PermSMBR—A New Hybrid Technology: Application on Green Solvent and Biofuel Production

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A new technology, the simulated moving bed membrane reactor (PermSMBR), was presented and applied for the production of the green solvent ethyl lactate and of the biofuel 1,1-diethoxyethane. Its conception was a result of process reintensification for oxygenates production, by integrating the simulated moving bed reactor with hydrophilic membranes to enhance the water removal, leading to high process performance. For ethyl lactate synthesis, the PermSMBR technology proved to have better performance than the reactive distillation (RD) and the simulated moving bed reactor (SMBR) processes; the RD and SMBR processes require more 152 and 165% of ethanol consumption than the new technology, respectively. For the 1,1-diethoxyethane production, the PermSMBR also leads to a decrease in ethanol consumption of 69% and a productivity enhancement of 53%, when comparing with the SMBR. © 2010 American Institute of Chemical Engineers *AIChE J,* 57: 1840–1851, 2011

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Introduction

The paradigm of chemical process engineering is changing. Traditional processes (where the reactor is followed by separation units to recover the desirable product, to remove the by-product, and to recycle the unconverted reactants to the reactor) are being replaced by integrated processes where reaction and separation occur in the same device. These integrated processes are of considerable interest for oxygenated compounds production (esters, acetals, ethers, etc.), that involves equilibrium-limited reactions that are favoured by the continuous removal of at least one reaction product. The term multifunctional reactor is often used to embrace reactive separation technologies, which main advantages are higher yields, reduction of energy requirements, decrease of solvents consumption and lower capital investments.[1] In the state of the art, the conventional multifunctional reactors used for equilibrium limited reactions are: reactive distillations (RD's), reactive extractions, membrane reactors and chromatographic reactors, among others. Regarding RD the best example is the methyl acetate synthesis developed and patented by the Eastman Kodak company.[2] The entire process is carried out in a single column and represents one-fifth of the capital investment and consumes one-fifth of the energy of the traditional process (reaction followed by separation by distillation).[3] However, there are some disadvantages in the use of RD for systems that exhibit azeotropes formation and/or other volatility restrictions regarding the boiling points of the reactants and/or products that makes RD unfeasible.[4] Membrane reactors are widely used and typical examples are pervaporation and vapor permeation reactors, where the catalyst is in fluidized[5,6] or fixed beds.[7–10]

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Table 1. Chemical Engineering Process Evolution

Traditional Process	Process Intensification	Process Reintensification
Reactor + separator • Distillation • Adsorption • Crystallization • Membranes • Extraction	Reactive separations • Reactive distillation • Membrane reactor • SMB reactor • Reactive extraction • Reactive crystallization	Reactive hybrid separations • SMB membrane reactor

Some authors also call membrane reactors to the processes where the reactor and membrane are housed in separate units in series or parallel.[11] Typically, the membrane is selective to water; the by-product formed on oxygenates production.[8,9,11] Chromatographic reactors include fixed bed (FBR),[12,13] pressure swing adsorption (PSAR),[14,15] and simulated moving bed reactors (SMBR),[16–18] among others. Some systems are enhanced by adding extra features to the multifunctional reactors, as the cyclic hybrid adsorbent-membrane reactor (HAMR), which combines the functionalities of PSAR and membrane separation with reaction into a single unit for hydrogen production.[19] From all the mentioned chromatographic reactors, the SMBR is the most commonly used in the process intensification for oxygenated compounds production. The SMBR process is implemented in the well-known SMB equipment,[20] in which the columns are packed with a solid (catalyst with adsorptive properties) or a mixture of solids (a catalyst and an adsorbent). The SMBR has several advantages, as the ones already mentioned for the reactive separations, but the most important is that usually works at lower temperatures than RD and membrane reactors. However, comparing to these processes, it has the disadvantage of product dilution with the desorbent which needs to be then separated and recycled to the SMBR unit. Another issue, that affects the process performance on oxygenates production, is that in several applications the feed comprises water (the by-product), which will lead to lower reactants conversion, product purity, and productivity. In the case of the SMBR unit it will also lead to higher desorbent consumption. Therefore, to decrease the desorbent consumption and increase productivity, it was developed a novel technology, the simulated moving bed membrane reactor (PermSMBR), which combines a reactor with two different separation techniques: chromatography (simulated moving bed) with membranes (pervaporation or vapor permeation), into a single device. This technology takes advantage of both processes, minimizing their weaknesses by the integration of both techniques. Of course that this integration reduces the flexibility of the process to find the operating conditions that satisfy, simultaneously, the equilibrium and kinetics of reaction, adsorption and membrane permeation. However, for many applications, the PermSMBR is a clean and economic alternative to conventional processes and even competitive when compared with other reactive separation technologies, as it will be shown in this work. One may say that, if reactive separations embrace the concept of Process Intensification, the reactive hybrid separations (as PermSMBR) embody the Process "Re-Intensification" (Table 1).

Due to its technological potential, the PermSMBR process was patented,[21] being a very promising technology for the synthesis of oxygenated compounds as esters, acetals and ethers, used as biofuels, solvents, and flavours, among others, given that there are many water selective membranes developed for organics dehydration. As examples, the following oxygenated compounds will be considered: (i) ethyl lactate, an important green solvent, that could replace a range of environment-damaging halogenated and toxic solvents[11]; and (ii) 1,1-diethoxyethane (diethylacetal), a biofuel that can be added to diesel up to 10%, reducing in 34.6% the particulate mass emissions and in 3.2% the NO_x emissions from fuel combustion and, additionally, decreases the net contribution of CO_2 emissions by 6.4%, since it is renewable.[22] Their synthesis involves liquid phase chemical equilibrium limited reactions between renewable chemicals, both catalysed in acid medium, having water as by-product. The ethyl lactate synthesis comprises the esterification reaction between ethanol and lactic acid:

$$\text{Ethanol } (A) + \text{Lactic Acid } (B1) \overset{H^+}{\longleftrightarrow} \text{Ethyl Lactate } (C1) + \text{Water } (D)$$

While, the production of diethylacetal involves the acetalization reaction of ethanol with acetaldehyde:

$$2\text{Ethanol } (A) + \text{Acetaldehyde } (B2) \overset{H^+}{\longleftrightarrow} \text{Diethylacetal } (C2) + \text{Water } (D)$$

The objective of this work is to present the PermSMBR technology and to assess its application for the production of ethyl lactate and 1,1-dietoxyethane. Therefore, the technical description of this new technology is addressed and a mathematical model is developed to describe the behaviour of the PermSMBR unit, considering it main features: inter and intraparticle mass transfer resistances, membrane concentration polarization and velocity variations due to reaction, adsorption/desorption and species permeation. This model is then applied to evaluate the PermSMBR process performance for different configurations (4 and 3 sections) and for different operating conditions (flowrates, temperature, permeate pressure). For given operating conditions, the flowrates that enable specified requirements of purity and conversion are represented by feasible regions, either reactive/separation region to maximize the productivity or regeneration region to minimize the ethanol consumption. Finally, this new technology is compared with the SMBR, which was already experimentally and theoretically evaluated for the synthesis of ethyl lactate and diethylacetal in previous works.[17,18,23] Additionally, for the ethyl lactate system, the PermSMBR is also compared with the RD process.[24]

Technical Description of the PermSMBR Technology

The PermSMBR consists of a set of columns connected in series, each column contains a set of membranes, and the catalyst/adsorbent is packed inside/outside the membranes depending on the position of the membrane active layer. The catalyst/adsorbent could be a mixture of catalyst and selective adsorbent or a solid that acts both as catalyst and as adsorbent. Typically, there are two liquid inlets (feed and desorbent) and two liquid outlets (extract and raffinate). For each column is collected a gas phase stream (permeate) containing the permeable species, and that are then assembled in

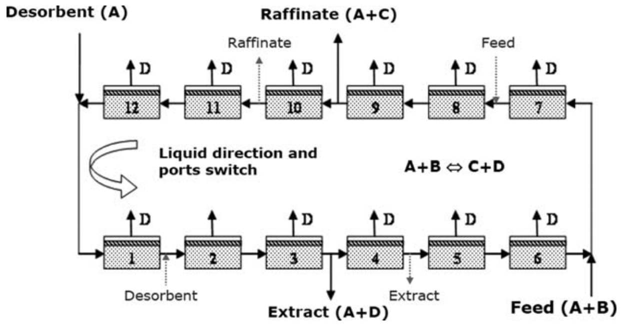

Figure 1. Schematic diagram of a PermSMBR unit with four sections and three columns per section.

