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Conversion Enhancement of Equilibrium-Limited Reactions in a Two-Membrane Reactor

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ABSTRACT

Analysis of two-membrane reactor performance is carried out on a simple, perfectly mixed reactor model. The influence of the design and operating parameters and physical properties of the system on conversion for equilibrium reactions of the type A ↔ B + C have been studied. Also, the effects of the presence of inerts at both the reaction and permeation sides of the reactor have been discussed. It has been shown that the two-membrane reactor exhibits superior performance as compared to the single-membrane reactor.

INTRODUCTION

In recent years there has been rising interest in studying inorganic membrane reactors for their use in conducting reversible gas-phase reactions (1–7). The process is based on the principle of selective removal of reaction products from the reaction zone, resulting in the conversion enhancement of equilibrium-limited reactions. Besides the increase in the reaction yield, the possibility of achieving product separation in the same unit makes this kind of process very attractive commercially. Most of the published literature in the area deals with single membrane reactors. In a recent study (8) we examined the idea of using a reactor that simultaneously houses two different types of membranes. This concept was previ-

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ously suggested for gas separations (9, 10). It was shown (8) that better overall process efficiency—reactant conversion and product separation—can be achieved with a two-membrane reactor than with a single-membrane reactor, especially if the reactant is the slowest permeating component. The present paper is a continuation of the previous study and focuses on reactant conversion. Its scope is to provide a more detailed analysis of the behavior of the two-membrane reactor in terms of design and operating variables and the physical properties of the system.

MATHEMATICAL MODEL

Consider the reversible gas reaction

$$A \Leftrightarrow bB + cC \tag{1}$$

taking place in the two-membrane reactor presented in Fig. 1. The model equations (Table 1) arising from component material balances are derived on the basis of the following assumptions: a) isothermal operation, b) ideal mixing of both the reaction and permeation sides content, c) elementary reaction mechanism, d) homogeneous membranes permeable to all the

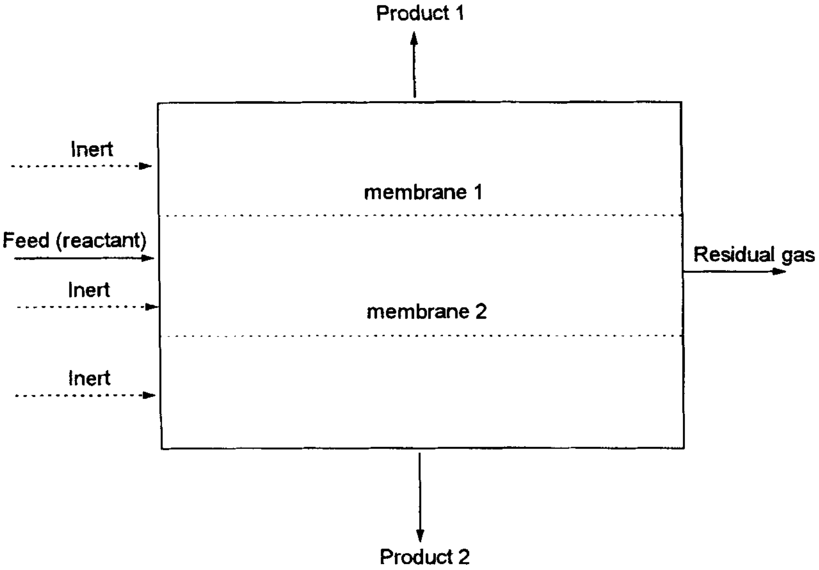

FIG. 1 Two-membrane reactor.

TABLE 1
Model Equations

Reaction side:

$$L^0x_i^0 + v_iVkPuf = Lux_i + \sum_{j=1}^{2} \frac{q_{ji}}{d_j} S_j(Pux_i - Pp_jy_{ji}); \qquad i = 1, N \tag{2}$$

Permeation side:

$$Lp_j^0y_{ji}^0 + \frac{q_{ji}}{d_j} S_j(Pux_i - Pp_jy_{ji}) = Lp_jy_{ji}; \qquad i = 1, N; \qquad j = 1, 2 \tag{3}$$

In dimensionless form:

$$\frac{1}{\text{Da}}\left(\frac{\phi x_i - x_i^0}{x_1^0}\right) - v_if + \sum_{j=1}^{2} \alpha_{ji}\delta_j(x_i - Pr_jy_{ji}) = 0; \qquad i = 1, N \tag{2a}$$

$$\frac{1}{\text{Da}}\left(\frac{\phi_jy_{ji} - Q_jy_{ji}^0}{x_1^0}\right) - \alpha_{ji}\delta_j(x_i - Pr_jy_{ji}) = 0; \qquad i = 1, N; \qquad j = 1, 2 \tag{3a}$$

Summation:

$$\sum_{i=1}^{N} x_i = 1 \tag{4}$$

$$\sum_{i=1}^{N} y_{ji} = 1; \qquad j = 1, 2 \tag{5}$$

For Reaction (1):

$$N = 3 \text{ (4 including inert)}$$

$$v_1 = -1, \quad v_2 = b, \quad v_3 = c, \quad v_4 = 0 \tag{6}$$

$$f = x_1^{-v1} - \frac{x_2^{v2}x_3^{v3}}{K_E}$$

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mixture components, e) component permeabilities equal to pure component ones, and f) the absence of chemical reaction at the permeation sides.

