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Design directions for ethyl lactate synthesis in a pervaporation membrane reactor

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ABSTRACT

Pervaporation membrane reactors (PVMR) can improve conversion of equilibrium reactions like esterification. However, it is important to select proper operating conditions for reaching a high conversion. Here, a systematic approach for studying the performance of a PVMR is presented. Three different tools, based on thermodynamic analysis, residue curves and design charts, were used to analyze the maximum conversion, the axial component concentration profile and the effect of selectivity and permeance on conversion in a PVMR for the esterification of lactic acid with ethanol to produce ethyl lactate. An operating window has been found and high conversions can be reached for the range $-5 < \log(P_e) < 4$ and $\log(D_{aR}) > 3$. However, there is a strong dependence of selectivity on the operating window. Conversion increases with temperature in a PVMR; however, the optimal operating temperature differs from where the highest conversion is reached.

Keywords: Pervaporation membrane reactor; Design directions; Ethyl lactate

1. Introduction

Ethyl lactate, also known as lactic acid ethyl ester, is a monobasic ester commonly used as a solvent. This compound is considered biodegradable and can be used as a water rinsible degreaser. Its importance is associated with the fact that toxic industrial solvents could be replaced by environmentally friendly solvents made with ethyl lactate. It is formed by esterification of lactic acid with ethanol. In general, esterification reactions usually suffer from chemical equilibrium limitations. In conventional processes, those reactions are accomplished on different reaction and separation unit operations, and recirculation of the unconverted reactants to the reactor is performed in order to improve the conversion. In recent years, multifunctional reactors have attracted growing interest in both industrial and academic sectors. Pervaporation membrane reactors (PVMR) appear as an attractive alternative [1,2]. They combine chemical reaction and separation by pervaporation in a single unit. In a PVMR, the driving force for mass transfer across the membrane is the difference of component partial pressure between both phases (retentate and permeate).

Three PVMR configurations have been studied for ethyl lactate synthesis: (i) batch reactor, where the esterification reaction takes place, followed by a

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membrane for water removal, and recycle of the retentate to the reactor [3,4], (ii) membrane inside a batch reactor [5], and (iii) a continuous integrated membrane reactor [6]. However, little has been reported about methodologies for the systematic analysis and design of a PVMR.

This work presents three different tools to analyze the maximum conversion, the axial component concentration profile, and the effect of selectivity and permeance on conversion in a continuous PVMR for the esterification of lactic acid with ethanol to produce ethyl lactate. The used tools are a thermodynamic analysis [7], residue curves [8], and design charts [9], respectively. An operating window in order to obtain high conversions is identified using the proposed tools.

2. Thermodynamic analysis

By using a PVMR is possible to shift the product concentration at equilibrium to higher values. Concentration of reactants and products change along the PVMR until an equilibrium is reached, where there is no reaction and permeation through the membrane. These concentrations at equilibrium are calculated by solving simultaneously the chemical reaction equilibrium (Eq. (1)) and a null driving force equation (Eq. (2)) for every compound across the membrane. Consequently, mass balances are required for the retentate side, where the reaction takes place, and the permeate side of the membrane. Such mole balances are presented in Table 1. Mole balances on the permeate side take into account sweep of an inert gas, which is fed only to the permeate side. This sweep gas reduces the concentration and partial pressure of every compound in the permeate.

Concentrations of every compound at equilibrium can be calculated by solving Eq. (1), for the equilibrium constant, and Eq. (2) for the null driving force through the membrane [10]), in this case, the three compounds that permeate the membrane (ethanol, ethyl lactate and water) with the mole fractions are presented in the last column of Table 1.

$$K_{\mathrm{eq}} = \prod_{i=1}^{\mathrm{NC}} a_i^{v_i} \tag{1}$$

$$x_i \gamma_i P_i^{\mathrm{sat}} = y_i \varphi_i P_{\mathrm{p}} \tag{2}$$

In Eq. (2), the driving force is the difference in partial pressure between retentate and permeate of each component. Thus, for the case under study, a total of 4 equations were solved by a multivariable Newton–Raphson method using MatLab®. Activity and fugacity coefficients were calculated using UNIFAC [11] and Peng Robinson equation of state [12], respectively. The equilibrium constant for the esterification of lactic acid with ethanol was fitted using experimental data, as function of temperature [13], to obtain:

$$K_{\mathrm{eq}} = 19.35 \exp\left(-\frac{515.13}{T}\right) \tag{3}$$

Table 1
Stoichiometric table with the mole balance for esterification of lactic acid with ethanol in a PVMR

