



## Separation of biodiesel and glycerol using ceramic membranes

Maria Carolina Sérgio Gomes\*, Nehemias Curvelo Pereira, Sueli Teresa Davantel de Barros

Department of Chemical Engineering, State University of Maringá, Maringá, Av. Colombo 5790, Bloco D90, CEP 87020-900, Paraná, PR, Brazil

### ARTICLE INFO

#### Article history:

Received 10 November 2009  
Received in revised form 4 February 2010  
Accepted 8 February 2010  
Available online 13 February 2010

#### Keywords:

Microfiltration  
Ceramic membranes  
Biodiesel  
Glycerol

### ABSTRACT

This study investigated the efficiency of microfiltration with ceramic membranes in the separation of biodiesel and glycerol. Runs in a micro- and ultrafiltration module were performed in batch mode using tangential filtration. The experiments were carried out with tubular  $Al_2O_3/TiO_2$  ceramic membranes with average pore size of 0.2, 0.4, and 0.8  $\mu m$  and filtration area of 0.005  $m^2$ . In the first part of the experiment, synthetic blends (feed solution) prepared with mass composition of 80% biodiesel, 10% glycerol, and 10% anhydrous ethanol were microfiltered at 60 °C and transmembrane pressures of 1.0, 2.0, and 3.0 bar. Membrane performance was evaluated based on the capacity to retain glycerol and on the permeate flux values. Experimental results showed that transmembrane pressure has a strong influence on biodiesel microfiltration. The best performance was obtained with the 0.2  $\mu m$  membrane and 2.0 bar transmembrane pressure. In these conditions and at the same temperature that was used in the previous experiments (60 °C), the influence of the ethanol concentration on the feed solution separation was evaluated. The highest ethanol concentration in the feed solution used, 20%, resulted in the highest glycerol concentration in the permeate. The lowest flux decline rate and the highest glycerol retention (99.6%), were achieved for the feed solution with 5% ethanol.

© 2010 Elsevier B.V. All rights reserved.

### 1. Introduction

The constant concerns about the environmental impact of vehicle emissions and the prospect of oil shortage have driven the discussion on the use of biodiesel. Biodiesel is an alternative fuel constituted of a mixture of alkyl esters of long-chain carboxylic acids produced from vegetable oils, animal fat, and residual fats [1,2].

Biodiesel fuel is essentially free of sulfur and aromatic compound and it has the potential to reduce the level of pollutants and the level of potential carcinogenic compounds, in contrast to mineral diesel. As the physico-chemical characteristics of esters are very similar to those of petroleum diesel, biodiesel can be used in any mixture with diesel. Additionally, it is renewable, biodegradable, non-toxic, and an excellent lubricant, which extends the useful life of diesel engines [1,3–5].

An important parameter in the quality control of biodiesel is the amount of free glycerol, molecular glycerol dissolved in biodiesel. Its maximum limit is 0.02%. A high free glycerol content may result in decantation, storage, and engine fuel injection system problems. Free glycerol is also associated with fuel tank bottom deposits, which attract other contaminants, such as water, which in turn increases engine corrosion and reduces the engine's useful life. Burning glycerol together with biodiesel may also result in

hazardous emissions [3,6]. Thus, one of the critical points in the production of biodiesel is the separation of free glycerol, mainly when the ethyl route is used, since the formation of stable emulsion during ethanolysis complicates the separation and purification of esters [7].

The most common way to produce biodiesel is by transesterification. During this reaction, a short-chain alcohol, such as methanol or ethanol, reacts with a triacylglycerol in the presence of a catalyst and forms glycerol and long-chain fatty acid esters [8,9]. After reaction, the final mixture is formed by alkyl esters, residual alcohol, glycerol, and the catalyst, along with mono-, di-, and triacylglycerol, which are intermediate reaction products [10]. Two phases are then formed, a heavier phase constituted of crude glycerol impregnated with excess alcohol, water and raw material impurities, and a less dense phase constituted of a mixture of either methyl or ethyl esters, depending on the type of alcohol used, and excess reaction alcohol and impurities [3].

At the end of the reaction, glycerol must be eliminated. Due to its low solubility in esters, separation is usually performed by either decantation or centrifugation. In the separation by decantation, the biodiesel and glycerol mixture is rested in tanks. The separation cost is low, but it is a slow process. In the centrifugation process, the mixture is fed into centrifuges for separation. Although the separation time is greatly reduced, the investment required and the operating costs are high [3,8].

Once the glycerol and biodiesel phase have been separated, it is necessary a step of ester refining. Each phase has a substantial amount of the excess alcohol that was used in the reaction, unused

\* Corresponding author. Tel.: +55 44 3305 2703.

E-mail address: [mcarolinagomes@yahoo.com.br](mailto:mcarolinagomes@yahoo.com.br) (M.C.S. Gomes).

catalyst and soaps. The purity level of biodiesel has strong effects on its fuel properties. The important parameters to determine if the product is ready for commercial applications are the amounts of water, alcohol, glycerol and catalyst [11].

