Article

Purification of Methyl Acetate/Water Mixtures from Chemical Interesterification of Vegetable Oils by Pervaporation

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Abstract: Biodiesel production through chemical interesterification of triglycerides requires an excess of methyl acetate that must be recovered once the reaction is finished and the catalyst is neutralized. The present study concerns with the purification of methyl acetate by pervaporation. PERVAP 2201 was chosen as pervaporation membrane due to its high hydrophilic character that makes it suitable for the elimination of water in methyl acetate. Runs were started from concentrations in the feed of 2–8 wt.% of water and working temperatures close to the boiling point of methyl acetate (50, 60, and 70 °C), to get the main design parameters, i.e., permeate flux and selectivity. High temperature favored the permeate flux without compromising the selectivity. However, the flux declines significantly when water contained in the feed is below 2 wt.%. This implies that pervaporation should be used, only to decrease the water content to a value lower than in the azeotrope (2.3% by weight). A solution-diffusion model relating the flux of the permeating compound with the activity of the compound in the feed and the operating temperature has been proposed. The model obtained can be used in the design of the pervaporation stage, thus allowing to know the permeate flux for the different operating conditions.

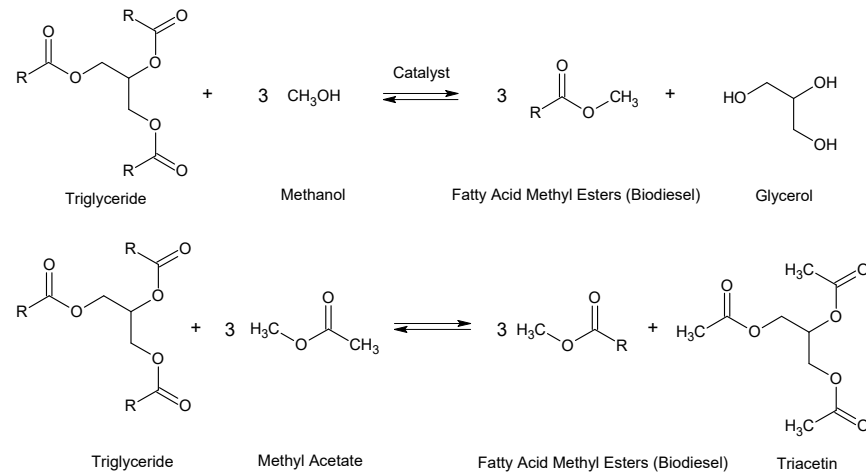**Keywords:** methyl acetate; interesterification; membrane

1. Introduction

The interesterification of triglycerides with methyl acetate, in place of methanol as it occurs in the transesterification reaction, gives triacetin as a product instead of glycerol [1–5]. During the interesterification reaction, one ester exchanges its alcohol group with another ester. The lack of alcohol as a reactant changes the polarity of the reaction media and the catalysts (usually alkaline methoxides, alkali metals, or alloys) become partially insoluble. The use of methyl acetate in the biodiesel production has been studied previously to solve problems related to methanol use, although only in the context of enzymatic [6–13] or supercritical [14–17] reactions. The interesterification of triglycerides requires an excess of methyl acetate that must be recovered once the reaction is finished. Therefore, a purification step of the methyl acetate is needed to remove contaminants such as water. A scheme of both interesterification and transesterification reaction is shown in Figure 1.

The way in which the catalyst is removed from the reaction medium will influence the subsequent purification of the remaining methyl acetate to be recycled to the reaction step. Depending on the process used in the removal of the catalyst (wet washing with deionized water and/or acids and dry washing with solid adsorbents), the methyl acetate can be contaminated by water.

In the case of methyl acetate-water mixtures, the distillation is the most suitable purification process, although it is limited by the presence of a minimum boiling point azeotrope for 2.3 wt.% of water [18]. For this mixture, pervaporation is a more appropriate alternative. Pervaporation consists in the selective evaporation of a component of a liquid

mixture when it is in contact with a dense membrane, so that one of the components of the mixture permeates preferentially through it [19]. Not depending on the balance between phases, it is a more efficient process than distillation in some difficult separations. In addition, because it is only necessary to evaporate a fraction of the feed mixture, the latent heat consumption is lower than that required in a distillation process, which represents a great energy advantage. For these reasons, pervaporation is very useful in the separation of azeotropes and mixtures of components whose boiling points are close, as well as to eliminate substances present in low concentrations [20].

