



Ultrafiltration polymeric membranes for the purification of biodiesel from ethanol



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ABSTRACT

The emerging industry of biodiesel obtained from ethanol and vegetable oil, presents a number of difficulties in the purification step of the obtained esters. Current processes use large amounts of water to remove the by-product of the transesterification reaction. This paper presents an alternative to the washing process of biodiesel, which involves the use of ultrafiltration membranes resistant to solvents and alkalis. For that, two lab-made hydrophobic polymeric membranes were prepared from poly(vinylidene fluoride) and poly(sulfone) as main materials. The synthesized membranes were used to reduce glycerol content of biodiesel solutions obtained from semi-refined soybean oil and ethanol, catalyzed by sodium hydroxide. The poly(vinylidene fluoride) membrane reached a glycerol rejection up to 67% (at 30 °C and 5 bar) from a biodiesel sample with 0.5 wt % of water added. Under the same operation conditions, the poly(sulfone) membrane showed a lower separation performance, with glycerol rejection of 48%. Moreover, stability tests demonstrated that poly(vinylidene fluoride) membrane was more stable to solvents, alkalis and temperature, compared to the poly(sulfone) membrane. A remarkable flux recovery after more than 45 cycles of biodiesel permeation (≈ 105 hs) was verified in poly(vinylidene fluoride) membrane, indicative of the high stability and low fouling of the membrane.

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1. Introduction

The use of fossil fuels as an energy source has negative environmental impacts. The challenge against global warming requires the generation of industrial policies focuses on reducing both, the emissions of greenhouse gases and the consumption of non-renewable fuels. Since the beginning of the XXI century, a large number of countries have developed policies that regulate and promote the biofuel industry (Ackrill and Kay, 2014). Brazil, EEUU and EU have promoted biodiesel and bio-ethanol production to reduce fossil fuel consumption. The growth trend in bio-fuels seems to continue during the coming decade in a $\approx 2\%$ annual (OECD/FAO, 2015), consolidating the industry. The last estimation by OECD/FAO (2015) points out that by the year 2024, around 38.000 M of liters of biodiesel (Fatty acid methyl ester,

FAME) will be produced. This high quantity comes mainly from a synthetic route that uses water as biodiesel (BD) purification resource.

The transesterification reaction between a vegetable oil (soybean, canola, palm) and a short chain alcohol, catalyzed by a strong base sodium methylate or sodium hydroxide, is the most frequent process used around the globe to obtain BD (Yusuf et al., 2011). However, other by-products are obtained such us: glycerol (GLY), soaps, rest of triglycerides (TG), monoglycerides (MG), diglycerides (DG), catalyst, water and solvent (Ma and Hanna, 1999). Alcohol frequently used is methanol (MeOH) because it promotes efficient separation of the reaction by-products and higher final conversions of FAME. Nevertheless, MeOH is obtained from non-renewable sources and poses a high toxicity. Ethanol (EtOH) is an interesting alternative to methanol as its use intensifies sustainability in the production of biodiesel (Liew et al., 2014). This alcohol is obtained from renewable resources and it has been evaluated by several researchers in BD production. For example, Uthman and Abdulkareem (2014) and Encinar et al. (2007) studied the

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ethanolysis of used frying oil to obtain BD to be used as fuel in compression ignition engines.

The liquid-liquid equilibria are relevant to understand the partition of compounds in glycerol-rich phase and ethyl ester rich phase and it is used in design separation processes. An interesting analysis of the equilibria of ternary systems present in BD production (BD, EtOH and GLY) was made by Machado et al. (2012). Compared to the methanolysis, ethanolysis produce fatty acids ethyl esters (FAEE) and a region of higher miscibility of the reaction products. When the initial volumetric ratio of EtOH exceeds 30% (v/v) just a single phase is obtained (Mendow and Querini, 2013; Mendow et al., 2011). Ethanol containing even low water amounts produces highly stable emulsions due to more content of soaps formed during the reaction (Eze et al., 2015; Kucek et al., 2007). High levels of soap in BD allow the formation of gels, which seriously affect the separation of the reaction products (Klossek et al., 2013; Machado et al., 2012). Therefore, water traces should be minimized in the synthesis when ethanol is used, in order to avoid the mentioned obstacles during the BD separation and purification steps (Klossek et al., 2013; Chen et al., 1984). After reaching the maximum conversion, phase separation occurs. The glycerol phase is removed while the alcohol excess in the ester phase is separated by flash evaporation. Then, the remaining ester phase is submitted to a series of hot water washes. It has been estimated that during the washing process 10 L of water by each liter of FAME are used (Atadashi et al., 2011). Clearly, the focus on water consumption reduction is mandatory.