The alcohol is removed from both the glycerol and ester stream using an evaporator or a flash unit. The primary purpose of the ester washing step is the removal of any soaps formed during the transesterification. In addition, the water provides a medium for addition of acid to neutralize the remaining catalyst and a means to remove the product salts [5,10].

The acid is added to the esters to neutralize remaining base catalyst and break the soaps formed during the reaction. Soaps react with acid producing free fatty acids and salts that are soluble in water. The salts are removed during the washing steps, while the free fatty acids remain in the biodiesel [3].

Additionally, the esters washing with water provides a reduction in the total glycerol contents that is one of the most important parameters to indicate if the final product meets the specification for trading [11].

The phase separation between esters and water is typically very clean and complete. However, the equilibrium solubility of water in esters is higher than the specified water content for B100. Therefore, after the washing step there will be more than the equilibrium amount of water present and vacuum driers are used to dry the biodiesel, that will be ready for storage [10].

Some studies have been carried out in an attempt to develop a more efficient separation method. Van Gerpen et al. [12] used synthetic mixtures of methyl esters and bi-distilled glycerol with and without the addition of distilled water to investigate phase separation after different mixture agitation times. They found that the presence of a large amount of water produces the solubilization of glycerol and allows its complete separation. The procedure proposed by Encinar et al. [7] to separate and purify the ethyl esters produced from used frying oil consisted of addition 25% of glycerol, based on the weight of the oil, after complete reaction. The glycerol added destabilized the emulsion and facilitated the separation of the phases. After separation the ethyl esters were purified by distilling the residual ethanol and removing remaining catalyst by successive rinses with distilled water.

Membrane separation is largely used in the purification of water, and in protein and gas separation. Many researchers have applied membrane separation technology to vegetable oil and oil emulsion processing with promising results for the industrial sector.

In the biofuel area, the use of processes with membranes is not very significant yet. Dubé et al. [13] developed a reactor for the production of biodiesel that uses a 0.05- $\mu\text{m}$  pore diameter carbon membrane and the methyl transesterification of canola oil. The membrane forms a barrier that prevents the presence of triglycerides and unreacted lipids in the product, which is desirable to ensure the quality of the produced biodiesel. Cao et al. [14] used a membrane reactor similar to that developed by Dubé et al. [13] to study the influence of carbon membrane pore sizes 0.05, 0.2, 0.5, and 1.4  $\mu\text{m}$ . They observed that the membrane pore diameter did not influence the conversion of triglyceride into fatty acid methyl esters, obtaining values over 90% and no trace of triglyceride in the permeate. He et al. [15] compared the efficacy of traditional biodiesel purification methods and hollow polysulfone and polyacrylonitrile fiber membranes. The membrane process avoided the emulsification of water and the esters, reduced refining losses when compared to the other methods, and afforded 99% biodiesel purity.

Thus, the objective of the present work was to evaluate the applicability of microfiltration with ceramic membranes to the separation of biodiesel and glycerol by the analysis of the permeate flux and of the quality of the product obtained by the analysis of free glycerol content. The influence of the mass concentration of

ethanol in the feed on the microfiltration process performance was also evaluated.

## 2. Materials and methods

### 2.1. Raw materials and reagents

Biodiesel obtained from soybean oil supplied by Biolix, Rolândia, Paraná State, anhydrous ethanol from plants of the region, and bi-distilled commercial glycerol were used in all microfiltration assays. The chemical reagents used in the analysis of free glycerol and to wash the membranes were purchased from Merck, Brazil.

### 2.2. Membranes

The ceramic membranes used in the experiments were made of tubular-type  $\alpha\text{-Al}_2\text{O}_3/\text{TiO}_2$  (Shumacher GmbH-Ti 01070), 250 mm long, 7 mm in diameter, and 0.005  $\text{m}^2$  filtration area, purchased from Andritz, Pomerode, Santa Catarina State, Brazil. Membranes with three pore sizes were used: 0.2, 0.4, and 0.8  $\mu\text{m}$ .

### 2.3. Experimental microfiltration module

The experimental equipment was constituted of a micro- and ultrafiltration pilot unit UF NETZSCH, Pomerode, Santa Catarina State, Brazil, model 027.06-1C1/07-0005/Al, that operates under tangential flow conditions. A detailed scheme of the experimental unit is given in Fig. 1.

The experimental module feed system consisted of a 5-L two-sleeve stainless steel tank and a positive displacement pump with a frequency inverter, which allowed its operation at varying flux rates, that is, with varying tangential filtration speed. Two manometers and a rotameter were used to measure the feed pump flux. The pump operating pressure was limited by a pressostat and a device prevented void operation. The membranes used were set on a stainless steel module fixed to the piping with flanges.

