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Theoretical analysis of conversion enhancement in isothermal polymeric catalytic membrane reactors

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Abstract

A theoretical study of polymeric catalytic membrane reactors (PCMR) is performed when a reversible A $\leftrightarrow$ B reaction is taking place inside the catalytic membrane. The PCMR is assumed to be isothermal, and with a perfectly mixed flow pattern for both retentate and permeate chambers. An analytical expression is derived to calculate the reactor conversion and the reactor conversion enhancement for the case in which the membrane permeability is the same for the reactant and product. When the membrane has different permeabilities for the reactant and product, a semi-analytical solution is presented. The results show that, at least theoretically, conversion above thermodynamic equilibrium can be achieved with the PCMR when the membrane has higher permeability for the product than for the reactant. It is also pointed out that, in the PCMR, the environment of the catalyst particle should be quite different from that existing in conventional reactors. This should change the properties of the catalyst particle and it must be carefully considered.

Keywords: Polymeric catalytic membrane reactors; Conversion enhancement; Gas phase reversible reaction; Permselectivity; Equilibrium constant

1. Introduction

Membrane reactors (MR), combining the use of membranes together with catalysts, provide an opportunity to achieve significant enhancement over the thermodynamic equilibrium conversion. Most of the recent research has been done on reactors incorporating inorganic membranes, due to the usually high temperatures involved and the sometimes aggressive chemical environments. However, there has been a recent interest in polymeric membranes operating at low temperatures for conducting gas phase [1–5] or liquid phase reactions [6–9]. In such conditions, inorganic membranes may be replaced by less expensive, more versatile polymeric membranes. Furthermore, a dense polymer membrane can actively take part in the reaction by influencing sorption and diffusion behavior of the reactants and products [10].

In the development of catalytic membrane reactors (CMR), some efforts have been reported concerning simulation work. Most of these studies were carried out for packed bed membrane reactors (PBMR) [5,11–20], where the membranes are permselective but not catalytically active. For these systems, it is well recognized that conversion above the thermodynamic equilibrium value can be obtained by selectively removing the product from the reaction zone. In other words, as in all membrane applications, the membrane with high permeability and permselectivity towards the product is favored.

There are also some studies considering polymeric catalytic membrane reactors (PCMR) where the catalyst is incorporated inside the membrane, either for liquid phase [21,22] or gas phase reaction [23–29]. When the PCMR was applied to a gas phase reaction, and whatever the reaction stoichiometry considered [23–29], it was concluded that a conversion above the thermodynamic equilibrium value could be achieved if the reactant diffusion coefficient was lower, or the sorption coefficient was higher, than that of the product. However, the relative conversion variable used in these papers

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Nomenclature

D_i	diffusion coefficient of component i (m^2/s)
H_i	Henry's sorption constant of component i (mol/(m^3 Pa))
k_d^m	direct reaction rate constant in membrane phase (s^{-1}))
K_e^g	gas phase reaction equilibrium constant
K_e^m	membrane phase reaction equilibrium constant
p	partial pressure in equilibrium with the concentration inside the membrane (Pa)
Q	volumetric flow rate (m^3/s)
r_m	apparent reaction rate in the membrane phase ($mol/m^3/s$)
$\mathfrak{R}$	universal gas constant (Pa m^3/mol/K)
S	membrane surface area (m^2)
T	absolute temperature (K)
x	dimensionless membrane spatial coordinate
X_{PCMR}	conversion of reactant A in the PCMR
X_e^g	thermodynamic equilibrium conversion
z	membrane spatial coordinate (m)

Greek symbols

Γ	dimensionless contact time
$\alpha_{B/A}$	membrane permselectivity
χ	Relative PCMR conversion (ratio between X_{PCMR} and X_e^g)
δ	thickness of the membrane
ϕ	Thiele modulus for catalyst particle
ϕ'	Modified Thiele modulus used in present work
γ	total pressure difference
λ_i	dimensionless permeability of component i
ν_i	stoichiometric coefficient of component i
ψ	dimensionless pressure
ζ	dimensionless volumetric flow rate

Superscript

F	feed side
P	permeate chamber
R	retentate chamber

Subscript

i	ith component
ref	reference component (reactant A in this paper)

to evaluate the performance of a PCMR considers that the reaction equilibrium constant in the membrane phase is numerically equal to the one in the gas phase. This assumption is very limitative. The present paper uses a simplified relationship between the reaction equilibrium constant for the gas phase and for the membrane phase, which can be obtained from the thermodynamics [30,31]. Inserting the relation for the equilibrium constants in the previous model [23–29], it is expected that different results are obtained. This is precisely the aim of this work where a hypothetical reversible reaction of the type $A \leftrightarrow B$ is considered. Conclusions are obtained for the model reaction $A \leftrightarrow B$ and extended for other equilibrium limited reactions.

In the present study, a PCMR is considered with perfectly mixed flow pattern in both the retentate and permeate sides and isothermal operation. The conversion reached in the PCMR is compared with the thermodynamic equilibrium one, which is the maximum possible conversion attained in a conventional reactor. Moreover, the influence of the membrane permselectivity, reaction equilibrium constant, Thiele modulus, dimensionless contact time and total pressure difference on the performance of the PCMR is briefly discussed.

2. Model development

The PCMR considered in the present work is sketched in Fig. 1, and it has been reported elsewhere [23–25]. A hypothetical reversible reaction of the type $A \leftrightarrow B$ is studied.

The model development is based on the following main assumptions [23–25]:

(1) Steady-state operation.
(2) Isothermal operation.
(3) Perfectly mixed flow pattern on the retentate chambers. Assuming a perfectly mixing flow pattern in the retentate chamber, the permeate chamber should have also a perfectly mixing flow pattern, once the emerging gas at the permeate side should have the same composition irrespective of the position in the membrane surface if the membrane is homogeneous.
(4) Negligible total pressure drop in the retentate and permeate chambers.
(5) Negligible external transport limitations in the gas-membrane interface.
(6) Fickian transport across the membrane.
(7) Henry's law describing the sorption/desorption equilibrium between the bulk gas phase and the membrane phase.
(8) Unitary activity coefficients.
(9) Constant diffusion and sorption coefficients.
(10) Homogeneous catalyst distribution throughout the membrane.