Membrane technology for biodiesel purification has received attention from the scientific community over the last decade (Shuit et al., 2012). It has been verified that membrane technology can reduce the water consumption during the BD purification step, leading to a significant impact on process costs. In spite of that, this technology requires a high initial capital investment. The membranes used for cleaning biodiesel are microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF) which are prepared from solvent resistant polymers or ceramic materials. Polymeric membranes have received the most attention mainly due to their high relative selectivity and low cost compared to ceramic membranes. Alves et al. (2013) studied the purification of biodiesel (FAME of soybean oil, methanol and potassium hydroxide) using different polymeric commercial membranes. As it was discussed above, the use of ternary miscibility diagram allows to optimize the separation process. Cheng et al. (2009) used this information for optimizing the efficiency of oil separation in biodiesel and alcohol mixture using a ceramic microfiltration membrane with a mean pore size of 0.14 μm . In their results, a total oil rejection was obtained when different mixture composition in biodiesel, oil, and methanol (two phases) were used. Gomes et al. (2015) used tubular UF membranes made of $\alpha\text{-Al}_2\text{O}_3/\text{TiO}_2$ in the treatment of transesterification mixtures obtained from several oils.

The BD samples used in the purification with membranes mentioned above had low percentages of GLY, soap, MG, DG and TG. More complex samples of BD using EtOH, with high contents of glycerol and soaps in the ester final phase, represent a new and interesting challenge. Furthermore, the stability of the membrane materials should be taken into account for such treatments. In this sense, the objectives of this work are: i) to prepare and characterize biodiesel (FAEE) from EtOH and semi-refined soybean oil, and ii) to evaluate the performance of UF process in the purification of the obtained BD using lab-made polymeric resistant solvent membranes. The membranes are synthesized from poly(vinylidene fluoride) (PVDF) and poly(sulfone) (PSf) as main materials.

2. Materials and methods

2.1. BD synthesis

2.1.1. Reagents

The catalyst, NaOH 97 wt%, was purchased to Ciccarelli (Argentina). Semi-refined soybean oil was kindly provided by Oleaginosa General Cabrera SAIC (Argentina). The main component concentrations of the semi-refined oil were: soap = 0.01 wt%, FFA (free fatty acids) = 0.14 wt%, H (moisture humidity) = 0.15 wt%, η (viscosity) = 44 cP and ρ (density) = 0.915 g/cm³. The anhydrous EtOH (water 0.5 wt%) used for the biodiesel synthesis and the permeation experiments was obtained from Bio4 S.A. Argentina. The process involved in EtOH manufacture was corn fermentation and subsequent purification via distillation and dehydration using zeolites. The EtOH characteristics from lab analysis have shown an acidic content (as acetic acid) < 20 ppm, H = 0.5 wt% and ρ = 0.79 g/cm³. 1,2,4-Butanetriol (1000 $\mu\text{g}/\text{mL}$ in pyridine) and Tricaprin (8000 $\mu\text{g}/\text{mL}$ in pyridine); GLY (500 $\mu\text{g}/\text{mL}$ in pyridine); MG, DG and TG (500 $\mu\text{g}/\text{mL}$ in pyridine), were purchase to Sigma-Aldrich. N-Methyl-N-(trimethylsilyl)trifluoroacetamide (MTFA) 98,5% and heptane (both Sigma-Aldrich) were used as silylating agent and solvent, respectively. For the moisture/humidity determination (Karl Fischer) HYDRANAL-Composite5[®] reagent and anhydrous methanol as solvent were purchased from Sigma Aldrich (Argentina) and Ciccarelli (Argentina) respectively.

2.1.2. Synthesis

Batch experiment was carried out in a 500 mL glass flask with mechanic agitation at atmospheric pressure. A molar ethanol-oil ratio of 5:1 and 1 wt% of NaOH based on the oil were used in the transesterification reaction. The operating temperature was 55 °C for 2 h reaction time (Mendow et al., 2011). The required amount of NaOH was dissolved in the right amount of EtOH. The reaction was performed at the agitation speed of 800 rpm. The transesterification products were transferred to a separating funnel and then allowed to settle for 10 h until to two immiscible phases were obtained. The non-polar FAEE rich phase was characterized and used for permeation experiment. The BD synthesis procedure is schematized in Fig. 1.

The quantification of total glycerol GT (GT = GLY, MG, DG and TG) was done by gas chromatography according to ASTM D 6584 method by using a Perkin Elmer Clarus 580 device coupled with a flame ionization detector (FID), and a ELITE 5HT 15 m \times 0.32 mm \times 10 μm Perkin Elmer GC capillary column. For determination of soap (as sodium oleate) it was used the AOCS titrimetric method Cc 17–95. The technique was carried out with an automatic titrator plus Metrom Titrimo[®], equipped with a Solvotrode Metrohm electrode for non-aqueous determinations. The biodiesel yield (% FAEE) after oil-alcohol catalyzed reaction was calculated from:

$$\%FAEE = \frac{m_{BD}}{m_{Oil}} 100 \quad (1)$$

where m_{BD} is the mass of crude biodiesel after transesterification reaction and m_{Oil} is the mass of soybean oil used as feedstock (Alves et al., 2013).