Figure 1. Scheme of transesterification (**up**) and interesterification (**down**) reaction.

The effectiveness of pervaporation for methyl acetate-water mixtures was checked for Borisov et al. [21]. Experiments were performed varying the concentration of methyl acetate (0–1.5 wt%) and the temperature (30, 40, and 50 °C). The intrinsic enrichment factor changes noticeably when the process parameters are varied, affecting the concentration polarization modulus value during the pervaporation process. The concentration polarization modulus increases with the temperature and feed flow rate, taking the value close to 1 at temperature of 50 °C and at the average feed flow rate equal to 1.34 cm s^{-1}.

For methyl acetate-methanol mixtures, it should be taken into account that the minor component to be removed is, in turn, the least volatile (boiling point of methanol and methyl acetate, 65 and 57 °C, respectively) which does not compensate for the use of distillation [22]. In this case, the adsorption with molecular sieves is an interesting alternative. Thanks to the smaller kinetic diameter of methanol (3.85 versus 4.94 Å of methyl acetate) and its greater polarity, the use of molecular sieve 5A allows the selective removal of methanol from the mixture. In a previous study, the technical feasibility of methyl acetate purification using the adsorption with a molecular sieve 5A was shown [23].

The aim of this work was the evaluation of the technical feasibility of the methyl acetate purification in mixtures with water using pervaporation process. The mechanism was be modeled, which allowed to determine the optimal operating conditions.

2. Materials and Methods

2.1. Materials

Methyl acetate (99%) was obtained from Sigma–Aldrich, Madrid, Spain. Pure water was obtained with a Milli-Q Advantage A10 Ultrapure Water Purification System (Millipore, Burlington, MA, USA).

2.2. Pervaporation Setup

The pervaporation setup was supplied by Sulzer Chemtech, GmbH. The installation diagram is shown in Figure 2. The feed tank (1) consists of a cylindrical tank of stainless steel and 2 L capacity. Said vessel has a jacket whose heating fluid (glycol) is driven from

a thermostatic bath (2) (Thermo Fischer Scientific DC 30), which allows the temperature to be controlled up to a maximum value of 150 °C. The temperature is measured with an analogic Gulbinat thermometer with a temperature range of 0–200 °C. The top cover of the tank is connected to three pipes. The feed inlet pipe to the tank (valve H08) allows to recirculate the liquid without having to pass through the membrane module. A second pipe provided with valve (H10) allows the air purge during the filling of the tank. The third pipe is used to fill the tank, having a funnel and a valve (H01). This pipe is connected in turn to a safety valve (3) (design pressure of 16 bar) and to the recirculation of the retentate from the membrane module (H05). The liquid mixture is pumped from the feed tank to the membrane module using a centrifugal pump (4) supplied by Speck (model HT/NPY 2251.0022). The flow through the pump can be regulated by the H03 valve that controls a bypass around the equipment. The measurement of the volumetric flow is made between the centrifugal pump and the entrance to the membrane module using a KROHNE rotameter, model DK 34 (flow range between 14 and 140 L h^{-1}). A needle valve (5) is located in the pipe that leads to the membrane module, which makes it possible to obtain samples of the feed. The valve is connected to a stainless-steel capillary coil immersed in a glass cooled with cold water.
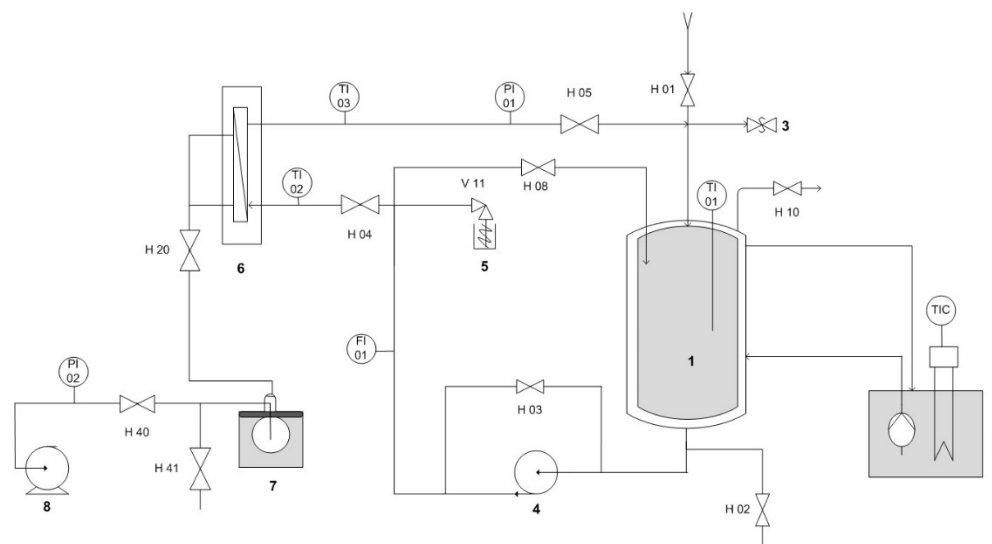
Figure 2. Pervaporation setup.