At switching time n the inlets (Feed and Desorbent) and outlets (Extract and Raffinate) are represented by thick arrows, and for switching time *n*+1 they are represented by dashed arrows.

a global permeate stream. Figure 1 shows a schematic representation of a PermSMBR unit, where a reaction of type $A+B \leftrightarrow C+D$ is considered, having a total number of columns of 12, arranged in a configuration 3-3-3-3, meaning three columns per section.

The reactants *A* and *B* are introduced into the unit through the feed stream. Moreover, one of the reactants (*A* in this case) is also used as desorbent. The selection of the most suitable reactant to be used as desorbent should consider:

(i) no oligomerization in acid medium;
(ii) negligible membrane permeation;
(iii) less viscous to reduce pressure drop;
(iv) preferably, the most easy to separate from the products to minimize solvent recovery cost;
(v) preferably, the adsorption selectivity relatively to the products should be intermediate to decrease the desorbent consumption[25];
(vi) less toxic, dangerous and harmful.

The products formed (*C* and *D*) are separated due to the different affinities of the adsorbent towards these species, being the more adsorbed product (*D*) collected in the extract and the less retained (*C*) in the raffinate. Additionally, the permeable product (*D*) is also removed by pervaporation through the permeate streams. All the liquid inlet/outlet streams are introduced/removed from the system through ports positioned between the columns, and at regular time intervals, called the switching time, these streams are shifted one column distance in direction of the fluid flow. In this way, the countercurrent motion of the solid is simulated and its velocity is equal to the length of a column divided by the switching time. A cycle is completed when the number of switches is equal to a multiple of the total number of columns. The PermSMBR is equipped with a rotary valve or with a set of valves arranged in such manner that any inlet/outlet stream may be introduced/withdrawn from any column. Additionally, it is necessary to supply vacuum or sweep gas flow to withdraw the permeate stream from each column. If necessary, the membrane flux might be deactivated in some columns by switching off the vacuum or cutting the sweep gas flow. Similarly to the SMBR, the position of the liquid inlet/outlet streams defines different sections existing in the PermSMBR unit, each one accomplishing a certain function and containing a given number of columns.

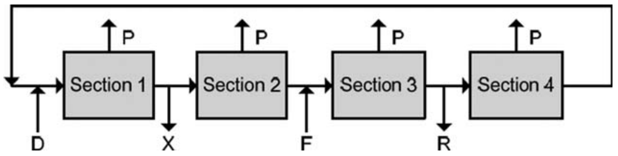

Figure 2. Schematic diagram of a PermSMBR unit with four sections: two inlet ports for feed (*F*) and desorbent (*D*) streams; two outlet ports for extract (*X*) and raffinate (*R*) streams; and outlet permeate streams (*P*).

The typical PermSMBR contains 4 sections, as represented in Figures 1 and 2:

- section 1 (between the desorbent and extract nodes), where the adsorbent is regenerated by desorption of the more strongly adsorbed product (*D*) from the solid using the desorbent (*A*);
- sections 2 (between the extract and feed nodes) and 3 (between the feed and raffinate nodes), where reaction takes place and the products *C* and *D* are separated as they are being formed, leading to reaction conversion beyond the thermodynamic equilibrium up to 100% of reactants conversion;
- section 4 (between the raffinate and desorbent nodes), where the desorbent is regenerated by adsorption of the less adsorbed product (*C*) and then it is recycled to section 1.

In all the sections, the permeable product D is continuously removed, enhancing the adsorbent regeneration (sections 1 and 4) and the reaction conversion (sections 2 and 3).

The PermSMBR can have different configurations depending on the total number of liquid streams fed/removed from the unit, which corresponds to the total number of sections. For example, the PermSMBR unit can be simplified to a unit of three sections: eliminating the extract stream, if the membrane is selective to the more adsorbed product (Figure 3); or eliminating the raffinate stream, if the membrane is selective to the less retained product (Figure 4). In the three sections unit, where the extract stream was eliminated (Figure 3), the reactants are fed continuously between sections 1 and 2, where reaction takes place and the formed products are separated. The less adsorbed product is collected at the outlet of section 2 (raffinate stream), while the most adsorbed product is removed through the membranes. The desorbent is introduced continuously into section 1 and it is regenerated into section 3, before being recycled to section 1. Using this operating configuration, it is not imperative to completely regenerate the adsorbent into section 1, before going to section 3, since the most adsorbed product can also be removed at the end of section 3 (through the membranes), without the contamination of

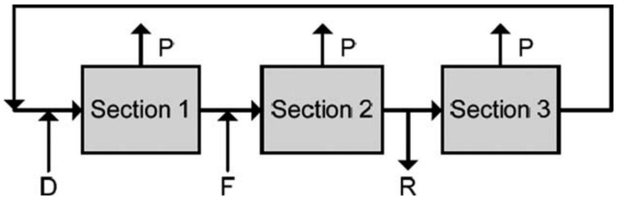

Figure 3. Schematic diagram of a PermSMBR unit with three sections: two inlet ports for feed (*F*) and desorbent (*D*) streams and one outlet port for raffinate (*R*) stream.

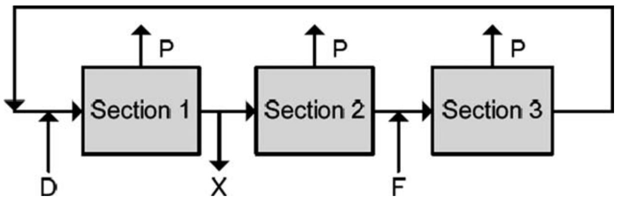

Figure 4. Schematic diagram of a PermSMBR unit with three sections: two inlet ports for feed (*F*) and desorbent (*D*) streams and one outlet port for Extract (*X*) stream.

raffinate stream. Considering Figure 4, the reactants are fed continuously between sections 2 and 3, where the reaction takes place and the products are separated as they are formed. The most adsorbed product is collected at the outlet of section 1 (extract stream), while the less adsorbed product is collected at the permeate streams. Once again, the desorbent is introduced continuously into section 1, and it is regenerated into section 3, before being recycled to section 1. However, in this operation mode, it is not necessary, to completely regenerate the desorbent on section 3, since the less retained component can be also removed at the beginning of section 1, through the selective membranes, preventing the extract contamination. Nevertheless, it is necessary to ensure the complete regeneration of the adsorbent in section 1.

In this work, hydrophilic membranes are used, and since water is the more retained component, the extract stream can be eliminated, leading to the configuration represented in Figure 3 that will be evaluated for the ethyl lactate synthesis.