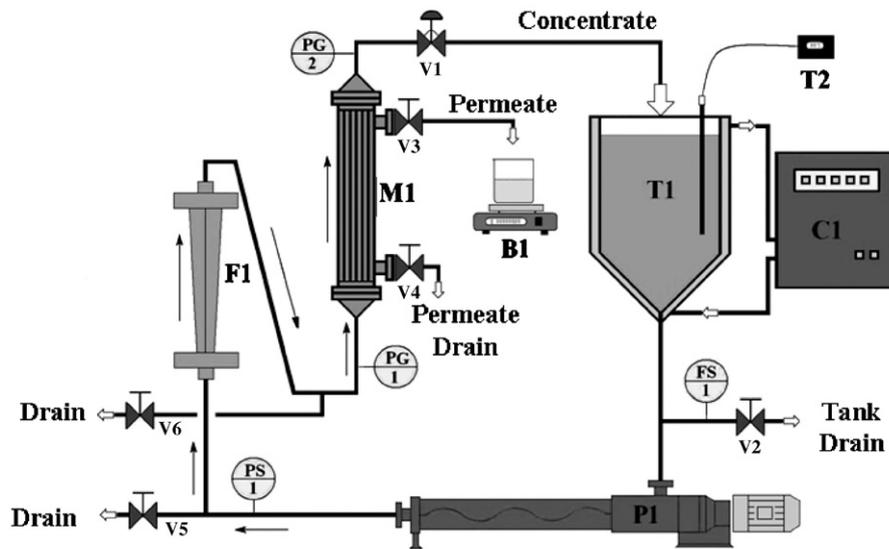
### 2.4. Microfiltration assays

Batches of synthetic mixtures of biodiesel, ethanol, and glycerol were prepared for analysis. Before each assay, the module was run with pure biodiesel without membrane to remove the remaining water. The feed mixture was then pumped in and the pressure was adjusted with a manual valve. The permeate was collected and the retentate was totally recirculated to the feed tank. The temperature was controlled with a thermostatic bath. A rheological study of glycerol demonstrated that an increase in the temperature causes a sharp decrease in the viscosity, which becomes less accentuated above 60 °C. Thus, the temperature of 60 °C was used in all experiments in order to provide a good performance of the pump which promotes the circulation of the mixture.

For the first stage, 3.5 kg of mixtures with mass composition of 80% biodiesel, 10% ethanol, and 10% glycerol were prepared. The mixture composition was chosen according to data published by Vicente et al. [16], who suggested the use of 100% molar excess ethanol in the reaction, corresponding to a mass of about 10% ethanol in the final mixture.

Each membrane was assayed in replicate at operating pressures of 1.0, 2.0, and 3.0 bar at 60 °C. All experiments were performed at maximum pump flux rate of 600  $\text{L h}^{-1}$ , which corresponds to a tangential speed of circa 4  $\text{m s}^{-1}$ . Some studies demonstrated that high cross-flow velocity is more effective to reduce fouling and a velocity around 3.0  $\text{m s}^{-1}$  was sufficient to prevent the formation of reversible fouling layer [17,18].

The second stage involved the identification of the membrane that gave the best results in relation to the permeate flux and free



<b>M1 – Membrane module</b>	<b>T2 – Thermometer</b>
<b>P1 – Circulating pump</b>	<b>B1 – Analytical balance</b>
<b>T1 – Feed tank</b>	<b>PG1, PG2 – Pressure gauges</b>
<b>F1 – Flow meter</b>	<b>FS1 – Flow controller</b>
<b>V1 – Pressure valve</b>	<b>PS – Pressure controller</b>
<b>V2, V3, V4, V5, V6 – Drain valves</b>	<b>C1 – Circulating Bath Temperature Control</b>

Fig. 1. Diagram of the micro- and ultrafiltration experimental unit.

glycerol retention. The chosen membrane was used in new microfiltration assays at the same pressure and temperature as used in the first assays by varying the initial concentration of anhydrous ethanol in the feed mixture. According to Van Gerpen et al. [10], the excess ethanol used in the reaction may vary from 60 to 100%. Thus, mixtures with mass composition of 70% biodiesel, 10% glycerol, and 20% ethanol and 85% biodiesel, 10% glycerol, and 5% ethanol, were prepared.

The permeate flux values were determined by the amount of permeate measured in a semi-analytical balance (BG 4000 – Gehaka), and the filtration time, Eq. (1):

$$J_{perm} = \frac{m_p}{A \cdot t} \quad (1)$$

where  $J_{perm}$  is the permeate flux ( $\text{kg/h m}^2$ ),  $m_p$  is the mass in kg,  $t$  is the filtration time in h, and  $A$  is the membrane permeation area in  $\text{m}^2$ .

### 2.5. Cleaning of the experimental module and the membranes

After each filtration process, the experimental unit was immediately cleaned to preserve the equipment and restore the permeability of the used membrane. Firstly, they were washed with water and detergent until most biodiesel was eliminated. Then, a 1% NaOH solution at 70 °C was recirculated for 45 min. Next, the module was rinsed with water and finally rinsed with deionized water.

The membranes were sonicated in a 1% NaOH solution at 70 °C and in deionized water at the same temperature.

Before starting the experiments, the hydraulic permeability of the membranes was evaluated to establish a cleaning parameter. The mean permeate flux values at 60 °C and 1.0 bar for the 0.2-, 0.4-, and 0.8- $\mu\text{m}$  membranes were 1800, 2300, and 2500  $\text{kg/h m}^2$ , respectively. After each cleaning cycle, the flux was measured with deionized water, thus ensuring the experiment reproducibility.