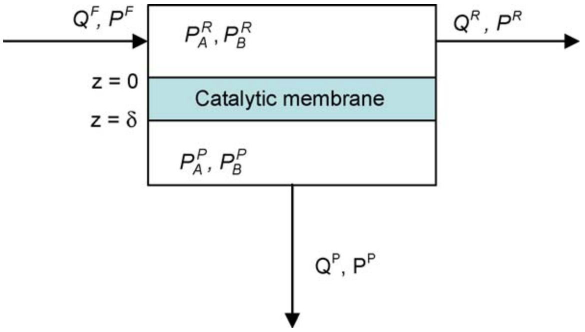

Fig. 1. Schematic diagram of the polymeric catalytic membrane reactor (PCMR).

(11) Reaction occurs only on the surface of catalyst particles.
(12) Equal concentration of reaction species in the catalyst surface and polymer (any relationship could be considered in principle, but this one simplifies the original problem).
(13) Elementary reaction rate law.

With these assumptions, the mass balance in the membrane is [23–25]:

$$D_i \frac{\mathrm{d}^2(H_i p_i)}{\mathrm{d}z^2} + \nu_i r_\mathrm{m} = 0 \quad i = \mathrm{A}, \mathrm{B} \tag{1}$$

where D_i is the diffusion coefficient of component i, H_i is the corresponding Henry's sorption coefficient, p_i the gas phase partial pressure in equilibrium with the concentration of component i inside the membrane ($C_i = H_i\, p_i$), z the spatial coordinate perpendicular to the membrane surface, ν_i the stoichiometric coefficient of component i ($\nu_\mathrm{A} = -1$, $\nu_\mathrm{B} = 1$) and r_m the membrane phase apparent reaction rate:

$$r_\mathrm{m} = k_\mathrm{d}^\mathrm{m}\left(H_\mathrm{A} p_\mathrm{A} - \frac{H_\mathrm{B} p_\mathrm{B}}{K_\mathrm{e}^\mathrm{m}}\right) \tag{2}$$

where k_d^m is the forward reaction rate constant and K_e^m is the reaction equilibrium constant when the reaction is taking place inside the membrane phase. Since we will compare the conversion reached in the PCMR with that obtained in a conventional reactor, it is more convenient to use the gas phase reaction equilibrium constant (K_e^g). The ratio of the reaction equilibrium constant in the gas phase and in the membrane phase is given by [31]:

$$K_\mathrm{e}^\mathrm{m} = \frac{H_\mathrm{B}}{H_\mathrm{A}} K_\mathrm{e}^\mathrm{g} \tag{3}$$

thus, Eq. (2) may be written as:

$$r_\mathrm{m} = k_\mathrm{d}^\mathrm{m} H_\mathrm{A}\left(p_\mathrm{A} - \frac{p_\mathrm{B}}{K_\mathrm{e}^\mathrm{g}}\right) \tag{4}$$

the boundary conditions for Eq. (1) are:

$$\begin{aligned} z &= 0, \quad p_i = p_i^\mathrm{R} \\ z &= \delta, \quad p_i = p_i^\mathrm{P} \end{aligned} \tag{5}$$

where p_i^R and p_i^P are the partial pressures of species i in the retentate and permeate chambers, respectively, and δ is the membrane thickness.

Partial and total mass balances in the retentate chamber are:

$$\begin{aligned} &\frac{Q^\mathrm{F} p_i^\mathrm{F}}{\Re T} - \frac{Q^\mathrm{R} p_i^\mathrm{R}}{\Re T} + S D_i H_i \left.\frac{\mathrm{d}p_i}{\mathrm{d}z}\right|_{z=0} = 0 \\ &\frac{Q^\mathrm{F} p^\mathrm{F}}{\Re T} - \frac{Q^\mathrm{R} p^\mathrm{R}}{\Re T} + S \sum_i D_i H_i \left.\frac{\mathrm{d}p_i}{\mathrm{d}z}\right|_{z=0} = 0 \end{aligned} \tag{6}$$

where p_i^F is the partial pressure of species i in the feed; p^F and p^P are the total pressures of the feed and effluent retentate, respectively; Q^F and Q^R are the total volumetric flow-rates of the feed and effluent retentate, respectively; $\Re$ is the universal gas constant, T is the absolute temperature and S is the membrane surface area.

Partial and total mass balances in the permeate chamber are:

$$\begin{aligned} &\frac{Q^\mathrm{P} p_i^{p}}{\Re T} + S D_i H_i \left.\frac{\mathrm{d}p_i}{\mathrm{d}z}\right|_{z=\delta} = 0 \\ &\frac{Q^\mathrm{P} p^\mathrm{P}}{\Re T} + S \sum_i D_i H_i \left.\frac{\mathrm{d}p_i}{\mathrm{d}z}\right|_{z=\delta} = 0 \end{aligned} \tag{7}$$

where Q^P is the total volumetric flow-rate of the effluent permeate.