PermSMBR Mathematical Model

The PermSMBR results from the integration of the pervaporation membrane reactor and the simulated moving bed reactor and, therefore, its model takes into account the following assumptions:

- axial dispersion flow for the bulk fluid phase;
- linear driving force (LDF) approximation for the inter and intraparticle mass transfer rates;
- multicomponent adsorption equilibrium at the adsorbent phase;
- liquid velocity variations due to reaction, adsorption/desorption and species permeation;
- constant porosity and length of the packed bed;
- membrane concentration polarization;
- isothermal operation.

In Figure 5, a schematic representation of the fluxes inside a membrane of the PermSMBR is shown: F is the molar flux in the feed side (retentate) and J is the permeate molar flux through the membrane.

The PermSMBR model equations are:

Bulk fluid mass balance to component i *in column* k

$$\frac{\partial C_{ik}}{\partial t}+\frac{\partial (C_{ik}u_k)}{\partial z}+\frac{(1-\varepsilon)}{\varepsilon}\frac{3}{r_p}K_{\mathrm{L},ik}\left(C_{ik}-\overline{C}_{p,ik}\right) = D_{\mathrm{ax},k}\frac{\partial^2 C_{ik}}{\partial z^2}-\frac{A_\mathrm{m}}{\varepsilon}J_{ik} \quad (1)$$

where C_{ik} and $\overline{C}_{p,ik}$ are the bulk and average particle concentrations in the liquid phase of species i in column k, respectively; $K_{\mathrm{L},ik}$ is the global mass transfer coefficient of the component i; ε is the bulk porosity; t is the time variable; z is the axial coordinate; $D_{\mathrm{ax},k}$ is the axial dispersion coefficient in column k; u_k is the interstitial velocity in column k; r_p is the particle radius; A_m is the membrane area per unit reactor volume; and J_{ik} is the permeate flux of species i in column k.

Pellet mass balance to component i, *in column* k

$$\varepsilon_p\frac{\partial \overline{C}_{p,ik}}{\partial t}+\left(1-\varepsilon_p\right)\frac{\partial q_{ik}}{\partial t}=\frac{3}{r_p}K_{\mathrm{L},ik}\left(C_{ik}-\overline{C}_{p,ik}\right)+\upsilon_i\rho_p\eta r\left(\overline{C}_{p,ik}\right) \quad (2)$$

where q_{ik} is the average adsorbed phase concentration of species i in column k in equilibrium with $\overline{C}_{p,ik}$, ε_p is the particle porosity, υ_i is the stoichiometric coefficient of component i, ρ_p the particle density, η is the effectiveness factor of the catalyst and r is the chemical reaction rate relative to the average particle concentrations in the fluid phase.

Interstitial fluid velocity variation calculated from the total mass balance

$$\frac{du_k}{dz}=-\frac{(1-\varepsilon)}{\varepsilon}\frac{3}{r_p}\sum_{i=1}^{n}K_{\mathrm{L},ik}V_{\mathrm{mol},i}\left(C_{ik}-\overline{C}_{p,ik}\right)-\frac{A_m}{\varepsilon}\sum_{i=1}^{n}J_{iK} \quad (3)$$

where $V_{\mathrm{mol},i}$ is the molar volume of component i; and n is the total number of components.

Initial and Danckwerts boundary conditions

$$t=0: \quad C_{ik}=\overline{C}_{p,ik}=C_{ik,0} \text{ and } q_{ik}=q_{ik,0} \quad (4)$$

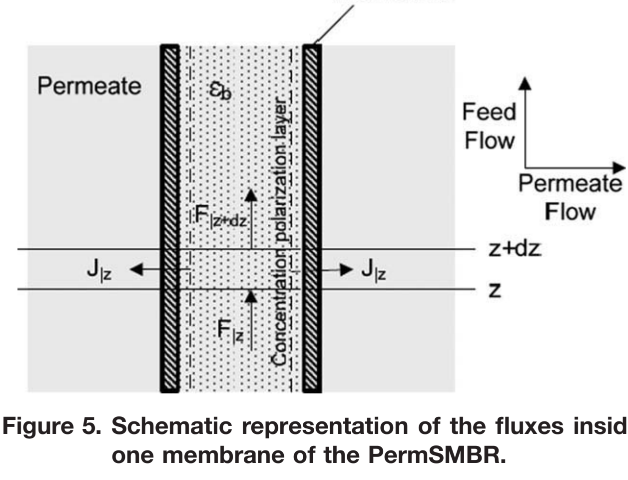

Figure 5. Schematic representation of the fluxes inside one membrane of the PermSMBR.

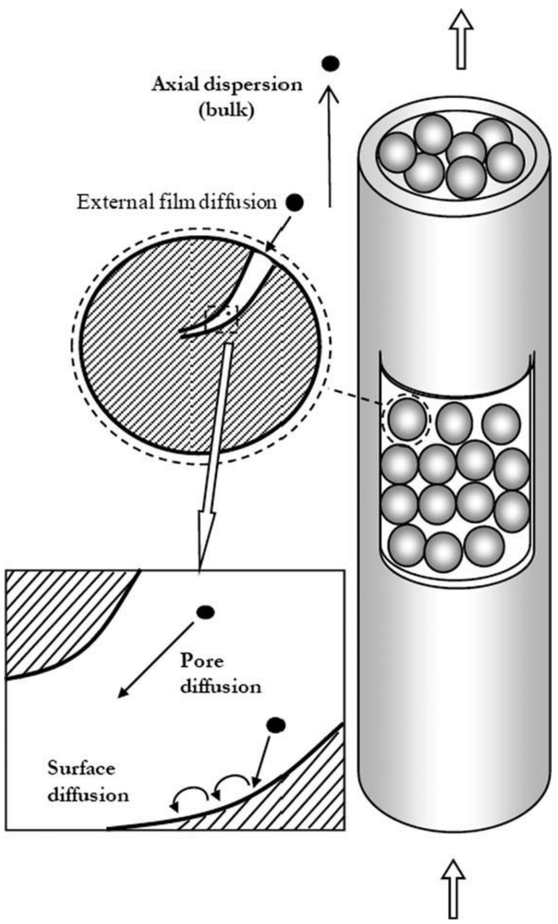

Figure 6. Schematic representation of the mass transfer mechanisms in a packed bed.

$$z = 0: \quad u_k C_{ik} - D_{ax,k} \left.\frac{\partial C_{ik}}{\partial z}\right|_{z=0} = u_k C_{ik,F} \tag{5a}$$

$$u_k = u_{k,0} \tag{5b}$$

$$z = L_c: \quad \left.\frac{\partial C_{ik}}{\partial z}\right|_{z=Lc} = 0 \tag{5c}$$

where the subscripts F and 0 refer to the feed and initial states, respectively.

Mass balances at the nodes of the inlet and outlet lines of the PermSMBR

Desorbent node $(j = 1)$:

$$C_{i(j=4,z=Lc)} = \frac{u_1}{u_4} C_{i(j=1,z=0)} - \frac{u_D}{u_4} C_i^D \tag{6a}$$

Extract $(j = 2)$ and Raffinate $(j = 4)$ nodes :

$$C_{i(j-1,z=Lc)} = C_{i(j,z=0)} \tag{6b}$$

$$\text{Feed node}: \ (j = 3): \quad C_{i(2,z=Lc)} = \frac{u_3}{u_2} C_{i(3,z=0)} - \frac{u_F}{u_2} C_i^F \tag{6c}$$

where,

$$u_1 = u_4 + u_{\mathrm{Ds}} \text{ Desorbent } (D) \text{ node ;} \tag{7a}$$

$$u_2 = u_1 - u_{\mathrm{X}} \text{ Extract } (X) \text{ node ;} \tag{7b}$$

$$u_3 = u_2 + u_{\mathrm{F}} \text{ Feed } (F) \text{ node ;} \tag{7c}$$

$$u_4 = u_3 - u_{\mathrm{R}} \text{ Raffinate } (R) \text{ node ;} \tag{7d}$$

The ratio between the fluid interstitial velocity, u_j, and the simulated solid velocity, $Us = L/t^*$, could be defined for each section giving a dimensionless parameter $\gamma_j = u_j/Us$, which will be used for the determination of the feasible operating conditions for specific purity and conversion requirements.

