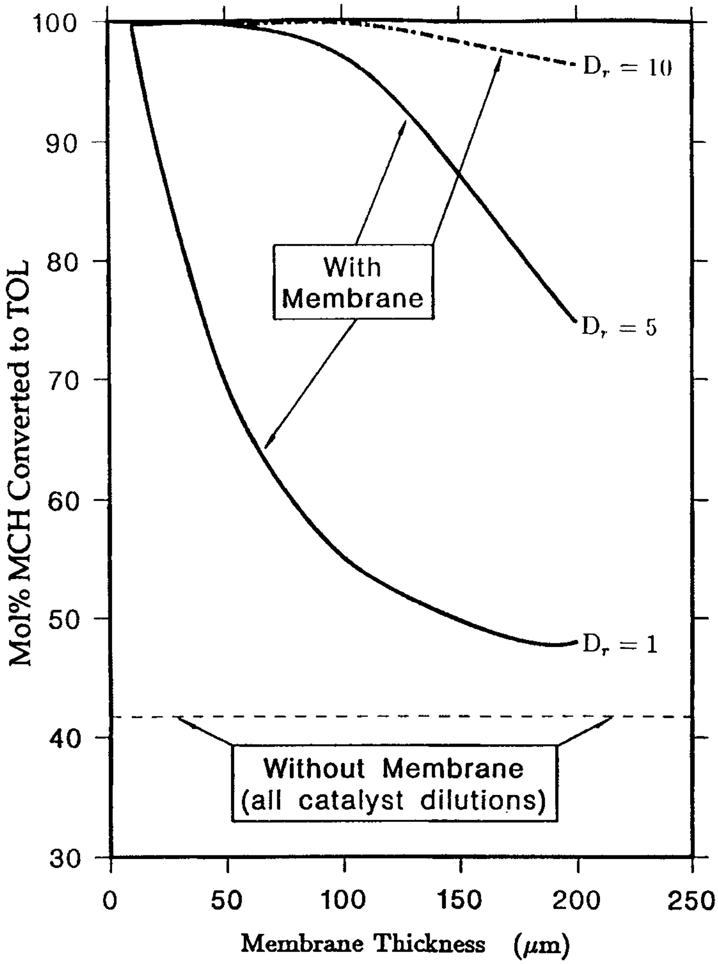

FIG. 6 Effect of catalyst dilution (D_r) with inert particles upon membrane reactor performance at 613 K, 1.5 MPa, and LHSV = 4 h^{-1}, Catalyst C2.

membrane, and undiluted catalyst, respectively. With a sufficiently active catalyst, the rate of H_2 generation significantly exceeds the permeation rate, and the increase in conversion beyond the equilibrium value due to H_2 removal is limited (1). However, if the permeation rate of H_2 approaches its rate of generation, as in the case of diluted catalysts, conversion can reach its maximum potential. These concepts are clearly illustrated by Fig. 7 where the percent H_2 separated by the membrane [(H_2 permeated)/(H_2 generated)] is plotted as a function of membrane thickness and catalyst dilution for the data of Fig. 6.

