Modeling of pervaporation processes controlled by concentration polarization

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Abstract

Pervaporation is considered a clean and energetically efficient process used for a wide range of applications, working separately or integrated into a hybrid process. In this work, a mathematical model has been developed accounting for the mass transport phenomena under non-isothermal conditions with strong contribution of polarization concentration that prevail in pervaporation systems.

The mathematical model incorporates characteristics of the module geometry, mass and heat transfer correlations and estimation of the system physicochemical properties. The equation-oriented simulation software g-PROMS® was used in the solution of the final problem.

Finally, the model was tested against a representative case study, pervaporative dehydration of cyclohexane, the solvent used in the manufacture of synthetic rubber. Model simulated curves described satisfactorily well the kinetic data of cyclohexane dehydration obtained in a pilot plant set-up. © 2006 Elsevier Ltd. All rights reserved.

Keywords: Pervaporation; Modeling; Plates-and-frames membrane module; Cyclohexane dehydration

1. Introduction

Pervaporation (PV) is presented in literature as an economic alternative for saving energy costs when combined in hybrid pervaporation–distillation processes, as reported by Huang (1991), and Jonquières et al. (2002). Azeotropic, close boiling- and high boiling-point mixtures are examples of said hybrid applications.

Solute removal by pervaporation is nowadays a common industrial application (Néel, 1997). One of the most famous plants, owing to its size, is the Betheneville plant for ethanol dehydration (France). In this industrial pervaporation application, plates-and-frames modules provided with hydrophilic polymeric membranes (commonly PVA) are used (Ho & Shirkar, 1992).

Although the number of works dealing with PV opportunities in the last decades is enormous, most part use simplified mathematical models to predict the separation flux (Ahmad, Lau, Abu Bakar, Abd. Shukor, 2005; Cao & Henson, 2002; Urtiaga, Gorri, & Ortiz, 1999). More recently, scarce contributions have considered non-isothermal description of the involved phenomena, under steady state conditions, to determine optimum operation. The works of Han, Li, Chen, and Wickramasinghe (2002), and Eliceche, Daviou, Hoch, and Ortiz (2002) can be mentioned as representative examples.

Simulation of the system behavior is an important tool in the design and optimization of an industrial pervaporation plant (Biegler, Grossmann, & Westerberg, 1997). The aim of this study is to develop a general mathematical model that gives a satisfactory description of PV separations under non-isothermal and non-stationary conditions that are usually encountered in industrial applications and for applications governed by polarization concentration. The equation-oriented simulation software g-PROMS® has been selected to solve the problem and to obtain results under different operation conditions. The model has been tested against experimental results of the dehydration of industrial cyclohexane obtained in a pilot plant that uses plates-and-frames membrane modules (Ortiz, Urtiaga, Ibáñez, Gómez, & Gorri, 2006).

2. Mathematical modeling of the PV process

Description of a PV operation working in batch mode under non-isothermal and non-stationary conditions needs the solution of simultaneous first order ordinary equations, which are mass
### Nomenclature

