Desalination and Water Treatment
www.deswater.com

51 (2013) 2387–2393
February

Taylor & Francis
Taylor & Francis Group

doi: 10.1080/19443994.2012.728058

Pervaporation membrane reactor design guidelines for the production of methyl acetate

Sandra Milena López-Zamora, Javier Fontalvo, Miguel Ángel Gómez-García*

Grupo de Investigación en Aplicación de Nuevas Tecnologías, Laboratorio de Intensificación de Procesos y Sistemas Híbridos, Departamento de Ingeniería Química, Facultad de Ingeniería y Arquitectura, Universidad Nacional de Colombia—Sede Manizales, Cra 27 No. 64-60, Apartado Aéreo 127, Manizales, Colombia
Email: magomez@unal.edu.co

Received 25 November 2011; Accepted 23 February 2012

ABSTRACT

Design guidelines were applied for the production of methyl acetate in a pervaporation membrane reactor. The limits of operation were determined. The shift in equilibrium is evaluated by a simple model involving simultaneously chemical equilibrium and transport across the membrane. This analysis establishes possibilities and limitations of a pervaporation membrane reactor. The performance of a continuous stirred tank reactor with a pervaporation membrane (PV-CSTR) is analyzed. To achieve conversions higher than 90%, conditions must satisfy $D_a > 150$ and $0.01 < P_e < 100$. Increasing temperature has a negative effect on membrane reactor conversion. The effect of sweep is important at high-permeate pressures. Two design charts were created to illustrate dynamics between permeation rates, reaction rates, and selectivity with conversion. The three powerful tools proposed for the analysis of a pervaporation membrane reactor described the system in a systematic way.

Keywords: Pervaporation membrane reactor; Design methodology; Design charts; Methyl acetate

1. Introduction

Methyl acetate is produced by esterification and is used as a volatile low toxic solvent in glues, fast drying paints, nail polish removers, and as an intermediate in the manufacture of pharmaceutical products. Conventional methyl acetate process uses an excess of one of the reactants—e.g. methanol. This is due in part because esterification reactions are limited by equilibrium. Since the challenge in modern chemical processing is to lower energy cost, increase conversion, and minimize space, membrane reactor technologies appear as an attractive option. This technology synergistically intensifies reaction–separation into a single process unit by removing one or more products, thereby shifting the equilibrium conversion and purifying the reaction mixture in-situ. Despite these advantages, a systematic design methodology has not been developed for pervaporation membrane reactors (PVMR). Some design guides have been proposed in the literature. Hasanoglu and Dincer, after an interesting experimental study, modeled the esterification of ethyl acetate coupled with separation in a PVMR [1]; Lim et al. worked with ethyl acetate production comparing different configurations for the reactor [2]; and

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*Corresponding author.

International Scientific Conference on Pervaporation, Vapor Permeation and Membrane Distillation, 8–11 September 2011, Toruń, Poland

Ivanovic and Leiknes considered the design of a biofilm membrane bioreactor [3]. However, a simultaneous analysis of thermodynamics, separation, and reaction kinetics is necessary for an integrated design of esterification membrane reactors.

In this work, three powerful tools are proposed in order to describe the PVMR in a systematical way. It combines thermodynamic analysis, retentate phase diagrams, and design charts to facilitate the design of membrane reactors and the selection of better operating conditions (e.g. those that lead to the higher conversion). The proposed thermodynamic analysis is the first step for the systematic design. This tool indicates whether or not exists an advantage in the use of a membrane reactor, and establishes its possibilities and limitations. Various authors have proposed several assumptions in order to predict the shift on the thermodynamic equilibrium conversion due to the presence of a membrane. Partial pressures for the methyl acetate process at equilibrium on both sides of the membrane (retentate and permeate) were investigated by Itoh [4,5]. Constant concentration profiles obtained by mass balance and kinetics were studied by Mohan and Govind [6] and Abashar and Al-Rabiah [7] and the activities at equilibrium for diffusing compounds using mole balances were investigated by Rezai and Traa [8]. In this work, this last methodology has been used for the methyl acetate case. On the other hand, retentate phase diagrams help to define operating conditions that favor reactive process over transport process. They are similar to those used for the analysis of distillation, but modified in order to describe membrane reactors. This method has been proposed and discussed for mixtures of three components in the literature [9–13]. Here that method was adapted for the four components of the esterification reaction under study. Thus, it is possible to know how the composition in the permeate is related with that in the retentate. Finally, two design charts were defined to establish the relation between conversion and membrane selectivity using molar balances as a function of dimensionless numbers of Peclet (P_e) and Damköhler (D_a). All mathematical models were solved with MatLab®.