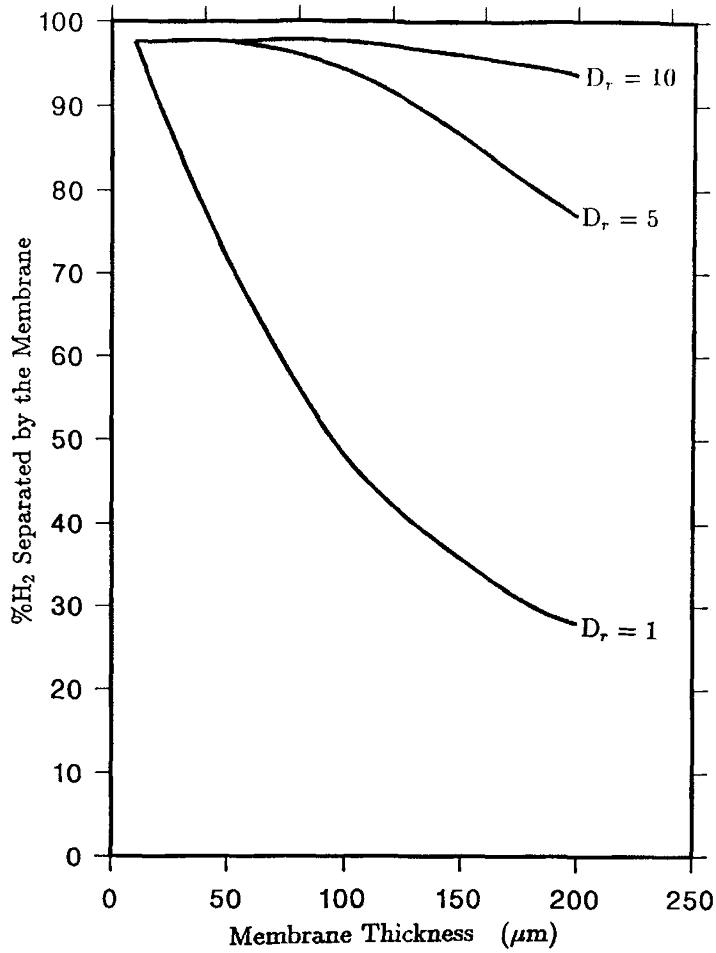

FIG. 7 Effect of catalyst dilution (D_r) upon the amount of H_2 separated relative to that generated at 613 K, 1.5 MPa, and LHSV = 4 h^{-1}, Catalyst C2.

Figure 8 shows the axial partial pressure of H_2 in the reaction side as a function of catalyst dilution with a 200-μm thick membrane for the same data.

The H_2 partial pressure reaches nearly the same maximum value about 2 cm into the catalyst bed for catalyst dilutions of 1 to 10, decreasing slightly near the reactor exit for the undiluted catalyst since little H_2 permeates relative to the amount produced, while the decrease is much greater for the diluted catalysts because less H_2 is generated.

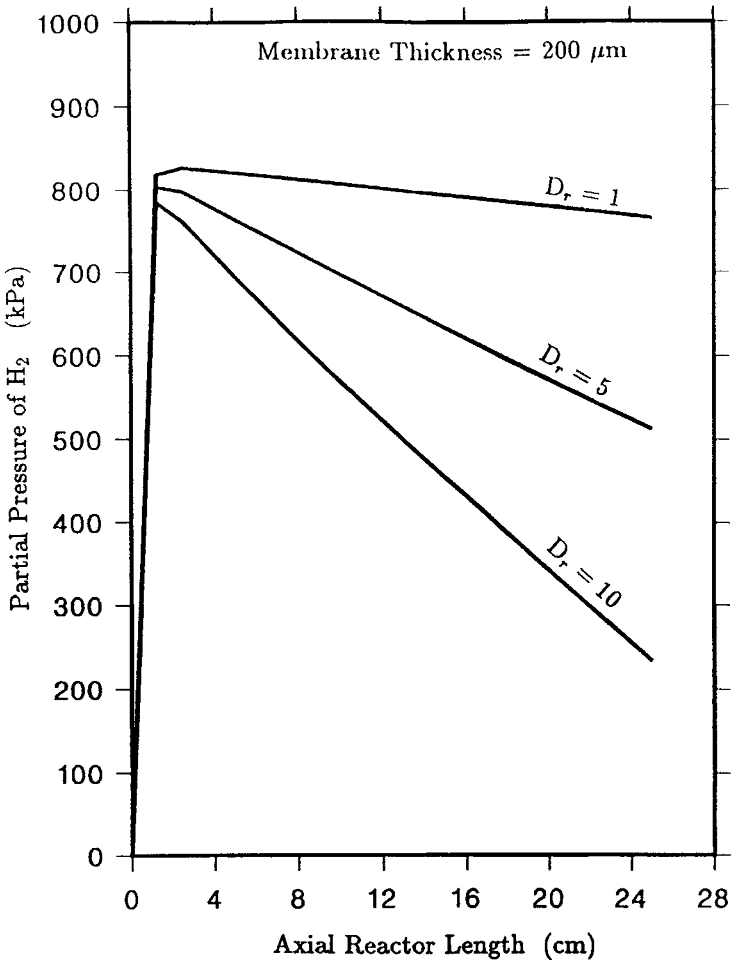

FIG. 8 Effect of catalyst dilution (D_r) upon the reactor axial partial pressure of H_2 at 613 K, 1.5 MPa, and LHSV = 4 h^{-1}, Catalyst C2.