The feed stream is fed to the membrane module (6) made of stainless steel, which has a flat plate configuration with an effective membrane area of 170 cm^2. At the entrance and exit (retentate) of the module, continuous temperature measurements are made by two thermocouples connected to a digital thermometer, GMH 3230 Greisinger, with a resolution of 0.1 °C. The membrane used (PERVAP 2201) has been supplied by Sulzer Chemtech, GmbH. It was chosen due to its high hydrophilic character that makes it suitable for the elimination of water in methyl acetate.

The vacuum generated on the permeate side of the membrane is obtained by means of a membrane vacuum pump (8), Vacuubrand, model MZ 2 NT, which generates a maximum vacuum of 7 mbar. The value of the vacuum pressure in the permeate area is measured with a Vacuubrand DVR 2 digital vacuum gauge located between the outlet of the membrane module and the vacuum pump. It allows a pressure reading between 1 and 1000 mbar. To regulate the generated vacuum, a valve open to the atmosphere (H41) is placed between the vacuum pump and the condensation trap.

Finally, the permeate obtained in the vapor phase is condensed in a condensation trap (7) located between the membrane module and the vacuum pump. It consists of a flask of 50- or 100-mL capacity, depending on the flow obtained, and is located on a Dewar vessel that uses liquid nitrogen as condensation agent.

2.3. Experimental Procedure

The pervaporation experiments were carried out as follows: the feed, formed by a binary methyl acetate-water mixture in different concentrations, was introduced into the liquid phase in the feed tank and heated to operating temperature using glycol as a heating agent. The feed was pumped (flow 115 L h^{-1}) to the membrane module and the retentate is recirculated back to the feed tank. On the permeate side, a vacuum of 15 mbar is applied generating a permeate stream in the vapor phase. This is condensed by a liquid nitrogen trap located between the membrane module and the vacuum pump.

2.4. Analytical Methods

Water content was measured with a Metrohm 831 Coulometric KF titrator (Switzerland). Methyl acetate was determined using a Hewlett Packard (USA) 6890 gas chromatograph. The analyses were performed using a DB-WAX column 30 m long, with an internal diameter of 0.32 mm and a thickness of 0.25 μm, and a split injection system with a split ratio of 50:1 at a temperature of 260 °C. The column pressure was set at 80 kPa. The oven temperature was set at 50 °C. The flame-ionization detector (FID) temperature was set at 250 °C. Analyses were performed in triplicate, being the estimated uncertainty of the concentration measurement less than 0.1%.

3. Results

3.1. Modelling of Experimental Results

The transport of the component that permeates passes through different stages:

(1) Transport from the feed fluid to the surface of the membrane.
(2) Solution of the component in the membrane.
(3) Diffusion of the component through the membrane.
(4) Desorption of the component in the permeate phase.
(5) Transport from the surface of the membrane to the vapor phase.

In the pervaporation processes, the resistance in the boundary layer of both the feed and the permeate side is usually considered negligible (stage 1). Therefore, it is considered that the limiting step of the process is the mass transfer through the membrane. To check this statement and using the studies of Cussler [24] and Sitaraman et al. [25], the values of the global resistance to the mass transfer and the individual resistances offered by the boundary layer of the liquid side and the membrane are shown in Table 1. In the experimental conditions tested in this work, the resistance in the liquid film of the feed has a maximum weight of 0.54% of the overall resistance. Thus, it can be stated that the mass transfer through the PERVAP membrane 2201 is the limiting stage.