2. Systematic design methodology

2.1. Thermodynamic analysis

In the esterification of acetic acid with methyl alcohol, the conversion is limited to ca. 70% in conventional processes [14]. It is expected a shift in the equilibrium conversion by removing one or more products of the reaction. It has been proved that water can be selectively removed from this system by pervaporation [11]. Our work is based on the experimental behavior of the commercial membrane PERVAP 2210 (Sulzur Chemtech). This membrane is principally permeable to water but allows permeation of small amounts of methanol and methyl acetate. The equilibrium calculation in a conventional reactor involves the molar balance presented in Table 1, where conversion is denoted as X_1.

For a membrane reactor, the equilibrium shift calculation includes two molar balances: one for the reaction side (retentate) and the other for the permeate side [8]. A sweep gas (nitrogen in this case) is used in the permeate side in order to increase the flux through the membrane. Both balances are coupled via the permeated component activities across the membrane. The corresponding balances are presented in Table 2, where R is defined as the $N_{\mathrm{sweep}}/N_{\mathrm{Ao}}$ ratio and X_2, X_3, and X_4 as the transported amount of methanol, methyl acetate, and water, respectively, relative to the limit reagent.

Membrane reactor equilibrium is reached when chemical equilibrium and transport of the compounds through the membrane are satisfied. Eq. (1) must be solved for a conventional reactor, while Eqs. (1) and (2) must be solved simultaneously for a membrane reactor. They were solved by a Newton–Raphson method implemented in MatLab®.

$$K_{\mathrm{eq}} = \prod_{i=1}^{n} a_i^{\nu_i} \tag{1}$$

$$a_{i,\mathrm{perm}} = a_{i,\mathrm{ret}} \tag{2}$$

where i corresponds to the permeated compounds. The esterification reaction occurs in liquid phase, therefore activity is given by: $a_i = x_i\gamma_i$. At the permeate, the compounds are in gaseous phase and their activity can be calculated as: $a_i = y_i\varphi_i P/P_{\mathrm{o}}$. Equilibrium constant, K_{eq}, is evaluated from the experimental data given by Pöpken et al. [15].

2.2. Retentate phase diagrams

As the reaction–separation process advances simultaneously, the variation of retentate concentration can be described by retentate phase diagrams. From molar and flux balances across the membrane, Eqs. (3) and (4) are obtained as follows [12]:

$$\frac{\mathrm{d}x_i}{\mathrm{d}z^*} = \left(x_i - \frac{n_i}{n_{\mathrm{T}}}\right) + D_{\mathrm{a}}(\nu_i - \nu_{\mathrm{T}}x_i)\frac{n_{\mathrm{T,ref}}}{n_{\mathrm{T}}}\frac{k}{k_{\mathrm{ref}}}\Re \tag{3}$$

Table 1
Stoichiometric table for a conventional reactor

Compound	In	Change	Out	Molar fraction out
Acetic acid (*A*)	N_{Ao}	$-N_{Ao}X_1$	$N_{Ao}(1-X_1)$	$\frac{N_{Ao}(1-X_1)}{(N_{Ao}+N_{Bo})}$
Methanol (*B*)	N_{Bo}	$-N_{Ao}X_1$	$N_{Bo}-N_{Ao}X_1$	$\frac{N_{Bo}-N_{Ao}X_1}{(N_{Ao}+N_{Bo})}$
Methyl acetate	0	$N_{Ao}X_1$	$N_{Ao}X_1$	$\frac{N_{Ao}X_1}{(N_{Ao}+N_{Bo})}$
Water	0	$N_{Ao}X_1$	$N_{Ao}X_1$	$\frac{N_{Ao}X_1}{(N_{Ao}+N_{Bo})}$
Total	$N_{Ao}+N_{Bo}$	0	$N_{Ao}+N_{Bo}$	1

Table 2
Stoichiometric table with the mole balance for the esterification reaction of acetic acid with methanol in a PVMR with R representing the $N_{\text{Sweep gas}}/N_{Ao}$ ratio being N_{Ao} the molar flow of acetic acid entering the reactor. X_1 is defined as the amount of acetic acid converted in the esterification reaction relative to the amount of acetic acid fed and X_2, X_3, and X_4 are defined as the amount of methanol, methyl acetate, and water permeated through the membrane, respectively, relative to the amount of acetic acid fed