PACKED BEDS–MEMBRANE UNITS SYSTEMS

A CMR of shell-and-tube configuration containing a tubular membrane inside every reactor tube may not be practically feasible in large-scale reactors because it is difficult to assemble a gas-tight system mechanically under industrial operating conditions, and it is not easy to charge the catalyst into the reactor tubes. However, conventional packed-bed reactors are routinely used in industry. Deploying membrane units in between two or more packed-bed reactors to separate the H_2 ex-situ could be advantageous. Because the reaction is strongly equilibrium limited, the axial H_2 partial pressure in packed-bed reactors reaches a maximum value at a distance of 2–4 cm down into the catalyst bed in most cases, as shown by the example of Fig. 9 at 633 K and 1.5 MPa for Catalyst C2.

The 25-cm long packed-bed reactor without membrane is divided into two sections of 4 and 21 cm length, respectively, and a membrane unit is placed between them in series to remove 90% of the H_2 leaving in the effluent from the first section so that the pressure of the permeated H_2 can be maintained at around ambient conditions. Pd–23% Ag membrane units giving the desired H_2 separation are commercially available and can be combined with existing preheaters between reactors in the case of endothermic reactions. This system of packed bed reactors–membrane units gives considerable improvement in the conversion of MCH to TOL over a shell-and-tube CMR with a 100-μm wall thick membrane. Also, the conversion is virtually independent of the LHSV over the 3–10 h^{-1} range as shown in Fig. 10, reflecting the attainment of a new equilibrium.

Furthermore, most mono- and bimetallic noble metal catalysts contain sulfur and/or chlorine. These may poison the membranes (22) in CMRs during the activation stage. The system of packed reactors–membrane units permits separate catalyst and membrane activation to diminish membrane poisoning. The membrane unit's permeation areas can be estimated by Eq. (5) by employing an averaged driving pressure ($\sqrt{P_H} - \sqrt{P_m}$) between the inlet to and outlet of the membrane unit. For example, 65 cm^2 of 100 μm thick membrane area per reactor tube is needed to give 90% H_2 separation at a LHSV of 4 h^{-1} for the conditions of Fig. 10. Figure 11 shows MCH conversion to TOL and the H_2 partial pressure as a function of the number of packed bed reactors–membrane units when a membrane unit is placed after each 4 cm long section of the reactor tube to remove 90% of the H_2 in the effluent.

The conversion increases as the number of staged membrane units increases, reaching almost 100% after three membrane units at 633 K, 1.5 MPa, and an industrially viable LHSV of 7 h^{-1}. The lower the H_2 pressure in the downstream side of the membrane (P_m) is, the more efficient the