Mass transfer parameters in the resin bed

The mass transfer effects in packed beds are due to four main mechanisms: axial mixing in the bulk mobile phase percolating between the stationary phase particles in the column (axial dispersion); mass transfer of molecules between the bulk mobile phase and external surface of the stationary phase particles (external mass transfer); diffusive migration through the pores inside the particles (internal diffusion); and surface diffusion. A schematic illustration of the mass transfer mechanisms that may occur in a packed bed is shown in Figure 6.

The axial dispersion coefficient (D_{ax}) is estimated from the empirical correlation, valid for liquids in packed beds[26]:

$$\varepsilon Pe_{\mathrm{p}} = 0.2 + 0.011\ \mathrm{Re}_{\mathrm{p}}^{0.48} \tag{8}$$

in which $Pe_{\mathrm{p}} = d_{\mathrm{p}}u/D_{\mathrm{ax}}$ and $Re_{\mathrm{p}} = \rho\ d_{\mathrm{p}}\ u/\eta$ are the Peclet and Reynolds numbers relative to particle, respectively.

The proposed model considers a global mass transfer coefficient for the resin beads (K_{L}), which combines the external and internal mass transfer coefficients for adsorbable species,[27] defined, for each component, as:

$$\frac{1}{K_{\mathrm{L}}} = \frac{1}{k_{\mathrm{e}}} + \frac{1}{\varepsilon_{\mathrm{p}} k_{\mathrm{i}}} \tag{9}$$

wherein k_{e} and k_i are the external and internal mass transfer coefficients, respectively. The external mass transfer coefficient was calculated as a function of the Reynolds number and the Schmidt number, using the Wilson and Geankoplis correlation,[28] while the internal mass transfer coefficient was estimated by $k_i = 5D_{\mathrm{in}}/(r_{\mathrm{p}}\tau)$.[29]

Membrane flux

The permeate flux (J_i) is defined as:

$$J_i = k_{\mathrm{ov},i}(a_i p_i^0 - y_i P_{\mathrm{perm}}) \tag{10}$$

where a_i is the activity of component i in bulk; p_i^0 is the saturation pressure of component i; P_{perm} is the total pressure on the permeate side; y_i is the molar fraction of component i in the vapor phase (permeate side), $y_i = J_i / \sum_{i=1}^{n} J_i$; and $k_{\mathrm{ov},i}$ is the global membrane mass transfer coefficient, which

Table 2. Rates of Reaction for the Synthesis of Ethyl Lactate[33] and Diethylacetal[34]

Reaction	Esterification	Acetalization
Catalyst	Amberlyst 15 wet	Amberlyst 18 and 15 wet
Reaction rate	$r = k_C \frac{a_A a_{B1} - a_{C1} a_D / K_{eq}}{(1 + K_{s,A} a_A + K_{s,D} a_D)^2}$	$r = k_C \frac{a_A a_{B2} - a_{C2} a_D / (K_{eq} a_A)}{(1 + K_{s,D} a_D)^2}$
Activity coefficients	UNIQUAC model	UNIFAC model

combines the resistance due to the diffusive transport in the boundary layer with the membrane resistance[30]:

$$\frac{1}{k_{ov,i}} = \frac{1}{Q_{memb,i}} + \frac{\gamma_i^* p_i^0 V_{mol,i}}{K_{bl}} \tag{11}$$

in which $Q_{memb,i}$ is the permeance of component i through the membrane; γ_i^* is the activity coefficient of component i; and K_{bl} is the boundary layer mass transfer coefficient. For laminar flow and Graetz number ($d_{int}^2\ u/(D_m\ L)$) much greater than one, the mass transfer coefficient for transport in the boundary layer, k_{bl}, is determined by the Lévêque correlation[31]:

$$Sh = 1.62 Re^{0.33} Sc^{0.33} \left(\frac{d_{int}}{L}\right)^{0.33} \qquad (\mathrm{Re} < 2300) \tag{12}$$

where $Sh = k_{bl}\ d_{int}\ / D_m$ and $Re = \rho\ d_{int}\ u/\mu$ are the Sherwood and Reynolds numbers relative to membrane, respectively; $Sc = \mu/(\rho\ D_m)$ is the Schmidt number; D_m is the solute diffusivity in the boundary layer; d_{int} is the inside diameter of the membrane; L is the membrane length; ρ and μ are the bulk liquid mixture density and viscosity, respectively. The prediction of the species diffusivity was made using the Perkins and Geankoplis method,[32] and further details concerning its calculation for diethylacetal and ethyl lactate systems can be found in previous works.[12,13]

The permeances of the species (involved in the ethyl lactate synthesis) trough the commercial hydrophilic silica membranes considered in this work were determined in a previous study and are given by[9]:

$$Q_{memb,A} = 2.36 \times 10^{-12} \exp\left(\frac{22.6 \times 10^3}{RT}\right) \quad (\mathrm{mol/(s\ m^2\ Pa)}) \tag{13}$$

$$Q_{memb,C1} = 1.99 \times 10^{-9} \exp\left(\frac{10.4 \times 10^3}{RT}\right) \quad (\mathrm{mol/(s\ m^2\ Pa)}) \tag{14}$$

$$Q_{memb,D} = 3.278 \times 10^{-11} \exp\left[\frac{32.3 \times 10^3}{RT} + \left(18.64 - \frac{50.4 \times 10^3}{RT}\right) x_D\right] \quad (\mathrm{mol/(s\ m^2\ Pa)}) \tag{15}$$

where x_D is the water mole fraction; T is the absolute temperature and R is the ideal gas constant. It was observed that lactic acid does not permeate trough the membrane. At 50°C, the permeance of water varies from 5.5×10^{-6} mol/(s m^2 Pa), at infinite dilution, up to 4.9×10^{-6} mol/(s m^2 Pa) at bulk conditions. Comparing to water, ethyl lactate and ethanol permeances (9.6×10^{-8} and 1.1×10^{-10} mol/(s m^2 Pa), respectively) are negligible. The acetaldehyde and diethylacetal permeances were assumed to be similar to those of ethanol and ethyl lactate, respectively, due to similarity in terms of molecular size and chemical composition. The vapor pressure of ethanol, lactic acid, acetaldehyde, diethylacetal, ethyl lactate and water, at 50°C, is 0.267, 0.001, 2.601, 0.147, 0.019, and 0.124 bar, respectively.

