SOLVENT RECOVERY FROM SOYBEAN OIL/N-HEXANE MIXTURES USING HOLLOW FIBER MEMBRANE

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Abstract - In this work, the separation of refined soybean oil/n-hexane mixtures was investigated using a commercial hollow fiber ultrafiltration membrane 50 kDa. Three alcohols with different chain lengths were tested for the conditioning of the membrane; n-propyl alcohol showed the highest n-hexane permeate flux after conditioning. There was a decrease in the rejection and an increase in permeate flux over time. This behavior may be related to swelling and membrane plasticization by the oil. Rejections from 10.0 to 28.7% and total permeate fluxes from 12.2 to 65.3 kg/m^{2}h were observed. An increase in the oil/n-hexane mass ratio and the pressure caused an increase in the rejection and permeate total flux for most assays. No degradation was observed in the membrane module.
Keywords: Soybean oil; n-Hexane; Solvent recovery; Hollow fiber; Ultrafiltration; Membrane conditioning.

INTRODUCTION

Membrane technology has been increasingly adopted by the food industry, mainly for the clarification of juices, wines and beers and the concentration of milk proteins. The interest in the application of membrane separations in the processing of vegetable oils to replace some of the traditional steps has also been growing in the last decade (Baker, 2004; Coutinho *et al*., 2009; Sarmento *et al*., 2004; Shahidi, 2005)

Membrane separation processes have advantages over conventional separation processes, including energy savings, the selectivity of the compounds obtained, the possibility of separation of thermolabile compounds, the simplicity of operating the system and a relatively easy scale up from lab to industrial scale

(Faria *et al*., 2002; Shahidi, 2005). In contrast to the conventional refining process, the membrane process can be conducted at low temperatures, preserving the heat sensitive components of technological interest of the oil, such as natural antioxidants. A more stable product, with thus better quality can be obtained using membranes (Ribeiro *et al*., 2008).

In the conventional processing of vegetable oils, distillation units operated under vacuum and other auxiliary equipment are used in the process. A possible thermal degradation of oil and an incomplete elimination of n-hexane are major disadvantages of this technology, besides the large amount of energy used in these processing steps (Reverchon and De Marco, 2006).

The low amount of energy consumption inherent to the membrane separation processes makes them a

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more attractive technique compared to technologies that use heat as a means of solvent separation. The membrane-based separation of organic solvents from vegetable oils can be conducted at low temperatures, avoiding the thermal degradation of valuable components in the final product, which is of great interest for the processing plant aiming at a consumer market that pays high prices for these superior products (Subramanian *et al*., 2004).

An ideal membrane for industrial solvent recovery should combine specific properties such as high oil rejection and permeate flux, as well as thermal, mechanical and chemical resistances. The major limitation for the implementation of membrane technology in the vegetable oil industry is the short supply of membranes that are stable to n-hexane and other organic solvents (Ribeiro *et al*., 2006).

Depending on the kind of mixture to be permeated, a pre-treatment step might be necessary. Among the main effects of pretreatment, we highlight the following: the effect of clustering in hydrophobic and hydrophilic sites in the surface layer of the membrane (Hilal *et al*., 2004); the removal of preservatives and wetting of the membrane surface and pores (Raman *et al*., 1996; Ribeiro *et al*., 2006); and the improvement of the permeate flux without significantly affecting the rejection (Arora *et al*., 2006; Marenchino *et al*., 2006). Organic solvents are used to improve the polarity of the membrane (the membrane becoming more polar or nonpolar) (Marenchino *et al*., 2006) or to prevent the closing of the pores present in some membranes when they are placed in contact with a mixture of hydrocarbons (García *et al*., 2006). The interactions between membrane and solvent can be
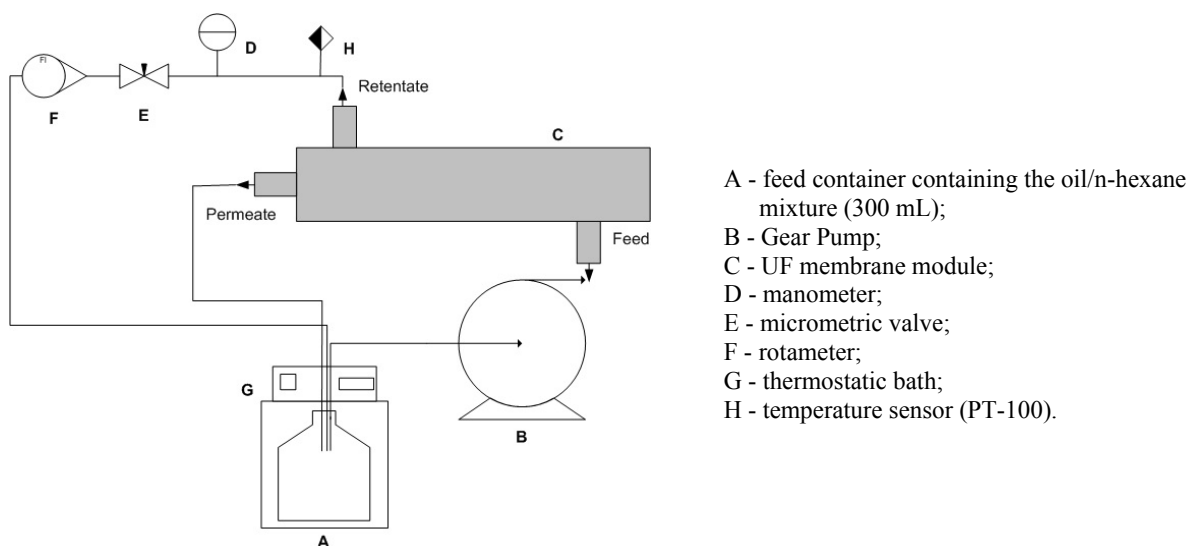
expected to change with changes in solvent properties such as dielectric constant, molecular size, dipole moment and the solubility parameter of Hildebrand (Machado *et al*., 1999; Darvishmanesh *et al*., 2009).