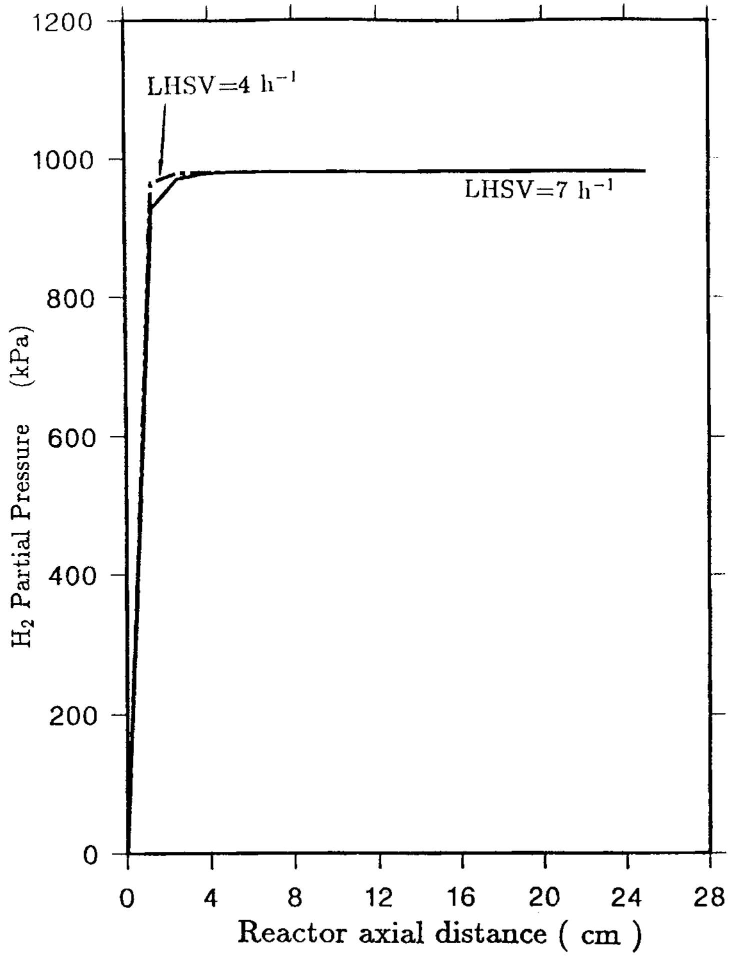

FIG. 9 Axial H_2 partial pressure in packed-bed reactor without membrane for MCH dehydrogenation at 633 K and 1.5 MPa, Catalyst C2 undiluted.

separation will be, but there is enough flexibility to operate the system with P_m around atmospheric pressure and thus avoid the use of a sweep gas.

CONCLUSIONS

The effect of the relative rates of MCH dehydrogenation to TOL and H_2 permeation through Pd–Ag membranes upon the performance of a

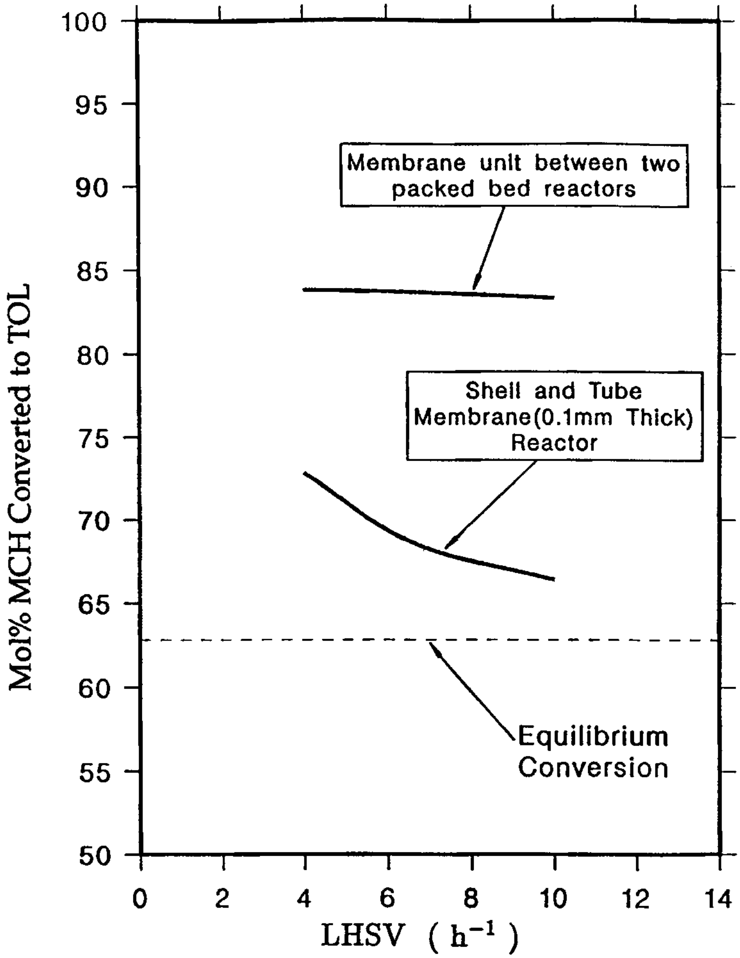

FIG. 10 Comparing the performance of a shell-and-tube membrane reactor with a combined packed bed–membrane unit system at 633 K and 1.5 MPa, Catalyst C2 undiluted.