Eqs. (1) and (4)–(7) in dimensionless form are as follows:

$$\begin{aligned} &\frac{\mathrm{d}^2\psi_i}{\mathrm{d}x^2} + \nu_i \frac{\phi'^2}{\lambda_i} \frac{\alpha_{\mathrm{B/A}} K_\mathrm{e}^\mathrm{g}}{1 + \alpha_{\mathrm{B/A}} K_\mathrm{e}^\mathrm{g}} \left(\psi_\mathrm{A} - \frac{\psi_\mathrm{B}}{K_\mathrm{e}^\mathrm{g}}\right) = 0 \\ &x = 0, \quad \psi_i = \psi_i^\mathrm{R} \\ &x = 1, \quad \psi_i = \psi_i^\mathrm{P} \end{aligned}, \tag{8}$$

$$\psi_i^\mathrm{F} - \zeta^\mathrm{R}\psi_i^\mathrm{R} + \Gamma \lambda_i \left.\frac{\mathrm{d}\psi_i}{\mathrm{d}x}\right|_{x=0} = 0 \tag{9}$$

$$1 - \zeta^\mathrm{R}\psi^\mathrm{R} + \Gamma \sum \lambda_i \left.\frac{\mathrm{d}\psi_i}{\mathrm{d}x}\right|_{x=0} = 0 \tag{10}$$

$$\zeta^\mathrm{P}\psi_i^\mathrm{P} + \Gamma \lambda_i \left.\frac{\mathrm{d}\psi_i}{\mathrm{d}x}\right|_{x=1} = 0 \tag{11}$$

$$\zeta^\mathrm{P}\psi^\mathrm{P} + \Gamma \sum \lambda_i \left.\frac{\mathrm{d}\psi_i}{\mathrm{d}x}\right|_{x=1} = 0 \tag{12}$$

where:

$$\begin{aligned} &\psi_\mathrm{A}^\mathrm{F} = \frac{P_\mathrm{A}^\mathrm{F}}{P_\mathrm{ref}}, \psi_\mathrm{A}^\mathrm{R} = \frac{P_\mathrm{A}^\mathrm{R}}{P_\mathrm{ref}}, \psi_\mathrm{A}^\mathrm{P} = \frac{P_\mathrm{A}^\mathrm{P}}{P_\mathrm{ref}}, \psi_\mathrm{B}^\mathrm{R} = \frac{P_\mathrm{B}^\mathrm{R}}{P_\mathrm{ref}}, \psi_\mathrm{B}^\mathrm{P} = \frac{P_\mathrm{B}^\mathrm{P}}{P_\mathrm{ref}}, \psi^\mathrm{P} = \frac{P^\mathrm{P}}{P_\mathrm{ref}}, \psi^\mathrm{R} = \frac{P^\mathrm{R}}{P_\mathrm{ref}} = 1 \\ &\zeta^\mathrm{F} = \frac{Q^\mathrm{F}}{Q_\mathrm{ref}}, \zeta^\mathrm{R} = \frac{Q^\mathrm{R}}{Q_\mathrm{ref}}, \zeta^\mathrm{P} = \frac{Q^\mathrm{P}}{Q_\mathrm{ref}} \\ &\lambda_i = \frac{D_i H_i}{D_\mathrm{ref} H_\mathrm{ref}} \left(\alpha_{\mathrm{B/A}} = \frac{D_\mathrm{B} H_\mathrm{B}}{D_\mathrm{A} H_\mathrm{A}}\right), x = \frac{z}{\delta} \\ &\phi' = \delta \sqrt{\frac{k_\mathrm{d}^\mathrm{m}}{D_\mathrm{A}}\left(1 + \frac{D_\mathrm{A}/D_\mathrm{B}}{K_\mathrm{e}^\mathrm{m}}\right)} = \delta \sqrt{\frac{k_\mathrm{d}^\mathrm{m}}{D_\mathrm{ref}}\left(1 + \frac{1}{\alpha_{\mathrm{B/A}} K_\mathrm{e}^\mathrm{g}}\right)}, \Gamma = \frac{S D_\mathrm{ref} H_\mathrm{ref} \Re T}{\delta Q_\mathrm{ref}}, \gamma = \frac{\psi^\mathrm{R}}{\psi^\mathrm{P}} \end{aligned}, \tag{13}$$

the subscripts i and ref refer to the ith and reference components, respectively, and the superscripts F, R, and P refer to the feed, retentate and permeate conditions, respectively. ψ designates the dimensionless pressure, and ζ the dimensionless volumetric flow rate. λ_i is the dimensionless membrane permeability. For convenience, we also define $\alpha_{B/A}$ as the membrane permselectivity (ratio between product (B) and reactant (A) permeability). Γ is the dimensionless contact time (ratio between the characteristic feed flow time and the characteristic permeance time of the reference component) and γ is the total pressure difference (ratio between retentate and permeate side total pressure). Feed conditions are taken as the reference for P_{ref} and Q_{ref}. Component A is taken as the reference for D_{ref} and H_{ref}. Variable ϕ' in Eq. (13) is similar to the Thiele modulus expression for a first-order reversible reaction and slab geometry of catalyst used by Froment and Bischoff [32]:

$$\phi = \delta\sqrt{\frac{k_{\mathrm{d}}}{D_{\mathrm{ref}}}\left(1+\frac{1}{K_{\mathrm{e}}}\right)} \tag{14}$$

however, for catalytic membrane systems there is not just one but two surface concentrations (retentate and permeate). It is then not possible to use the generalized Thiele modulus definition [32]:

$$\phi = \delta\frac{r_{\mathrm{A}}(C^{\mathrm{s}})}{\sqrt{2}}\left[\int_{C^{\mathrm{eq}}}^{C^{\mathrm{s}}} D_{\mathrm{A}}(C)r_{\mathrm{A}}(C)\mathrm{d}C\right]^{-1/2} \tag{15}$$

for obtaining a consistent Thiele modulus definition for the present system (where C^{s} is the concentration on the surface of the catalyst particle).

In this way, variable ϕ' should be viewed as a modified Thiele modulus. A similar expression was used by Winkelman and Beenackers [33], when modeling a gas–liquid reactive absorption process, where reactant and product had different diffusion coefficients in liquid phase.

