Pervaporation: Promissory Method for the Bioethanol Separation of Fermentation

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It is clear that biofuels have a positive impact in the social, environmental and economic aspects of our world. In Brazil, ethanol is produced from sugarcane and is mainly used as a biofuel for cars. However, much research is being done in order to reduce the price of ethanol. With this goal in mind, pervaporation is being studied as a recovery process for ethanol from wine from fermentation, and to simplify the distillation step in order to reduce its production costs. More specifically, this research project studies ethanol separation by pervaporation from ethanol-water mixtures. The pervaporation was evaluated at 30 °C using a hydrophobic membrane of Polydimethylsiloxane (PDMS) for ethanol recovery, using ethanol concentrations characteristic of sugarcane fermentation.

 Keywords: Fermentation, ethanol, membranes processes, pervaporation.

1. Introduction

Biomass is a promising alternative for energy and chemicals derived from petroleum and other fossil based fuels. That is the case for the bioethanol that is produced from sugarcane in Brazil and from corn in the US (Dias et al., 2013; Renouf et al., 2008). In Brazil, bioethanol is used in its hydrous form in Flex Fuel vehicles and as anhydrous ethanol to mix with gasoline (Goldemberg et al., 2008), which is then made up of 25% ethanol.

A significant portion of the ethanol production process consists of the separation/dehydration stage. This has motivated the development of alternative processes to reduce its production costs. Economic analyses made through the internal return rate method have shown the economic feasibility of the membranes processes (Basile and Nunes, 2011). These processes allow the selective separation of components in a solution without thermal damage through the use of membranes (Basile and Nunes, 2011), which are considered technically important in industries where they have been used for purification of aqueous streams, concentration and recovery of valuable products, production of potable water, concentration or removal of dissolved ions, splitting gas streams, removal or recovery of specific gases, and separation and concentration of liquid mixtures (Bruschke, 1995). Among the different membrane processes are microfiltration, ultrafiltration, nanofiltration, reverse osmosis, electrodialysis, gas separation, and the pervaporation process (Bruschke, 1995). The last one can be considered an attractive process for the continuous removal of ethanol from fermentation wine, decreasing production costs and increasing its profitability (Basile and Nunes, 2011; Le et al., 2013; Luccio et al., 2002; Vane, 2005).

2. Pervaporation

Pervaporation is a process in which the component of interest, in liquid state, is removed from a matrix liquid (feed) through a membrane by the application of a differential pressure (low pressure) between the walls thereof, sufficient to bring the component into a gaseous state and get it removed on the other side of the membrane, obtaining a flow with a high concentration of the desired component (permeate) in gas state and

another flow with low concentration of the desired component (retentate). This process can be operated by applying a pressure differential between the membrane walls through a vacuum pump or a carrier gas, thus obtaining a gaseous flow that is subsequently condensed into the permeate (Figure 1) (Feng and Huang, 1997).
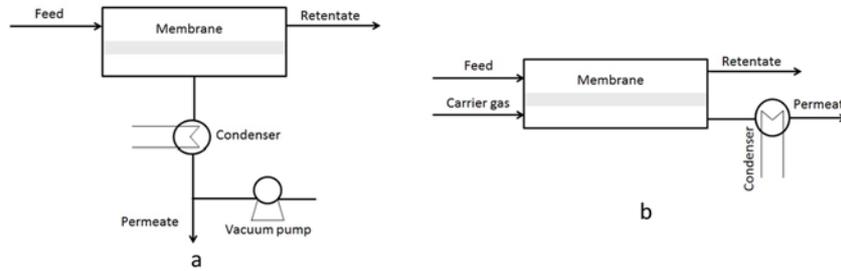

Figure 1: Alternative operation of pervaporation process. a) Vacuum pervaporation, b) carrier gas pervaporation.

In biofuels, pervaporation is a promising process as an extractive unit to be coupled to the fermentation unit for ethanol recovery (Sharma and Rangaiah, 2012), as used in this project, or, as is more common, together with a distillation unit for ethanol dehydration or even to remove water-ethanol at azeotropic mixtures (Hömmerich and Rautenbach, 1998).

2.1 Membrane

The membrane is the most important part of pervaporation—it is where the phenomenon of separation is taking place through a solution-diffusion mechanism. As such, the membrane must satisfy three important requirements: productivity, selectivity, and stability (Feng and Huang, 1997).

Membrane productivity: is characterized by permeation flux, J, which is a measure of the quantity of a component that permeates through a specific area of membrane in a given unit of time (Xiangli et al., 2007).