Side	Compound	In	Change	Out	Molar fraction out
Retentate	Acetic acid (*A*)	N_{Ao}	$-N_{Ao}X_1$	$N_{Ao}(1-X_1)$	$\frac{N_{Ao}(1-X_1)}{N_{Ao}(1-X_2-X_3-X_4)+N_{Bo}}$
	Methanol (*B*)	N_{Bo}	$-N_{Ao}(X_1+X_2)$	$N_{Bo}-N_{Ao}(X_1+X_2)$	$\frac{N_{Bo}-N_{Ao}(X_1+X_2)}{N_{Ao}(1-X_2-X_3-X_4)+N_{Bo}}$
	Methyl acetate	0	$N_{Ao}(X_1-X_3)$	$N_{Ao}(X_1-X_3)$	$\frac{N_{Ao}(X_1-X_3)}{N_{Ao}(1-X_2-X_3-X_4)+N_{Bo}}$
	Water	0	$N_{Ao}(X_1-X_4)$	$N_{Ao}(X_1-X_4)$	$\frac{N_{Ao}(X_1-X_4)}{N_{Ao}(1-X_2-X_3-X_4)+N_{Bo}}$
	Total	$N_{Ao}+N_{Bo}$	$-N_{Ao}(X_2+X_3+X_4)$	$N_{Ao}(1-X_2-X_3-X_4)+N_{Bo}$	1
Permeate	Sweep: N_2	$N_{Ao}R$	0	$N_{Ao}R$	$\frac{R}{R+X_2+X_3+X_4}$
	Methanol (*B*)	0	$N_{Ao}X_2$	$N_{Ao}X_2$	$\frac{X_2}{R+X_2+X_3+X_4}$
	Methyl acetate	0	$N_{Ao}X_3$	$N_{Ao}X_3$	$\frac{X_3}{R+X_2+X_3+X_4}$
	Water	0	$N_{Ao}X_4$	$N_{Ao}X_4$	$\frac{X_4}{R+X_2+X_3+X_4}$
	Total	$N_{Ao}R$	$N_{Ao}(X_2+X_3+X_4)$	$N_{Ao}(R+X_2+X_3+X_4)$	1
	Overall balance	$N_{Ao}(R+1)+N_{Bo}$	0	$N_{Ao}(R+1)+N_{Bo}$	–

$$n_i = \dot{p}_i(a_{i,\text{perm}} - a_{i,\text{ret}}) \tag{4}$$

In this case, the reaction law for the methyl acetate production, using Amberlite-15 as catalyst, is described by Eqs. (5) and (6) as defined experimentally elsewhere [14,15]:

$$\Re = \frac{\left(a'_{\text{HOAc}}a'_{\text{MeOH}} - \frac{a'_{\text{MeOAc}}a'_{\text{H}_2\text{O}}}{K_{\text{eq}}}\right)}{a'_{\text{HOAc}} + a'_{\text{MeOH}} + a'_{\text{MeOAc}} + a'_{\text{H}_2\text{O}}} \tag{5}$$

$$k = 8,497 \times 10^9 \exp\left(\frac{-60,470}{RT}\right) \tag{6}$$

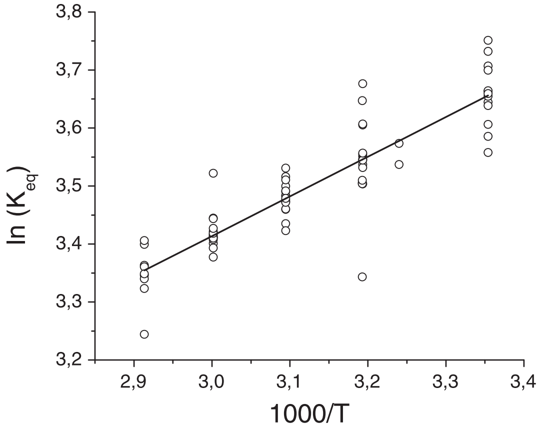

Fig. 1. Equilibrium constant calculated from experimental data [15,16].

According to experimental data [14], the permeabilities of components through the commercial membrane PERVAP 2210, in mol/(m^2 s), are described by Eqs. (7)–(9):

$$\dot{p}_{H_2O} = 2.01 \times 10^1 \exp\left(\frac{-3,173}{T}\right) \tag{7}$$

$$\dot{p}_{\mathrm{MeOH}} = 2.92 \times 10^5 \exp\left(\frac{-6,756}{T}\right) \tag{8}$$

$$\dot{p}_{\mathrm{MeOAc}} = 7.88 \times 10^7 \exp\left(\frac{-9,385}{T}\right) \tag{9}$$

The acetic acid does not permeate. The water permeability becomes 4–5 times higher than that for methanol and 57 times higher than that for methyl acetate at 323 K, a common temperature used for the esterification reaction under study.