Reaction rates

The reaction rate of the esterification and acetalization are shown in Table 2, and their kinetic and thermodynamic parameters were experimentally determined in previous works.[33,34]

Adsorption equilibrium

The multicomponent adsorption is described by the extended Langmuir isotherm model:

$$\overline{q}_i = \frac{Q_i K_i \overline{C}_{p,i}}{1 + \sum_{j=1}^{NC} K_j \overline{C}_{p,j}} \tag{16}$$

where Q_i and K_i are the total molar capacity per unit volume of resin and the equilibrium constant for component i, respectively. The adsorption parameters over Amberlyst 15-wet were experimentally determined at 20 and 50°C for the ethyl lactate system[13]; and at 15°C for diethylacetal system.[12] In this work, the operating temperature is set at 50°C and, therefore, for diethylacetal system, an approximation is made considering that adsorption parameters at 50°C are the same as those at 15°C. The validity of this approximation is corroborated by the data obtained for the ethyl lactate system for different temperatures.[13] As can be seen in Figure 7, the ethanol/water breakthrough curves at 20 and 50°C, obtained in a fixed bed column packed with Amberlyst 15-wet, are very similar. Deviations are mainly due to liquid density variations due to temperature that affect the total concentration of liquid mixtures.

PermSMBR Performance Parameters

Similarly to SMBR, the PermSMBR performance parameters are important indicators that will be used to evaluate the process feasibility under different operating conditions and to compare both technologies.

Purity

The purity of the raffinate and extract streams at cyclic steady state over a complete cycle is defined as:

Raffinate purity :

$$PUR\ (\%) = 100 \frac{\int_t^{t+N_C t*} C_{R,C}\, dt}{\int_t^{t+N_C t*} \left(C_{R,B} + C_{R,C} + C_{R,D}\right) dt} \tag{17a}$$

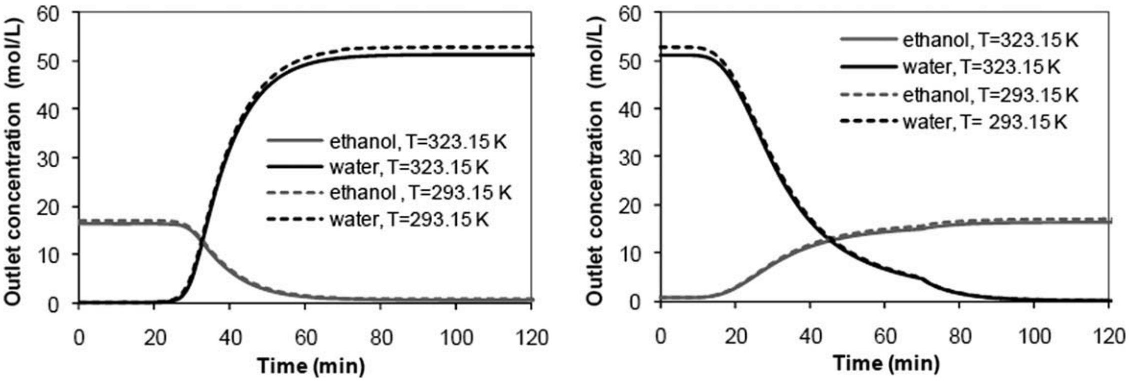

Figure 7. Breakthrough curves: outlet concentration of ethanol and water as a function of time at two different temperatures, 293.15 and 323.15 K.

(a) water displacing ethanol; (b) ethanol displacing water.

$$\text{Extract purity}: \ \text{PUX}\ (\%) = 100 \frac{\int_t^{t+N_c t*} C_{X,D} dt}{\int_t^{t+N_c t*} \left(C_{X,B}+C_{X,C}+C_{X,D}\right) dt} \tag{17b}$$

The numerator of the above equations indicates the quantity of the target component collected in the product stream (extract or raffinate) within a complete cycle, while the denominator indicates the sum of the products and unconverted reactants collected with exception of the reactant used as desorbent.

Conversion

The limiting reactant conversion is calculated through the amount fed during a cycle discounting the amounts withdrawn at extract and raffinate streams, according to the next

$$\text{equation}: \ X = 1 - \frac{Q_X \int_t^{t+N_c t*} C_{X,B} dt + Q_R \int_t^{t+N_c t*} C_{R,B} dt}{Q_F C_{F,B} N_c t*} \tag{18}$$

Productivity

The productivity, PR, is an important indicator from the economic point of view and, is defined considering the target product produced, ethyl lactate or diethylacetal, and withdrew from the raffinate stream.

$$\text{PR}\left(\frac{kg_C}{\text{day} L_{\text{adsorbent}}}\right) = \frac{Q_R \int_t^{t+N_c t*} C_{R,C} dt}{(1-\varepsilon) V_{\text{unit}} N_c t*} \tag{19}$$

This parameter indicates how much product is produced per amount of adsorbent/catalyst used in the unit.

Desorbent consumption

Other important performance parameter is the desorbent consumption, DC, which reflects on the costs involved in the separation of the solvent from the products.

$$\text{DC}(L_A/Kg_C) = N_c t * \frac{Q_D C_{D,A} + Q_F(C_{F,A} - \upsilon_A X C_{F,B})}{Q_R \int_t^{t+N_c t*} C_{R,C} dt} \tag{20}$$

This parameter is calculated from the total amount of desorbent (ethanol) fed to the system through the feed and desorbent streams, discounting the amount consumed by reaction.

Numerical solution

The above model equations were solved numerically by using the gPROMS-general PROcess Modelling System version: 3.1.3. The mathematical model involves a system of partial and algebraic equations (PDAEs). The axial domain was discretized using third order orthogonal collocation in finite elements method (OCFEM). Ten finite elements per column with two collocation points in each element were used. The system of ordinary differential and algebraic equations (ODAEs) was integrated over time using the DASOLV integrator implementation in gPROMS. For all simulations was fixed a tolerance equal to 10^{-5}. It is assumed that a PermSMBR simulation has reached the cyclic steady state when the columns profiles in two consecutive cycles have less than 1.0% of relative deviation and the global mass balance is verified with less than 1.0% of relative error.

PermSMBR Geometrical Specifications

The PermSMBR unit considered consists in 12 columns where each column has 13 commercial hydrophilic tubular membranes (Pervatech BV) to dehydrate the reaction medium. Regarding the position of the membrane separation layer, it is possible to have different configurations. In the case of the silica membranes from Pervatech, the selective layer is inside the tube and consequently, it was considered that these membranes were packed with the resin Amberlyst 15-wet, that acts as catalyst and as selective adsorbent, in the lumen side (inside the membrane tube). The PermSMBR characteristics (length of the bed and number of membranes) were set by imposing the same mass of catalyst and effective cross-sectional area (εA) than that of the SMBR, to compare the performance of both processes in equivalent conditions. The PermSMBR porosity was estimated from the experimental results obtained in fixed bed columns with ratio between tube diameter and particle diameter of ten.[35] The characteristics of the columns are presented in Table 3.

Ethyl Lactate Synthesis

The ethyl lactate synthesis using the SMBR was previously studied, at 50°C.[18] Ethanol, that is one of the reactants, was also selected as desorbent since fulfils all the requirements mentioned in section 1.2. The lactic acid is commonly available as an

Table 3. Characteristics of the Columns for Both SMBR[17,18] and PermSMBR

	SMBR	PermSMBR
Solid weight (A15)	47.6 g	47.6 g
Length of the bed (L)	23.00 cm	25.45 cm
Internal diameter (D_i)	2.6 cm	0.7 cm*
Bed porosity (ε)	0.400	0.424
Bulk density (ρ_b)	390 kg/m^3	374 kg/m^3
Number of membranes	–	13

*Related to membrane internal diameter.

aqueous solution and, therefore, it is not suitable to be used as desorbent since the water content is typically about 10–15%. Additionally, it is very viscous which would lead to high pressure drops and would increase the mass transfer resistances, reducing the unit productivity. The best SMBR performance was obtained for the following operation conditions: feed of lactic acid solution (85 wt % in water); desorbent of ethanol (99.5 wt % in water); configuration of 3-3-4-2; switching time of 2.1 min; desorbent and recycle flowrates of 58 and 27 mL/min, respectively ($\gamma_1 = 3.654$ and $\gamma_4 = 1.161$). In this work, the PermSMBR will be evaluated and compared with the SMBR to demonstrate that the ethyl lactate production is enhanced by the integration of water permselective membranes in the SMBR unit and, therefore, equivalent operation conditions will be used. Using the same flowrates in section 1 and 4, it is necessary to use a switching time (t^*) of 2.323 min to keep the same γ_1 and γ_4. Additionally, it was set a vacuum pressure of 10 mbar in the permeate side of the PermSMBR unit. Aiming to evaluate the equivalence between the two units, the SMBR was compared to the PermSMBR in absence of permeation by using the operating conditions mentioned before and setting feed and extract flow rates of 7 and 39 mL/min, respectively, for both units. It can be verified in Table 4 that the performance parameters are very similar for both processes.