- **a**: mass transport shape factor
- **b**: energy transfer shape factor
- **Bi**: Biot number; \( Bi = hL/\lambda \)
- **C**: solute concentration within the module feed (kg m\(^{-3}\))
- **C\text{exp}**: experimental dimensionless concentration
- **C\text{in}**: solute concentration at the inlet of the membrane module (kg m\(^{-3}\))
- **C\text{in}^T**: solute concentration at the inlet of the feed tank (kg m\(^{-3}\))
- **C\text{out}**: solute concentration at the outlet of the membrane module (kg m\(^{-3}\))
- **C\text{out}^T**: solute concentration at the outlet of the feed tank (kg m\(^{-3}\))
- **C\text{p}**: liquid heat capacity (J kg\(^{-1}\) K\(^{-1}\))
- **C\text{ps}**: solid heat capacity (J kg\(^{-1}\) K\(^{-1}\))
- **C\text{sim}**: simulated dimensionless concentration
- **C\text{t}**: solute concentration within the feed tank (kg m\(^{-3}\))
- **C\text{0}**: initial solute feed concentration (kg m\(^{-3}\))
- **d\text{h}**: hydraulic equivalent diameter (m)
- **D**: diffusion coefficient (m\(^2\) s\(^{-1}\))
- **e\text{F}**: feed plate thickness (m)
- **e\text{H}**: holed plate thickness (m)
- **F**: volumetric flow rate of the feed (m\(^3\) s\(^{-1}\))
- **G\text{Z}**: Graetz number, \( Gr = (d\text{h}L)ReSc \)
- **h\text{F}**: liquid boundary layer heat transfer coefficient (W m\(^{-2}\) K\(^{-1}\))
- **H**: height of the plate-and-frame duct (m)
- **J\text{SOL}**: flux of solvent through the membrane (kg m\(^{-2}\) s\(^{-1}\))
- **J\text{W}**: flux of solute through the membrane (kg m\(^{-2}\) s\(^{-1}\))
- **k\text{l}**: liquid boundary layer mass transfer coefficient (m s\(^{-1}\))
- **K\text{ov}**: overall mass transfer coefficient of solute transport (m s\(^{-1}\))
- **L**: length of the module plates (m)
- **M\text{B}**: molecular weight of solvent (g mol\(^{-1}\))
- **N**: number of experimental points
- **Nu**: Nusselt number
- **Pr**: Prandtl number
- **R**: ideal gas constant (J mol\(^{-1}\) K\(^{-1}\))
- **Re**: Reynolds number
- **Sc**: Schmidt number, \( Sc = \mu/\rho D \)
- **Sh**: Sherwood number
- **t**: time (s)
- **T**: temperature of the fluid at an axial position within the module (K)
- **T\text{C}**: critical temperature (K)
- **T\text{out}**: solute temperature at the outlet of the membrane module (K)
- **T\text{r}**: reduced temperature (K)
- **T\text{R}**: room temperature (K)
- **T\text{s}**: temperature of the feed plate at an axial position within the module (K)
- **T\text{s}2**: temperature of the holed plate at an axial position within the module (K)
- **v\text{e}**: average linear velocity of the fluid at an axial position within the module (m s\(^{-1}\))
- **V\text{C}**: critical volume (m\(^3\)mol)
- **V\text{C}S**: saturated liquid volume (m\(^3\)mol)
- **V\text{F}**: feed volume (m\(^3\))
- **w**: acentric factor
- **W**: width of the plate-and-frame duct (m)
- **z**: axial coordinate
- **Z\text{c}**: compressibility factor

<table>
<thead>
<tr>
<th>Greek letters</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \lambda ): feed thermal conductivity (W m(^{-1}) K(^{-1}))</td>
</tr>
<tr>
<td>( \lambda\text{SOL} ): solvent latent heat of vaporization (J kg(^{-1}))</td>
</tr>
<tr>
<td>( \lambda\text{VW} ): solute latent heat of vaporization (J kg(^{-1}))</td>
</tr>
<tr>
<td>( \mu ): viscosity (kg m(^{-1}) s(^{-1}))</td>
</tr>
<tr>
<td>( \mu\text{B} ): viscosity of the liquid bulk (kg m(^{-1}) s(^{-1}))</td>
</tr>
<tr>
<td>( \mu\text{w} ): liquid viscosity at the plate wall (kg m(^{-1}) s(^{-1}))</td>
</tr>
<tr>
<td>( \rho ): liquid density (kg m(^{-3}))</td>
</tr>
<tr>
<td>( \rho\text{s} ): solid density (kg m(^{-3}))</td>
</tr>
<tr>
<td>( \sigma\text{w} ): weighted standard deviation</td>
</tr>
<tr>
<td>( \xi ): association parameter for the solvent</td>
</tr>
</tbody>
</table>

and heat balances, together with algebraic expressions to obtain the transport flux across the pervaporation system. Hydrodynamic influence over the process performance requires a correct geometrical description of the membrane module.

#### 2.1. PV membrane modules

Plates-and-frames modules are commonly used for industrial PV applications. The most typical configuration consists of a stack in which a set of individual structural units are arranged in series to create individual chambers. As shown in Fig. 1, each structural unit (sandwich) comprises one stainless steel feed plate, and two stainless steel sheets perforated with small holes. In this basic unit, the membranes are placed on one side of the perforated plates. The stack of structural units is shown in Fig. 1(b). The ‘sandwiches’ are separated by metallic netting, in such a way that the individual chambers are isolated from each other. Finally, the stack is placed between two endplates. The number of ‘sandwiches’ together with the dimensions of the plates provide the membrane area available in the module.