Table 1. Global and individual resistances to the mass transfer.

Temperature (°C)	Water (wt. %)	$1/Q_{g,w}$ (kg h^{-1} m^{-2} Pa^{-1})	$1/Q_{bl,w}$ (kg h^{-1} m^{-2} Pa^{-1})	$1/Q_{m,w}$ (kg h^{-1} m^{-2} Pa^{-1})
50	2.2	173,239	84	173,155
50	6.6	21,220	61	21,159
70	2.1	172,808	125	172,684
70	7.0	27,535	148	27,387

$Q_{g,w}$: global permeation coefficient of water; $Q_{bl,w}$: permeation coefficient of water in the boundary layer; $Q_{m,w}$: permeation coefficient of water in the membrane.

Furthermore, since a high vacuum is used in the permeate zone, desorption occurs instantaneously (stage 4), the resistance in the boundary layer of the permeate is practically null (stage 5), and the concentration of the permeate component can be considered on that side approaches zero. Therefore, the only steps to be considered will be the solution-diffusion stages (stages 2 and 3).

If we consider the diffusion (stage 3) of a pure component through the membrane, it can describe the process through a relationship like Fick's law:

$$J_i = -D_i \frac{dC_i}{dl} \tag{1}$$

where J_i, D_i, and C_i are the flux, the diffusivity, and the concentration in the membrane for the i component, respectively; l is the membrane thickness.

The diffusivity increases with the concentration. This phenomenon is due, mainly, to phenomena of plasticization and swelling that the polymer undergoes when it comes into contact with the permeating compound that allows the molecules to move more easily inside. There are numerous models that describe the dependence of diffusivity with concentration, with the exponential model being the most accepted for polymeric membranes [20]:

$$D_i = D_{i0} exp(A_i C_i) \tag{2}$$

where D_{i0} is the diffusion coefficient of i to infinite dilution and A_i is a plasticization coefficient, which represents the interaction between the polymer and the component that permeates. Starting from the exponential model (2) and substituting in the law of Fick (1), we arrive at Equation (3):

$$J_i = -D_{i0} exp(A_i C_i) \frac{dC_i}{dl} \tag{3}$$

Integrating along the thickness of the membrane:

$$J_i \int_0^l dl = -\int_{C_i^{Fm}}^{C_i^{Pm}} D_{i0} exp(A_i C_i) dC_i \tag{4}$$

$$J_i = \frac{D_{i0}}{A_i l} \left[exp\left(A_i C_i^{Fm}\right) - exp\left(A_i C_i^{Pm}\right) \right] \tag{5}$$

where C_i^{Fm} and C_i^{Pm} are the concentrations on the surface of the membrane in the feed and permeate side, respectively. Since the concentration in the permeate is practically zero, the expression can be simplified to:

$$J_i = \frac{D_{i0}}{A_i l} \left[exp\left(A_i C_i^{Fm}\right) - 1 \right] \tag{6}$$

To include the effect of the solution stage (stage 2), the concentration in the membrane is related to the activity of component i in the feed, by means of a partition coefficient [20]:

$$C_i^{Fm} = K_i a_i^F \tag{7}$$

being K_i, the distribution coefficient and a_i^F, the activity of component i in the feed. In addition, it is necessary to include the effect of temperature on the diffusivity. For this, an Arrhenius-type equation has been considered:

$$D_{i0} = D_{i00} exp\left(\frac{-E_a}{RT}\right) \tag{8}$$

being D_{i00} the pre-exponential term of the Arrhenius equation and E_a the activation energy of the diffusion process. Including Equations (7) and (8) in Equation (6):

$$J_i = \frac{D_{i00}}{A_i l} exp\left(\frac{-E_a}{RT}\right) \left[exp\left(A_i K_i a_i^F\right) - 1 \right] \tag{9}$$

This model relates the flux of the permeating compound with the activity of said compound in the feed and the operating temperature. The activity values of the water in the methyl acetate-water mixture are calculated by the following expression:

$$a_a^F = \gamma_a^F X_a^F \tag{10}$$

where a_a^F, X_a^F, and γ_a^F are the activity, molar fraction, and the activity coefficient of the water in the feed, respectively. The activity coefficient was calculated with the UNIQUAC equation using the data provided by [26].