Side	Substance	In	Change	Out	Molar fraction out
Reaction	Lactic acid	$\dot{n}_{\mathrm{LA},0}$	$-X_1\dot{n}_{\mathrm{LA},0}$	$(1-X_1)\dot{n}_{\mathrm{LA},0}$	$\frac{(1-X_1)}{(1+\theta_{\mathrm{Eth}}-\Phi_2-\Phi_3-\Phi_4)}$
	Ethanol	$\theta_{\mathrm{Eth}}\dot{n}_{\mathrm{LA},0}$	$(-X_1-\Phi_2)\dot{n}_{\mathrm{LA},0}$	$(\theta_{\mathrm{Eth}}-X_1-\Phi_2)\dot{n}_{\mathrm{LA},0}$	$\frac{(\theta_{\mathrm{Eth}}-X_1-\Phi_2)}{(1+\theta_{\mathrm{Eth}}-\Phi_2-\Phi_3-\Phi_4)}$
	Ethyl lactate	0	$(X_1-\Phi_3)\dot{n}_{\mathrm{LA},0}$	$(X_1-\Phi_3)\dot{n}_{\mathrm{LA},0}$	$\frac{(X_1-\Phi_3)}{(1+\theta_{\mathrm{Eth}}-\Phi_2-\Phi_3-\Phi_4)}$
	Water	0	$(X_1-\Phi_4)\dot{n}_{\mathrm{LA},0}$	$(X_1-\Phi_4)\dot{n}_{\mathrm{LA},0}$	$\frac{(X_1-\Phi_4)}{(1+\theta_{\mathrm{Eth}}-\Phi_2-\Phi_3-\Phi_4)}$
	Total	$(1+\theta_{\mathrm{Eth}})\dot{n}_{\mathrm{LA},0}$	$(-\Phi_2-\Phi_3-\Phi_4)\dot{n}_{\mathrm{LA},0}$	$(1+\theta_{\mathrm{Eth}}-\Phi_2-\Phi_3-\Phi_4)\dot{n}_{\mathrm{LA},0}$	1
Permeate	Sweep gas	$R_{\mathrm{S}}\dot{n}_{\mathrm{LA},0}$	0	$R_{\mathrm{S}}\dot{n}_{\mathrm{LA},0}$	$\frac{R_{\mathrm{S}}}{(R_{\mathrm{s}}+\Phi_2+\Phi_3+\Phi_4)}$
	Ethanol	0	$\Phi_2\dot{n}_{\mathrm{LA},0}$	$\Phi_2\dot{n}_{\mathrm{LA},0}$	$\frac{\Phi_2}{(R_{\mathrm{s}}+\Phi_2+\Phi_3+\Phi_4)}$
	Ethyl lactate	0	$\Phi_3\dot{n}_{\mathrm{LA},0}$	$\Phi_3\dot{n}_{\mathrm{LA},0}$	$\frac{\Phi_3}{(R_{\mathrm{s}}+\Phi_2+\Phi_3+\Phi_4)}$
	Water	0	$\Phi_4\dot{n}_{\mathrm{LA},0}$	$\Phi_4\dot{n}_{\mathrm{LA},0}$	$\frac{\Phi_4}{(R_{\mathrm{s}}+\Phi_2+\Phi_3+\Phi_4)}$
	Total	$R_{\mathrm{S}}\dot{n}_{\mathrm{LA},0}$	$(\Phi_2+\Phi_3+\Phi_4)\dot{n}_{\mathrm{LA},0}$	$(R_{\mathrm{s}}+\Phi_2+\Phi_3+\Phi_4)\dot{n}_{\mathrm{LA},0}$	1
Overall balance		$(1+\theta_{\mathrm{Eth}}+R_{\mathrm{s}})\dot{n}_{\mathrm{LA},0}$	0	$(1+\theta_{\mathrm{Eth}}+R_{\mathrm{s}})\dot{n}_{\mathrm{LA},0}$	–

In Fig. 1, ethyl lactate conversion is shown as function of temperature. For a conventional tubular reactor (TR), conversion increases with temperature, due to the endothermic behavior of this reaction. However, in a PVMR, conversions are higher than that in a TR and the ratio between conversion in a PVMR and that in a TR increases with temperature. Due to the higher amount of water and ethyl lactate transported through the membrane at higher temperatures, conversion of lactic acid increases. The driving force for transport of water and ethyl lactate not only improves at higher temperatures, but also improves at higher sweep gas flows and lower permeate pressures. By introducing a sweep gas, molar concentrations of each component in the permeate side decreases and, consequently, its driving force of mass transport through the membrane rises. Thus, acid lactic conversion increases with temperature, higher sweep gas ratios and lower permeate pressures (results not shown).

It will be desirable to operate a PVMR where conversion is maximum, which is reached at high temperatures. However, Fig. 1 shows that at high temperatures and conversions, lactic acid concentrations are higher, while ethyl lactate concentrations are lower. Thus, at high temperatures, the high concentration of lactic acid will increase the separation costs of the mixture downstream the PVMR. There is a temperature where ethyl lactate concentration is maximum (335 K) and where separation costs of the retentate stream could be reduced. However, it will be necessary to perform an economical evaluation in order to identify an optimal operating temperature for the PVMR.