A good description of the plates-and-frames pervaporation modules can be found in Neel (1997), and Mulder (1996). The feed-flow pattern depends on the module configuration, where the plates are usually assembled in series or mostly in parallel to reduce pressure drop. Fig. 2 shows the common parallel feed distribution within a plates-and-frames membrane module. The feed flows upwards to the retentate outlet. Permeate vapors...
are collected in individual chambers behind the membranes and headed towards the condenser.

2.2. Model hypothesis

The mathematical model, although of wide applicability, will be developed for description of systems where concentration polarization usually influences significantly mass and heat transport, dehydration of organic solvents are among representative examples.

Mass transport assumptions:
(1) Although the considered PV process operates under batch conditions, the driving force is small enough to consider that a pseudo-steady state can be approached inside the PV module, where changes of solute concentration within the membrane module occur mainly in the axial position and the contribution of the concentration variation at the module entrance is negligible. This hypothesis allows important simplifications in the mathematical description of the system (Ji, Sikdar, & Hwang, 1994; Psaume, Aptel, Aurelle, Mora, & Bersillon, 1988; Urtiaga, Gorri, Ruiz, & Ortiz, 2001).
(2) Plug flow and negligible axial diffusion (Han et al., 2002; Marriott, Sørensen, & Bogle, 2001).
(3) Solution-diffusion model is used to describe solute flux with a driving force expressed as a function of the solute concentration (Gómez, Daviou, Ibáñez, Eliceche, & Ortiz, 2006; Gómez, Ibáñez, Ortiz, & Grossmann, 2006; Jiraratananon, Chanachai, & Huang, 2002).
(4) Negligible influence of membrane resistance. The liquid boundary layer mass transfer coefficient ($k_l$) governs the overall mass transport kinetics.

Heat transport assumptions:
(5) Two different mechanisms are usually responsible for heat losses: the latent heat of vaporization of the permeate through the membrane; and the heating of the PV module by the hot fluid as a result of operating conditions. Other possible causes have been neglected since the module is operated adiabatically.
(6) Non-stationary state has been assumed in the description of the temperature drop.
(7) Plug flow, as considered for mass transport, in the heat balances.
(8) Each ‘sandwich’ consists of two hole plates and a feed plate (see Fig. 3). The hot fluid inside each flow channel heated up a hole plate and half of the feed plate.
(9) No heat transport resistance inside the plates and uniform temperature profiles. Low Biot numbers are expected since the thickness of the plates use to be very low. This
assumption is in accordance with the proposed 1D model. Higher Biot numbers would require consideration of the plate resistance to heat flux and a 2D model would be necessary.

(10) The main resistance to heat transport is located at the boundary layer of the feed fluid over the plate.

(11) Heat losses to the environment are negligible (module thermally isolated).

Similar assumptions are taken into account in the literature for plate-and-frames heat exchangers (Georgiadis & Macchietto, 2000).

2.3. Model equations

2.3.1. Heat and mass transfer correlations

Table 1 shows a compendium of mass transfer correlations reported in the literature to describe the resistance through the liquid boundary layer in laminar flow. The Sherwood number is usually expressed as a function of the Reynolds and Schmidt numbers. In these correlations, the classical Graetz problem, that is usually expressed as a function of the Reynolds and Schmidt numbers, is replaced by the Prandtl number could be proposed as follows:

\[
Nu = \frac{h_{Fd}}{\lambda} = b \left( Re \frac{d_h}{L} \right)^{1/3}
\]  

(2)

When the wall temperature is lower than that in the bulk, the liquid viscosity varies significantly through the fluid layer. This behavior distorts the velocity profile across the boundary layer and affects the temperature profile and, subsequently, the heat transfer coefficient. This effect is accounted for in the Nusselt number by introducing a correction factor:

\[
Nu = \frac{h_{Fd}}{\lambda} = b \left( Re \frac{d_h}{L} \right)^{1/3} \left( \frac{\mu_B}{\mu_W} \right)^{0.14}
\]  

(3)

The parameter ‘b’ in Eq. (3) depends on the thermal boundary condition and plate geometry. A wide range of ‘b’ values, from 0.73 to 4.5 (Shah et al., 1988), has been reported in the open literature for laminar flow regime. This wide variety has been attributed to the complexity of plate patterns (corrugation, path flows, etc.) usually found in plate-and-frame geometries. Thus, this range of ‘b’ values should be used only as orientative and specific values must be obtained from experimental data.