3.2. Pervaporation Results

The pervaporation of the methyl acetate-water mixture obtained after washing of crude biodiesel with deionized water has been studied. In this work, concentrations of water in methyl acetate between 8 and 2 wt.% have been explored. These values are in the range of the solubility of water in methyl acetate at 50 °C (11.2 wt.%) and the minimum boiling point azeotrope (2.3 wt.%), respectively. The tests were carried out at three different temperatures (50, 60, and 70 °C) close to the boiling temperature of the methyl acetate. The dehydration of methyl acetate requires the use of a hydrophilic membrane; therefore, the membrane of Sulzer PERVAP 2201 has been used, which has an active layer of polyvinyl alcohol (PVA).

The behavior of a pervaporation membrane in the separation of a liquid mixture is mainly characterized by two parameters: productivity and selectivity. Productivity is evaluated by the mass flux of the permeating compound, in this case, water (J_a). On the other hand, the selectivity of a membrane is generally quantified by the separation factor (α_{ab}), which is defined from Equation (11):

$$\alpha_{ab} = \frac{C_a^P / C_b^P}{C_a^F / C_b^F} \tag{11}$$

where C^P and C^F are the mass concentrations of water (a) and methyl acetate (b), in the mixture of permeate and feed, respectively. The water permeates flux data for the different conditions studied are shown in Figure 3.
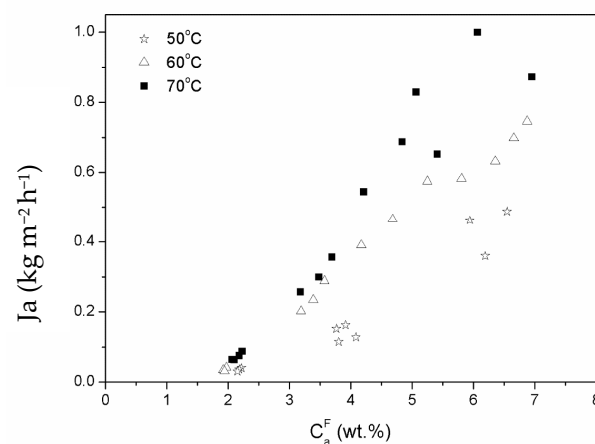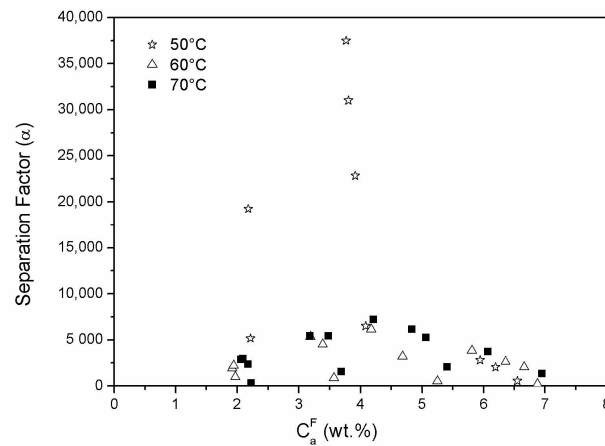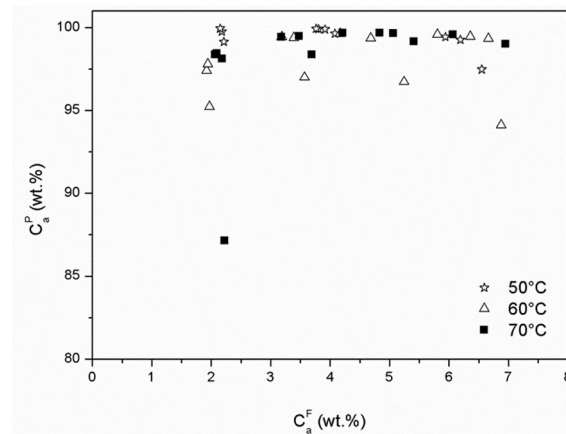
Figure 3. Water permeate flux for different temperatures and concentrations.

To complete the pervaporation study, the separation factor obtained in these experiments is shown in Figure 4.

Figure 4. Separation factor for different temperatures and concentration values.

In Figure 5, it can be observed the concentration of water in the feed and permeate for different temperatures.

Figure 5. Concentration of water in the feed and permeate for different temperatures.