In the literature, the analytical solutions for Eq. (8) (two components) are expressed in two different formulations [25,33]. The solution presented by Winkelman and Beenackers [33] is adopted here because it provides an analytical solution for the set of dimensionless mass balance equations (Eqs. (9)–(12)). Winkelman and Beenackers's solution was originally used to describe simultaneous absorption/desorption with reversible first-order chemical reaction in gas–liquid absorption. It can be adopted and re-written in the dimensionless form as:

$$\begin{aligned}\psi_A ={}& \frac{\sinh[\phi'(1-x)]}{\sinh(\phi')}\,\frac{\alpha_{\mathrm{B/A}}K_{\mathrm{e}}^{\mathrm{g}}\psi_{\mathrm{A}}^{\mathrm{R}}-\alpha_{\mathrm{B/A}}\psi_{\mathrm{B}}^{\mathrm{R}}}{1+\alpha_{\mathrm{B/A}}K_{\mathrm{e}}^{\mathrm{g}}} \\ &+\frac{\sinh(\phi'x)}{\sinh(\phi')}\,\frac{\alpha_{\mathrm{B/A}}K_{\mathrm{e}}^{\mathrm{g}}\psi_{\mathrm{A}}^{\mathrm{P}}-\alpha_{\mathrm{B/A}}\psi_{\mathrm{B}}^{\mathrm{P}}}{1+\alpha_{\mathrm{B/A}}K_{\mathrm{e}}^{\mathrm{g}}} \\ &+(1-x)\frac{\psi_{\mathrm{A}}^{\mathrm{R}}+\alpha_{\mathrm{B/A}}\psi_{\mathrm{B}}^{\mathrm{R}}}{1+\alpha_{\mathrm{B/A}}K_{\mathrm{e}}^{\mathrm{g}}}+x\frac{\psi_{\mathrm{A}}^{\mathrm{P}}+\alpha_{\mathrm{B/A}}\psi_{\mathrm{B}}^{\mathrm{P}}}{1+\alpha_{\mathrm{B/A}}K_{\mathrm{e}}^{\mathrm{g}}}\end{aligned} \tag{16}$$

$$\psi_{\mathrm{B}} = \psi_{\mathrm{B}}^{\mathrm{R}}+\frac{\psi_{\mathrm{A}}^{\mathrm{R}}-\psi_{\mathrm{A}}}{\alpha_{\mathrm{B/A}}}-\left[\frac{(\psi_{\mathrm{A}}^{\mathrm{R}}-\psi_{\mathrm{A}}^{\mathrm{P}})}{\alpha_{\mathrm{B/A}}}+(\psi_{\mathrm{B}}^{\mathrm{R}}-\psi_{\mathrm{B}}^{\mathrm{P}})\right]x \tag{17}$$

when Eqs. (16) and (17) are substituted into the retentate and permeate sides mass balance equations, Eqs. (9)–(12), they can be simplified and lead to the following six algebraic equations:

$$1-\zeta^{\mathrm{R}}-\frac{\zeta^{\mathrm{P}}}{\gamma}=0 \tag{18}$$

$$\frac{\zeta^{\mathrm{P}}}{\gamma}=\Gamma\alpha_{\mathrm{B/A}}\left[\frac{1-\alpha_{\mathrm{B/A}}}{\alpha_{\mathrm{B/A}}}(\psi_{\mathrm{A}}^{\mathrm{R}}-\psi_{\mathrm{A}}^{\mathrm{P}})+\left(1-\frac{1}{\gamma}\right)\right] \tag{19}$$

$$\begin{aligned}&\psi_{\mathrm{A}}^{\mathrm{F}}-\zeta^{\mathrm{R}}\psi_{\mathrm{A}}^{\mathrm{R}}-\zeta^{\mathrm{P}}\psi_{\mathrm{A}}^{\mathrm{P}} \\ &\quad=\Gamma\frac{\alpha_{\mathrm{B/A}}}{1+\alpha_{\mathrm{B/A}}K_{\mathrm{e}}^{\mathrm{g}}}\,\frac{\phi[\cosh(\phi')-1]}{\sinh(\phi')} \\ &\qquad\times\left[(1+K_{\mathrm{e}}^{\mathrm{g}})(\psi_{\mathrm{A}}^{\mathrm{R}}+\psi_{\mathrm{A}}^{\mathrm{P}})-\left(1+\frac{1}{\gamma}\right)\right]\end{aligned} \tag{20}$$

$$\begin{aligned}\zeta^{\mathrm{p}}\psi_{\mathrm{A}}^{\mathrm{P}}={}&\Gamma\frac{\alpha_{\mathrm{B/A}}}{1+\alpha_{\mathrm{B/A}}K_{\mathrm{e}}^{\mathrm{g}}}\left[\frac{\phi'}{\sinh(\phi')}[(K_{\mathrm{e}}^{\mathrm{g}}+1)\psi_{\mathrm{A}}^{\mathrm{R}}-1]\right. \\ &-\frac{\phi'\cosh(\phi')}{\sinh(\phi')}\left[(K_{\mathrm{e}}^{\mathrm{g}}+1)\psi_{\mathrm{A}}^{\mathrm{P}}-\frac{1}{\gamma}\right] \\ &\left.+\frac{1-\alpha_{\mathrm{B/A}}}{\alpha_{\mathrm{B/A}}}(\psi_{\mathrm{A}}^{\mathrm{R}}-\psi_{\mathrm{A}}^{\mathrm{P}})+\left(1-\frac{1}{\gamma}\right)\right]\end{aligned} \tag{21}$$

$$\psi_{\mathrm{A}}^{\mathrm{R}}+\psi_{\mathrm{B}}^{\mathrm{R}}=1 \tag{22}$$

$$\psi_{\mathrm{A}}^{\mathrm{P}}+\psi_{\mathrm{B}}^{\mathrm{P}}=\frac{1}{\gamma} \tag{23}$$