2.2. Membranes

2.2.1. Materials

Membranes were made of poly(vinylidene fluoride), MW: 570–600 kDa and poly(sulfone), MW: 75–81 kDa. These polymers were supplied by Solvay & CIE. Nonwoven polyester (provided by Separem) was used as support. The non solvent additive methyl

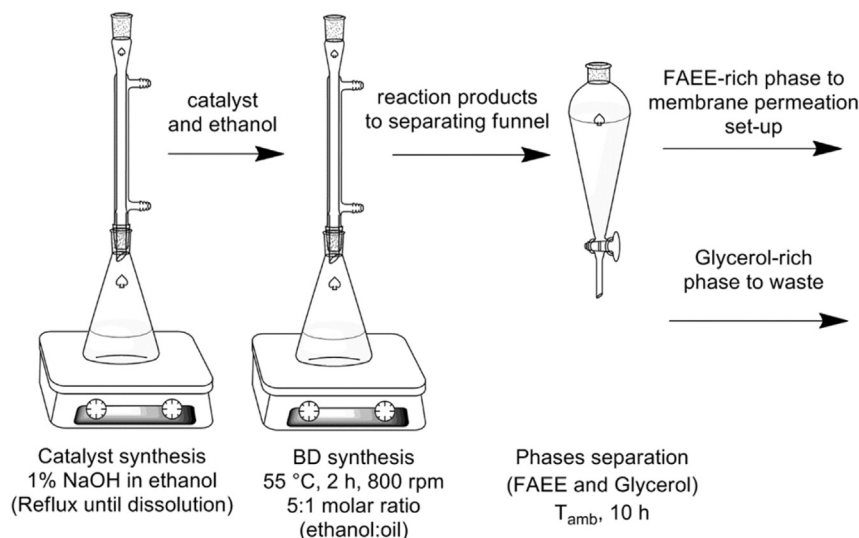


Fig. 1. BD synthesis scheme.

cellosolve (MC) of MW = 76.09 Da, was purchased from Sigma Aldrich. The solvent *N,N*-dimethylformamide (DMF) and non solvent tetrahydrofuran (THF), were obtained from Merck.

2.2.2. Preparation

Two new UF membranes with low pore size were prepared following the phase inversion process (Kesting, 1985). Based in our previous researches (Masuelli et al., 2009; Ochoa et al., 2003, 2001a), and the studies of other authors Gryta, and Barancewicz. (2010) and Han, and Nam, (2002), relative high concentrations of the main polymers (PVDF, PSF) were used in the casting solutions. In order to obtain a close distribution of pore with small size, a certain amount of MC and 1 mL of THF was added to the casting solutions. The MC was used because its molecule size is similar to those solutes with lower molecular weight present in BD solutions. The solutes compositions (wt%) of the casting solution used in the membrane preparation are listed in Table 1, where the symbols and number of the membrane classification refers to polymer and MC additive compositions in the casting solution, respectively. In the membrane preparation procedure the flat polyester support was fixed on a glass plate and the polymeric solution was cast at 25 °C in air, using a Gardner knife gap of 300 μm. The solvent was allowed to evaporate for 30 s. Then, the cast film was immersed in a coagulation bath containing distilled water at 25 °C and then transferred to fresh water for 24 h. All of the membranes were stored in water.

2.2.3. Characterization

A lab scale cross-flow test cell (Minitan system, Millipore) was used to characterize the water permeability and the molecular weight cut-off (MWCO) of the membranes. The membrane sample was placed in the cell and the water permeate flux (J_w) through the membrane was measured as a function of transmembrane pressure ($\Delta p = 0.2\text{--}1$ bar) at $T = 30$ °C. The water permeability ($L_{h,w}$) was calculated from Darcy's law ($L_{h,w} = J_w/\Delta p$). An important parameter to characterize the mean pore size of the membrane is its MWCO.

Table 1
Casting solution composition.

Membrane	Polymer solution (wt%)	Methyl cellosolve (wt%)
PVDF-20-5	20	5
PSF-23-7	23	7

MWCO refers to the lowest solute molecular weight (in Daltons) in which 90% of the solute, with a known molecular weight, is retained by the membrane. To determine the MWCO, aqueous solutions of 0.1 wt% poly(ethylene glycol) (PEG, from Fluka) of different molecular weight (1.3–20 kDa) were permeated in the cross-flow test cell. The PEG permeations were performed following the procedure reported elsewhere (Ochoa et al., 2001b). The PEG concentrations in the permeate and retentate were determined by refractometry using a GPR 11–37, Index Instruments. PEG rejections, %R, were calculated according to Eq. (4) and they were used in the membrane MWCO estimation.