Reactive/separation region: PermSMBR versus SMBR

PermSMBR operating conditions to obtain products with specific purity requirement are obtained from the reactive/separation region in the $\gamma_2 - \gamma_3$ plane, which is a feasible region in terms of the operating conditions in sections 2 and 3, for given conditions on sections 1 and 4 (γ_1 and γ_4) that ensures complete regeneration of adsorbent and desorbent, respectively. The reactive/separation regions for the SMBR/PermSMBR setting a criteria of 95% for extract and raffinate purity and, also, for the lactic acid conversion were determined from the average concentrations over a cycle obtained by the SMBR/PermSMBR model at cyclic steady state. The cyclic steady state mathematical model was successively solved for several values of γ_2 and γ_3, keeping the values of $\gamma_1 = 3.654$ and $\gamma_4 = 1.161$. The γ_3 value must be higher than γ_2, since the diagonal $\gamma_2 = \gamma_3$ corresponds to zero feed flow rate. The algorithm used in the construction of the reactive/separation region begins by setting a feed flow rate of 0.01 ml/min and the value of γ_2 equal to 1.161. Then, the feed flow rate was kept constant and the γ_2 values were gradually increased. The value of γ_3 was calculated from the mass balance in the feed node for each value of γ_2. For each set of γ_2 and $\gamma_{3,}$ the conversion and the purities of extract and raffinate were estimated and the values that satisfy the criteria of 95% were selected to build the reaction/separation region. After this set of simulations, the feed flow rate was increased and the same procedure was repeated. The simulations procedure ends when is achieved the maximum value of feed flow rate that gives required product purities and conversion (vertex of the reaction/separation region). Above that feed flow rate value the requirements cannot be fulfilled for any pair of values of γ_2 and γ_3. The PermSMBR and SMBR reactive/separation regions, determined for the criteria of 95% for extract and raffinate purities and for lactic acid conversion and setting the conditions of $\gamma_1 = 3.654$ and $\gamma_4 = 1.161$, is shown in Figure 8. The PermSMBR reactive/separation region is larger than the one of the SMBR, which indicates better performance of the new technology. Since water is removed more efficiently, the lactic acid conversion in sections 2 and 3 is increased and the adsorbent regeneration in section 1 is improved, which allows processing higher feed flow rates without the contamination of the raffinate stream. The PermSMBR productivity is enhanced due to water selective removal through the membranes, which is reflected by the maximum feed flow rate of 12.1 mL/min processed in the unit, which is higher than the one processed in the SMBR

Table 4. Comparison Between SMBR and PermSMBR in Absence of Permeation

	SMBR	PermSMBR*
PUX (%)	99.92	99.94
PUR (%)	96.19	97.85
X (%)	99.51	99.37
PR ($Kg_{\mathrm{EL}}.L_{resin}^{-1}$ day^{-1})	14.64	14.63
DC (L_{Eth}/kg$_{\mathrm{EL}}$)	5.98	5.98

*Results obtained from the PermSMBR model considering zero flux through the membranes (equal to a SMBR).

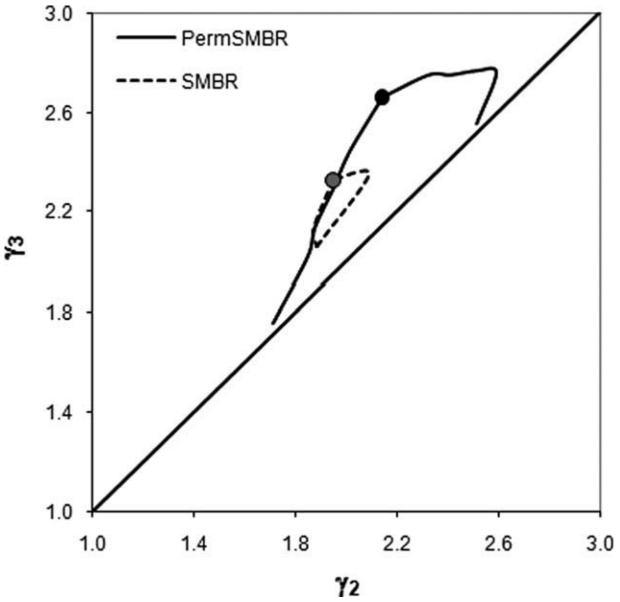

Figure 8. Reactive/separation region for PermSMBR and SMBR processes (PermSMBR switching time of 2.323 min and SMBR switching time of 2.1 min).

Table 5. Performance Parameters of the SMBR and PermSMBR for the EL Synthesis

	SMBR	PermSMBR	Improvement
PR ($Kg_{EL}.L_{resin}^{-1}$ day^{-1})	18.06	24.19	33.94 %
DC (L_{Eth}/kg$_{EL}$)	4.75	3.41	28.21 %

(8.8 mL/min). Additionally, the PermSMBR desorbent consumption is reduced as more ethanol is converted (decreasing the numerator of Eq. 20) and more ethyl lactate is produced (increasing the denominator of Eq. 20). In Figure 8, the vertex of the reactive/separation region (V) represents the maximum feed flow rate allowed in each unit, where both extract and raffinate streams have a purity of 95%. The highest throughput indicates the optimal operating condition that leads to the best performance, which is presented in Table 5. The ethyl lactate synthesis on the PermSMBR benefits its productivity in about 34% and, additionally, decreases the desorbent consumption in 28% which will reduce downstream costs since the products are less diluted.

PermSMBR with three sections

As stated before, the PermSMBR technology can be operated with different configurations and different number of sections. Depending on the permeable product, the most/less adsorbed, it is possible to remove the extract/raffinate stream, leading to a PermSMBR with 3 sections (PermSMBR-3s). Since the membranes are selective to water, the by-product formed in the ethyl lactate synthesis, it might be convenient to simplify the PermSMBR unit from 4 to 3 sections, eliminating the extract stream, which change the previous configuration 3-3-4-2 to 6-4-2. Using the operating conditions mentioned before, and setting the feed and desorbent flow rates at 8 and 25 mL/min, respectively, the desorbent consumption of the PermSMBR-3s (see Table 6 for $P_{perm} = 10$ mbar) is lower than that obtained at optimal conditions of the PermSMBR with 4 sections (Table 5); however, the remaining performance parameters are worst and the purity requirement is not fulfilled. This could be improved by changing the flowrates of each section or by adjusting the permeate pressure, as shown in Table 6. Lactic acid conversion and ethyl lactate purity are the parameters most significantly improved. The analysis of internal concentration profiles at the cyclic steady-state, shown in Figure 9, allows a better understanding of the PermSMBR unit behaviour. The reduction of the permeate pressure from 10 mbar, to 6 mbar and 0 mbar, increases the water permeation flux (Eq. 10), enhancing significantly the resin regeneration on section 1, which avoids water to pass from section 1 to section 3 and increases the ethyl lactate purity. Since the reaction is equilibrium limited, this decrease on water content near the raffinate port prevents the ethyl lactate hydrolysis, increasing the lactic acid conversion, as consequence. A SMBR unit to have the same raffinate purity, lactic acid conversion and ethyl lactate productivity as the PermSMBR-3s ($P_{perm} = 6$ *mbar*), would have to operate under the following conditions: configuration of 3-3-4-2, $t^* = 2.1$ min, $Q_F = 8$ *mL*/min, $Q_x = 38$ mL/min, $Q_D = 58$ mL/min and $Q_{Rec} = 27$ mL/min. However, this would imply a desorbent consumption of 5.20 L_{Eth}/kg$_{EL}$, which is 165% higher than the one needed for the PermSMBR-3s at 6 mbar.