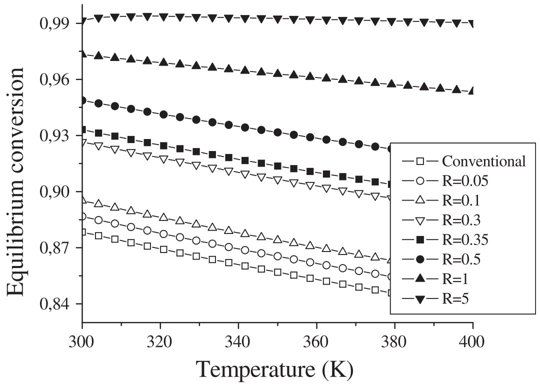

Fig. 2. Equilibrium conversion shift in a membrane reactor as a function of temperature at several sweep ratios. $\theta_B = 1$ and $p = 1$ atm.

2.3. Mathematical model for membrane reactors

In this work, a continuous stirred tank reactor with a pervaporation membrane (PV-CSTR) is analyzed. It can be represented by Eq. (10).

$$\dot{F}_{io} - \dot{F}_i + v_i D_{\mathrm{a}} \Re - \frac{D_{\mathrm{a}} \delta \dot{p}_i a_{i,\mathrm{ret}}}{\dot{p}_{H_2O}} = 0 \tag{10}$$

3. Results and discussion

3.1. Thermodynamic analysis

Equilibrium constant for the reaction was calculated from experimental data [15,16]. Its value decreases, while temperature increases (Fig. 1).

The reaction equilibrium constant can be described as a function of temperature as presented in Eq. (11):

$$K_{\mathrm{eq}} = 3.90126 \exp\left(-\frac{5,688.3}{T}\right) \tag{11}$$

Membrane reactor analysis was developed with several sweep gas relations and stoichiometric feed composition ($N_{\mathrm{Ao}} = N_{\mathrm{Bo}}$). The results are presented in Fig. 2. Potential improvement in conversion as a result of the use of a membrane is evident. In fact, there is a direct relation between high conversions and high sweep ratio (R).

3.2. Retentate phase diagrams

Retentate phase diagrams were evaluated at 323 K and several Damköhler numbers. They are presented in Fig. 3. Their values include the main characteristics of both the reaction and separation processes: when no chemical reaction occurs, $D_{\mathrm{a}} = 0$; when $D_{\mathrm{a}} = 1$, the reaction rate is comparable to the permeation rate; and in the absence of a membrane: $D_{\mathrm{a}} = \infty$. The high water permeability generates a decrease of this component content in the retentate, so lines in the tetrahedron move from its pure composition (instable node) direction to the compounds whose permeability is lower: methyl acetate (stable node) and acetic acid. The retentate curves are not directed to methanol in which permeability can be considered as intermediate. This behavior is consistent with the literature [11]. It is also observed that the curves are closer to the desired product (methyl acetate) when Damköhler number (D_{a}) is high. This is due to a higher reaction rate that allows a fast decrease of water at the retentate side reaching higher concentrations of the desired product.