The hydrophobic character of the membranes was determined by measuring the water-membrane contact angle (θ) by the sessile-drop technique using a contact angle device (Micromeritics Instrument Corporation, Norcross, A, USA) (Romero-Dondiz et al., 2016; Firman et al., 2013). Three drops of water were measured for each membrane sample. The contact angle value was measured dropping water on the membrane surface in a 1501 Micromeritics contact anglemeter. The average contact angles (θ) were evaluated from the following expression (User manual of Micromeritics's contact angle device):

$$\cos \theta = 1 - \sqrt{\frac{Bh^2}{(1 - Bh^2/2)}} \quad (2)$$

where $B = \rho g/2\gamma$, being g the gravity acceleration (980 cm/s²), ρ bi-distilled water density (0.9971 g/cm³), γ interfacial tension of bi-distilled water (71.97 erg/cm²), and h the height of the liquid drop.

The morphology of the membranes was analyzed using a JMS-35 JEOL scanning electron microscope. In order to observe the membrane cross section, samples were fractured in liquid nitrogen and coated with gold.

2.3. Ultrafiltration experiments

All permeation trials were conducted in a dead-end filtration set-up. The stainless Steel 316 L test cell (Sterlitech HP4750, USA) has an inner diameter of 5.1 cm, the height of 19.9 cm, and maximum volume capacity of 300 mL. The membrane was supported on a sintered porous stainless-steel disc. Membrane diameter was 4.9 cm with an effective area $A = 14.6 \times 10^{-4}$ m². The feed solution was magnetically mixed with a (Teflon coated) stirred bar

at a constant speed of 500 rpm. The transmembrane pressure (Δp) was supplied by a nitrogen cylinder connected to the top of the cell and the temperature was kept constant by the temperature-controller of the magnetic stirred. The permeate flux J ($L/(m^2 h)$) was determined by measuring the volume of permeate collected (ΔV) during the operation time (Δt) and calculated from (Ochoa et al., 2001a):

$$J = \frac{1}{A} \frac{\Delta V}{\Delta t} \quad (3)$$

2.3.1. EtOH permeability

The membrane sample is placed in the test cell and preconditioned by loading the reservoir with pure EtOH, leaving it for 24 h. The reservoir was charged with pure solvent and the EtOH permeate flux, J_{EtOH} , was measured as a function of transmembrane pressure ($\Delta p = 3\text{--}7$ bar) at different temperatures ($T = 30\text{--}40$ °C). Solvent permeate flux values were used to evaluate EtOH permeability ($L_{h,EtOH} = J/\Delta p$). Each experiment was carried out in triplicate.

2.3.2. BD permeation

Once the pure solvent measurements were performed, the BD permeation experiments were carried out with the obtained BD, without and with the aggregated of distilled water (0.2 and 0.5 wt %). The cell reservoir was charged with 250 mL of BD mixture and stirred at a constant speed of 500 rpm. The transmembrane pressure and temperature were varied from 5 to 7 bar and 30–40 °C, respectively. The permeate was collected through a port beneath the membrane support. The experiments were stopped after 140 min. All permeation trials were performed in triplicate. The BD permeate flux was evaluated from Eq. (3) and the percentage of rejection solute i ($R\%$) was calculated according to the following equation:

$$\%R = \left(1 - \frac{C_{i,p}}{C_{i,r}}\right) \times 100 \quad (4)$$

where $C_{i,p}$ and $C_{i,r}$ are the permeate and retentate concentration of solute i , respectively.

2.3.3. Membrane stability

Membranes were re-used after each BD permeation experiment. In order to analyze the stability of the membranes after BD permeation, membranes were cleaned in situ by rinsing with EtOH under stirring for 30 min. Then, the cell was filled again with EtOH and allowed to permeate for 1 h at 5 bar and 30 °C. Finally, the cell was filled with EtOH and allowed to permeate for 40 min at 3–7 bar and 30 °C, and the EtOH flux was determined. After that, the new EtOH permeability, $L_{h,EtOH}^*$, was evaluated to establish a standard of cleanliness. The flux recovery ratio (FRR), defined in Eq. (5), was used to measure the membrane stability.