In this set of equations, the input parameters are $\psi_{\mathrm{A}}^{\mathrm{F}}, \gamma, \Gamma, \phi, K_{\mathrm{e}}^{\mathrm{g}}$ and $\alpha_{\mathrm{B/A}}$, and the output parameters are $\psi_{\mathrm{A}}^{\mathrm{R}}, \psi_{\mathrm{A}}^{\mathrm{P}}, \psi_{\mathrm{B}}^{\mathrm{R}}, \psi_{\mathrm{B}}^{\mathrm{P}}, \zeta^{\mathrm{R}}$ and ζ^{P}. Then, the PCMR conversion, X_{PCMR}, defined as the conversion of the reactant species (component A) that can be obtained by the PCMR, is calculated in terms of feed and output gas phase compositions and flow rates:

$$X_{\mathrm{PCMR}}=\frac{\psi_{\mathrm{A}}^{\mathrm{F}}-\zeta^{\mathrm{R}}\psi_{\mathrm{A}}^{\mathrm{R}}-\zeta^{\mathrm{P}}\psi_{\mathrm{A}}^{\mathrm{P}}}{\psi_{\mathrm{A}}^{\mathrm{F}}} \tag{24}$$

The relative PCMR conversion (χ_{PCMR}), defined as the ratio between the reactor conversion (X_{PCMR}) and the thermodynamic gas phase equilibrium conversion ($X_{\mathrm{g}}^{\mathrm{e}}$), is:

$$\chi_{\mathrm{PCMR}}=\frac{X_{\mathrm{PCMR}}}{X_{\mathrm{g}}^{\mathrm{e}}} \tag{25}$$

The thermodynamic equilibrium conversion depends on the gas phase reaction equilibrium constant and feed composition:

$$X_{\mathrm{g}}^{\mathrm{e}}=\frac{(K_{\mathrm{e}}^{\mathrm{g}}+1)\psi_{\mathrm{A}}^{\mathrm{F}}-1}{(K_{\mathrm{e}}^{\mathrm{g}}+1)\psi_{\mathrm{A}}^{\mathrm{F}}} \tag{26}$$

Basically, Eqs. (18)–(23) can be solved by numerical methods [24,25]. However, for a specific case, i.e. when the membrane has the same permeability for the reactant and product ($\alpha_{B/A} = 1$), an analytic solution can be derived, as follows:

$$\zeta^{R} = 1 - \Gamma\frac{\gamma - 1}{\gamma} \tag{27}$$

$$\zeta^{P} = \Gamma(\gamma - 1) \tag{28}$$

$$\begin{aligned}\psi_{A}^{R} = {}& \frac{1}{1 + K_{e}^{g}} \\ & + \frac{\hbar + \gamma - 1}{\Gamma(\hbar^2 - {}^2) + \Gamma[\gamma + (1/\gamma) + (1/\Gamma) - 2](\hbar - 1) + \gamma} \\ & \times \frac{(1 + K_{e}^{g})\psi_{A}^{F} - 1}{1 + K_{e}^{g}}\end{aligned} \tag{29}$$

$$\begin{aligned}\psi_{A}^{P} = {}& \frac{1}{\gamma}\left[\frac{1}{1 + K_{e}^{g}}\right. \\ & + \frac{}{\Gamma(\hbar^2 - {}^2) + \Gamma[\gamma + (1/\gamma) + (1/\Gamma) - 2](\hbar - 1) + \gamma} \\ & \left.\times \frac{(1 + K_{e}^{g})\psi_{A}^{F} - 1}{1 + K_{e}^{g}}\right]\end{aligned} \tag{30}$$

$$\psi_{B}^{R} = 1 - \psi_{A}^{R} \tag{31}$$

$$\psi_{B}^{P} = \frac{1}{\gamma} - \psi_{A}^{P} \tag{32}$$

where

$$\hbar = \frac{\phi' \cosh(\phi')}{\sinh(\phi')}, \qquad = \frac{\phi'}{\sinh(\phi')}$$

Substituting Eqs. (27)–(32) into Eqs. (24)–(25), both the PCMR conversion and the relative PCMR conversion, for the case in which the membrane has the same permeability for the reactant and the product ($\alpha_{B/A} = 1$), can be calculated with the following expressions:

$$X_{PCMR} = \left\{1 - \frac{[1 - \Gamma + (\Gamma/\gamma)]\hbar + \Gamma(\gamma - 1) + (\gamma - 1)[1 - \Gamma + (\Gamma/\gamma)]}{\Gamma(\hbar^2 - {}^2) + \Gamma[\gamma + (1/\gamma) + (1/\Gamma) - 2](\hbar - 1) + \gamma}\right\}\frac{(1 + K_{e}^{g})\psi_{A}^{F} - 1}{(1 + K_{e}^{g})\psi_{A}^{F}} \tag{33}$$

$$\chi_{PCMR} = 1 - \frac{[1 - \Gamma + (\Gamma/\gamma)]\hbar + \Gamma(\gamma - 1) + (\gamma - 1)[1 - \Gamma + (\Gamma/\gamma)]}{\Gamma(\hbar^2 - {}^2) + \Gamma[\gamma + (1/\gamma) + (1/\Gamma) - 2](\hbar - 1) + \gamma} \tag{34}$$

When the reactant and product have different permeabilities in the membrane ($\alpha_{B/A} \neq 1$), the set of equations (Eqs. (18)–(23)) are solved by a Matlab program. A fast and accurate simulation can be obtained for such a simple algebraic equations system.

3. Results and discussion

3.1. The membrane permeability is the same for the reactant and product

In this condition, the PCMR conversion (X_{PCMR}) and relative PCMR conversion (χ_{PCMR}) can be computed by Eqs. (33) and (34). An analysis of Eq. (34) shows that the relative PCMR conversion approaches its maximum value of unit when the Thiele modulus tends to infinite ($\phi' \to \infty$, $\hbar \to \infty$, $\to 0$, $\chi_{PCMR} \to 1$). This means that a conversion enhancement over the thermodynamic equilibrium will never occur when the membrane permeability is the same for the reactant and product. Since the reaction product has the same transport properties as the reactant in the membrane, there is no separation effect and it is impossible to obtain a conversion enhancement relative to the thermodynamic equilibrium value.