Table 6. Performance Parameters of a 3 Sections PermSMBR for Different Permeate Pressures

P_{perm}	10 mbar	6 mbar	0 mbar
PUR (%)	92.85	96.15	99.63
X (%)	97.56	99.18	99.86
PR ($Kg_{EL}.L_{resin}^{-1}$ day^{-1})	16.27	16.51	16.59
DC (L_{Eth}/kg$_{EL}$)	2.00	1.96	1.95

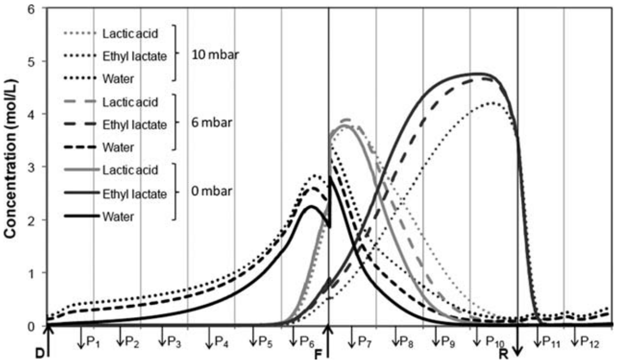

Figure 9. Influence of permeate pressure on the concentration profiles at the middle of the switching time at cyclic steady state for the PermSMBR-3s with configuration 6-4-2.

Comparison between PermSMBR, SMBR, and RD technologies

The ethyl lactate synthesis by means of RD, using Amberlyst 15-wet as catalyst, was successfully implemented by Asthana et al.[24]; and the best productivity of 40.63 $Kg_{EL}.L_{resin}^{-1}$ day^{-1} was obtained, when ethanol and an 88 wt % lactic acid solution were fed in a molar ratio of 3.6 (ethanol/lactic acid), using a bottom temperature of 128°C, achieving 95% of lactic acid conversion and 95% of ethyl lactate purity.[24] The best performances obtained on the SMBR and PermSMBR processes at 50°C, for 95% of ethyl lactate purity and lactic acid conversion are shown in Table 7; which are worse than that of the RD process. The productivities are being limited by the reaction rate since low temperatures (50°C) were used, and would be easily improved by increasing the operating temperature. Moreover, both SMBR and PermSMBR processes use a higher excess of ethanol to desorb the water, leading to higher ethanol consumption. This can be improved in the PermSMBR technology eliminating the extract stream, which is enabled by the water removal through the membranes. Once permeation will be overloaded, it would be also advantageous to operate at higher temperature. Therefore, when operating the PermSMBR with 3 sections (PermSMBR-3s) at 70°C ($t^* = 2.323$ min, $Q_F = 20.5$ mL/min, $Q_D = 34.0$ mL/min and $Q_{Rec} = 23.5$ mL/min,, $P_{perm} = 6$ mbar) the performance increases significantly (see Table 7). Comparing with the RD, an improvement of 60.37% in terms of ethanol consumption is achieved, for almost the same ethyl lactate productivity, even operating at lower temperatures. These results illustrate the great potential of this new technology. A fair comparison of technologies must be done in terms of economical assessment.

Table 7. Performance Parameters for RD, SMBR, and PermSMBR Technologies

	RD[24]	SMBR	PermSMBR	PermSMBR-3s
PR ($\mathrm{kg_{EL}}$ L_{resin}^{-1} day^{-1})	40.63	18.06	24.19	41.17
DC ($L_{\mathrm{Eth}}/\mathrm{kg_{EL}}$)	2.17	4.75	3.41	0.86

Diethylacetal Synthesis

Diethylacetal was successfully produced by means of the SMBR technology, using a mixture of acetaldehyde and ethanol as feed, ethanol as desorbent and Amberlyst 15-wet as both catalyst and adsorbent.[17] The use acetaldehyde as desorbent would be very advantageous to reduce the cost of desorbent recovery due to its low boiling point. However, since acetaldehyde oligomerization occurs onto the resin surface in absence of ethanol, it cannot be used as desorbent. In presence of ethanol, acetaldehyde oligorimerization is inhibited, being the acetalization the preferable reaction. Although the SMBR process for diethylacetal production has not the limitations of the ethyl lactate system (which has lower reaction rate, water content in the feed and higher mass transfer limitations due to lactic acid viscosity), the PermSMBR technology might decrease desorbent consumption and therefore it will be evaluated for the diethylacetal production. As mentioned before, the acetaldehyde permeance was considered equal to the one of the ethanol, which is almost negligible. However, the acetaldehyde vapor pressure (2.6 bar at 50°C) is much higher than that of ethanol (0.27 at 50°C), which implies a high driving force for the membrane flux. To avoid acetaldehyde losses trough the membranes, the vacuum was deactivated on the columns of sections 2 and 3, were the reaction occurs. The PermSMBR performance was calculated for the following operation conditions: feed of 51% of acetaldehyde in ethanol; configuration of 3-3-3-3; temperature of 50°C; switching time of 4.1 min; desorbent and recycle flow rates of 50 and 20 mL/min, respectively ($\gamma_1 = 3.654$, $\gamma_4 = 1.161$); feed flow rate of 13 mL/min and extract flow rate of 34 mL/min; leading to a productivity of 21.97 $Kg_{\mathrm{EL}}.L_{resin}^{-1}$ day^{-1} and a desorbent consumption of 3.20 $L_{\mathrm{Eth}}/\mathrm{kg_{EL}}$. The internal concentration profiles at the cyclic steady-state for those conditions (see Figure 10) show that is possible to obtain almost complete acetaldehyde conversion (99.98%) and pure diethylacetal (99.997%).

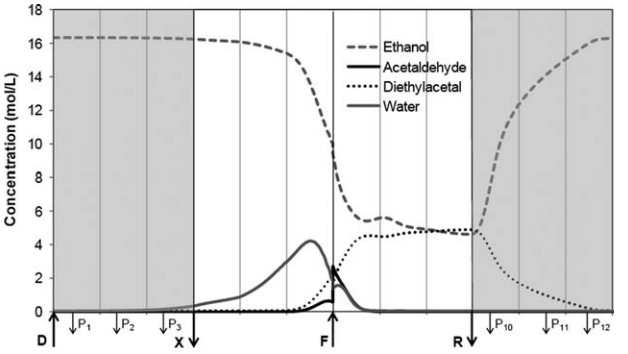

Figure 10. Concentration profiles at the middle of the switching time at cyclic steady state for the PermSMBR.