$$FRR = \frac{L_{h,EtOH}^*}{L_{h,EtOH}} \quad (5)$$

3. Results and discussion

3.1. Biodiesel characteristics

After transesterification reaction and 10 h of settling at 20 °C, the obtained BD solution showed a high content of fatty acids ethyl

esters (FAEE $\approx 87\%$, Eq. (1)) and other minor components. The apparent pH and the density of the BD solution were $pH_{app} = 11.7 \pm 0.2$ and $\rho = 0.88 \pm 0.01$ g/cm³. The residual amount of EtOH measured by evaporation was 7.8% v/v. The concentrations of total glycerol calculated as in ASTM D 6584 were GT (wt %) = 1.74% (GLY 1.31%, MG 1.55%, DG 0.15%, TG 0.03%) and 1.06% of soaps by potentiometric titration. The composition of the minor components was slightly higher to those reported by others authors (Mendow et al., 2011; Othman et al., 2010; Kucek et al., 2007). Mendow et al. (2011), in their studies of ethyl ester production by homogeneous alkaline transesterification, reported a concentration of 0.4% of total glycerides and 0.5% content of soaps. The lower concentrations of total glycerol (≈ 4.3 times) and soaps (≈ 2.5 times), compared to our results, were consistent with the relatively high water content in the EtOH used in our BD synthesis.

Detailed studies on the complexity of the mixtures of fatty acid ethyl ester (FAEE) can be found in Eze et al. (2015), Mendow and Querini (2013) and Machado et al. (2012). The main conclusions from these works were that the formation of FAEE was accompanied by high amounts of soaps, leading to stable emulsions of water-soap-glycerol-esters. This fact makes the phase separation becomes a difficult task to perform. For example, for fatty acid methyl esters (FAME) after the reaction, the final amount of soap in the ester layer is less than 0.1 wt%; while in FAEE this value is ≈ 0.4 wt% (Mendow et al., 2011). These values are the result of studying systems with very low water content in MeOH and EtOH (0.035 wt% and 0.115 wt% respectively) and low water content in the refined sunflower oil.

3.2. Characterization of membranes

Figs. 2 and 3 show SEM micrographs of asymmetric PSf-23-7 and PVDF-20-5 flat sheet membranes, respectively. Figs. 2(a) and 3(a) show a clear differentiation between the textures of both membranes surfaces, being the PVDF membrane the rougher. Cross section micrograph of PSf-23-7 asymmetric membrane (Fig. 2b) shows two well-defined regions, a thin dense layer (selective) on the top consisting of packed nodule aggregates of polymer, and underneath a thicker porous spongy sub-structure, whereas the sub-structure under the skin layer of PVDF-20-5 membrane (Fig. 3b) is formed by finger-like macrovoids. This can be in part due to the higher viscosity of the PSf casting solution (23 wt%), compared with the PVDF solution (20 wt%). An increase of the casting solution viscosity causes a decrease in the mass transfer rate during coagulation process, and consequently a decrease in the macrovoid formation (Ochoa et al., 2003).

Table 2 shows the characterization results of the synthesized membranes obtained from different methods, i.e. contact angle, permeability, PEG rejection, MWCO, and FRR. The contact angle value of PSf membrane was 18° lower than the PVDF membrane, indicating its higher hydrophilic character. In theory, the more hydrophilic character would allow a greater permeability of hydrophilic solvents. Table 2 shows that the water and ethanol permeabilities of the PVDF-20-5 membrane are larger than those of the PSf-23-7 one. This discrepancy is due to the fact that the solvent permeability depends on multiple factors, among them: pore size and pore density of the dense layer (porosity), dense layer thickness, porous sub-structure characteristics, etc. (Susanto and Ulbricht, 2009). Hence the explanation and comparison of the obtained permeabilities is not an easy task to accomplish.

The $L_{h,EtOH}/L_{h,w}$ ratios were 1.94 and 0.57 for PVDF-20-5 and PSf-23-7 membranes respectively. The relatively low permeability of ethanol in the PSf membrane may be ascribed to the interaction between the solvent and the membrane material (swelling effect). From this, it is possible to infer that some shrinkage of the smallest

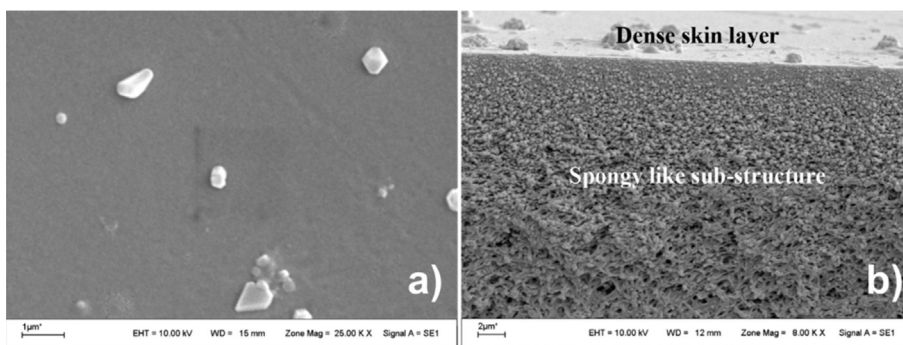


Fig. 2. SEM micrograph of PSf-23-7 membrane: a) surface, b) cross section.