On the other hand, Fig. 2 shows the molar fractions calculated for the permeate stream at several temperatures that correspond to those evaluated for the retentate stream showed in Fig. 1. Also, the permeated total molar flow per mole fed (lactic acid and ethanol) to the PVMR is shown. Water molar fractions are relatively constant and change approximately between 0.45 and 0.50, while ethanol molar fraction decreases with temperature between 0.1 and 0.4. Ethyl lactate molar fraction is higher at higher temperatures and changes between 0.1 and 0.4, approximately. Considering that water concentration is approximately constant, separation costs downstream the PVMR could be low if the PVMR is operated at low or high temperature where ethyl lactate or ethanol molar fractions are low, respectively. Also, keeping in mind the previous analysis of Fig. 1, that takes into account the retentate molar fraction, it is important to develop an economical evaluation of the separation costs downstream the PVMR to identify an optimal operating temperature for the PVMR. This optimal temperature will not necessarily correspond to that of the maximum conversion.

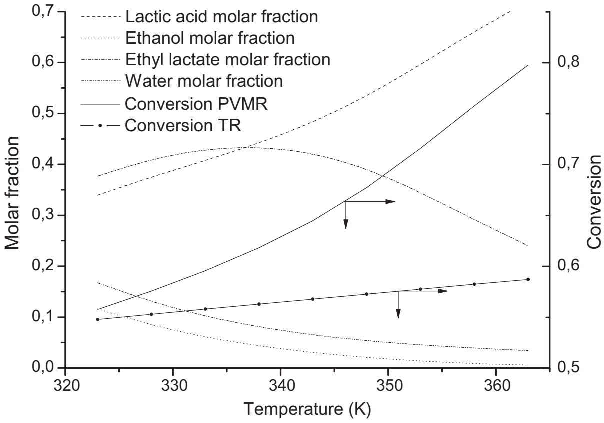

Fig. 1. Conversion of lactic acid and retentate molar fractions at equilibrium in a PVMR, as function of temperature. $\theta_{\mathrm{Eth}} = 1$, $P_{\mathrm{P}} = 0.1$ bar, and without sweep.

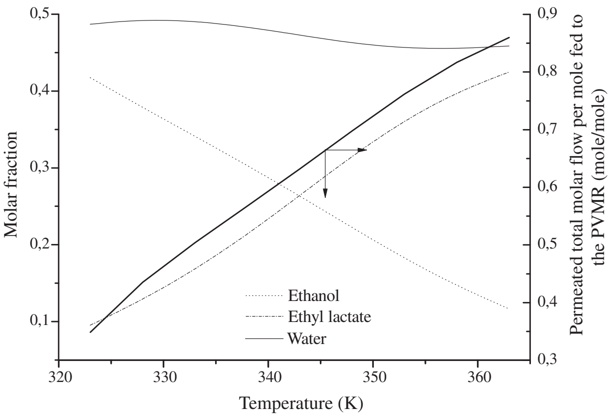

Fig. 2. Ethanol, ethyl lactate, and water molar fraction in the permeate at equilibrium in a PVMR and the permeated total molar flow per mole fed (lactic acid and ethanol) to the PVMR as function temperature. $\theta_{\mathrm{Eth}} = 1$, $P_{\mathrm{P}} = 0.1$ bar, and without sweep.

The permeated total molar flow increases with temperature, as shown in Fig. 2, so not only at a high temperature there is a higher ethyl lactate concentration, but also a higher total amount of it. At equilibrium and at high temperatures, the ester concentration in the permeate side is even higher than that in the retentate. Thus, if a more selective membrane is used for the PVMR, the ethyl lactate concentration and its molar flow will be reduced in the permeate side, while it is increased in the retentate side, reducing treatment costs downstream.

3. Residue curves for a PVMR

In general, residue curves describe the change in composition of the retentate as function of the length of the reactor in continuous processes or as a function of time for batch processes [8]. The PVMR considered in this study essentially consists of a shell and tube configuration, with catalyst pellets (Ambertlyst 15—wet ion exchange resin) located inside the membrane tube as presented in Fig. 3.

The experimental device for ethyl lactate synthesis consists of a commercial hydrophilic membrane supplied by Pervatech BV (the Netherlands) [13]. That membrane has a modified silica (methyl silica) selective layer coated onto gamma alumina. The separation layer is applied inside of an asymmetric ceramic tube that has an outer diameter of 10 mm, an inner diameter of 7 mm, and a length of 50 cm. It has an effective membrane area per tube of about 110 cm^2 (five tubular membranes were used, giving an effective area of about 550 cm^2) [13]. The mathematical model developed to describe the behavior of the PVMR is based on isothermal, plug flow assumptions with negligible pressure drop. Neither concentration nor temperature polarization effects where considered. Although, a specific configuration was used as a base case, the results presented below can be applied for other types of membrane reactors. The driving force for permeation is the pressure gradient created either by a pressure difference between the feed and the permeate sides or by the use of a sweep gas on the permeate side (Fig. 3). Thus, it is possible to define the following balances in the retentate:

$$\frac{\mathrm{d}(Fx_i)}{\mathrm{d}z} = -J_i\frac{A_\mathrm{m}}{L} + A_\mathrm{t}\varepsilon_\mathrm{cat}v_i k\Re \tag{4}$$

$$\frac{\mathrm{d}(F)}{\mathrm{d}z} = -J_\mathrm{T}\frac{A_\mathrm{m}}{L} + A_\mathrm{t}\varepsilon_\mathrm{cat}v_T k\Re \tag{5}$$