Besides the reaction-specific parameter, the chemical equilibrium constant, K_E, the dimensionless model parameters affecting the reactor performance are as follows. The Damkohler number, Da, is the ratio of the maximal forward reaction rate to the reactant feed flow rate. The rate ratio, δ_j, is the ratio of the maximal permeation rate of the fastest gas through membrane j to the maximal forward reaction rate. With respect to reactor design parameters, the Da number is proportional to the reactor volume, while δ_j is proportional to the membrane area and is inversely proportional to membrane thickness and reactor volume. The pressure ratio, Pr_j, represents the ratio of pressure on the permeation side j to the reaction side pressure. The permselectivity, α_{ji}, represents the ratio of the permeability of component i through membrane j to the permeability of the fastest gas through the same membrane ($0 < \alpha_{ji} < 1$). A convenient way of expressing relative component permeabilities is by permeability ratios, T_j^{I} and T_j^{II}, which are defined as ratios of permselectivities (or permeabilities) of the reactant and either of the products (I for B, II for C) for membrane j:

$$T_j^{\mathrm{I}} = \frac{\alpha_{j1}}{\alpha_{j2}}; \qquad T_j^{\mathrm{II}} = \frac{\alpha_{j1}}{\alpha_{j3}}; \qquad j = 1, 2 \tag{7}$$

Additional parameters needed to describe the system in the presence of any inert will be described later.

Upon specifying the feed stream composition and parameter values, the model equations can be solved for the unknown residue and permeate flow rates (ϕ and ϕ_j) and compositions (x_i and y_{ji}).

RESULTS AND DISCUSSION

The performance of a membrane reactor is evaluated by reactant conversion, X, or conversion ratio, X_{R} (conversion obtained in a membrane reactor/equilibrium conversion). In order to provide a unique basis for comparison of the performance of a two-membrane reactor and a single-membrane one, it is assumed that

$$Pr_1 = Pr_2 = Pr \tag{8}$$

and

$$\delta_1 = \delta_2 = \delta/2 \tag{9}$$

where Pr and δ refer to a one-membrane reactor. Further, it is assumed that one of the membranes of a two-membrane reactor, in the view of component permeabilities, behaves like a single-membrane reactor, while the other membrane is supposed to be reversely permselective with respect to products, which implies

$$T_1^{\mathrm{I}} = T_2^{\mathrm{II}} = T^{\mathrm{I}}; \qquad T_1^{\mathrm{II}} = T_2^{\mathrm{I}} = T^{\mathrm{II}} \tag{10}$$

where T^{I} and T^{II} refer to the one-membrane reactor.

In the analysis, by taking $T_1^{\mathrm{I}} < T_1^{\mathrm{II}}$, it is implied that the permeability ratio T_1^{I} characterizes the fast product and T_1^{II} characterizes the slow product. Two cases of practical interest are considered. In Case I the reactant is the slowest permeating component ($T_1^{\mathrm{I}} < 1$, $T_1^{\mathrm{II}} < 1$), while in Case II the reactant permeability value is between the permeability values of products ($T_1^{\mathrm{I}} < 1$, $T_1^{\mathrm{II}} > 1$).

Reaction (1) with $b = c = 1$ is considered, and the feed is taken to be a pure reactant $x_1^0 = 1$, $x_2^0 = x_3^0 = 0$. The ranges of parameter values are selected so as to comply with those likely to be encountered in practice (1): rate ratio, δ, 0.1 to 5.0; Damkohler number, Da, 5.0 to 50; pressure ratio, Pr, 0.0 to 1.0; equilibrium constant, K_{E}, 0.0001 to 0.5; permselectivity, α, 0.0 to 1.0.

Absence of Inert

Ideally, a maximal conversion ratio, X_{Rmax}, would be obtained in an infinite membrane reactor (Da$\rightarrow\infty$; to consume all reactant), operating at a zero pressure ratio and at a very small but positive rate ratio (to reduce reactant loss) (1). It has been shown (Figs. 2a, 2b) that this ideal upper limit on conversion ratio (for given K_{E}) is higher for the two- than for the one-membrane reactor in both Cases I and II. While complete reactant conversion ($X = 1$) would be obtained if membranes were impermeable to the reactant ($T_1^{\mathrm{I}} = T_1^{\mathrm{II}} = 0$), with increasing reactant permeability and decreasing permeability of the slow product ($T_1^{\mathrm{I}} > 0$ and $T_1^{\mathrm{II}} > 0$) the maximal attainable conversion decreases for both reactor types. Better achievement of the two-membrane reactor is due to simultaneous removal of both reaction products from the reaction zone, which, by enhancing conversion, prevents the excessive loss of unconverted reactant from the reaction zone.