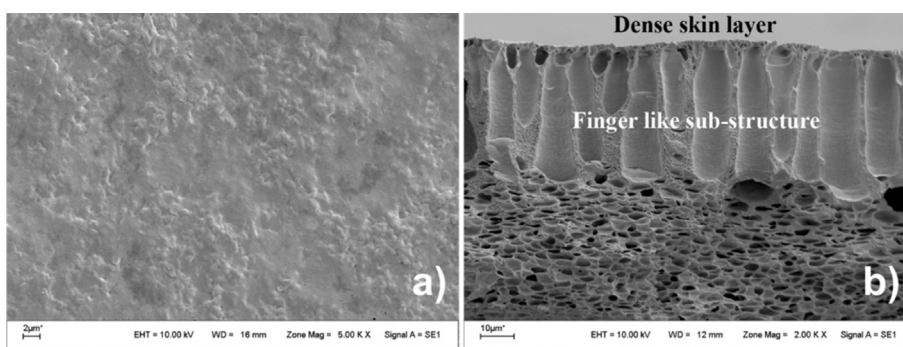


Fig. 3. SEM micrograph of PVDF-20-5 membrane: a) surface, b) cross section.

Table 2

Membrane parameters and permeabilities (T = 30 °C).

Membrane	θ	$L_{h,w}$ L/(m ² h bar)	$L_{h,EtOH}$ L/(m ² h bar)	FRR	PEG MW (kDa)	R% (PEG)	MWCO (kDa)	r_p (nm)
PVDF-20-5	80.9	12.4	24.1	0.94 ± 0.13	20	100	7	4.4
					10	98		
					6	86		
					4	47		
					1.3	21		
PSf-23-7	62.2	9.0	5.2	0.88 ± 0.09	20	100	5	4.0
					10	100		
					6	94		
					4	83		
					1.3	33		

The $L_{h,EtOH}^*$ average values can be deduced from FRR and $L_{h,EtOH}$ data (Eq. (5)).

pores in the dense layer of PSf membrane has occurred, reducing the ethanol flux. A remarkable FRR was verified in both membranes (0.94 for PVDF and 0.88 for PSf) after more than 45 cycles of BD permeation (≈ 105 hs) indicating a high stability and low membrane fouling.

Once water permeability was determined, measurements with PEG were carried out in order to obtain the mean pore size according to the method reported elsewhere (Ochoa et al., 2001b). The r_p data were included in Table 2.

3.3. Biodiesel permeability

All permeation trials were carried out in triplicate and mean values of permeate flux (J) with time were determined by Eq. (3). A good reproducibility in the permeation data was observed, within 5% deviation. Fig. 4 shows the variation of permeate flux with time through the UF membranes at 30 °C, $\Delta p = 5$ bar, and 0.5 wt% of water added. There was a slight drop in permeate flux through the membranes in the first 40 min and then it practically remained

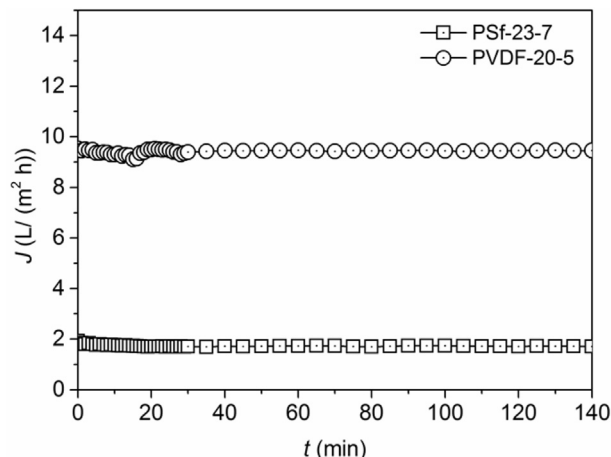


Fig. 4. BD permeate flux with operational time (T = 30 °C, $\Delta p = 5$ bar and 0.5% water).

constant. This decrease in the initial flow can be attributed to a very low membrane fouling (soap primary adsorption and concentration polarization effects). Similar flux decline behavior was nearly observed in everyone of the experimental runs. The other permeate flux results are reported in the supplementary information (SI). The average permeate flux values between $t = 100$ min and $t = 120$ min, J^* , were used as reference fluxes to evaluate the membrane permselectivity performance. Table 3 summarizes the average values of J^* and rejection at $T = 30$ °C and 40 °C, $\Delta p = 5$ and 7 bar for the synthesized asymmetric membranes. The data show the expected trend for each synthesized membrane, where the permeate flux increased with both, the transmembrane pressure (pressure driven process) and temperature (lower solvent viscosity). Furthermore, the data showed that when the permeability increased there was a decrease in selectivity (lower GLY and GT rejections), in agreement with the general behavior of UF membranes.