When the membrane has the same permeability for the reactant and product, the relative PCMR conversion depends only on the Thiele modulus, dimensionless contact time and total pressure difference. This is illustrated in Fig. 2. The relevant variables used in the calculation are: $K_{e}^{g} = 1$ and $\psi_{A}^{F} = 1(\psi_{B}^{F} = 1 - \psi_{A}^{F} = 0)$. It can be seen that the relative reactor conversion always increases with the Thiele modulus. In general, the Thiele modulus reflects the relative rate of the reaction processes compared to the diffusion across the membrane. A low Thiele modulus value indicates that species move through the membrane with small probability of reaction. A high Thiele modulus, on the other hand, means that species are rapidly consumed at the catalyst surface, and thus just a small fraction permeates through the membrane, leading to a high PCMR conversion. We also can find that the relative reactor conversion is greatly influenced by the dimensionless contact time. The relative reactor conversion increases with the dimensionless contact time mainly because the loss of reactants decreases as the retentate stream flowrate decreases and/or membrane permeability increases. The other conclusion that can be made from Fig. 2 is that the total pressure difference can enhance or penalize the conversion, depending on the Thiele modulus values. In the low Thiele modulus regime, where reaction controls, a low total pressure difference will decrease the reactant loss and thus favor the reactor conversion. On the other hand, at high Thiele modulus values (diffusion controlled regime), a large total pressure difference will increase the driving force of the diffusion process. However, the influence of the total pressure difference is inconspicuous in most conditions. A notable influence of the total pressure difference on the reactor conversion enhancement can only be observed when the dimensionless contact time is high.

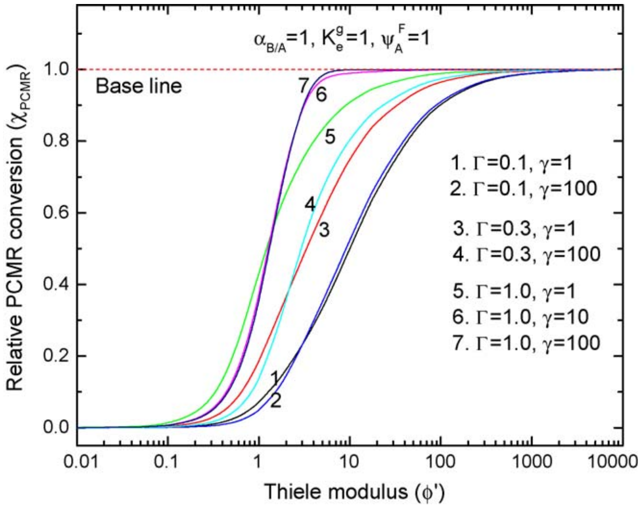

Fig. 2. Influence of the Thiele modulus, dimensionless contact time and total pressure gradient on the relative PCMR conversion ($\alpha_{B/A}$ = 1).

3.2. *The permeabilities are different for the reactant and product*

3.2.1. *Effect of the permselectivity*

Fig. 3 shows the relative reactor conversion enhancement obtained in the PCMR when the membrane has different permselectivities for the reactant and product. The other parameters used in the simulations are: $\gamma = 100$, $\Gamma = 0.15$, $K_e^g = 1$ and $\psi_A^F = 1$.

As can be seen from this figure, a PCMR conversion well above the thermodynamic equilibrium value can be achieved when the membrane has a higher permeability for the product than for the reactant. This is due to the membrane positive separation effect. When the product is selectively removed from the reaction zone ($\alpha_{B/A} > 1$), the reaction equilibrium is shifted forward and thus a reactor conversion enhancement is obtained. The higher is the membrane permselectivity ($\alpha_{B/A} \geq 1$), the more significant is the reactor conversion enhancement (curves 1–3). On the other hand, when the reactant permeates through the membrane faster than the product ($\alpha_{B/A} < 1$), the reaction equilibrium shift is hindered by the 'negative' membrane separation effect: the higher permeability of the reactant through the membrane penalizes the conversion. In such a condition, the higher the membrane permselectivity for the reactant ($\alpha_{B/A} \leq 1$), the more seriously it penalizes the reactor conversion (curves 3–5).

When the product permeates through the membrane faster than the reactant ($\alpha_{B/A} > 1$), it can be seen that the relative conversion reaches a peak well above the thermodynamic value in a medium Thiele modulus region and then the relative conversion gradually decreases to the unit when the Thiele modulus further increases. This happens because in the medium Thiele modulus range, in which the PCMR operates in the intermediate regime, when the product is selectively removed from the reaction zone the reaction equilibrium is shifted forward and thus a reactor conversion enhancement is attained. As the Thiele modulus further increases, the reaction becomes so fast that the membrane separation effect is getting more and more offset. Finally, when the Thiele modulus approaches infinity, the reaction reaches equilibrium instantaneously throughout the membrane and the reactor conversion approaches the thermodynamic equilibrium value.

As discussed so far, it can be concluded that a PCMR conversion exceeding the thermodynamic equilibrium can be achieved by selecting a membrane with a higher permeability for the product than for the reactant. In other words, the PCMR conversion enhancement does not depend on the diffusion or sorption coefficients separately but depends on the membrane permselectivity, which is the product of both parameters.