For more realistic reactor designs and operating conditions, the two-membrane reactor provides larger conversion (Figs. 3, 4a, 4b). In both Cases I and II the conversion ratio for the two-membrane reactor increases with an increase of rate ratio until all components are consumed from the reaction zone. However, for the one-membrane reactor in Case II, there is an optimal rate ratio above which the backward reaction is favored (1). The results show that at a low enough pressure ratio ($Pr\rightarrow 0$), the ideal conversion ratio, X_{Rmax}, can be closely approached in a realistic two-membrane reactor almost independently of the Da number, provided the appropriate rate ratio is chosen. For the one-membrane reactor, however, in Case II and at high equilibrium conversions (Fig. 4b), the choice of higher Da number would be more important.

As seen from Figs. 2a, 2b, 4a, and 4b, the introduction of the second membrane would be most effective for those reactions with low equilibrium conversion (low K_{E} values).

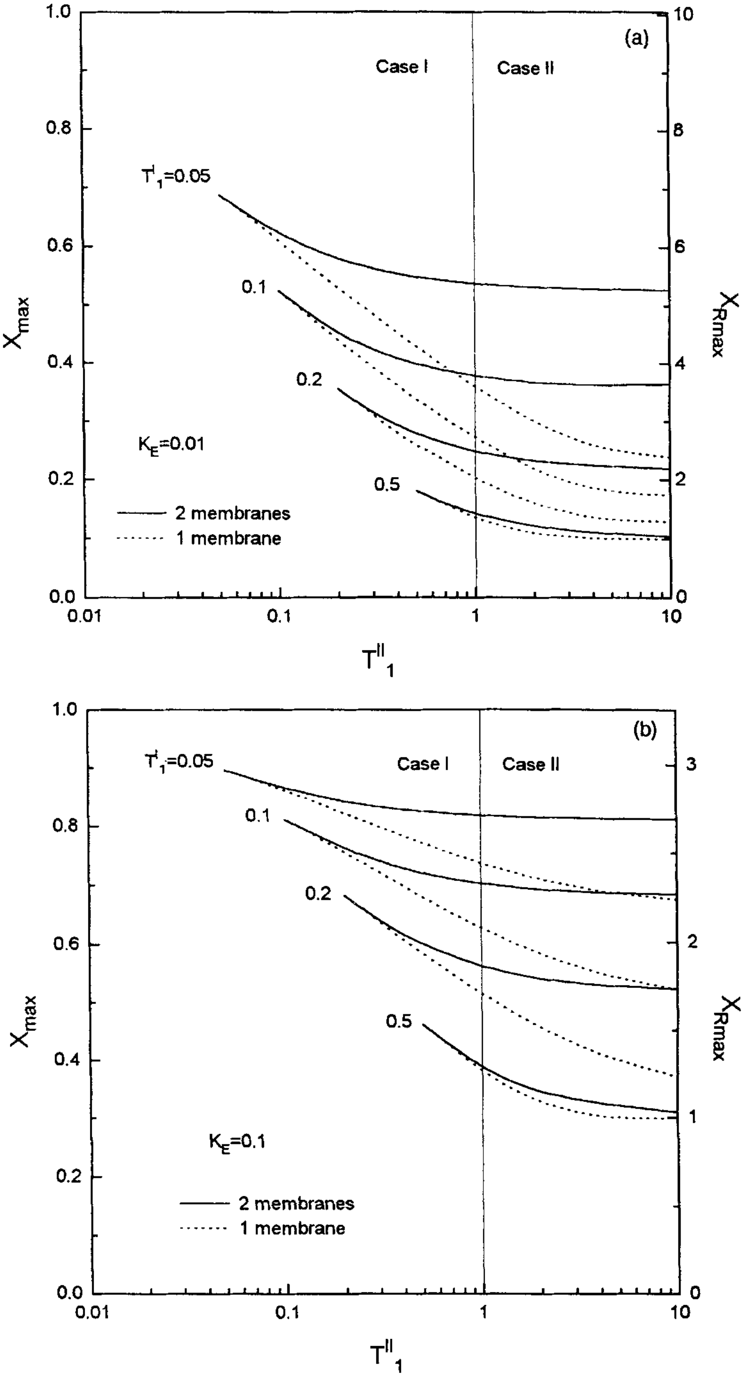

FIG. 2 Dependence of maximal conversion in membrane reactor, X_{max}, on T^I_1 (reactant to fast product permeability ratio) and T^{II}_1 (reactant to slow product permeability ratio).