2.3.2. Temperature dependent properties

Some of the variables involved in the description of mass and heat transport depend significantly on temperature. Therefore, suitable correlations or theoretical equations must be supplied for description of temperature influence in the physicochemical parameters: diffusivity coefficient of solute in solvent, feed fluid density, latent heat of vaporization, specific heat capacity, thermal conductivity, and liquid viscosity. Table 2 reports some of the correlations often used in the prediction of these properties.

2.3.3. Mass and heat balances

Considering the above assumptions, the resulting balances, including boundary conditions and connectivity equations, can be written as follows.

<table>
<thead>
<tr>
<th>Correlation</th>
<th>System</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ Sh = a \left( Re \frac{Sc}{d_h} \right)^{1/3} ]</td>
<td>a = 1.85; tubes or rectangular ducts</td>
<td>Hwang and Kammermeyer (1975)</td>
</tr>
<tr>
<td>[ Sh = 3.66 + \frac{0.0668(Re \cdot Sc(d_h/L))}{1 + (0.04(Re \cdot Sc(d_h/L)))^{3/3}} ]</td>
<td>a = 1.85; tubes approximate solution</td>
<td>Skelland (1974)</td>
</tr>
<tr>
<td>[ Sh_{avg} = 1.62Gz^{1/3} \left[ 1 + 0.0742 \frac{(Gr \cdot Sc(d/L))^{3/4}}{Gz} \right] ]</td>
<td>a = 1.85; tubes or flat circuits; Gz ≥ 10</td>
<td>Sellsars, Tribus, and Klein (1959); Lixin and Hwang (1999)</td>
</tr>
<tr>
<td>[ Sh_{avg} = 1.47Gz^{1/3} \left[ 1 + 0.0989 \frac{(Gr \cdot Sc(h/L))^{3/4}}{Gz} \right] ]</td>
<td>Theoretical; vertical parallel plates, forced and natural convection; opposite effects (--)</td>
<td>Ruckenstein and Rajagopolan (1980)</td>
</tr>
</tbody>
</table>
Table 2

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Reference</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusivity coefficient (D_{AB}^p)</td>
<td>Wilke–Chang + Olander (Wankat, 1994)</td>
<td>(\frac{D_{AB}^p}{T} = 7.4 \times 10^{-8}(\xi M_B) / 2.3V_0^{0.6})</td>
</tr>
<tr>
<td>Density (\rho)</td>
<td>Rackett equation (Poling, Prausnitz, &amp; OiCONNell, 2001)</td>
<td>(V_i = V_c Z_e^{(1-T_i)/T_i}2^{7/3})</td>
</tr>
<tr>
<td>Latent heat of vaporization (\lambda_v)</td>
<td>Pitzer equation (Poling et al., 2001)</td>
<td>(\frac{\lambda v}{RT_e} = 7.08(1 - T_i)^{0.354} + 10.95u(1 - T_i)^{0.456})</td>
</tr>
<tr>
<td>Heat capacity (C_p)</td>
<td>Perry, Green, &amp; Maloney, 2001</td>
<td>(C_p = C_1 + C_2 T + C_3 T^2 + C_4 T^3)</td>
</tr>
<tr>
<td>Thermal conductivity (\lambda)</td>
<td>Latini et al. (Poling et al., 2001)</td>
<td>(\lambda = A(1 - T_i)^{0.38} / T_i^{1.6})</td>
</tr>
<tr>
<td>Liquid viscosity (\mu)</td>
<td>Andrade correlation (Poling et al., 2001)</td>
<td>(\ln(\mu) = A + B/T + C\ln(T))</td>
</tr>
</tbody>
</table>

\(a\) Parameter temperature dependence considered in referred expression.