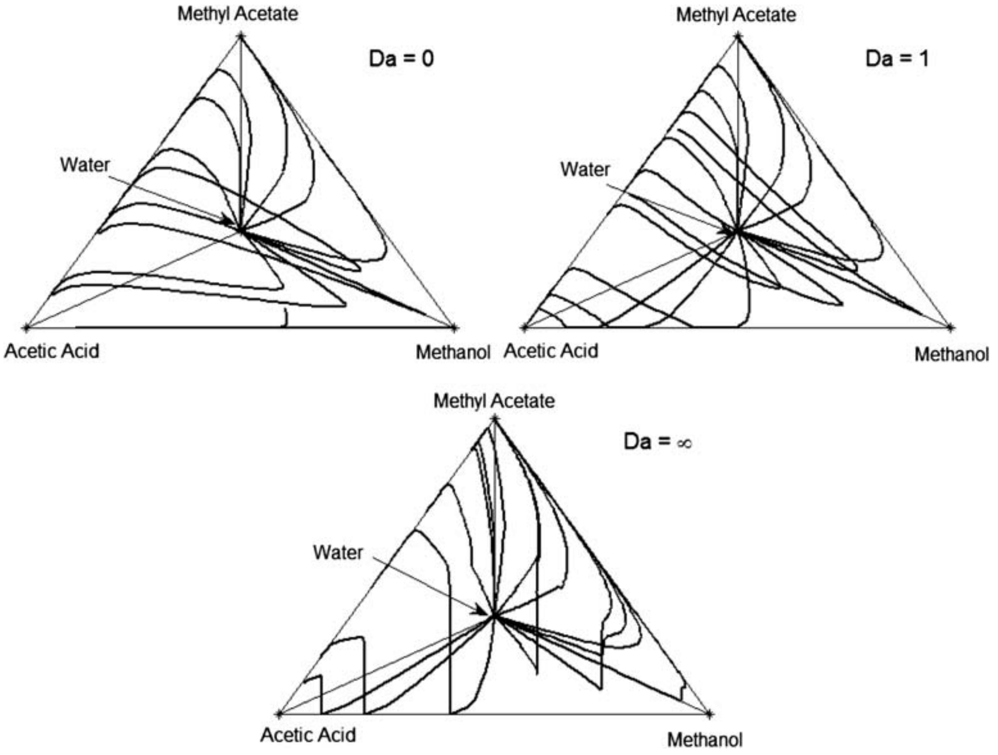

Fig. 3. Retentate phase diagrams for the acetic acid esterification with methanol at different driven forces. When no chemical reaction occurs: $D_a = 0$; when reaction rate is comparable to the permeation rate $D_a = 1$; when no permeation exists: $D_a = \infty$. $T = 323$ K; $R = 5$ (chosen from results presented in Fig. 2); and $\theta_B = 1$; $P_{\text{Permeate}} = 10$ mbar.

3.3. Reactor configuration

Membrane reactors conversion was analyzed for several Damköhler and Peclet numbers. Results are presented in Fig. 4. The higher the Damköhler number is, the higher the conversion will be. It is interesting to note that there is an optimum value of δ. However, it depends on Damköhler number. For example, when $D_a = 500$, the conversion reach values as high as 96% for the PV-CSTR, while, for a conventional reactor it only reaches 87%.

Fig. 5, obtained from the solution of the PV-CSTR model, illustrates one of the proposed design chart for the methyl acetate esterification process. It includes the contour of exit conversion of the PV-CSTR as a function of P_e and D_a, calculated at 323 K. Five distinctive sections appeared in the design space. In Section A, where D_a has low values, conversion is kinetically controlled and is independent of P_e. In Section B, conversion depends of both P_e and D_a. Thus, kinetics and selective permeation highly influence the performance of the PV-CSTR. When P_e has low values, Section C, conversion is controlled by selective permeation and independent of D_a. Conversion in Section D (shadow area) has the highest values, where effectively large values of D_a (>150) and intermediate values of P_e ($0.01 < P_e < 100$) prevail. Finally, in Section E, conversion seems to be kinetically controlled but dependent of D_a (since conversion increases with the increase of D_a).

The relation between conversion, membrane selectivity, and Peclet number, for $D_a = 200$, can be observed in Fig. 6. The increase in P_e, keeping constant the

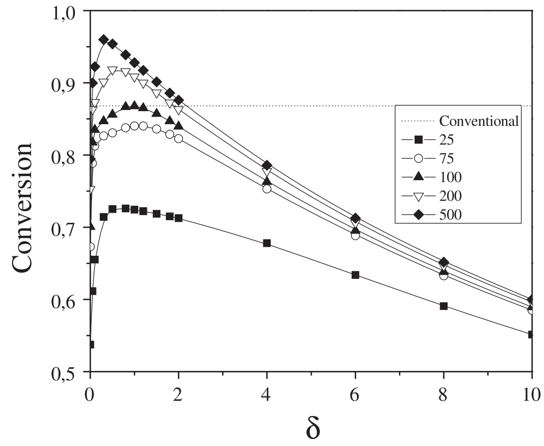

Fig. 4. Comparison of a PV-CSTR and a conventional reactor performances for the methyl acetate esterification process. $T = 323$ K, $\theta_B = 1$, and $R = 5$ (chosen from results presented in Fig. 2).