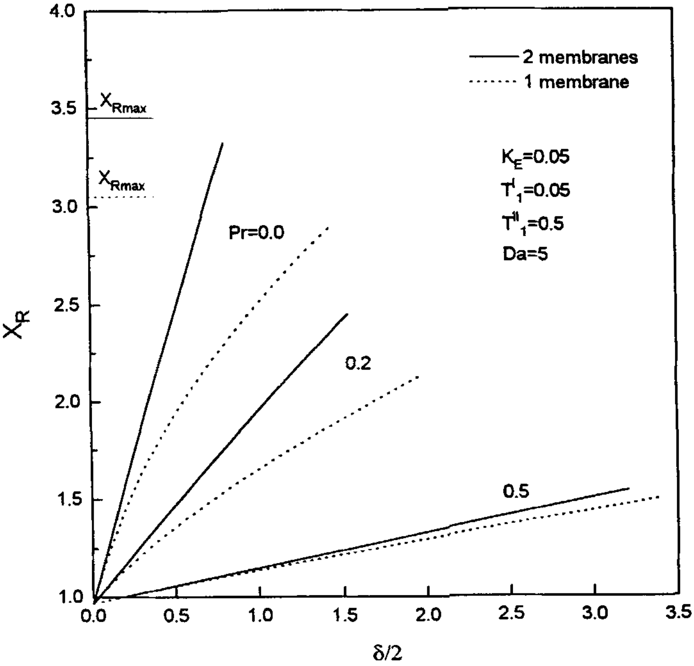

FIG. 3 Effect of pressure ratio on conversion.

Presence of Inert

The influence of an inert gas on membrane reactor performance is twofold (1). On the reaction side, the presence of an inert is beneficial for those reactions in which there is an increase in volume, since the partial pressures of products will be decreased. The presence of an inert at the permeation side causes the decrease of partial pressures of permeating components and thus (at finite pressure ratios) promotes permeation rates.

Before we proceed with the analysis, let us denote inert permeability ratios by

$$T_j^{III} = \frac{\alpha_{j1}}{\alpha_{j4}}, \quad j = 1, 2 \tag{11}$$

and assume

$$T_1^{III} = T_2^{III} = T^{III} \tag{12}$$

where T^{III} denotes the permeability ratio of an inert for the single-membrane reactor.

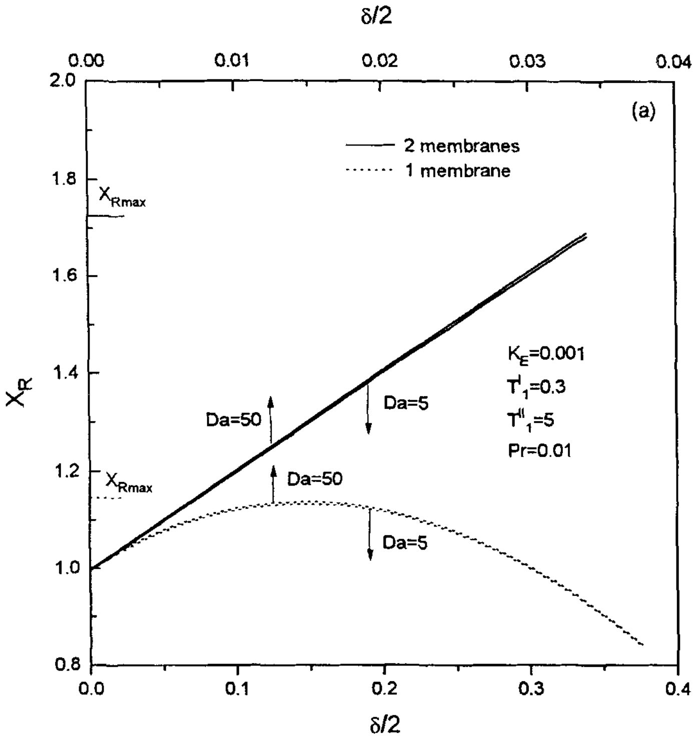

FIG. 4 Influence of Da number and rate ratio variations on conversion.