By applying the chain rule on Eq. (4), substituting Eq. (5) and rearranging terms, is possible to obtain for each component:

$$\frac{\mathrm{d}(x_i)}{\mathrm{d}z^*} = \left(x_i - \frac{J_i}{J_T}\right) + D_\mathrm{am}(v_i - v_\mathrm{T}x_i)\frac{J_\mathrm{T,ref}}{J_T}\Re \tag{6a}$$

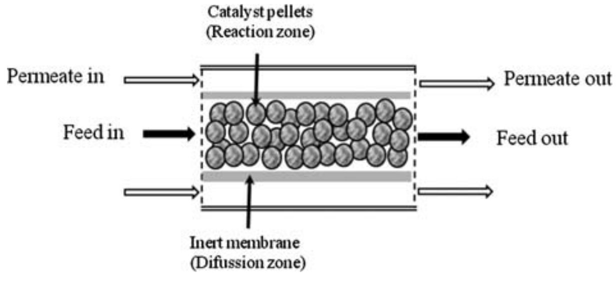

Fig. 3. Schematic diagram of a pervaporation membrane reactor with catalyst in the feed side (retentate).

where the following dimensionless parameters are introduced:

$$z^* = \frac{J_\mathrm{T}A_\mathrm{m}}{LF}\mathrm{d}z \tag{6b}$$

$$D_\mathrm{am} = \frac{A_\mathrm{t}\varepsilon_\mathrm{cat}kL}{J_\mathrm{T,ref}A_\mathrm{m}}\mathrm{d}z \tag{6c}$$

where D_am is the Damköhler number based on membrane flux. The component and total fluxes through the membrane can be evaluated by:

$$J_i = p_i(x_i\gamma_i P_i^\mathrm{sat} - y_i P_\mathrm{p}) \tag{7a}$$

$$J_\mathrm{T} = \sum J_i \tag{7b}$$

The permeance of each component (p_i), mol/(m^2 s Pa), as function of composition and temperature is [6]:

$$p_\mathrm{Eth} = 2.36 \times 10^{-12}\exp\left(\frac{-22.6 \times 10^3}{RT}\right) \tag{8a}$$

$$p_\mathrm{LA} = 0 \tag{8b}$$

$$p_\mathrm{EL} = 1.99 \times 10^{-09}\exp\left(\frac{-10.42 \times 10^3}{RT}\right) \tag{8c}$$

$$p_\mathrm{W} = 3.278 \times 10^{-11}\exp(18.64x_\mathrm{w}) \times \exp\left(-\frac{5037x_\mathrm{w} - 32,326}{RT}\right) \tag{8d}$$

In Eqs. (4), (5) and (6a), the dimensionless reaction rate $\Re$ is:

$$\Re = \frac{\left(a_\mathrm{Eth}a_\mathrm{LA} - \dfrac{a_\mathrm{EL}a_\mathrm{W}}{K_\mathrm{eq}}\right)}{(1 + K_\mathrm{Eth}a_\mathrm{Eth} + K_\mathrm{W}a_\mathrm{W})^2} \tag{9}$$

Table 2 presents the reaction rate constant (k) and the adsorption and equilibrium constants of Eq. (9) used in this study [13].

Residue curves are obtained by the integration of Eq. (6) with the fluxes and dimensionless reaction rate given by Eqs. (7) and (9), respectively. The residue curve maps obtained for esterification of lactic acid with ethanol are presented in Fig. 4 for six values of D_am. The value of D_am is high for low levels of permeation through the membrane; the opposite occurs for very high permeation. Thus, two limits can be identi-

Table 2
Kinetic parameters for the ethyl lactate synthesis [13]

Temperature (K)	k mol/(g min)	K_{W}	K_{Eth}	K_{eq}
293.15	0.035	15.82	4.16	3.34
323.15	0.225	15.77	3.71	3.93

fied: (i) for very large D_{am}, reaction proceeds without any component removal by the membrane and concentration of every compound evolves like in a conventional reactor, the maximum molar fraction of ethyl lactate is around 0.56, and (ii) when $D_{\mathrm{am}} = 0$, a maximum molar fraction of ethyl lactate can be achieved (ca. 0.79), which is 41% higher than that in a conventional esterification reactor. This molar fraction corresponds to the maximum ethyl lactate concentration that can be achieved in a PVMR at 323.15 K. Also, residue curves start on the component with the highest permeance, which is water, move to the component of intermediate permeance, which are ethyl lactate or ethanol depending on composition, and end on the component with the lowest permeance, being lactic acid. Pure water and lactic acid appear as unstable and stable nodes, respectively. Pure ethanol or ethyl lactate could be considered as saddle points. For the range $0.01 < D_{\mathrm{am}} < 1$, the ethyl lactate concentration is high and water transport across the membrane is higher than the water production. However, a sudden change in ethyl lactate concentration is detected when kinetics and transport driving forces are compared. Then, when the transport across the membrane becomes the determining step, the reactive system behavior appears to be like that of a conventional tubular reactor. No changes are detected for $D_{\mathrm{am}} > 10$.