The performance of this new reactor was also compared with the one of the SMBR for the production of diethylacetal. The reactive/separation regions were determined for both processes imposing, once again, 95% criteria for extract and raffinate purities and acetaldehyde conversion and ensuring complete regeneration on sections 1 and 4 ($\gamma_1 = 5.302$, $\gamma_4 = 1.515$). The operating conditions used for SMBR are the same as those for PermSMBR, with exception of the switching time that was set at 3.7 min to keep the same γ_1 and γ_4. Additionally, the PermSMBR and the SMBR process were also evaluated through the regeneration regions for the same purity and conversion criteria, which define the operation conditions on sections 1 and 4, for given conditions on sections 2 and 3 ($\gamma_2 = 2.727$, $\gamma_3 = 3.712$). Theoretically, the minimum value of γ_1 has to be equal to γ_2, since it corresponds to zero extract flow rate; and the maximum value of γ_4 has to be equal to γ_3, since it corresponds to zero raffinate flow rate. The procedure to determine the regeneration region, where the vertex corresponds to the minimum desorbent flow rate that fulfils the defined criteria, is similar to that described for the reaction/separation region. The reactive/separation and regeneration regions are shown in Figure 11, proving that the diethylacetal production is improved using the PermSMBR technology, being possible to process higher feed flowrates (24.9 mL/min) than the ones processed when using the SMBR (17.7 mL/min) to obtain the same purity and conversion requirements, which implies higher productivity (+53.12%) and lower desorbent consumption (−40.50%) when this new reactor is used (see Table 8). The size of the regeneration region using the PermSMBR is larger than the one using the SMBR; and at the optimal operating conditions, the PermSMBR allows a reduction on the desorbent consumption of about 69% when compared with the SMBR for processing the same feed flow rate. For the PermSMBR, it is worth to mention that the lowest desorbent consumption is achieved when the extract flowrate is equal to zero, i.e. when this new technology is operated with just 3 sections eliminating the extract stream.

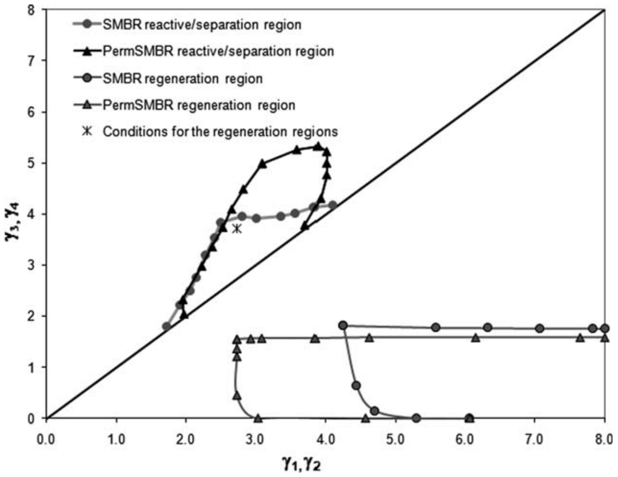

Figure 11. Reactive/separation and regeneration regions for PermSMBR (t^* = 4.1 min) and SMBR (t^* = 3.7 min) processes: T = 50°C and configuration 3-3-3-3.

Table 8. Performance Parameters for SMBR and PermSMBR Technologies for the Diethylacetal Production

	SMBR	PermSMBR	Improvement (%)
PR ($Kg_{EL}.L^{-1}_{resin}$ day^{-1})	27.40	41.95	53.12%
DC (L_{Eth}/kg$_{Ac}$)	2.47	1.47	40.50%

Conclusions

The PermSMBR, a new patented technology that combines the Simulated Moving Bed Reactor and Membrane Reactor into a single unit, was presented. The performance was evaluated through the developed mathematical model, which considers: (i) axial dispersion flow for the bulk fluid phase; (ii) inter and intraparticle mass transfer rates described by a linear driving force approximation; (iii) adsorption equilibrium described by the multicomponent Langmuir isotherm; (iv) reaction kinetics based on the Langmuir-Hinshelwood model; (v) membrane flux described by the solution-diffusion model; (vi) membrane concentration polarization; (vii) liquid velocity variations due to reaction, adsorption/desorption and species permeation; and (viii) isothermal operation.

The PermSMBR proved to be more effective than the SMBR when applied to the ethyl lactate and 1,1-diethoxyethane synthesis, having higher productivities and lower desorbent consumptions, for the same purity and conversion criteria.

For further improvement of the ethanol consumption, the extract stream containing ethanol/water was eliminated, leading to the 3 sections PermSMBR (PermSMBR-3s), which was studied for the ethyl lactate production. For an ethyl lactate productivity of about 16 $Kg_{EL}L^{-1}_{resin}$ day^{-1}, at 50°C, the SMBR ethanol consumption is 165% higher than the one of the PermSMBR-3s (sub-section 1.4.1.2). It was shown that the temperature has a significant effect onto the processes performance, which is controlled by the kinetics of the esterification reaction. The RD process at 128°C (bottom temperature) requires more 152% of ethanol consumption than the PermSMBR-3s at 70°C, for a productivity of about 41 $Kg_{EL}L^{-1}_{resin}$ day^{-1}.

Concluding, the PermSMBR is a competitive technology, even compared with other intensified processes, that allows significant reduction of solvent consumption and, consequently, lower downstreaming costs associated to the separation units, for complete reactants conversion, high productivity and purity.

Notation

a_i = liquid-phase activity of component i in bulk side
A_m = membrane area per unit reactor volume ($m^2_{membrane}/m^3_{bulk}$)
C = liquid phase concentration (mol/L)
D_{ax} = axial dispersion coefficient (m^2/min)
D_m = molecular diffusivity (m^2/min)
DC = desorbent consumption (L/mol)
d_p = particle diameter (m)
J_i = permeate flux of species i (mol/(m^{2}min))
K_L = global mass transfer coefficient
k_{ov} = global membrane mass transfer coefficient (mol/(m^{2}sPa))
L = column length (m)
n = total number of components
Pe_p = Peclet number relative to particle
p_i^0 = saturation pressure of component i (bar)
P_{perm} = total pressure on the permeate side (bar)
PR = raffinate productivity (kg$_{EL}$/(L_{resin}.day))
PUR = raffinate purity (%)
PUX = extract purity (%)
q = solid phase concentration in equilibrium with the fluid concentration inside the particle (mol/L)
Q = volumetric flowrate (L/min)
Q_{memb} = permeance (mol min^{-1} m^{-2} Pa^{-1})
r = rate of reaction (mol kg^{-1} min^{-1})
Re = Reynolds number
Re_p = Reynolds number relative to particle
r_p = particle radius (m)
t = time variable (min)
t^* = switching time (min)
U_s = solid velocity (m/min)
u = interstitial velocity (m/min)
$V_{mol,i}$ = molar volume of species i (L/mol)
X = lactic acid conversion
y_i = molar fraction in the vapor phase of component i
z = axial coordinate (m)

Greek letters

γ = dimensionless velocity ratio
γ^* = activity coefficient
ε = bulk porosity
ε_p = particle porosity
υ_i = stoichiometric coefficient of component i
ρ_p = particle density
μ = viscosity (cP)
η = effectiveness factor of the catalyst
τ = tortuosity

Subscripts

i = relative to component i ($i = A, B1, B2, C1, C2, D$)
j = relative to section in SMBR (j = 1, 2, 3, 4)
k = relative to column in SMBR
0 = relative to initial conditions
A = relative to ethanol
$B1$ = relative to lactic acid
$B2$ = relative to acetaldehyde
$C1$ = relative to ethyl lactate
$C2$ = relative to diethylacetal
D = relative to water
F = relative to the feed
p = relative to the particle
R = relative to raffinate
Rec = relative to recycle
X = relative to extract

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