Consider the situation in which an inert is introduced to the permeation side j ($y_{j4} = 1$ and $y_{ji} = 0$, $i = 1, 3$) at flow rate Q_j and assume

$$Q_1 = Q_2 = Q/2 \tag{13}$$

where Q is the flow rate of an inert to the single-membrane reactor. In Fig. 5 the influence of $Q/2$ on conversion as a function of the rate ratio is presented. As seen from this figure, at high inert flow rates there is an optimal rate ratio at which maximal conversion is obtained. At this point the effects of an inert presence at both the reaction (note, $Pr = 1$) and permeation sides are superimposed. With an increase of the rate ratio above the optimal value, the loss of reactant prevails, resulting in a decrease of conversion. However, at low inert flow rates the maximal conversion is obtained at the limit $\delta \rightarrow \infty$, where the effect of membrane selec-

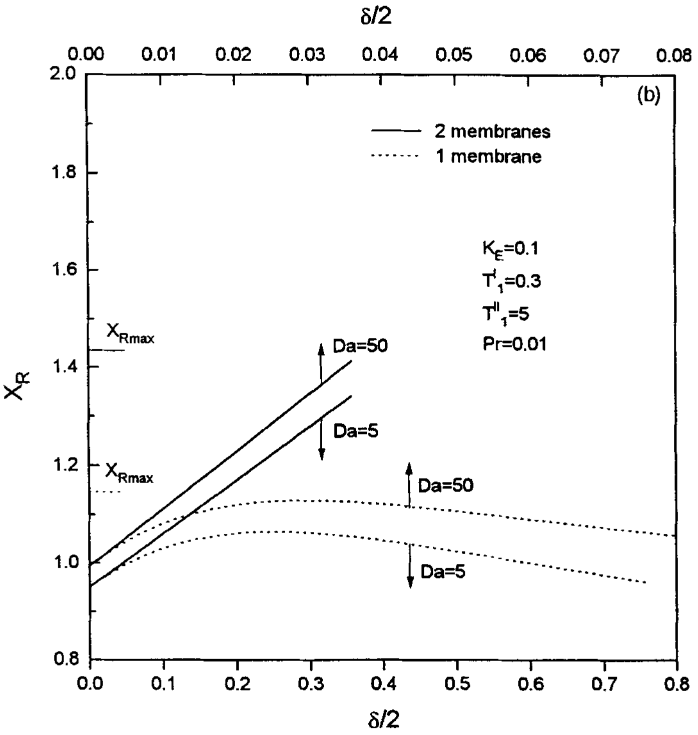

FIG. 4 Continued

tivity disappears. Obviously, higher inert flow rates favor conversion enhancement; the effect is more evident for a two-membrane reactor.

Our results confirm the conclusions reached by Mohan and Govind (1) that the best reactor efficiency is obtained at a pressure ratio of unity (to allow for the permeation of any inert to the reaction zone) and at large residence times on the reaction side (large Da number), which will not be documented here. Concerning the influence of the inert permeability ratio, T_1^{III}, it is, as seen from Table 2, of little significance (slightly better results can be obtained for lower permeabilities in Case I and for higher inert permeabilities in Case II). Thus, by adopting the maximal realistic values for Da and the inert flow rate, Fig. 6, which shows the limits on attainable conversion enhancement, was constructed. Compared to Fig. 2, a significant improvement over $X_{\max}$ can be observed.

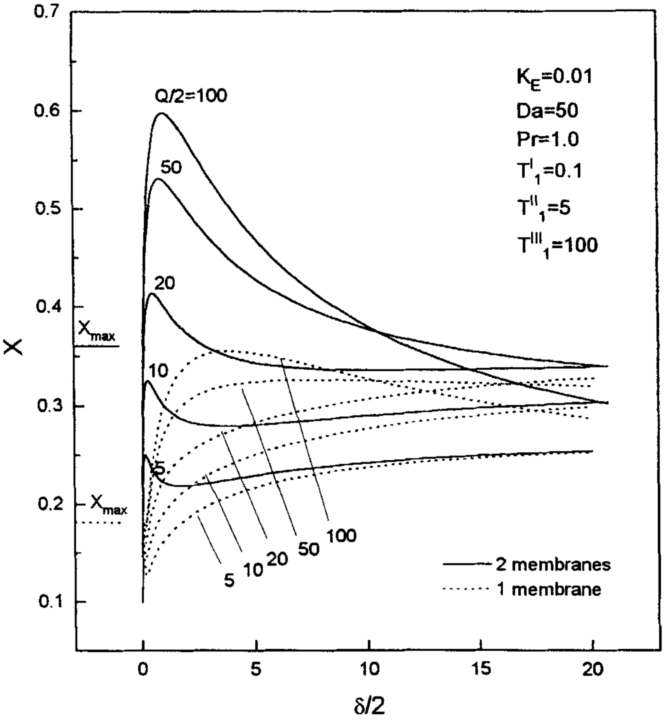

FIG. 5 Influence of permeation side inert flow rate on conversion.