### 2.6. Analysis of free glycerol content in biodiesel

The free glycerol content of the permeate was determined by the official AOCS method for the analysis of free glycerol in oils and fats (Ca 14-56) with modifications, as proposed by Dantas [19]. The titration method used is based on the reaction of glycerol in aqueous medium with excess sodium periodate to form formaldehyde, formic acid, and iodic acid, and later the addition of potassium iodate to react with the formed sodium periodate and the iodic acid.

The titration method with periodate presents low cost in comparison with gas chromatography. Besides, this methodology is simple, quick and sufficiently reliable [6]. Sala and Bondioli [20] evaluated the method that employs periodate as an oxidant reagent for determining glycerol and conclude that glycerol analyses carried out with this method were very successful in terms of precision and accuracy. Similar results were obtained by Naviglio et al. [21] in the study of determination of esterified glycerol and glycerides in oils by means of periodate method after transesterification. They demonstrated that the method is easily repeatable and accurate.

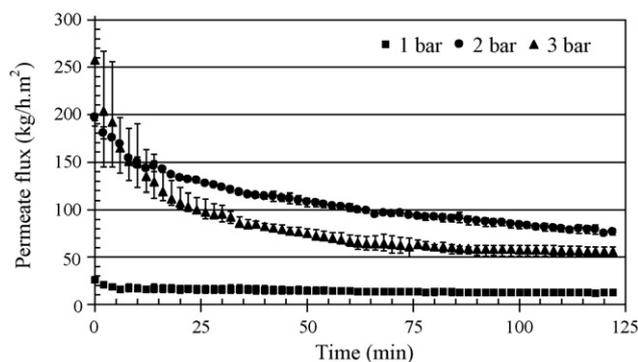
The feed and permeate free glycerol contents were analyzed in triplicate in each microfiltration assay and the standard deviation was calculated. The coefficient of retention of glycerol (%R) was calculated with Eq. (2):

$$\%R = \frac{[(C_{al} - C_{per}) \times 100]}{C_{al}} \quad (2)$$

In this equation,  $C_{al}$  and  $C_{per}$  are the mass fractions of free glycerol in the feed and the permeate, respectively.

### 2.7. Influence of the concentration of ethanol in the microfiltrate mixture

The mixture of biodiesel, glycerol, and ethanol forms an emulsion, which is defined as a mixture with at least two immiscible phases in the form of a uniform macroscopic or microscopic dis-



**Fig. 2.** Permeate flux of the 0.2  $\mu\text{m}$  membrane as a function of the filtration time for the biodiesel, glycerol, ethanol mixture (80:10:10% mass) at 1.0, 2.0, and 3.0 bar and  $T=60^\circ\text{C}$ .

persed system [22]. Depending on the emulsification process, the diameter of the droplets of the dispersed phase in the continuous phase may range from 0.1  $\mu\text{m}$  to 0.01 mm [23]. In the mixture studied here, free glycerol, the dispersed phase, was dispersed in the form of droplets in the biodiesel, the continuous phase.

In a two-phase ester–glycerol system, the alcohol distributes between the two phases. For 90% ester and 10% glycerol mass concentrations, which are required for complete transesterification, the mass percentage of methanol is approximately 60% in the ester-rich phase, and 40% in the glycerol-rich phase [10].

The formation of a dispersed phase and the size of the droplets formed depend on the interface tension between the continuous and the dispersed phase. The reduction of the interface tension makes the formation of smaller droplets in the dispersed phase easier [24].

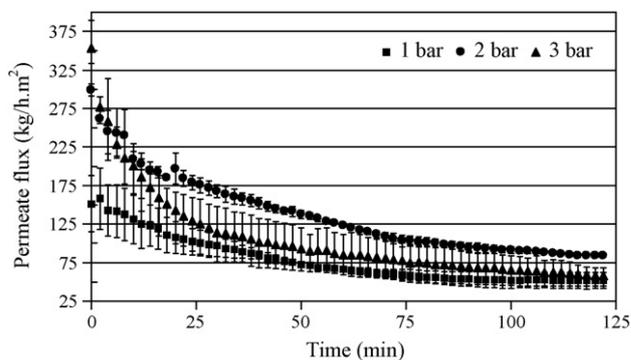
### 3. Results and discussion

#### 3.1. Influence of the transmembrane pressure

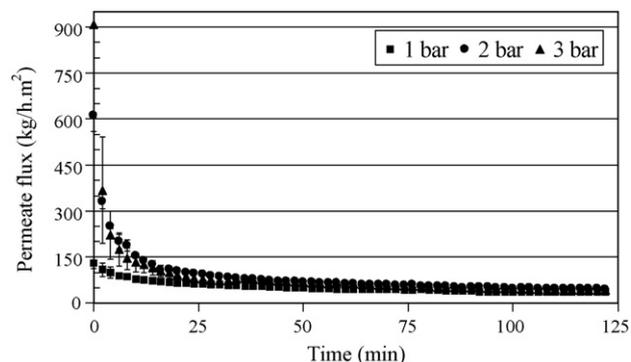
The total microfiltration time, approximately 2 h, was determined to enable stabilization flux in all experimental conditions. Thus, the concentration factor, which is defined as the ratio between the initial mixture volume and the concentrate volume, varied from 1.07 to 1.66. Mean values of replicate experiments were used to plot the curves and calculate the standard deviations.