Solute concentration description within the plates-and-frames module is expressed by means of mass balance:

\[
F \frac{dC}{dz} = -WJ_W \tag{4}
\]

boundary conditions : \(z = 0, \quad C = C_{in}\) \tag{5}

In a general pervaporation system, the flux in terms of the partial vapor pressure difference may be expressed as \(J = P_i(x_{eq} Y_0) p_{flat}^s - p_{hi}) / l\) where \(P_i\) is the overall permeability, and \(l\) the membrane thickness. However, the driving force in pervaporation could equally well have been expressed in terms of concentration differences (Wijmans & Baker, 1995). Considering Henry law for dilute solutions and resistance-in-series model, the flux can be written as \(J = K_{ov}(C_{in} - (p_{hi}/H_i))\) where \(K_{ov}\) is the overall mass transfer coefficient \((K_{ov} = P_i H_i / l)\). Finally, in pervaporation the permeate pressure is commonly very close to 0 due to the use of a vacuum pump and thus \(p_{hi} \approx 0\), leading to the simplified flux expression \(J_W = K_{ov}C\).

Determination of the relative importance of the kinetic resistances in the pervaporation system by taking into account the contribution of the PV membrane behaviour would define the relationship between the overall and individual mass transport coefficients (Gómez, Daviou, et al., 2006; Gómez, Ibáñez, et al., 2006). In this work, and as a result of the negligible influence of the membrane resistance, it can be assumed that \(K_{ov} \approx k_1\).

Feed tank, assuming that it behaves as an ideal stirred vessel.

\[
V_T \frac{dC_T}{dt} = F(C_{in} - C_{out}) \tag{6}
\]

initial condition : \(t = 0, \quad C = C_0\) \tag{7}

Connectivity expressions between the module and the feed tank.

\[
C_{out} = C_{in} \tag{8}
\]

\[
C_{in} = C_{out} \tag{9}
\]

The heat transport balances describe the temperature evolution within the PV membrane module in three different elements, i.e., fluid (feed stream), feed plate and holed sheet.

Fluid (feed stream) heat balance

\[
H_\rho C_p \left( \frac{\partial T}{\partial t} + v_z \frac{\partial T}{\partial z} \right) = -(J_{SOL} \lambda v_{SOL} + J_W \lambda v_W
\]

\[+ h_F(T - T_0) + h_F(T - T_{S2}) \tag{10}\]

initial condition : \(t = 0, \quad T = T_R\) \tag{11}

boundary conditions : \(z = 0, \quad T = T_0\) \tag{12}

Feed plate heat balance

\[- \left( \frac{e_F}{2} \right) \rho_s C_p s_0 \left( \frac{dT_s}{dr} \right) = h_F(T_s - T) \tag{13}\]

initial condition : \(t = 0, \quad T_s = T_R\) \tag{14}

Holed sheet heat balance

\[- e_H \rho_s C_p s_0 \left( \frac{dT_{S2}}{dr} \right) = h_F(T_{S2} - T) \tag{15}\]

initial condition : \(t = 0, \quad T_{S2} = T_R\) \tag{16}

where \(e_F\) and \(e_H\) are the approximate thicknesses of the feed plate and the holed sheet. In both expressions, the density and heat capacity of the plates were considered constant within the operation range of temperature.

Thus, Eqs. (1)–(16) constitute the mathematical model able to describe the solute concentration evolution as a result of the pervaporation process under non-isothermal conditions. Application of the model requires also of the correlations used for prediction of temperature dependent variables that are shown in Table 2.

3. Method of solution

The set of differential and algebraic equations presented in the mathematical model were solved simultaneously using the equation-oriented simulation software g-PROMS®. The integration of this model required additional information in the form of property correlations, geometrical parameters and mass transport correlations. In addition, the suitable values of the shape
parameters ‘a’ and ‘b’ of Eqs. (1) and (3), respectively must be determined for the membrane module used. A set of possible values of the parameter ‘a’ has been compiled from the open literature in Table 1. The selection of the most accurate parameter value for a defined plate-and-frame membrane module requires experimental data together with an estimation tool like gEST, provided in g-PROMS®. Fig. 4 shows the program structure and the main variables needed for description of the full PV problem.