TABLE 2
Effect of Inert Permeability Ratio ($T_1^{\rm III}$) on Conversion (X); Inert Introduced to Permeation Side[a]

		$T_1^{\rm I} = 0.1$			$T_1^{\rm I} = 0.5$		
$Q/2$	$T_1^{\rm III}$	$T_1^{\rm II} = 0.1$	$T_1^{\rm II} = 1$	$T_1^{\rm II} = 10$	$T_1^{\rm II} = 0.5$	$T_1^{\rm II} = 1$	$T_1^{\rm II} = 10$
100	100	0.76	**0.63**	**0.59**	0.48	**0.42**	**0.35**
			0.53	0.29		0.42	0.25
	1	0.75	**0.62**	**0.59**	0.47	**0.42**	**0.35**
			0.53	0.33		0.42	0.26
50	100	0.72	**0.57**	**0.53**	0.45	**0.41**	**0.32**
			0.49	0.29*		0.40	0.30*
	1	0.70	**0.56**	**0.52**	0.45	**0.39**	**0.33**
			0.48	0.29*		0.39	0.30*

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[a] Boldfaced numbers indicate a two-membrane reactor. Asterisks indicate optimum at a boundary ($\delta/2 = 30$).

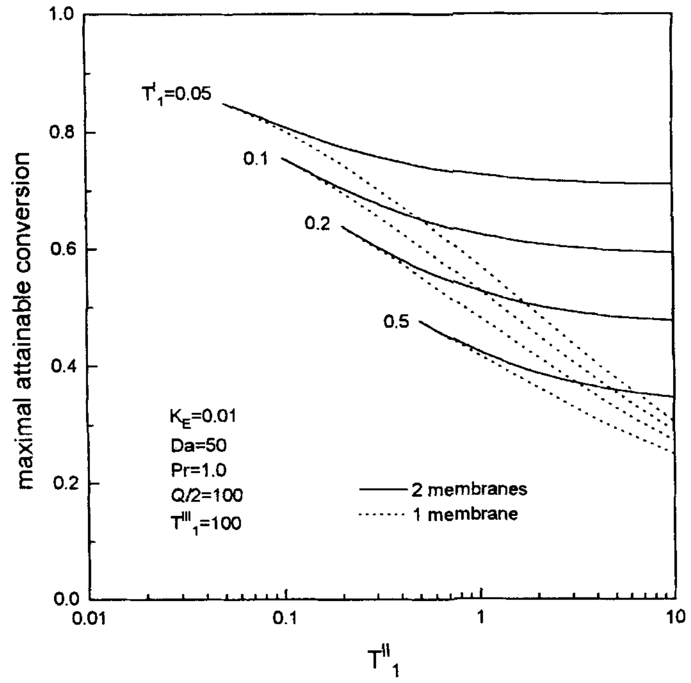

FIG. 6 Limits of attainable conversion; inert introduced to permeation side.

Now, consider the opposite situation in which the inert gas is introduced not to the permeation but to the reaction zone $(x_1^0 + x_4^0 = 1)$. Its quantity is defined by the following parameter:

$$F = x_4^0/x_1^0 \qquad (14)$$

In order to establish the limits on conversion enhancement that could be achieved by adding the inert to the reaction zone, the analysis should be carried out for the maximal realistic value of the Da number. Clearly, the pressure ratio should approach a value of zero to obtain the maximal permeation rate (Fig. 7). Meanwhile, the inert permeability ratio, T_1^{III}, should be large enough to keep the inert in the reaction zone. Analysis of the influence of parameter F (Fig. 8 and Table 3) has shown that the largest conversion (with small variations) for the two-membrane reactor in both Cases I and II and for the single membrane reactor in Case I is obtained in the range $0.1 \leq F \leq 1$. For the single membrane reactor in Case II, larger values of parameter F are preferred. In Fig. 9 the maximal

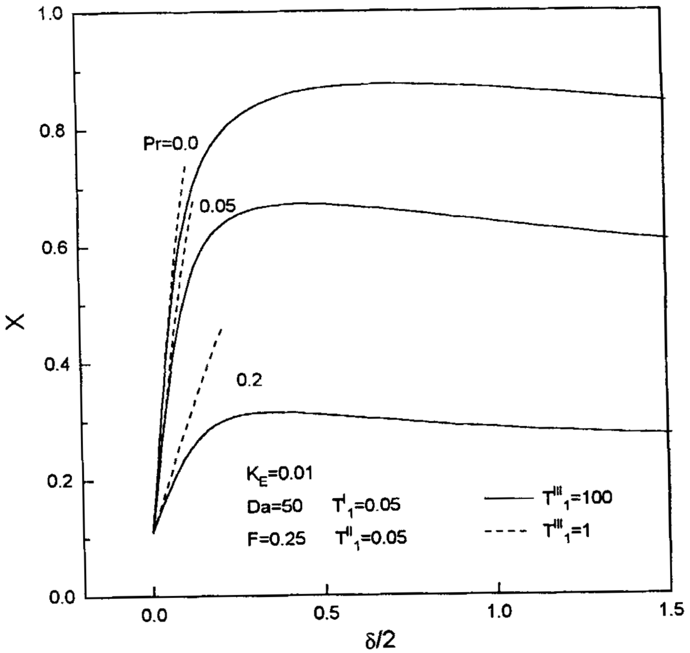

FIG. 7 Effect of pressure ratio and T_1^{III} (reactant to inert permeability ratio) on conversion; inert introduced to reaction side.