Fig. 2 shows the curve of the permeate flux as a function of the filtration time for the 0.2- $\mu\text{m}$  membrane and the three pressure values used. At 0.1 bar, this membrane gave the lowest stabilized permeate flux, 12.2  $\text{kg/h m}^2$ , which is six-fold smaller than the highest value obtained in this study. However, this condition resulted in the largest retention of glycerol, 99.6%.

The 0.4  $\mu\text{m}$  membrane gave the highest permeate flux values for all the used pressures when compared to the other membranes, as shown in Fig. 3. The highest stabilized permeate flux of this membrane was 83.6  $\text{kg/h m}^2$  at 2.0 bar for 99.3% glycerol retention.



**Fig. 3.** Permeate flux of the 0.4  $\mu\text{m}$  membrane as a function of the filtration time for the biodiesel, glycerol, ethanol mixture (80:10:10% mass) at 1.0, 2.0, and 3.0 bar and  $T=60^\circ\text{C}$ .



**Fig. 4.** Permeate flux of the 0.8  $\mu\text{m}$  membrane as a function of filtration time for the biodiesel, glycerol, ethanol mixture (80:10:10% mass) at 1.0, 2.0, and 3.0 bar and  $T=60^\circ\text{C}$ .

Despite the initial high fluxes of the membrane with 0.8  $\mu\text{m}$  pore diameter, it presented the largest decreases in permeate flux (Fig. 4) as well as the highest percent mass of glycerol in the permeate, 0.1%. It is likely that the glycerol agglomerates formed were about the same size as the membrane pores, permeating or even completely blocking the pores and consequently reducing the flux.

Figs. 2–4 show that the curves obtained for all conditions describe a typical membrane separation behavior, with a sharp reduction in the permeate flux soon after the beginning of the process caused by the concentration polarization. The continuous flux reduction with time indicates that other “incrustation” phenomena, such as pore blocking or molecule adsorption on the membrane surface, must also occur [17,25].

The highest stabilized permeate flux of each membrane was obtained at 2.0 bar. Likewise, the stabilized flux increased with the increase in pressure from 1.0 to 2.0 bar. At 3.0 bar, the permeate flux was the highest. However, higher flux decrease rates were also observed at this pressure, reaching values lower than those obtained at 2.0 bar, that is, the increase in pressure from

**Table 1**

Steady-state permeate flux and glycerol retention values for membranes with 0.2, 0.4, and 0.8  $\mu\text{m}$  pore diameter at 1.0, 2.0, and 3.0 bar and  $T=60^\circ\text{C}$ .

Average pore diameter ( $\mu\text{m}$ )	Pressure (bar)	Permeate flux ( $\text{kg/h m}^2$ )	Glycerol content in permeate (% mass)	Glycerol retention (%)
0.2	1	12.2	$0.04 \pm 0.004$	99.6
0.2	2	78.4	$0.06 \pm 0.009$	99.4
0.2	3	56.1	$0.06 \pm 0.005$	99.4
0.4	1	52.2	$0.05 \pm 0.003$	99.5
0.4	2	83.6	$0.07 \pm 0.015$	99.3
0.4	3	60.0	$0.10 \pm 0.010$	99.0
0.8	1	36.0	$0.06 \pm 0.008$	99.4
0.8	2	46.3	$0.08 \pm 0.010$	99.2
0.8	3	41.3	$0.10 \pm 0.016$	99.0

2.0 to 3.0 bar resulted in a reduction of the stabilized permeate flux.

Koltuniewicz et al. [26] studied the microfiltration of oil–water emulsions with ceramic membranes with pore diameter of 0.1  $\mu\text{m}$  at two different pressures, 0.6 and 0.8 bar. At the low pressure, the initial permeate flux was smaller than at the high pressure. However, after approximately 150 min of operation, the two flux values were equal. After a long filtration time, the flux at 0.6 bar was higher than at 0.8 bar. These results and the ones obtained in the present study indicate an increased trend for the membrane to clog up at higher pressures.

Table 1 gives the steady-state permeate flux and glycerol retention values of each assay.

In Brazil, the National Agency for Petroleum, Natural Gas, and Biofuels (ANP) specifies biodiesel B100 based on the standards of the Brazilian Technical Standards Association (Associação Brasileira de Normas Técnicas, ABNT), the International Organization for Standardization (ISO), and the European Committee of Standardization (Comité Européen de Normalization, CEN). The maximum amount of free glycerol allowed in biodiesel is 0.02% mass [27]. In the present study, the concentrations of glycerol in the permeate ranged from 0.04 to 0.1% (mass), being close to the specification value for commercialization and thus demonstrating the potential for microfiltration to be used as a substitute of traditional process of biodiesel purification.

Çetinkaya and Karaosmanoglu [11] used a refining method of washing with hot water to purify biodiesel produced by methanolysis of used cooking oil. The glycerol content of the crude ester phase after separation of the phases by decantation was determined to be 0.338 wt%. Seven consecutive washing steps with hot distilled water at 50 °C were necessary to meet the required limit value. Although a minimum free glycerol content of 0.011 wt% was obtained, this process requires a large amount of water and produces a waste stream that needs a treatment before discharge.