4. Case study

To facilitate understanding of model applicability, the performance of the pervaporation process at a pilot plant scale studied satisfactorily in the R&D facilities of the Spanish company Dynasol Elastomeros S.A. was selected as a case of study. A PV pilot plant set-up comprising a plate-and-frame PLC-06 CM-Celfa module (total membrane area of 3 m²), with similar characteristics to an industrial installation, coupled to a 20 l feed tank was installed and conditioned to operate in batch mode. The characteristics of this membrane module are shown in Table 3. A detailed description of this set-up can be found at Ortiz et al. (2006) together with the results obtained in successful experiments carried out to decrease the solute content of 17 l of cyclohexane, from an average value of 100 mg kg⁻¹ to less than 10 mg kg⁻¹. The liquid boundary layer resistance was experimentally checked to be the most important limitation in the kinetics of solute transport fro the industrial solvent due.

5. Simulation results and discussion

After integrating the mass and heat balances, Eqs. (1)–(16) with the g-PROMS® software tool, simulated results for different conditions were obtained. Table 4 shows model details in terms of the total number of equations, variables and parameters involved. Table 5 compiles the values of the transport and the temperature dependent variables obtained for a flow rate of 5.00×10⁻⁵ m³ s⁻¹ and initial solute content in feed of 119 mg kg⁻¹. Eqs. (1) and (3) were used to predict the influence of temperature and flow rate variables on the liquid resistance.

Table 3
Geometrical parameters of PLC 06 membrane module

<table>
<thead>
<tr>
<th>Module geometrics</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Total membrane area (m²)</td>
<td>3</td>
</tr>
<tr>
<td>Flow pattern</td>
<td>Parallel</td>
</tr>
<tr>
<td>Number of sandwich</td>
<td>21</td>
</tr>
<tr>
<td>Number of membrane sheets</td>
<td>42</td>
</tr>
<tr>
<td>Membrane sheet area (m²)</td>
<td>0.07</td>
</tr>
<tr>
<td>Plates length (m)</td>
<td>0.426</td>
</tr>
<tr>
<td>Plates width (m)</td>
<td>0.18</td>
</tr>
<tr>
<td>Flow channel height (m)</td>
<td>8.50E⁻⁰⁴</td>
</tr>
<tr>
<td>Feed plate thickness (m)</td>
<td>5.00E⁻⁰³</td>
</tr>
<tr>
<td>Holed plate thickness (m)</td>
<td>2.50E⁻⁰³</td>
</tr>
</tbody>
</table>

Table 4
Details of the mathematical model developed

<table>
<thead>
<tr>
<th>Model details</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Axial steps</td>
<td>200</td>
</tr>
<tr>
<td>Time steps</td>
<td>6</td>
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<tr>
<td>Model equations</td>
<td>4236</td>
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<tr>
<td>Differential</td>
<td>601</td>
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<td>Algebraic</td>
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<td>Variables</td>
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<td>9</td>
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<td>Unknown</td>
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<tr>
<td>Initial conditions</td>
<td>601</td>
</tr>
<tr>
<td>Parameters</td>
<td>12</td>
</tr>
</tbody>
</table>
Table 5
Values of the variables involved in the problem description for a flow rate of $5.00 \times 10^{-5}$ m$^3$ s$^{-1}$ and initial solute content in feed of 119 mg kg$^{-1}$

<table>
<thead>
<tr>
<th>Transport variables</th>
<th>Axial position within the membrane plates</th>
</tr>
</thead>
<tbody>
<tr>
<td>$z = 0$ m</td>
<td>$z = 0.1$ m</td>
</tr>
<tr>
<td>$Sh$</td>
<td>2.77</td>
</tr>
<tr>
<td>$Re$</td>
<td>17.05</td>
</tr>
<tr>
<td>$Sc$</td>
<td>241.8</td>
</tr>
<tr>
<td>$Nu$</td>
<td>0.071</td>
</tr>
<tr>
<td>$Pr$</td>
<td>9.78</td>
</tr>
<tr>
<td>$k_l$ (m s$^{-1}$)</td>
<td>0.018</td>
</tr>
<tr>
<td>$h_F$ (W m$^{-2}$ K$^{-1}$)</td>
<td>4.69</td>
</tr>
</tbody>
</table>