Membrane selectivity: is the ability to permeate a specific compound through the membrane. It is expressed by a separation factor, α, which is a dimensionless quantity dependent on the concentration of the permeate component (Equation 1) (Alvarez 2005).

$$\alpha = \left(\frac{\chi_{i,p}}{1-\chi_{i,p}}\right)\left(\frac{1-\chi_{i,f}}{\chi_{i,f}}\right) \qquad (1)$$

Where $\chi_{i,p}$ and $\chi_{i,f}$ are the molar fractions of permeate component in the feed and permeate, respectively.

Membrane stability: is defined as the ability of a membrane to maintain both the permeability and selectivity under specific system conditions for an extended period of time (Feng and Huang, 1997).

In terms of their characteristics, the membranes used for pervaporation are made from both asymmetric and composite non-porous materials (Purchas and Sutherland, 2002) and present high productivity, good selectivity, and long-termstability (Le et al., 2013). Thus, the most commonly reported membrane for the recovery of biofuels is PDMS (Li et al., 2013; Li et al., 2011), a hydrophobic membrane selective for alcohols, such as ethanol and butanol, and VOCs from dilute aqueous solutions due to their elastomeric characteristics that gives excellent film-forming ability, thermal stability, and chemical and physiological inertness (Yadav et al., 2013). It is due to all these characteristics that it was used in this research project.

2.2 Pervaporation Model

Two most used models that described the mass transfer phenomenon of the components through the membrane are: the pore flow model and the solution-diffusion model. The second model is accepted by the majority of membrane researchers (Feng and Huang, 1997) and was used in the development of this project. The solution-diffusion model is based on three steps: i) Solution of the components through the feed/membrane interface, ii) Diffusion of the components through the membrane, and iii) Desorption of the components of the permeate side (Alvarez at al., 2008). Thus, the pervaporation model developed by Alvarez (2005) was used in this project.

The PERVAP simulator was developed using FORTRAN language (Compaq Visual Fortran Professional Edition 6.6.a). Activity coefficients of the components in the feed phase (γ_i) were determined using the UNIFAC method. The prediction of the diffusion coefficient (D_i^m) was carried out using the free-volume theory. The free-volume parameters were estimated from viscosity and temperature data of pure

components and the binary interaction parameter between the component and the polymer was determined using the group-contribution lattice-fluid equation of state (Araujo et al., 2008; Alvarez et al., 2008).

The diffusion coefficient of component i (ethanol) in the membrane, (D_i^m), was predicted by the free-volume theory described by equation (2).

$$D_i^m = D_0(1 - \phi_1)^2(1 - 2\chi\phi_1)\exp\left(\frac{-E}{RT}\right) exp\left(-\frac{\omega_1 \hat{V}_1^* + \xi\omega_2 \hat{V}_2^*}{\frac{K_{11}}{\gamma}\omega_1(K_{21} - T_{g1} + T) + \frac{K_{12}}{\gamma}\omega_2(K_{22} - T_{g2} + T)}\right) \qquad (2)$$

Where D_0 is a constant pre-exponential factor, E is the energy required to overcome attractive forces from neighboring molecules, γ is an overlap factor for free-volume, $\hat{V}_1^*$ and $\hat{V}_2^*$ are the specific critical hole free volumes of component i and the polymer required for jump, ω_1 is the solvent weight fraction, ω_2 is the polymer weight fraction, ξ is the ratio of critical molar volume of solvent jumping unit to that of polymer jumping unit, K_{11} and K_{21} are the solvent free-volume parameters, K_{12} and K_{22} are polymer free-volume parameters, ϕ_1 is the component volume fraction, χ is the component/polymer interaction parameter, T_{gi} is the solvent glass transition temperature, T is the temperature, and R is the gas constant. The Free-volume parameters used in this research project are shown in table 1.

Table 1: Free-volume parameters (Alvarez 2005)

Parameters	Ethanol	Water
$\hat{V}_1^*$ (cm^3/g)	0.985	1.071
$\frac{K_{11}}{\gamma}$ (cm^3/g K)	0.312×10-3	2.180×10-3
$K_{21} - T_{g1}$ (K)	111.80	-152.29
D_0 (cm^2/s)	11.6×10-4	8.55×10-4
χ	0.170	0.003
ξ	0.831	0.236
E (cal/mol)	0	0

The permeate flux, J, to components i (ethanol) and i (water) are predicted by equations 3 and 4.

$$J_i = \frac{D_i^m}{l\bar{\gamma}_i^m}\left(\chi_{i,f}\gamma_{i,f} - \frac{\chi_{i,f}\alpha P}{1 + (\alpha - 1)\chi_{i,f}}\right) \qquad (3)$$

$$J_j = \frac{D_j^m}{l\bar{\gamma}_j^m}\left(\chi_{j,f}\gamma_{j,f} - \frac{(1 - \chi_{i,f})pP_i^{sat}}{P_j^{sat}[1 + (\alpha - 1)\chi_{i,f}]}\right) \qquad (4)$$

where, J is the permeate flux (mol/m^{2}h), $\chi_{i,f}$ is the mole fraction to component i in the feed, P^{sat} is the vapor pressure (kPa), p is the relative pressure, $\bar{\gamma}_i^m$ and $\gamma_{i,f}$ are the activity coefficients to component i in the membrane and feed respectively (m^3/mol), D_i^m is the diffusion coefficient (m^2/h) to component i in the membrane, and α is the selectivity.