According to Table 1, an increase in the transmembrane pressure leads to a reduction in the retention of free glycerol, and, as previously mentioned, a pressure over 2.0 bar leads to a reduction in the permeate flux. A higher pressure may force the permeation of glycerol through the membrane pores, reducing the filtration area because of pore blocking and thus reducing the permeate flux. The same behavior was reported by Wang et al. [28] for the ultrafiltration of oil–water emulsions using alumina membranes with pore diameter in the order of 0.1–0.2  $\mu\text{m}$ . A flux decrease was observed at the same time as the oil rejection rate for pressures higher than 2.0 bar, indicating the oil permeation through the membrane. Ribeiro et al. [29] also reported a reduction in oil retention at high pressures in a study of recovery of solvent from oil–solvent micelle by polymer membranes. Shu et al. [30] used ceramic membranes in the treatment of oil–water microemulsions and observed oil in the permeate even when the oil droplet diameter was larger than the membrane pores, possibly because of the deformation of oil droplets. An alternative explanation proposed for the incomplete rejection is the coalescence of the oil droplets on the membrane surface, which may have resulted in the formation of a continuous oil phase and permeation through the membrane.

To determine the optimal process conditions, the permeate flux and glycerol retention values were analyzed simultaneously. Although the stabilized fluxes at 2.0 bar were very close for membranes with pore diameters of 0.2 and 0.4  $\mu\text{m}$ , the higher glycerol concentration in the permeate for the 0.4  $\mu\text{m}$  membrane at 3.0 bar suggests that a smaller pore diameter must be used to obtain a better quality permeate.

The membrane with pore diameter of 0.2  $\mu\text{m}$  at 2.0 bar performed the best, giving a steady-state permeate flux of 78.4  $\text{kg/h m}^2$  and glycerol retention of 99.4%. Hua et al. [31] studied the micro-

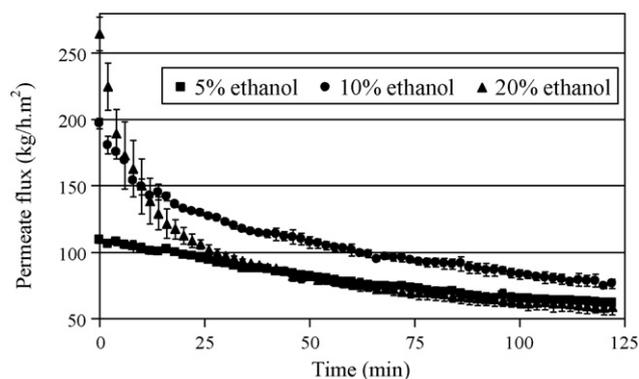


Fig. 5. Permeate flux of the 0.2  $\mu\text{m}$  pore diameter membrane as a function of filtration time for the biodiesel, glycerol, and ethanol mixtures and ethanol concentrations of 5, 10, and 20% (% mass) at 2.0 bar and  $T=60^\circ\text{C}$ .

filtration of oil emulsions with ceramic membranes with pore diameter of 0.5  $\mu\text{m}$ . They concluded that the pressure that reduced fouling the most was 2.0 bar.

In the present study, the permeate obtained with the 0.2- $\mu\text{m}$  pore diameter membrane at 2.0 bar after the evaporation of the alcohol had the best mean kinematic viscosity, 4.44  $\text{mm}^2/\text{s}$  at 40 °C, and density of 0.8739  $\text{g}/\text{cm}^3$  at room temperature. These results agree with those found in literature. Brandão et al. [32] obtained biodiesel with kinematic viscosity of 4.77  $\text{mm}^2/\text{s}$  at 40 °C and density of 0.886  $\text{g}/\text{cm}^3$  at 25 °C by the transesterification of soybean oil with mixtures of methanol–ethanol after the separation of glycerol by decantation and washing with acidic water.

### 3.2. Influence of the ethanol concentration on the microfiltered mixture

After determining the best condition for the separation of biodiesel and glycerol, that is, the smallest pore diameter membrane and pressure of 2.0 bar, the influence of the concentration of ethanol on the feed mixture during microfiltration was investigated. Fig. 5 shows the permeate flux curves against the microfiltration time of the mixtures with initial ethanol percent masses of 5, 10, and 20%.

The highest ethanol concentration in the initial mixture afforded high initial fluxes; however, its flux decrease rate was the greatest. It was observed that the concentration of ethanol affected the glycerol droplet size distribution, since for the same operating pressure, the glycerol content in the permeate for a higher ethanol concentration was over four-fold that for a lower alcohol concentration, as shown in Table 2.

The analysis of fouling in oil emulsions is complex, as an emulsion has a droplet size range and distribution variations as a result of distortions or coalescence [33]. It is known from the literature that the creation of the dispersed phase and the size of the dispersed phase droplets are highly dependent on the interfacial tension between the continuous phase and the dispersed phase. The ethanol acts as a surfactant in the system, reducing the surface tension between biodiesel and glycerol, maximizing their superfi-

Table 2  
Permeate flux and free glycerol retention for different ethanol concentrations in the feed mixture.