Once the influence of the temperature and the concentration of the feed in the permeate flux and selectivity was known, the modelling of the results obtained was carried out. For this purpose, the solution-diffusion model described by Equation (9) has been used. In this case, with water being the major component that permeates, Equation (9) is expressed as follows:

$$J_a = \frac{D_{a00}}{A_a l} exp\left(\frac{-E_a}{RT}\right)\left[exp\left(A_a K_a a_a^F\right) - 1\right] \tag{12}$$

The estimated parameters were $D_{aoo}/(A_a l)$, E_a, and $A_a K_a$. The values of these parameters that minimized the value of the objective function were determined, being the objective function, the sum of the squared differences between the experimental and the theoretical value. The obtained values are shown in Table 2.

Table 2. Parameter values for equation [12].

Parameter	Value
$D_{aoo}/(A_a l)$	15.01
E_a (kJ mol^{-1})	52.05
$A_a K_a$	4.38

To corroborate the validity of the model, the parity graph of the experimental and theoretical data of the water permeate flux is shown in Figure 6.
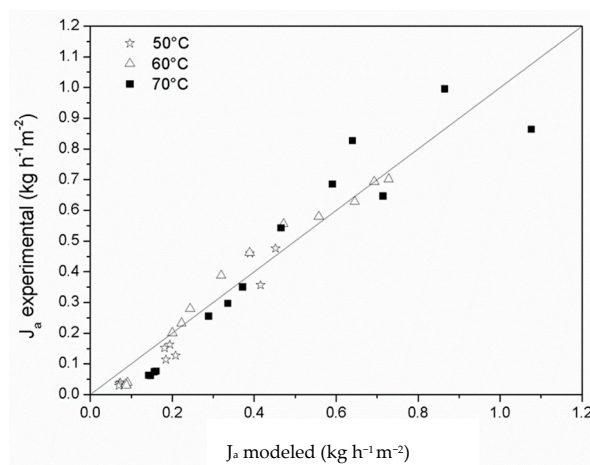
Figure 6. Experimental and modeled values for water permeate flux.

4. Discussion

It can be observed in Figure 3 that the water permeate flux increases with temperature. This is due to the polymer chains becoming more flexible improving the diffusion of water through the membrane. In addition, the vapor pressure of the components of the liquid phase is also increased, which means a greater driving force. On the other hand, it has also been observed that the use of higher concentrations of water increases the flux of permeate that passes through the membrane due to the swelling suffered by the membrane. According to this phenomenon, by increasing the water content of the feed, the hydrophilic membrane swells, making the polymer chains more flexible and improving the transport of the component through the membrane [27].

Therefore, from the point of view of the permeate flux, it is advisable to use a pervaporation temperature of 70 °C. However, it should be noted that the flux is significantly reduced below 2 wt.% of water in the feed. This implies that pervaporation should be used, only to decrease the water content to a value lower than that of the azeotrope (2.3 wt.%), and after that, the purification process with another operation like distillation should be continued.

It can be seen that the selectivity of the pervaporation process is very high (Figure 4). The highest selectivity value is obtained for the conditions where the permeate flux is lower, i.e., temperature of 50 °C and water concentration in the feed of 2–4 wt.%. The main reason is that by increasing the flux, there is the possibility that the permeate stream is contaminated with methyl acetate from the feed. However, there is no clear trend in the separation factor. This may be due to the high concentration of water in the permeate stream (Figure 5).

As can be seen, the permeate stream has a water content close to 100%. Therefore, the possible variations in the separation factor are not due to the operating conditions, but to the experimental error itself.

According to Figure 6, the model obtained can be used in the design of the pervaporation stage, thus allowing to know the permeate flux for the different operating conditions. In view of the results obtained, a temperature of 70 °C will be used, since it allows obtaining a greater permeate flux, without compromising the selectivity. Regarding the concentration in the feed, this process should not be used for concentrations lower than 2 wt.% since the flux values obtained are very low.

5. Conclusions

The pervaporation allows to selectively separate the water from the methyl acetate. The selectivity is not particularly affected by temperature, which makes it easier to work at the highest temperature (70 °C) to obtain higher permeate fluxes. The solution-diffusion model employed correctly correlates the results obtained at different temperatures and

feed concentrations. The use of this operation is discouraged below 2 wt.% of water due to the low permeate fluxes obtained.

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