BD permeation data with PSf-23-7 membrane at 40 °C could not be determined due to membrane rupture during the permeation tests. The information available about the stability of these polymers is scarce. Only a few providers report on compatibility against different solvents and some publications report the resistance to chemical attack, especially against oxidants such as chlorine (Rouaix et al., 2006). The post-reaction alkalinity of BD mixture obtained in this work was remarkable ($\text{pH}_{\text{app}} = 11.7$). However, the PSf and PVDF polymers are stable in a wide range of pH (1–13) and mainly PVDF membranes are more resistant in alkaline media (Li et al., 2008; Zeman and Zydny, 1996). The solvent-polymer interactions are more likely to promote membrane breakdown. In the presence of low molecular weight alcohols (i.e. methanol, isopropanol) and esters, the PSf membranes have shown a limited resistance to large exposure times. For example, the data sheet of PSf (Solvay, 2016) mentions the poor stability of PSf to esters. A prolonged exposure time to FAEE in conjunction with moderate temperature and strong basic media could be responsible for the observed membrane collapse.

In order to evaluate the variables more significant that affects the permeate flux; an analysis of variance (ANOVA) was carried out using data from Table 3. For statistical analysis, the InfoStat program was used (Di Rienzo et al., 2011). The model fit (R^2) for the PVDF-20-5 membrane was 0.97. The p-values of the operative variables % water added, T and Δp were <0.0001 , therefore, the three operative variables had a significant statically effect on the permeate flux with a 99% confidence level. Moreover, the interaction between variables did not show significant effects, due to that the p-values of the interactions were greater than 0.01. Multiple comparison analysis indicated that the only case that did not show significant statically difference was the condition 30 °C and 7 bar compared to the condition of 40 °C and 5 bar. This is because of compensation between an

increase of T and decrease of Δp to these two conditions specifically. The model fit (R^2) for the PSf-23-7 membrane was 1.0. The p-values of the operative variables %water add and Δp were <0.0001 , therefore, the two operative variables had a significant statistical effect on the permeate flux with a 99% confidence level. Moreover, the interaction between variables showed significant effects due to that the p-value of the interactions was less than 0.01. Multiple comparison analysis indicated that the differences in the permeate flux between 0.2 and 0.5%water added did not show significant statistical differences to both Δp .

The PVDF-20-5 membrane presented higher permselectivity characteristics compared to the PSf-23-7, being the permeate flux of PVDF higher than PSf membrane for all the operating conditions studied. The best permselective performance of PVDF-20-5 membrane was achieved at $\Delta p = 5$ bar, $T = 30$ °C and 0.5 wt% water added, reaching permeate flux of 9.5 L/(m²h) and rejection of 67.3% and 60.6% for GLY and GT, respectively. At the same operational conditions, the PSf membrane showed permeate flux 5.7 times lower (1.7 L/(m² h)) and rejections of 48% GLY and 45.4% GT.

Even if there are several studies in the literature related to the application of membrane technique for different BD mixtures, many of them are related with synthetic or artificial BD (FAME) and commercial MF-UF membranes. In their purification of FAME from refined canola, Saleh et al. (2010) used a commercial poly(acrylonitrile) UF membrane of 100 kDa MWCO. The FAME samples with different percentages of water, soap and MeOH, were used in their permeation tests. The initial concentration of GLY in BD samples (0.04 wt%) was close to the values permitted by ASTM D6751-07b standard ($<0.02\%$). The best permeation performance was obtained with the sample without MeOH and with 0.02% of water, at 5.5 bar and 25 °C, achieving GLY rejections of 63–70% and a decrease permeate flux from ≈ 13 to ≈ 7 L/(m²h), during 3 hs of operation time. In their studied of BD purification (FAME of soybean oil, methanol, and potassium hydroxide), Alves et al. (2013) used polymeric commercial membranes with different MWCO. Only the UF poly(ether sulfone) membrane of 10 kDa MWCO showed a reduction of glycerol ($R_{\text{GLY}} = 31\%$) within the levels permitted by the international standard ASTM D6751 (0.02% GLY). The glycerol removal was improved when 0.2% of water was added to the original BD mixture, achieving 69% of GLY rejection at 4 bar with an abrupt decrease of permeate flux from 70 to 30 kg/(m²h) during the first 55 min of operation time. After that, the flux decrease continuously, indicating a relatively high fouling. A remarkable glycerol rejection of 99% from FAME (palm oil, methanol, and potassium hydroxide) was achieved by Atadashi et al. (2012) using an MF ceramic membrane (0.22 μm mean pore size), at 2 bar transmembrane pressure (Δp) and 40 °C. The initial concentration of GLY was 0.14%. There was a pronounced flux decay during the experimental test indicating a high fouling of the membrane. After 45 min of permeation time, the BD flux was 9.08 kg/(m²h). Other relevant results were published by Gomes et al. (2015). They obtained high glycerol rejection using tubular UF ceramic membranes (0.05 μm and 20 kDa) in the treatment of BD obtained from ethylic transesterification of soybean and canola oils. BD from degummed and crude oils showed almost the same low concentration of glycerol in the permeate stream (0.012%, at 50 °C and $\Delta p = 1$ bar) with the membrane of 0.05 μm pore size. High permeate fluxes were obtained and their decline ranged from 14% to 26%, reaching values of 98–100 kg/(m²h) at 95 min of test time. This behavior was attributed to the presence of the larger size of glycerol agglomerates, which are formed in the presence of free fatty acids in the oil used. The BD from refined canola and soybean oils showed a high percentage of glycerol in the permeate (12%) under the same experimental conditions.