Ethanol in feed (% mass)	Permeate flux ( $\text{kg/h m}^2$ )	Glycerol in permeate (% mass)	Glycerol retention (%)
5	63.1	0.04 $\pm$ 0.004	99.6
10	78.4	0.06 $\pm$ 0.009	99.4
20	59.5	0.19 $\pm$ 0.013	98.1

cial contact area and causing the formation of small droplets of the disperse phase. Decrease in the interfacial tension makes it easier to break down the glycerol droplets into smaller ones [22,24]. This is due to the fact that ethanol has both a polar group and an apolar group. The apolar group will absorb the biodiesel phase while the polar group will absorb the glycerol phase, causing an increasing in the solubility between the phases [34].

Higher ethanol concentrations resulted in smaller droplet diameters of glycerol dispersed in biodiesel, led to the permeation of the glycerol through the membrane, according to Table 2. As a result, when the initial mixture had a large concentration of ethanol, 20%, the glycerol droplet permeation through the membrane was larger.

The feed mixture with 5% ethanol submitted to microfiltration afforded a low permeate flux reduction ratio over time, which reached a stationary value of 63.1 kg/h m<sup>2</sup>. Furthermore, this condition resulted in the largest retention of glycerol, 99.6%.

The membrane cleaning method used was efficient, and after each washing cycle, the initial membrane flux for deionized water was restored.

#### 4. Conclusions

A new separation route using membranes to obtain biodiesel with minimum free glycerol content was proposed. Ceramic membranes with pore diameters of 0.2, 0.4, and 0.8 μm separated biodiesel and glycerol efficiently. The preliminary results demonstrated the potential of this technology to improve the process of separation of biodiesel. The applied transmembrane pressure proved to be an extremely important variable in the microfiltration of biodiesel. Values over 2.0 bar reduced the retention of glycerol. For the three investigated membranes, the highest stable permeate flux was obtained at 2.0 bar.

The best performance was that of the membrane with pore diameter of 0.2 μm at 2.0 bar, which gave a stable permeate flux of 78.4 kg/h m<sup>2</sup> and glycerol retention of 99.4%.

The concentration of ethanol in the feed mixture submitted to microfiltration affected the behavior of the emulsion so that a higher concentration of ethanol led to a lower retention of glycerol. The glycerol content in the permeate for 20% ethanol was four-fold that for the lowest ethanol concentration.

In conclusion, a 5% ethanol percent mass in the feed submitted to microfiltration with a 0.2-μm pore diameter membrane gave the best results, with a stable permeate flux of 63.1 kg/h m<sup>2</sup> and glycerol retention of 99.6%.