The selectivity is calculated from equation 1.

The composition of component i in the permeate, $\chi_{i,p}$, is determined from permeate component partial fluxes (Equation 6).

$$\chi_{i,p} = \frac{J_i}{J_i + J_j} \qquad (5)$$

This model has been validated and used in the pervaporation separation of aqueous mixtures of ethanol (Alvarez et al., 2008), phenol (Moraes et al., 2009) and ethyl butyrate (Araujo et al., 2008).

3. Simulation

The simulations were carried out in the PERVAP simulator developed and validated by Alvarez (2005). This software is based on the solution-diffusion model to represent the mass transport of the permeate components through the membrane. The free-volume parameters are calculated using viscosity data, the temperature of pure components, and the binary interaction parameter (component/polymer). The specific critical hole free-volume was estimated by the additive method of atomic constant of "Sugden".

This ethanol recovery study was carried out through the use of a PDMS membrane of 25 µm at 303.15 K and was divided into two steps. The first step was the study of the effect of the feed ethanol mole fraction

on the behaviour of the permeate flux of ethanol and water, separation factor of ethanol, and the ethanol composition in the permeate. These studies were carried out specifying a permeate pressure of 0.133 kPa, a temperature of 30 °C, and an ethanol feed mole fraction ranging from 0 to 0.05, equivalent to 0 to 12 wt %, which is within normal range for sugarcane fermentation. In the second step, the effect of permeate pressure on the permeate flux of ethanol and water and on the separation factor of ethanol were studied using an ethanol solution of 0.033 mole fraction, which is equivalent to 8 wt %.

4. Results and discussion

In the present study, an increment of permeate flux of ethanol (0.056 to 2.037 mol/m^2.h) and a decrease of permeate flux of water (9.835 to 9.427 mol/m^2.h) were observed within the studied ethanol mole fraction range (0.001 to 0.05) (Figure 2.a). Despite working with a *hydrophobic* membrane, a near-constant flow of water is obtained in the permeate along with an increasing flow of ethanol. Increasing the concentration of ethanol in the feed also results in an increase in the flow of ethanol in the permeate. Therefore, an increase in the feed molar fraction of ethanol up to 0.05 results in up to 0.21 permeate molar ethanol fraction (Figure 2.b), equivalent to 40.7 wt % (Figure 2.c). Thus, the pervaporation is a promissory process for ethanol recovery. Likewise, a decrease of the separation factor (5.67 to 5.11) was observed as a function of the increase of ethanol mole fraction in the feed (Figure 2.d). However, this factor suggest that, in the simulated operating conditions, the pervaporation model estimates a separation factor greater than 5.11, which is an expected value for this separation in this type of membrane.
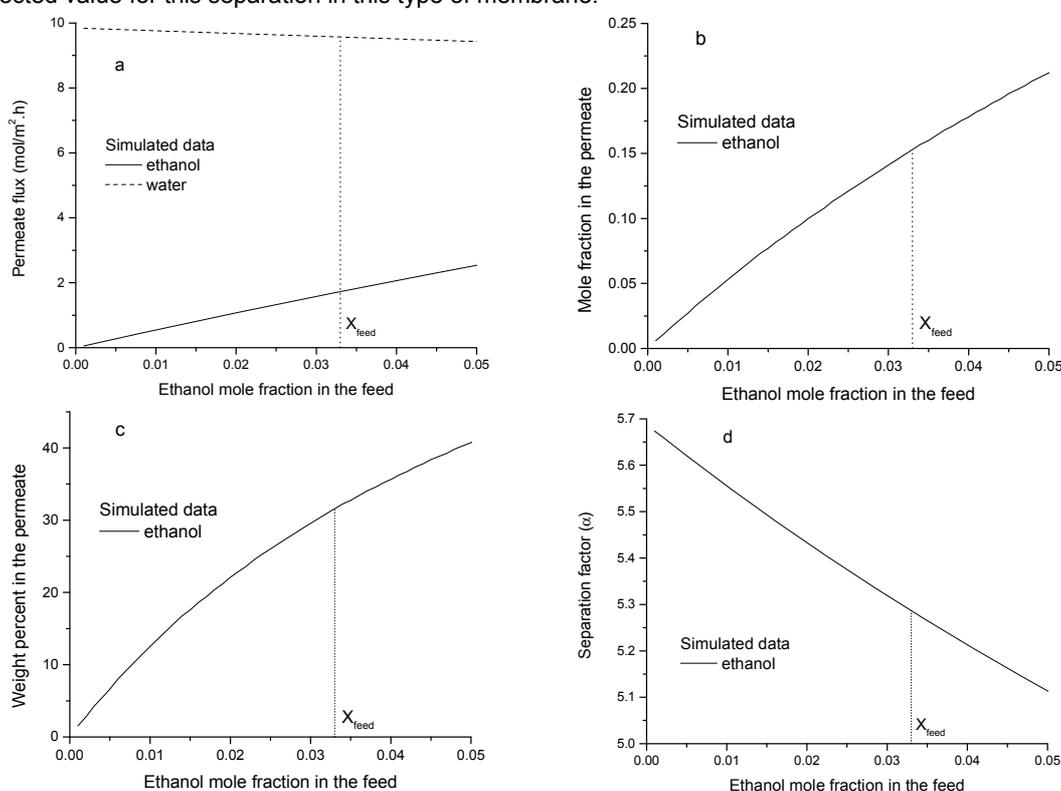