The published results show that there are a number of variables involved in the performance of BD purification, between these

Table 3
BD permeation fluxes at steady state and rejection factors.

Membrane	% Water added	T (°C)	Δp (bar)	J^* (L/(m ² h))	$R_{\text{GLY}} \%$	$R_{\text{GT}} \%$
PSf-23-7	–	30	5	10.5 ± 0.4	16.2	13.7
			7	12.8 ± 0.3	17.0	15.5
	0.2	5	5	1.9 ± 0.1	18.9	22.7
			7	2.4 ± 0.1	36.2	32.7
	0.5	5	5	1.7 ± 0.1	48.0	45.4
			7	2.3 ± 0.1	23.4	26.5
PVDF-20-5	0.2	30	5	7.4 ± 0.3	24.7	23.7
			7	10.5 ± 0.4	20.9	23.5
	0.2	40	5	11.6 ± 0.6	14.0	13.9
			7	14.9 ± 0.7	10.8	9.3
	0.5	30	5	9.5 ± 0.4	67.3	60.6
			7	13.1 ± 0.6	64.5	59.2
	0.5	40	5	12.5 ± 0.6	61.0	61.6
			7	18.1 ± 0.7	58.1	52.0

variables is worth mentioning i) the reagents used in the transesterification reaction: alcohol (FAME or FAEE), catalyst, oil crude, degummed or refined; and the amount of water, soaps, glycerides, etc. present in the solution to be treated, and ii) the physico-chemical and structural characteristics of the membranes used. Another important factor that has not been discussed in the aforementioned works is the useful life period of the membranes. From this, it is difficult to make a comparison on the purification performance of BD when solutions and membranes with different characteristics are employed.

As it was pointed out in Section 3.1, our BD samples showed values ≈ 1 wt% in soaps as a consequence of the 0.5 wt% of water in EtOH and around 0.15 wt% in semi-refined soybean oil. This high soap concentration makes difficult the removal of glycerol and by-products from the reaction. However, the obtained values of permeability and rejection of GLY and GT, as well as the high stability achieved with the PVDF membrane, encourage us to continue the development of more efficient membranes for BD purification.

4. Conclusions

In this study, a thorough analysis of BD preparation and purification with lab-made UF polymeric membranes is provided. Two solvent resistant membranes with molecular weight cut-off of 7 and 5 kDa were prepared from poly(vinylidene fluoride) and poly(sulfone) as main materials. Biodiesel was produced from ethyl transesterification of semi-refined soybean oil. The obtained BD solution ($\text{pH}_{\text{app}} = 11.7$) showed a high content of fatty acids ethyl esters, 1.74% of total glycerol, 1.06% of soaps, and other minor components. The PVDF membrane presented higher permselectivity characteristics compared to the PSf. The PVDF membrane performance was improved when 0.5% of water was added to the BD solution, reaching permeate flux of 9.5 L/(m²h) and rejection of 67.3% and 60.6% for GLY and GT, respectively, at $T = 30$ °C. A remarkable flux recovery after more than 45 cycles of BD permeation (≈ 105 hs) was verified in PVDF membrane, indicating the high stability and low fouling of the membrane. Despite the good performance of separation of these membranes, it is necessary to improve the permeability and selectivity values obtained, in order to reach adequate values of GLY and GT defined by BD regulations. These improvements could make membrane technology more competitive with conventional processes for BD purification.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jclepro.2016.09.130>.

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