4. Analysis of the PVMR performance in terms of permeance and selectivity

Permeance is the tendency of a given component to move across the membrane matrix, a high value of permeance produces a high rate of mass transfer. On the other hand, the selectivity is the tendency of a given component to be transported through the membrane more easily than other component that is taken as a reference. Eq. (4) can be easily reorganized in a dimensionless form in order to include permeance and selectivity to obtain the following [9].

For the shell side (retentate):

$$\frac{\mathrm{d}Y_i^o}{\mathrm{d}\xi} = -\alpha_i \sqrt{\frac{M_i}{M_{\mathrm{W}}}} \left(\frac{Y_i^o}{\sum Y_i^o} \gamma_i \frac{p_i^{\mathrm{sat}}}{p_r^o} - \frac{Y_i^I}{\sum Y_i^I} r_{\mathrm{p}} \right) \frac{1}{P_{\mathrm{e}}} + v_i \Re D_{\mathrm{aR}} \tag{10}$$

For the tubes side (permeate):

$$\frac{\mathrm{d}Y_i^I}{\mathrm{d}\xi} = \alpha_i \sqrt{\frac{M_i}{M_{\mathrm{W}}}} \left(\frac{Y_i^o}{\sum Y_i^o} \gamma_i \frac{p_i^{\mathrm{sat}}}{p_{\mathrm{r}}^o} - \frac{Y_i^I}{\sum Y_i^I} r_{\mathrm{p}} \right) \frac{1}{P_{\mathrm{e}}} \tag{11}$$

where the dimensionless numbers P_{e} and D_{aR} are defined as follows:

$$P_{\mathrm{e}} = \frac{F_{\mathrm{LA,o}}}{2\pi R_i N_{\mathrm{T}} L p_{\mathrm{W}}} \tag{12}$$

$$D_{\mathrm{aR}} = \frac{A_{\mathrm{t}} \varepsilon_{\mathrm{cat}} k_{\mathrm{ref}} L}{F_{\mathrm{LA,o}}} \tag{13}$$

In Damköhler number D_{aR}, Eq. (13) is based on the lactic acid feed flow to the PVMR, while in D_{am}, Eq. (6c) is based on the total flux through the membrane. $\Re$ was already defined in Eq. (9) and the selectivity parameter, α_i, is defined according to the Graham law as follows:

$$\alpha_i = \frac{p_i}{p_{\mathrm{W}}} \sqrt{\frac{M_{\mathrm{W}}}{M_i}} \tag{14}$$

If lactic acid is the limit reactant, conversion in the PVMR can be calculated as:

$$X = 1 - \frac{(Y_{\mathrm{LA}}^{\mathrm{I}} + Y_{\mathrm{LA}}^{\mathrm{o}})}{(Y_{\mathrm{LA,o}}^{\mathrm{I}} + Y_{\mathrm{LA,o}}^{\mathrm{I}})} \tag{15}$$

A design chart can be generated by integrating Eq. (10), for a constant value of conversion (Eq. (15)), as function of D_{aR} and P_{e} (Fig. 5).

Three distinctive sections can be identified in the design chart of Fig. 5. In section A, at low values of D_{aR} the reaction is slow and the conversion is dominated by the kinetics, the permeation rate through the membrane does not significantly affect the conversion value. In section B, conversion shows very little changes with D_{aR} and P_{e}. In section C, for larger values of D_{aR} the reaction rate is high and the selective permeation of the products through the membrane becomes important (low values of P_{e}) shifting the equilibrium concentration to higher conversions. The size of section C depends on membrane selectivity (not presented here) increasing lactic acid conversion for a given D_{aR} and P_{e} at higher selectivities. High conversions can be reached for log (P_{e}) between −5 and 4 and log (D_{aR}) > 3 for a selectivity of 1.