3.2.2. *Effect of the gas phase reaction equilibrium constant*

Fig. 4 shows the influence of the gas phase reaction equilibrium constant on the relative reactor conversion when $\gamma = 100$, $\Gamma = 0.15$, $\psi_A^F = 1$ and $\alpha_{B/A} = 5$. For a wide range of Thiele modulus, we can see that a higher reactor conversion enhancement can be obtained for the reaction with lower

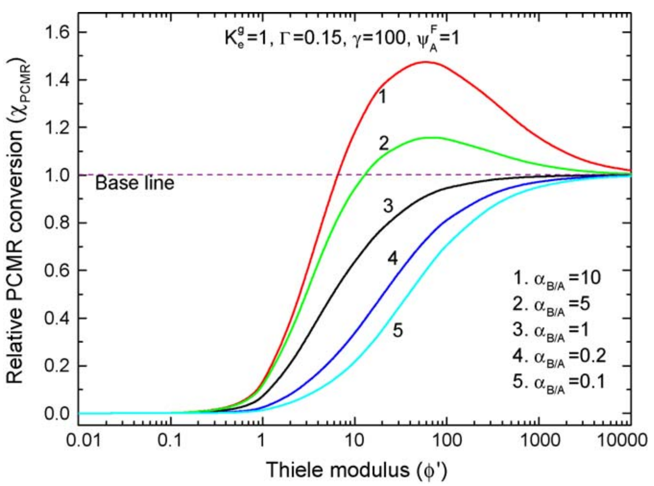

Fig. 3. Influence of the membrane permselectivity and Thiele modulus on the relative PCMR conversion.

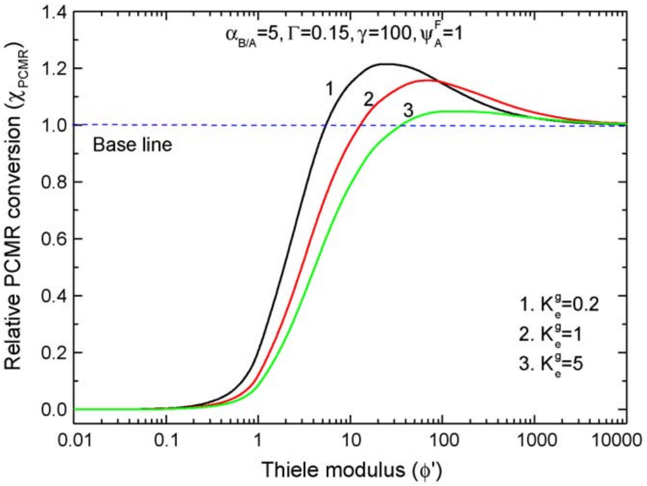

Fig. 4. Influence of the reaction equilibrium constant and Thiele modulus on the relative PCMR conversion ($\alpha_{B/A} > 1$).

Table 1
Maximum PCMR conversion and conversion enhancement ($\psi_A^F = 1$)

System	X_e^g	X_{PCMR}^{max}	χ_{PCMR}^{max}	Conditions for χ_{PCMR}^{max}
$\alpha_{B/A} = 10$, $K_e^g = 1$	0.5	0.9091	1.8182	(1) $\gamma \to \infty$; (2) total permeation condition (TPC); (3) medium Thiele modulus
$\alpha_{B/A} = 5$, $K_e^g = 1$	0.5	0.8333	1.6667	
$\alpha_{B/A} = 5$, $K_e^g = 5$	0.8333	0.9615	1.1539	
$\alpha_{B/A} = 5$, $K_e^g = 0.2$	0.1667	0.5	3	
$\alpha_{B/A} \leq 1$			1	$\phi' \to \infty$

equilibrium constant. A high equilibrium constant means the equilibrium conversion is high itself. So, it is difficult to obtain a high conversion enhancement. Considering the extreme case of $K_e^g \to \infty$ (irreversible reaction), we can never obtain a conversion enhancement. On the other hand, it was found that, in some conditions, the reaction with a high equilibrium constant leads to higher reactor conversion enhancement in high Thiele modulus region.

Assuming a feed condition of $\psi_A^F = 1$, we found that the maximum relative conversion depends on the membrane permselectivity and gas phase reaction equilibrium constant (Table 1). When the permeability of the product is smaller than or equal to that of the reactant ($\alpha_{B/A} \leq 1$), the maximum relative reactor conversion is the unit, which can be approached when the Thiele modulus tends to infinite ($\phi' \to \infty$, $\chi_{PCMR} \to 1$). For the case in which the product permeates through the membrane faster than the reactant ($\alpha_{B/A} > 1$), the maximum conversion above the thermodynamic equilibrium can be obtained for: (1) a very large total pressure difference ($\gamma \to \infty$); (2) the total permeation condition (TPC) [24,25] and (3) medium Thiele modulus range. As an example, Table 1 gives the maximum PCMR conversion and maximum relative PCMR conversion in various combinations of membrane permselectivity and gas phase reaction equilibrium constant.

Basing on simulated results (not all of these results are shown in Table 1), a simple correlation was found which relates the maximum relative conversion with the membrane permselectivity and gas phase reaction equilibrium constant:

$$\chi_{PCMR}^{max} = \frac{\alpha_{B/A} + \alpha_{B/A} K_e^g}{1 + \alpha_{B/A} K_e^g} \quad (\alpha_{B/A} \geq 1, \psi_A^F = 1) \tag{35}$$

3.2.3. *Effect of the total pressure difference and dimensionless contact time*

As pointed in previous sections, it is possible to obtain a PCMR conversion exceeding the thermodynamic equilibrium value by selecting a membrane with a higher permeability for the product than that for the reactant. However, to what extend the reactor conversion will be enhanced is tightly related to other conditions, such as the Thiele modulus, the total pressure difference and the dimensionless contact time. As the influence of the Thiele modulus on the reactor conversion has been extensively discussed, in this section it is shown how the total pressure gradient and dimensionless contact time affect the PCMR performance.

Fig. 5 clearly shows that, even though the reaction product permeates through the membrane faster than the reactant ($\alpha_{B/A} = 5$), when the dimensionless contact time is small ($\Gamma = 0.02$ in this case), a reactor conversion over the thermodynamic equilibrium value can only be achieved when the total pressure difference is large enough ($\gamma = 100$ and 1000 in this case). As compared with Fig. 2, we can see from Fig. 5 that for medium to high Thiele modulus values the total pressure difference plays a more important role when the membrane has different permeabilities for the reactant and product. This is a direct consequence of the membrane separation effect since the transport of reaction species through the membrane is related to their concentration gradient.