Temperature dependent properties

<table>
<thead>
<tr>
<th>$T^*$ (K)</th>
<th>$T_s$ (K)</th>
<th>$D_s$ (m$^2$ s$^{-1}$)</th>
<th>$\lambda$ (W m$^{-1}$ K$^{-1}$)</th>
<th>$\rho$ (kg m$^{-3}$)</th>
<th>$\lambda_{W}$ (J kg$^{-1}$)</th>
<th>$\lambda_{VSOL}$ (J kg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>332.9</td>
<td>331.16</td>
<td>$3.06 \times 10^{-9}$</td>
<td>3</td>
<td>740.6</td>
<td>2,445,944</td>
<td>362,339</td>
</tr>
<tr>
<td>333</td>
<td>313.87</td>
<td>$3 \times 10^{-9}$</td>
<td>742.3</td>
<td>2,451,444</td>
<td>2,456,888</td>
<td>363,479</td>
</tr>
<tr>
<td>333</td>
<td>313.88</td>
<td>$2.94 \times 10^{-9}$</td>
<td>744</td>
<td>2,456,888</td>
<td>2,462,222</td>
<td>364,596</td>
</tr>
<tr>
<td>312.48</td>
<td>311.17</td>
<td>$2.86 \times 10^{-9}$</td>
<td>745.61</td>
<td>2,462,222</td>
<td>2,467,388</td>
<td>365,688</td>
</tr>
<tr>
<td>311.17</td>
<td>309.93</td>
<td>$2.81 \times 10^{-9}$</td>
<td>747.21</td>
<td>2,467,388</td>
<td>2,472,550</td>
<td>366,745</td>
</tr>
<tr>
<td>312.48</td>
<td>311.17</td>
<td>$2.81 \times 10^{-9}$</td>
<td>747.21</td>
<td>2,472,550</td>
<td>2,477,711</td>
<td>366,745</td>
</tr>
</tbody>
</table>

Taking into account the membrane module selected for simulation and described in Table 3, the values of the parameters ‘$a$’ and ‘$b$’ included in the mass and heat transport correlations were estimated by means of the gEST tool available in the g-PROMS® software using available experimental data (Ortiz et al., 2006). A resultant value of 1.08 was finally obtained from estimation of the parameter ‘$a$’ in Eq. (1). The result is close to the literature value proposed by Sellars and shown in Table 1. For comparison purposes, Fig. 5 shows the concentration profiles obtained over time using two different literature values of the parameter ‘$a$’, together with experimental data obtained under similar operation conditions. A value of 0.081 was assigned to the parameter ‘$b$’ in the heat transport correlation given by Eq. (3). The calculated value of the heat transport coefficient ($h_F$) at 333 K was 4.4 W m$^{-2}$ K$^{-1}$, that is in accordance with low values of the Biot number (below 0.1), indicating negligible heat transport resistance inside the plate.

Fig. 5 shows the influence of temperature (that changes along the plates length of the membrane module) and the feed flow rate on the liquid boundary layer mass transport coefficient. Solid curves correspond to simulated values. When the feed enters the membrane module at 333 K, there is a decrease of the temperature as long as it contacts the membrane plates, heating up the module. This effect is less significant at higher flow rates being temperature drops between feed and retentate lower. As expected, higher mass transport coefficients were found as the temperature and flow rate of the retentate increased, thus making the liquid boundary layer influence less significant on the dehydration kinetics. The effect of a temperature drop of 40 K across

![Fig. 5. Water concentration profiles at the module retentate for different values of the parameter ‘$a$’. Flow rate 5.00 × 10$^{-5}$ m$^3$ s$^{-1}$. (♦) Experimental data; (––) estimated ‘$a$’ value; (—) Lévéque value (1.615); (- –) Sieder-Tate value (1.815).](image)

![Fig. 6. Influence of temperature and flow rate on the liquid boundary layer mass transfer coefficient.](image)
the module leads to a 26.6% reduction of the initial $k_1$ value (333 K) proving the importance of the variable in the process performance. The influence of the fluid flow rate on the mass transport coefficient is even more significant. The dehydration kinetics increased almost four times when the flow rate changed from 0.01 to 0.3 m$^3$/s$^{-1}$ (maximum flow rate allowed) at a constant temperature value. The developed model can be used for the prediction of the dehydration behavior, with low feed solute content, in a plates-and-frames pilot plant module that operated in batch mode under non-isothermal conditions.