#### References

- [1] F. Ma, M.A. Hanna, Biodiesel production: a review, *Bioresource Technology* 70 (1999) 1–15.
- [2] K.G. Georgogianni, M.G. Kontominas, E. Tegou, D. Avlonitis, V. Gergis, Biodiesel production: reaction and process parameters of alkali-catalyzed transesterification of waste frying oils, *Energy and Fuels* 21 (2007) 3023–3027.
- [3] G. Knothe, J. Van Gerpen, J. Krahl (Eds.), *The Biodiesel Handbook*, AOCS Press, Champaign, IL, 2005.
- [4] E.M. Shahid, Y. Jamal, A review of biodiesel as vehicular fuel, *Renewable and Sustainable Energy Reviews* 12 (2008) 2484–2494.
- [5] A. Demirbas, *Biodiesel: A Realistic Fuel Alternative for Diesel Engines*, Springer-Verlag London Ltd., London, 2008.
- [6] M.R. Monteiro, A.R.P. Ambrozini, L.M. Lião, A.G. Ferreira, Critical review on analytical methods for biodiesel characterization, *Talanta* 77 (2008) 593–605.
- [7] J.M. Encinar, J.F. González, A. Rodríguez-Reinares, Ethanolysis of used frying oil. Biodiesel preparation and characterization, *Fuel Processing Technology* 88 (2007) 513–522.
- [8] J. van Gerpen, Biodiesel processing and production, *Fuel Processing Technology* 86 (2005) 1097–1107.
- [9] Y. Zhang, M.A. Dubé, D.D. McLean, M. Kates, Biodiesel production from waste cooking oil. 1. Processing design and technological assessment, *Bioresource Technology* 89 (2003) 1–16.
- [10] J. van Gerpen, B. Shanks, R. Pruszko, D. Clements, G. Knothe, *Biodiesel Production Technology*. National Midwest Research Institute, first ed., Renewable Energy Laboratory, Colorado, 2004.
- [11] M. Çetinkaya, F. Karaosmanoglu, Optimization of base-catalyzed transesterification reaction of used cooking oil, *Energy and Fuels* 18 (2004) 1888–1895.
- [12] J.H. van Gerpen, E.G. Hammond, L.A. Johnson, S.J. Marley, L. Yu, I. Lee, A. Monyem, Determining the Influence of Contaminants on Biodiesel Properties, The Iowa Soybean Promotion Board, Iowa State University, 1996.
- [13] M.A. Dubé, A.Y. Tremblay, J. Liu, Biodiesel production using a membrane reactor, *Bioresource Technology* 98 (2007) 639–647.
- [14] P. Cao, A.Y. Tremblay, M.A. Dubé, K. Morse, Effect of membrane pore size on the performance of a membrane reactor for biodiesel production, *Industrial & Engineering Chemistry Research* 46 (2007) 52–58.
- [15] H.Y. He, X. Guo, S.L. Zhu, Comparison of membrane extraction with traditional extraction methods for biodiesel production, *JAOCs* 83 (2006) 457–460.
- [16] G. Vicente, A. Coteron, M. Nartinez, J. Aracil, Application of the factorial design of experiments and response surface methodology to optimize biodiesel production, *Industrial Crops and Products* 8 (1998) 29–35.
- [17] H. Choi, K. Zhang, D.D. Dionysiou, D.B. Oerther, G.A. Sorial, Effect of permeate flux and tangential flow on membrane fouling for wastewater treatment, *Separation and Purification Technology* 45 (2005) 68–78.
- [18] H. Choi, K. Zhang, D.D. Dionysiou, D.B. Oerther, G.A. Sorial, Influence of cross-flow velocity on membrane performance during filtration of biological suspension, *Journal of Membrane Science* 248 (2005) 189–199.
- [19] M.B. Dantas, Obtenção, caracterização e estudo termoanalítico de biodiesel de milho, MSc Thesis, Departamento de Química/Universidade Federal da Paraíba, 2006.
- [20] M. Sala, P. Bondioli, Caratterizzazione analitica del glicerolo. Considerazioni sperimentali, *Rivista Italiana delle Sostanze Grasse* 75 (1998) 305–309.
- [21] D. Naviglio, R. Romano, F. Pizzolongo, A. Santini, A. de Vito, L. Schiavo, G. Nota, S.S. Musso, Rapid determination of esterified glycerol and glycerides in triglyceride fats and oils by means of periodate method after transesterification, *Food Chemistry* 102 (2007) 399–405.
- [22] P. Pittia, D. Mastrocola, M.C. Nicoli, Effect of colloidal properties of oil-in-water emulsions on ethanol liquid–vapour partition, *Food Research International* 38 (2005) 585–595.
- [23] S. van der Graaf, C.G.P.H. Schroen, R.M. Boom, Preparation of double emulsions by membrane emulsification—a review, *Journal of Membrane Science* 251 (2005) 7–15.
- [24] G. Yilmaz, R.O.J. Jongboom, J.J.G. van Soest, H. Feil, Effect of glycerol on the morphology of starch-sunflower oil composites, *Carbohydrate Polymers* 38 (1999) 33–39.
- [25] L. Song, Flux decline in crossflow microfiltration and ultrafiltration: mechanisms and modeling of membrane fouling, *Journal of Membrane Science* 139 (1998) 183–200.
- [26] A.B. Koltuniewicz, R.W. Field, T.C. Arnot, Cross-flow and dead-end microfiltration of oily-water emulsion. Part I: Experimental study and analysis of flux decline, *Journal of Membrane Science* 102 (1995) 193–207.
- [27] ANP, 2008. National Petroleum Agency. ANP Resolution Number 7, March 19, 2008. Available at <http://www.anp.gov.br/petro/biodiesel.asp> in January 2010.
- [28] P. Wang, N. Xu, J. Shi, A pilot study of the treatment of waste rolling emulsion using zirconia microfiltration membranes, *Journal of Membrane Science* 173 (2000) 159–166.
- [29] A.P.B. Ribeiro, J.M.L.N. Moura, L.A.G. Gonçalves, J.C.C. Petrus, L.A. Viotto, Solvente recovery from soybean oil/hexane miscella by polymeric membranes, *Journal of Membrane Science* 282 (2006) 328–336.
- [30] W. Shu, C. Liangyin, C. Wenmei, Fouling-resistance composite membranes for separation of oil-in-water microemulsions, *Chinese Journal of Chemical Engineering* 14 (2006) 37–45.
- [31] F.L. Hua, Y.F. Tsang, Y.J. Wang, S.Y. Chan, H. Chua, S.N. Sin, Performance study of ceramic microfiltration membrane for oily wastewater treatment, *Chemical Engineering Journal* 128 (2007) 169–175.
- [32] K.S.R. Brandão, F.C. Silva, U.M. Nascimento, M.C. Sousa, A.M.C. Mouzinho, A.G. Souza, M.M. Conceição, K.R.M. Moura, Produção de biodiesel por transesterificação do óleo de soja com misturas de metanol–etanol, 2006. Available at <http://www.biodiesel.gov.br/rede.html> in January 2010.
- [33] T.C. Arnot, R.W. Field, A.B. Koltuniewicz, Cross-flow and dead-end microfiltration of oily-water emulsions. Part II. Mechanisms and modeling of flux decline, *Journal of Membrane Science* 169 (2000) 1–15.
- [34] C.Y. Lin, S.A. Lin, Effects of emulsification variables on fuel properties of two- and three-phase biodiesel emulsion, *Fuel* 86 (2007) 210–217.