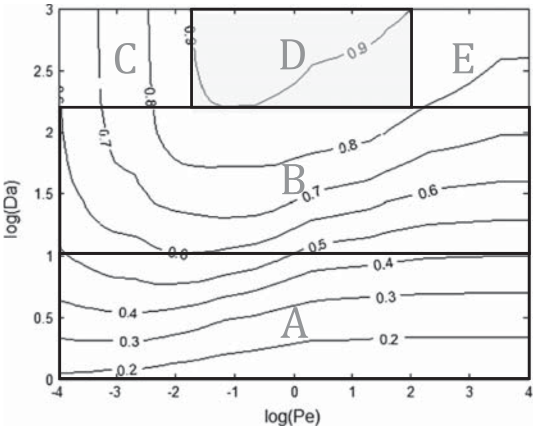

Fig. 5. Design guideline for a PV-CSTR. Shadow zone represents the best conditions for reactor operation. Simulation conditions: T = 323 K; $R = 5$ (chosen from results presented in Fig. 2); $\theta_B = 1$; and $P_{\text{Permeate}} = 10$ mbar.

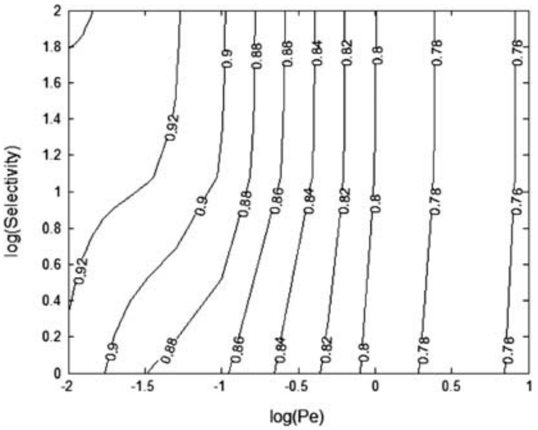

Fig. 6. Design guideline for a PV-CSTR in function of selectivity. Simulation conditions: T = 323 K; $R = 5$ (chosen from results presented in Fig. 2); $\theta_B = 1$; and $P_{\text{Permeate}} = 10$ mbar.

membrane selectivity, results in lower conversions. Thus, a change in P_e must include a change on selectivity if preserving conversion is the objective. Low P_e numbers, $0.01 < P_e < 100$, (high permeation rates), are recommended because in this way higher conversions are obtained.

4. Conclusions

A systematic methodology for the design of membrane reactors for the production of methyl acetate was proposed. Advantages for this kind of reactive system configuration and process parameters could be defined in advance when the proposed systematic methodology is used. For the methyl acetate case, equilibrium conversion decreases as reaction temperature increases. A continuous stirred tank reactor with a pervaporation membrane (PV-CSTR) was analyzed. Compared with the conventional process, higher conversions can be obtained when a pervaporation membrane reactor is used. Conversions higher than 90% are achieved for the PV-CSTR when $D_a > 150$ and $0.01 < P_e < 100$. The effect of sweep is important at high-permeate pressures.

Symbols

A — area
a_i — activity of i component
a'_i — modified activity of i component (= $K_i a_i / MM_i$))
D_a — Damköhler number (=$kW/F_{\text{ref,o}}$)
F_i — dimensionless molar flow of i component at reactive side (=$F_i/F_{\text{ref,o}}$)
K — reaction constant
K_{eq} — equilibrium constant
N_{io} — initial flow of i
n_i — molar flow of i component through the membrane
n_T — total molar flow through the membrane
P — pressure
P_o — reference pressure
p_i — permeability of i component
P_e — Peclet number $(= F_{\text{ref},o}/(AP_{H_2O}))$
R — relation between sweep gas and acetic acid flow (=$N_{\text{sweep}}/N_{\text{Ao}}$)

$\Re$ — reaction rate law
R_g — Universal gas constant
T — temperature (K)
W — catalyst weight
X_1 — acetic acid conversion
$X_{2,3,4}$ — molar fraction of permeants through the membrane: (2) methanol, (3) methyl acetate, and (4) water
x_i, y_i — molar fraction of i component
z^* — dimensionless axial coordinate

Greek symbols

δ — rate ratio $(= (AP_{H_2O})/kW))$
Φ_i — fugacity coefficient of the i component
γ_i — activity coefficient of the i component
v_i — stoichiometric coefficient of the i component
v_T — total mole change in the reaction

Subscripts

H_2O — water
HOAc — acetic acid
MeOAc — methyl acetate
MeOH — methanol
perm — permeate
ref — reference state
ret — retentate

Acknowledgment

The authors thank to the Dirección de Investigaciones of the Universidad Nacional de Colombia, Sede Manizales, for financial support of this research.

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