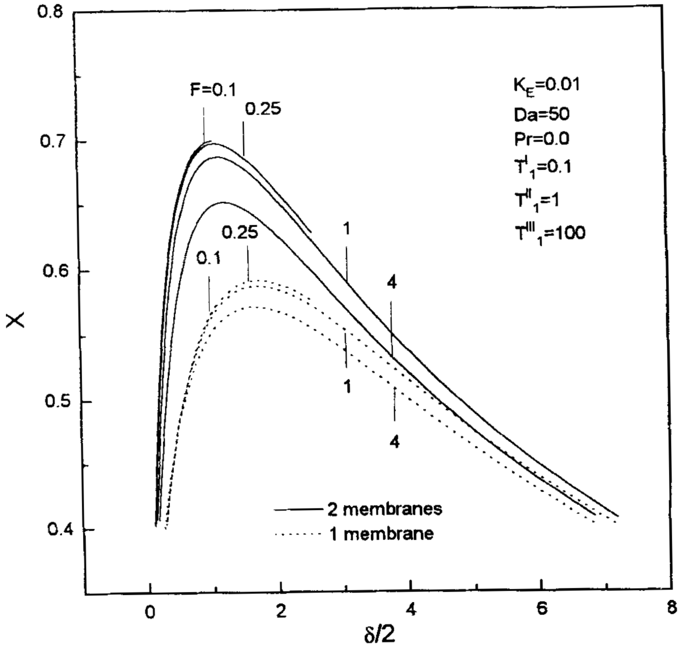

FIG. 8 Influence of proportion of inert in reaction side feed on conversion.

TABLE 3
Effect of Proportion of Inert (F) in Reaction Side Feed on Conversion (X)[a]

		$T_1^{\mathrm{I}} = 0.05$			$T_1^{\mathrm{I}} = 0.02$		
K_E	F	$T_1^{\mathrm{II}} = 0.05$	$T_1^{\mathrm{II}} = 1$	$T_1^{\mathrm{II}} = 10$	$T_1^{\mathrm{II}} = 0.2$	$T_1^{\mathrm{II}} = 1$	$T_1^{\mathrm{II}} = 10$
0.01	0.1	0.84	**0.80**	**0.80**	0.68	**0.56**	**0.51**
			0.66	0.38		0.48	0.22
	0.25	0.88	**0.80**	**0.80**	0.68	**0.58**	**0.55**
			0.66	0.43		0.52	0.28
	1	0.86	**0.79**	**0.78**	0.67	**0.57**	**0.54**
			0.65	0.45		0.52	0.32
	4	0.8	**0.74**	**0.73**	0.64	**0.56**	**0.53**
			0.63	0.51		0.51	0.35
0.1	0.1	0.96	**0.92**	**0.92**	0.86	**0.79**	**0.77**
			0.84	0.67		0.74	0.51
	0.25	0.95	**0.92**	**0.91**	0.85	**0.79**	**0.76**
			0.84	0.69		0.74	0.53
	1	0.93	**0.90**	**0.89**	0.84	**0.78**	**0.75**
			0.83	0.74		0.73	0.56
	4	0.87	**0.84**	**0.84**	0.79	**0.74**	**0.72**
			0.79	0.75		0.71	0.63

[a] Boldfaced numbers indicate a two-membrane reactor.

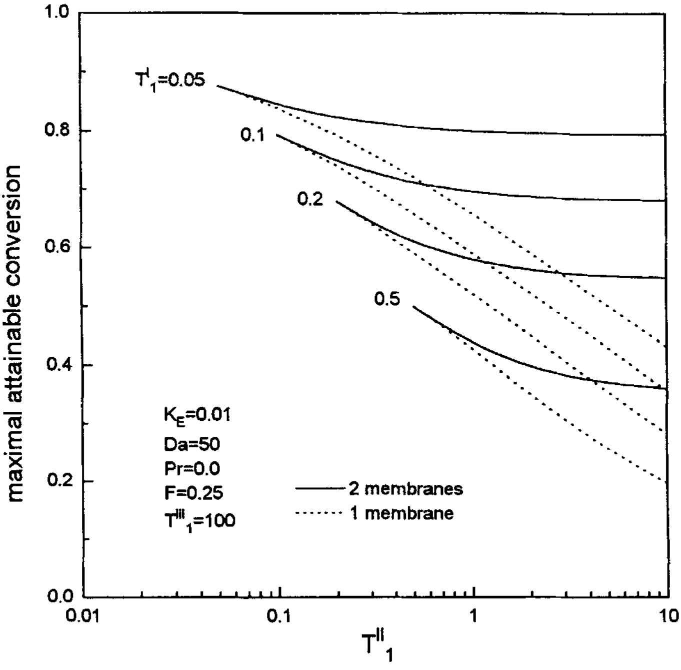

FIG. 9 Limits of attainable conversion; inert introduced to reaction side.

attainable conversions are presented for $F = 0.25$. With reasonable tolerance (except for the single-membrane reactor in Case II), these can be taken to represent the upper limits on conversion enhancement.