Fig. 6 presents the PVMR conversion as function of P_{e} number and membrane selectivity (ethanol/water) for a fixed $D_{\mathrm{aR}} = 10$. High conversions can be

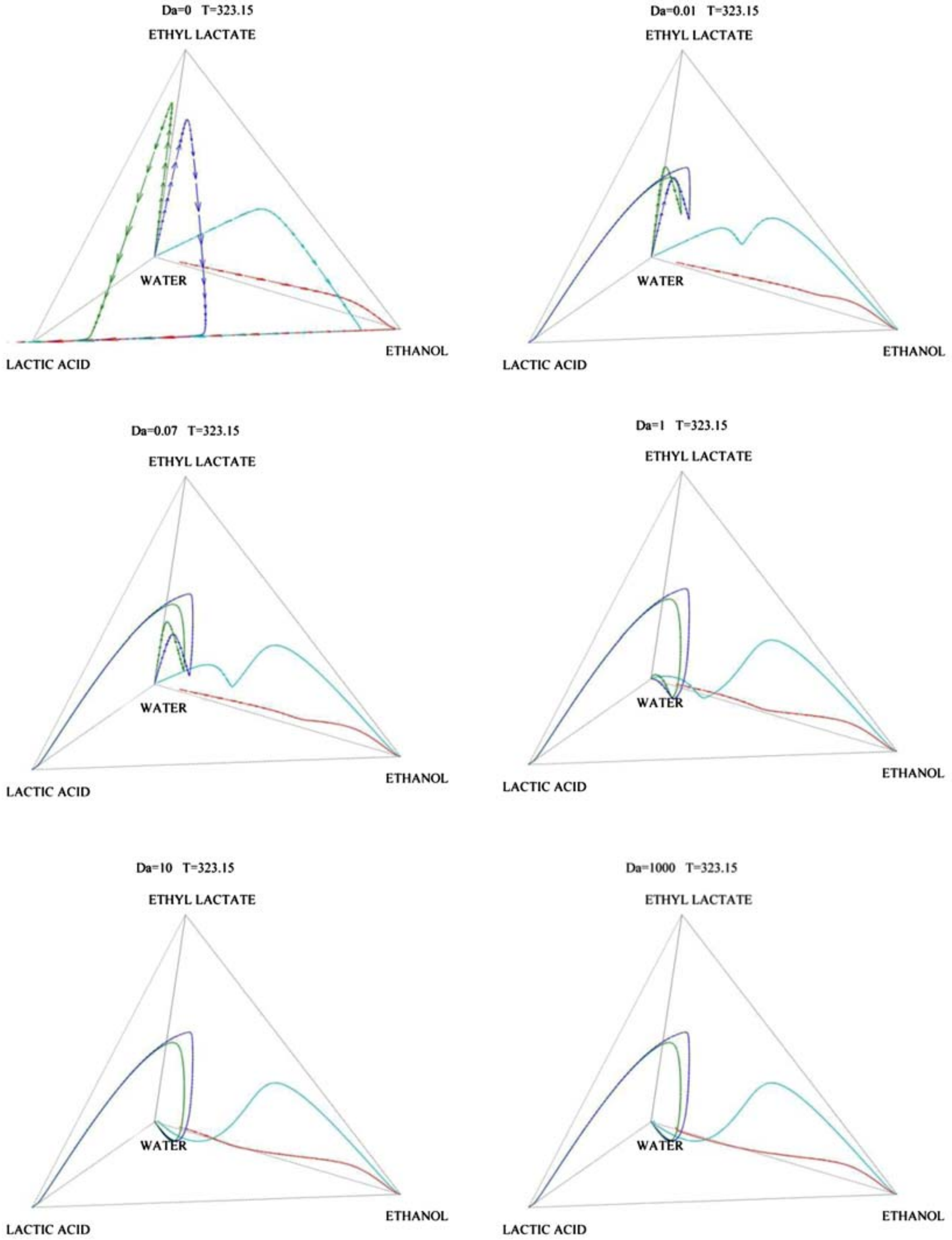

Fig. 4. Residue curves for lactic acid esterification with ethanol at three values of D_{am}. $T = 323.15$, $P_{\mathrm{r}} = 1$ atm, and $r_{\mathrm{p}} = 0$.

reached at low values of P_{e}. On the other hand, at high values of P_{e}, the lower residence time in the reactor causes a decrease in the exit conversion. For a specific selectivity, there are two values of P_{e} that can attain the same conversion. At a low P_{e}, water permeation becomes important shifting conversion to higher values. While for a higher P_{e}, the ethanol permeance decreases in order to keep a specific selectivity, thus the ethanol concentration in the retentate remains high increasing conversion.