Fig. 7 shows the influence of both temperature and flow rate variables on the solute concentration in the retentate. As mentioned above, the temperature in the membrane module increases with flow rate as it can be seen for each of the plotted curves. Higher temperatures and flow rates clearly lead to a decrease in the retentate outlet concentration of solute. Thus, this model can be used as a tool for design purposes of future industrial applications of the technology. The methodology of minimization of the membrane area required in a larger-scale process has

Fig. 8. Concentration and temperature evolution. (■) Experimental concentration; (—) simulated concentration; (♦) experimental temperature; (--) simulated temperature. The error bar on the temperature data show the possible error of the temperature controller. Flow rate: (a) $3.33 \times 10^{-5}$ m$^3$/s$^{-1}$; (b) $4.17 \times 10^{-5}$ m$^3$/s$^{-1}$; (c) $5.00 \times 10^{-5}$ m$^3$/s$^{-1}$; (d) $6.00 \times 10^{-5}$ m$^3$/s$^{-1}$; (e) $6.67 \times 10^{-5}$ m$^3$/s$^{-1}$; (f) influence over concentration and temperature profiles.
been reported elsewhere (Gómez, Daviou, et al., 2006; Gómez, Ibáñez, et al., 2006), specifying the optimal connection between membrane modules and the optimal values of operation variables.

Finally, the simulation results of the model were validated by means of the comparison of the predicted downstream profiles of concentration and temperature with the available experimental data. Simulations were obtained at the same conditions as those used during the experimental analysis (Ortiz et al., 2006). Fig. 8(a–e) show the comparison between experimental and simulated results of the evolution of the concentration and temperature profiles at the retentate, when the flow rate changed in the range of 3.33 × 10⁻⁵ to 6.67 × 10⁻⁵ m³ s⁻¹. Experiments were carried out with industrial cyclohexane as to the fact that the contribution of the vaporization of the permeate became less significant in this case (below 15% of the total cooling). Concentration polarization was appreciated as the main mass transport resistance, in accordance with the assumption of negligible membrane resistance proposed in the formulation of the mass balance Eq. (4). Fig. 8(f) shows the effect of the flow rate on both the dimensionless concentration and temperature of the retentate. This behaviour is explained through the significant contribution of concentration polarization to the overall mass transport rate. As shown in Fig. 8(a–e), the differences between the experimental and the simulated profiles were very small. The error bar on the temperature data shows the possible measure error in the temperature controller.

The parity graph of the simulated concentration values versus the experimental data is given in Fig. 9. Ninety per cent of the results of C_star_sim fall within the interval C_star_sim ± 10% C_star_exp, proving that the model developed in this work describes satisfactorily well the separation process. Additionally, the standard weighted deviation defined by Eq. (17) was calculated. The obtained value was below 5%, which confirms the validity of the proposed model assumptions.

\[
\sigma_w = \sqrt{\frac{\sum_{i=1}^{N} \left( \frac{C_{\text{sim}}^* - C_{\text{exp}}^*}{C_{\text{exp}}^*} \right)}{N - 1}}
\]  

(17)

The simulated temperature profiles showed a maximum deviation of 2 K with the experimental data. This falls in the range of the error bar in the figures that represents the possible error of the temperature controller device. This means that the proposed heat model could reproduce the experimental data accurately.

6. Conclusions

In this study, a mathematical model has been developed able to describe the behaviour of pervaporation processes with strong control of concentration polarization under common non-isothermal and non-stationary conditions using plates-and-frames membrane modules. For this purpose, module geometry and mass and heat transport rates in the system were incorporated. Existing correlations that relate the Sherwood and Nusselt numbers to the Reynolds, Schmidt and Prandtl numbers were used and fitting parameters ‘a’ and ‘b’ were estimated. Simulation results have shown significant influence of temperature and flow rate over the liquid mass transport coefficient.

Finally, taking into account the geometrical considerations of a pilot plant membrane module and the mass and heat transport assumptions made in the description of the pervaporative cyclohexane dehydration, the model proved to be useful for prediction of the concentration and temperature profiles at the retentate. Ninety percent of the simulated concentration values fell within the interval C_exp ± 10%C_exp and the standard weighted deviation was below 5%, thus confirming the model assumptions. Deviation between simulated and experimental was within a maximum range of 2 K.

The resulting model can be used in design and scale-up calculations of industrial applications of the pervaporation technology.

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