Fig. 6 illustrates the influence of the dimensionless contact time on the relative conversion. For the case in which the product permeates through the membrane faster than the reactant, the relative conversion increases significantly with the dimensionless contact time. This is expected, because a high dimensionless contact time means that the fraction of species that enter into the membrane is higher, which will reduce the loss of the reactant. From Fig. 6, it can also be seen that the maximum relative conversion can be approached at the total permeation condition when a large total pressure gradient is applied ($\gamma = 100$ in this case). The value of the maximum relative conversion is consistent with the prediction of Eq. (35).

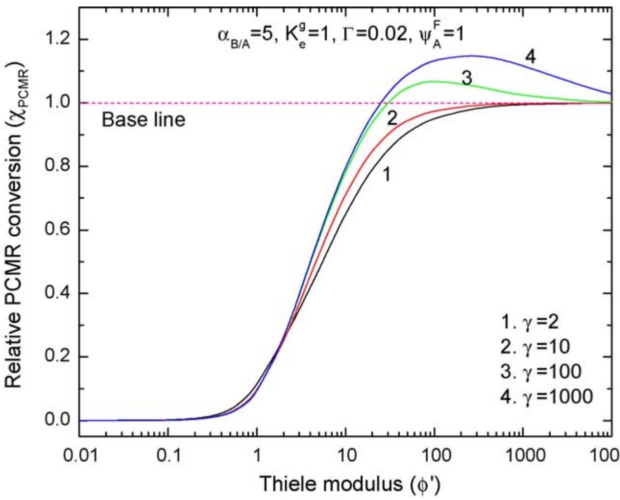

Fig. 5. Influence of the total pressure difference and Thiele modulus on the relative PCMR conversion ($\alpha_{B/A} > 1$).

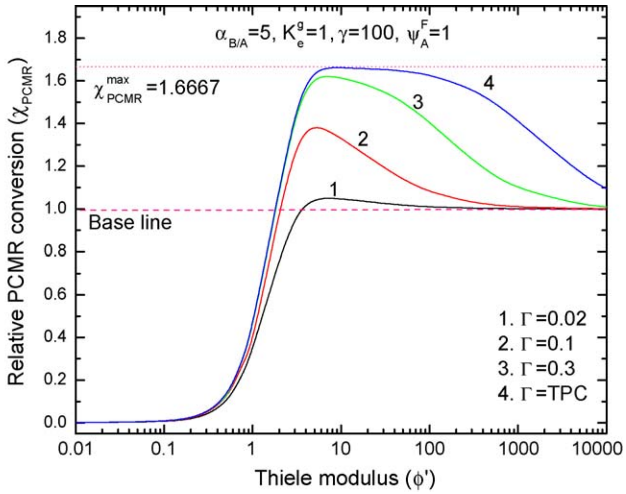

Fig. 6. Influence of the dimensionless contact time and Thiele modulus on the relative PCMR conversion ($\alpha_{B/A} > 1$).

3.3. Effect of the membrane properties on the catalyst performance

Previous sections show that, theoretically, a conversion enhancement over the thermodynamic equilibrium one can be obtained by selecting a membrane with higher permeability for the reaction product than that of the reactant. However, in this analysis, the catalyst is considered as a 'black box'. How the specific conditions, especially the membrane properties affect the catalyst state and properties is not taken into account. As pointed by Miachon and Dalmon [34], the environment of the catalyst in the polymeric catalyst membrane reactor may be quite different from that existing in conventional reactors. This originates changes of the catalyst properties.

The analysis above has shown that the PCMR conversion greatly depends on the Thiele modulus, which is defined as $\phi' = \delta\sqrt{k_d^m/D_A(1 + 1/\alpha_{B/A}K_e^g)}$ (for the $A \leftrightarrow B$ reaction studied in the present work). In this definition, for a specific gas phase reaction and a selected membrane, the exact values of the membrane thickness (δ), diffusivity (D_A) and permselectivity ($\alpha_{A/B}$) and reaction equilibrium constant (K_e^g) can be well estimated. However, the membrane phase direct reaction rate constant (k_d^m) is a factor which is affected by the membrane properties and it should be different in comparison to conventional systems, e.g. CSTR or packed bed reactor. As shown above, $K_e^m = k_d^m/k_i^m = H_B/H_A K_e^g$. So, a change of the sorption coefficients will change the ratio k_d^m/k_i^m (possibly both k_d^m and k_i^m change), as K_e^g depends only on the temperature. In this regard, it is impossible to anticipate how the membrane properties will alter the catalyst performance (k_d^m) and consequentially the Thiele modulus and PCMR conversion, even qualitatively. How the polymeric membrane properties affect the catalyst performance will be the aim of a future work.

4. Conclusions

The performance achieved by an isothermal polymeric catalytic membrane reactor, with a perfectly mixed flow pattern, was studied for a reversible $A \leftrightarrow B$ gas phase reaction. The PCMR conversion was calculated both analytically, for the case in which the membrane has the same permeability for the reactant and product, and numerically, otherwise. It was found that all the factors which may affect the performance of the PCMR can be combined into six dimensionless groups: Thiele modulus, dimensionless contact time, total pressure difference, feed composition, gas phase reaction equilibrium constant and membrane permselectivity. The simulation results show that, at least theoretically, the PCMR can overcome the thermodynamic equilibrium limitations when the reaction product permeates preferentially through the membrane. This conclusion should hold for any equilibrium limited reaction.

The performance of catalyst particles is affected by the membrane properties in the PCMR. It is clear that a change of the ratio between the reactant and product sorption coefficients should change the ratio between the forward and reverse membrane phase reaction rate constants. Accordingly, the Thiele modulus value could be changed. At this point, it is difficult to make a precise prediction of the PCMR performance.

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