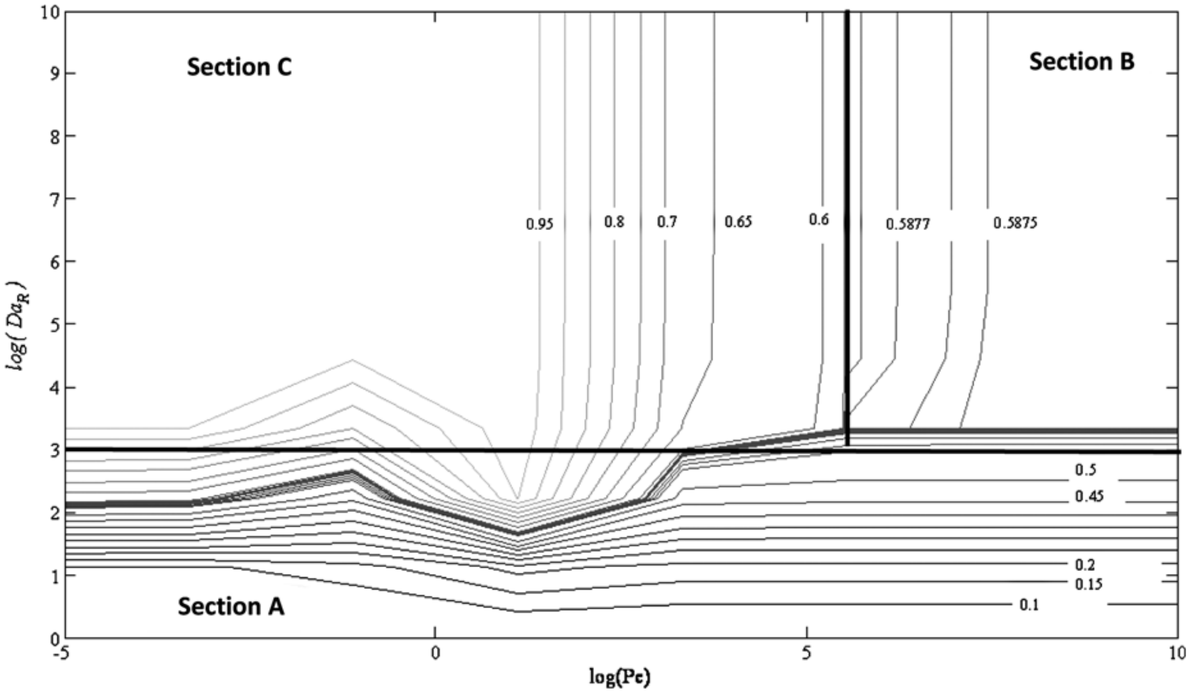

Fig. 5. Isoconversion lines of lactic acid as function of D_{aR} and P_{e} for an isothermal PVMR. $T = 363.15$; $P_r = 1\,\mathrm{atm}$; $P_p = 0.1\,\mathrm{atm}$; $\theta_{\mathrm{Eth}} = 1$; and $\alpha = 1$.

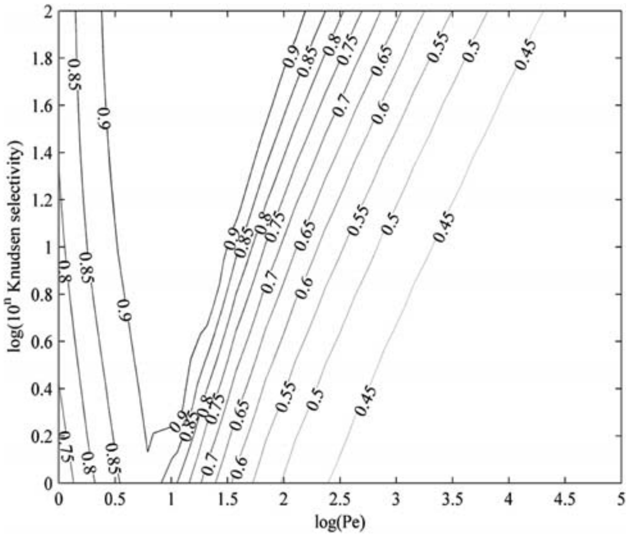

Fig. 6. Contour of exit conversion in a PVMR as a function of P_{e} and Knudsen selectivity.

5. Conclusions

Three different tools, based on thermodynamic analysis, residue curves and design charts, are presented to determine the maximum conversion, the axial component concentration profile, and the effect of selectivity and permeance on conversion in a continuous pervaporation membrane reactor (PVMR) for the esterification of lactic acid with ethanol to produce ethyl lactate. An operating window has been found and high conversions can be reached for log(P_{e}) between −5 and 4 and log(D_{aR}) higher than 3. However, the operating window highly depends on selectivity. At higher operating temperatures of the PVMR, higher conversions can be reached, but higher lactic acid concentrations in the retentate are also found. Consequently, the optimal operating temperature differs from that for the highest conversion and has to be calculated from an economic analysis. A systematic approach for studying a PVMR was presented. These tools can be applied to other PVMRs where an equilibrium reaction takes place.