CONCLUSIONS

It is demonstrated that by applying a two-membrane reactor instead of a single-membrane one for a reversible gas reaction, considerable conversion enhancement can be obtained. The efficiency of the two-membrane reactor is most prominent at low reactant permeabilities.

To achieve a given conversion, the two-membrane reactor involves lower operating and/or fixed costs (higher *Pr* ratio, lower Da number). In contrast to the single-membrane reactor, the two-membrane reactor allows for greater flexibility in choosing the Da number and rate ratio values.

The advantages of the two-membrane reactor are intensified by introducing an inert to the reactor. If the inert is introduced to the permeation sides, high inert flow rates would be necessary for the ultimate efficiency. On the other hand, a low pressure ratio would be necessary if the inert is introduced to the reaction zone, and the permeability of the inert should be low.

Although the proposed two-membrane reactor concept has not been experimentally verified so far, some recent investigations in solid electrolyte membranes (4, 6) could possibly provide two permselective membranes, each one specialized in a particular product.

The final choice between single- and two-membrane reactors depends on the relative costs of the two assemblies.

SYMBOLS

A, B, C	reactant and two reaction products, respectively
Da	Damköhler number, $VkPu/L^0x_1^0$
d_j	membrane thickness (m)
F	dimensionless inert flow rate at reaction side inlet
f	dimensionless raction rate expression
k	forward reaction rate constant (mol/m^3·Pa·s)
K_E	equilibrium constant in terms of mol fractions
L^0	flow rate at reaction side inlet (mol/s)
Lp_j	permeate flow rate (mol/s)
Lp_j^0	flow rate at permeation side inlet (mol/s)
Lu	residue flow rate (mol/s)
Pe_j	permeability of the fastest gas through membrane j (mol/m·Pa·s)

Pp_j	permeation side pressure (Pa)
Pr_j	pressure ratio, Pp_j/Pu
Pu	reaction side pressure (Pa)
Q_j	dimensionless inert flow rate to permeation side, Lp_j^0/L^0
q_{ji}	permeability of gas i through membrane j (mol/m·Pa·s)
S_j	membrane area (m^2)
T_j^{I}, T_j^{II}, T_j^{III}	permeability ratios of products B, C, and inert, respectively
V	reaction side volume (m^3)
X	conversion of reactant
X_{E}	equilibrium conversion
X_{R}	conversion ratio, X/X_{E}
x_i	mole fraction of gas i in residue
x_i^0	mole fraction of gas i on the reaction side inlet
y_{ji}	mole fraction of gas i in permeate j
y_{ji}^0	mole fraction of gas i on the permeation side inlet
α_{ji}	permselectivity of gas i for membrane j, q_{ji}/Pe_j
δ_j	ratio of permeation rate to reaction rate, Pe_jS_j/d_jkV
ϕ	dimensionless residue flow rate, Lu/L^0
ϕ_j	dimensionless permeate flow rate, Lp_j/L^0

Subscripts

i	substance (in order A, B, C, inert)
j	membrane

REFERENCES

1. K. Mohan and R. Govind, *AIChE J.*, *34*, 1493 (1988).
2. A. M. Champaigne, T. T. Tsotsis, R. G. Miner, and I. A. Webster, *Chem. Eng. Sci.*, *45*, 2423 (1990).
3. H. P. Hsieh, *Catal. Rev. Sci. Eng.*, *33*, 1 (1991).
4. N. Itoh, M. A. Sanchez C., W.-C. Xu, K. Haraya, and M. Hongo, *J. Membr. Sci.*, *77*, 245 (1993).
5. J. K. Ali, E. J. Newson, and D. W. T. Rippin, *Chem. Eng. Sci.*, *49*, 2129 (1994).
6. A. G. Dixon, W. R. Moser, and Y. H. Ma, *Ind. Eng. Chem. Res.*, *33*, 3015 (1994).
7. G. Saracco, G. F. Versteeg, and W. P. M. Swaaij, *J. Membr. Sci.*, *95*, 105 (1994).
8. M. N. Tekić, R. N. Paunović, and G. M. Ćirić, *Ibid.*, *96*, 213 (1994).
9. J. E. Perrin and S. A. Stern, *AIChE J.*, *31*, 1167 (1985).
10. A. Sengupta and K. K. Sirkar, *Ibid.*, *33*, 529 (1987).

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