Figure 2. Simulated data of the influence of ethanol mole fraction in the feed on: a) Permeate flux, b) Mole fraction in the permeate, c) Weight percent (wt %) in the permeate, d) separation factor.

In Figure 3.a, a decrease of the permeate flux both for ethanol (1.732 to 0.301 mol/m^2.h) and water (9.636 to 1.484 mol/m^2.h) as a function of permeate pressure (0.1 to 4.2 kPa) is observed, and the flux falls more rapidly for water. The graph shows that, at lower permeate pressures, the pervaporation favors the ethanol recovery. However, in this condition more water is extracted from the feed, reducing the purity of ethanol on the permeate. Likewise, the influence of permeate pressure on the separation factor shows that at higher permeate pressures the membrane is more selective for ethanol (Figure 3.b). Therefore, the pervaporation model shows a reasonable behaviour for the PDMS membrane. This being the case, one should consider using a relatively high pressure in order to obtain less-hydrated ethanol and to avoid greater energetic costs in the vacuum pump.
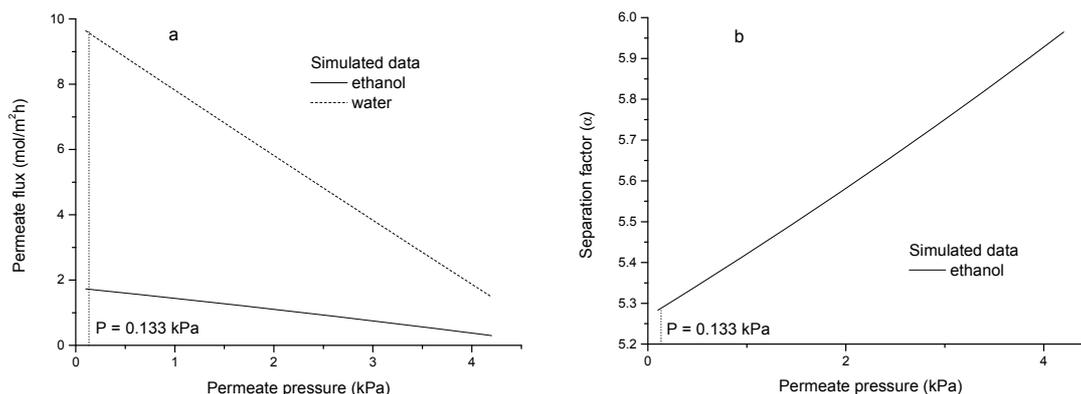
Figure 3. Simulated data of the influence of permeate pressure on: a) Permeate flux, b) Separation factor.

Thus, the pervaporation model showed that, from a solution at 0.033 ethanol mole fraction (equivalent to 8 wt %) with temperature at 303.15 K and permeate pressure at 0.133 KPa, a permeate flux of 1.726 mol/m^2.h of ethanol and 9.568 mol/m^2.h of water is obtained. Likewise, the ethanol mole fraction in the permeate is 0.153 (equivalent to 31.59 wt %), obtained at separation factor 5.23 (Figures 2 and 3). This means that the process turned an 8 wt% ethanol solution into a 31.59 wt% ethanol solution, which is a major increase in the ethanol concentration, demonstrating that the process functions as intended.

5. Conclusions

According to the obtained results, it was observed that for the PDMS membrane and the set of conditions used in this research project for the recovery of ethanol, a higher permeate ethanol concentration is obtained even when the ethanol concentration is low in the feed, as shown by separation factor, which could fit well with existing conditions in industrial plants. Additionally, this membrane provided good ethanol separation, as was verified in the ethanol concentration in the permeate.

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