CMR has been analyzed. The study shows that a catalyst for MCH dehydrogenation with no TOL inhibition in conjunction with a membrane <50 μm thick performs exceptionally well in a CMR, giving conversions considerably above equilibrium values at favorable operating conditions of 633 K, 1.5 MPa, and economically viable space velocities. Such a catalyst can be found among the monometallic noble metal catalysts. Unlike conventional packed-bed reactors, catalyst dilution with inert particles in a CMR increases conversion. Using just one membrane unit between two

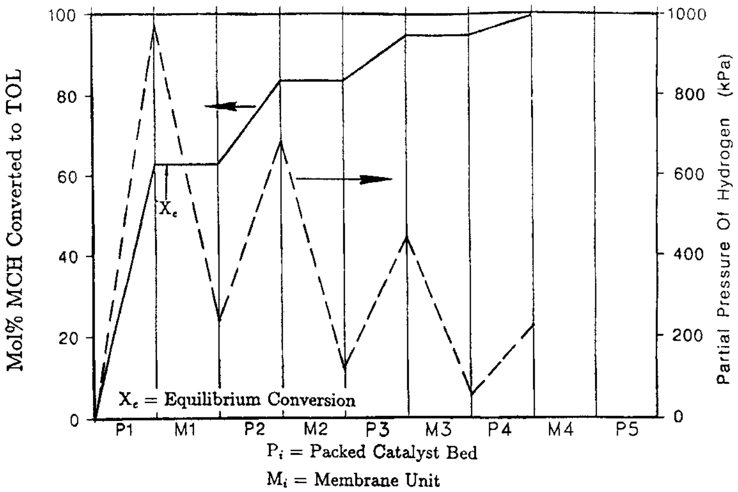

FIG. 11 Performance of combined packed-bed reactors and membrane units at 633 K, 1.5 MPa, LHSV = 7 h^{-1}, and a constant overall reactor length of 25 cm, Catalyst C2 undiluted.

conventional packed-bed reactors to separate the H_2 ex-situ gives significant improvement in performance over the shell-and-tube type CMR, resulting in conversions considerably in excess of the equilibrium values and virtually independent of the LHSV over the 3–10 h^{-1} range. The models also show that thinner membranes and high activity catalysts could further improve the performance of CMRs.

NOMENCLATURE

A_1	preexponential factor of the reaction ($kmol \cdot s^{-1} \cdot kgCat^{-1} \cdot kPa^{-1}$)
A_2	preexponential factor of the TOL inhibition constant (kPa^{-1})
D_r	catalyst dilution ratio
E_1	apparent activation energy of the reaction ($J \cdot mol^{-1}$)
E_2	apparent adsorption enthalpy of TOL ($J \cdot mol^{-1}$)
f_H	H_2 flow rate, reaction side ($kmol \cdot s^{-1}$)
f_{mch}	MCH flow rate, reaction side ($kmol \cdot s^{-1}$)
f_{tol}	TOL flow rate, reaction side ($kmol \cdot s^{-1}$)
k_1	reaction rate constant ($kmol \cdot s^{-1} \cdot kgCat^{-1} \cdot kPa^{-1}$)
k_2	apparent equilibrium constant of TOL inhibition (kPa^{-1})
K_{eq}	reaction equilibrium constant (kPa^3)
L	reactor and membrane lengths (m)

LHSV	feed volume/h/reactor volume occupied by the catalyst (h^{-1})
P_m	H_2 pressure in the downstream side of the membrane (kPa)
P_H	partial pressure of H_2 in the reaction side (kPa)
P_{mch}	partial pressure of MCH in the reaction side (kPa)
P_{tol}	partial pressure of TOL in the reaction side (kPa)
Q_H	rate of H_2 permeation ($kmol \cdot s^{-1} \cdot m^{-2}$)
R	gas constant (8.3144 $J \cdot mol^{-1} \cdot K^{-1}$)
r_{im}	inside radius of the membrane (m)
r_{lm}	log mean radius of the membrane (m)
r_m	outside radius of the membrane (m)
R_r	inside radius of the reactor (m)
T	temperature (K)
t_m	membrane wall thickness (m)
ΔH_r	enthalpy of the reaction ($J \cdot mol^{-1}$)
ϑ	the rate of reaction ($kmol \cdot s^{-1} \cdot kgCat^{-1}$)
ρ_b	bulk density of the catalysts ($kg \cdot m^{-3}$)

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