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Symbols

A_{m} — membrane area per unit membrane modules volume, $\mathrm{m}^2/\mathrm{m}^3$
A_{t} — sectional area, m^2
a_i — activity coefficient of component i, –
D_{am} — Damköhler number based on membrane flux, –

D_{aR} — Damköhler number based on reactor lactic acid feed flow, –
F — total molar flow rate, mol s^{-1}
F_i — molar flow rate of species i in the retentate side, $\mathrm{mol_i\,s^{-1}}$
J_i — molar flux of component i through membrane, $\mathrm{mol_i/(m^2\,s)}$
J_{T} — total molar flux through membrane, $\mathrm{mol/(m^2\,s)}$
k — forward reaction rate constant, mol/(g min)
k_o — rate constant at inlet condition, mol/(g min)
K_i — adsorption constant of component i, –
K_{eq} — equilibrium constant, –
L — reactor length, m
M_i — molecular weight of component i, $\mathrm{(g/mol)_i}$
N_{T} — number of tubes
$\dot{n}_i$ — Mol of component i, $\mathrm{mol_i}$
P_{e} — Peclet number, –
p_i^{sat} — saturated vapor pressure of component i, bar
p_i — permeability of species i, $\mathrm{mol/(m^2\,s\,Pa)}$
P_{r} — pressure ratio (shell pressure/tube pressure), –
P_{T} — total pressure of system, bar
r_{P} — transmembrane pressure ratio (permeate pressure/retentate pressure), –
$\Re$ — dimensionless reaction rate on residue curves equation, –
R — Universal gas constant or sweep ratio, J/(mol K) or –
R_{i} — inner radius of shell, m
R_{o} — outer radius of tube, m
R_{s} — sweeping gas ratio, –
T — temperature, K
u_i — permselectivity of component i respect to the faster transport component, –
x_i — liquid phase mole fraction of component i, –
X_i — conversion of component i, –
y_i — vapor phase mole fraction of component i, –
Y_i — dimensionless mole flow rate of species i, –
z^* — dimensionless length, –

Greek symbols

α_i — selectivity of species i to water, –
γ_i — activity coefficient, –
$\varepsilon_{\mathrm{cat}}$ — catalyst loading density, –
θ_i — feed mol ratio, –
Φ_i — ratio of the amount permeated through the membrane of component i to the lactic acid flow fed to the PVMR
ξ — dimensionless axial distance, –
ρ_{cat} — catalyst density, $\mathrm{kg/m^3}$
V_{ij} — Stoichiometric coefficient of species i on the j reaction, –
V_i — Stoichiometric coefficient of component i, –
V_{T} — total mole change of reaction, –
φ_i — Fugacity coefficient, –

Superscripts

I — properties on the tube side
o — properties on the shell side

Subscripts

eq — equilibrium
Eth — ethanol
EL — ethyl lactate
LA — lactic acid
W — water
ref — at reactor inlet conditions

References

[1] A. Hasanoglu, S. Dincer, Modelling of a pervaporation membrane reactor during esterification reaction coupled with separation to produce ethyl acetate, Desalin. Water Treat. 35 (2011) 286–294.

[2] I. Ivanovic, T. Leiknes, Membrane reactor design as a tool for better membrane performance in a biofilm MBR (BF-MBR), Desalin. Water Treat. 25 (2011) 259–267.

[3] K. Wasewar, S. Patidar, V.K. Agarwal, Esterification of lactic acid with ethanol in a pervaporation reactor: Modeling and performance study, Desalination 243 (2009) 305–313.

[4] D.J. Benedict, S.J. Parulekar, S.P. Tsai, Pervaporation-assisted esterification of lactic and succinic acids with downstream ester recovery, J. Membr. Sci. 281 (2006) 435–445.

[5] K. Tanaka, R. Yoshikawa, C. Ying, H. Kita, K.I. Okamoto, Application of zeolite T membrane to vapor-permeation-aided esterification of lactic acid with ethanol, Chem. Eng. Sci. 57 (2002) 1577–1584.

[6] C.S.M. Pereira, S.P. Pinho, V.M.T.M. Silva, A.E. Rodrigues, Batch and continuous studies for ethyl lactate synthesis in a pervaporation membrane reactor, J. Memb. Sci. 361 (2010) 43–55.

[7] S.A.S. Rezai, Y. Traa, Equilibrium shift in membrane reactors: A thermodynamic analysis of the dehydrogenative conversión of alkanes, J. Memb. Sci. 319 (2008) 279–285.

[8] Y.S. Huang, K. Sundmacher, E.U. Schlünder, Feasibility analysis of membrane reactors-discovery of reactive arheotropes, Catal. Today 104 (2005) 360–371.

[9] W.S. Moon, S.B. Park, Design guide of a membrane for a membrane reactor in terms of permeability and selectivity, J. Memb. Sci. 170 (2000) 43–45.

[10] R.W. Baker, Membrane technology and applications, John Wiley and Sons, Chichester, 2004.

[11] R. Wittig, J. Lohmann, J. Gmehling, Vapor−liquid equilibria by UNIFAC Group Contribution. 6. Revision and Extension, Ind. Eng. Chem. Res. 42 (2003) 183–188.

[12] J.R. Elliott, C.T. Lira, Introductory Chemical Engineering Thermodynamics, Prentice-Hall, Upper Saddle River, NJ, 1999.

[13] C.S.M. Pereira, S.P. Pinho, V.M.T.M. Silva, A.E. Rodrigues, Thermodynamic equilibrium and reaction kinetics for the esterifcation of lactic acid with ethanol catalyzed by acid ion exchange resin, Ind. Eng. Chem. Res. 47 (2008) 1453–1463.