In this context, the objective of this study was to investigate the separation of refined soybean oil/n-hexane mixtures using a hollow fiber ultrafiltration membrane, testing the effect of pre-treatment on the membrane permeability to n-hexane.

MATERIALS AND METHODS

Membrane and Equipment

Permeation assays were performed using a hollow fiber ultrafiltration (UF) membrane module, supplied by PAM Membranas Seletivas Ltda. (Rio de Janeiro, Brazil). The membrane material is poly(ethersulfone)/poly(vinylpyrrolidone) PES/PVP) with a nominal molecular weight cut off (MWCO) of 50 kDa. The fiber module was 0.26 m long and 1.8 cm in diameter and contained 75 fibers. The membrane area was 0.036 m^2. The typical water flux at 1 bar of these membranes is 120 kg/m^2.h. The system was operated with a feed volume of 300 mL at a fixed flow rate of 2 L/min using a gear pump (Micropump, Cole Parmer Model 72211-15, max. pressure 7 bar). Figure 1 presents the schematic diagram of the experimental apparatus used for the assays. The system was run with complete recycle of permeate and retentate streams, i.e., the feed concentration was kept constant during the permeation run.

A - feed container containing the oil/n-hexane mixture (300 mL);
B - Gear Pump;
C - UF membrane module;
D - manometer;
E - micrometric valve;
F - rotameter;
G - thermostatic bath;
H - temperature sensor (PT-100).

Figure 1: Schematic diagram of the apparatus used for the separations of soybean oil/n-hexane mixtures using a hollow fiber UF membrane.

Membrane Conditioning

Preliminary tests of solvent permeation (n-hexane, Vetec, Rio de Janeiro, Brazil) showed that a membrane-conditioning step was necessary, since the flux obtained was much lower than the nominal water flux of the module. This behavior was attributed to the hydrophilic character of membrane, due to the presence of PVP on its surface (Simone *et al.*, 2010). Thus, pre-treatments were tested for conditioning the membrane before the permeation assays with oil/solvent mixtures. The solvents tested in the membrane conditioning were ethyl alcohol, n-propyl alcohol, and n-butyl alcohol. All solvents were analytical grade (>99%, Vetec).

Initially, the ultrapure water (Milli-Q, Millipore, São Paulo, Brazil) flux was compared to the data reported by the manufacturer. For solvent exchange, the excess of the previous solvent was removed from the module, pump and tubing, and the system was washed three times with 600 mL of the new solvent. In the last washing step, the solvent was left in contact with the module for 24 hours. This latter procedure was not carried out with ethanol, since the manufacturer reported that the epoxy glue was unstable upon prolonged contact with ethanol. All steps were carried out at 25 °C.

Oil/n-Hexane Mixture Permeation

After membrane conditioning, the permeation of refined soybean oil/n-hexane mixtures was carried out with oil to hexane mass ratios of 1:1, 1:4 and 1:5 (w/w) at pressures of 0.9, 1.1 and 1.3 bar. The system pressurization was performed by restricting the valve E in the system (Fig. 1). The feed flow rate of the mixture was 120 kg/h. The volumetric flow rate was measured with a rotameter placed in the retentate stream and converted to a mass flow rate by using the density of the mixture measured at the operating temperature with a digital densimeter (model DMA4500, Anton Paar, Ashland, VA, USA). All permeation tests were carried out in duplicate and at 25 °C. Variability in the results was within ±10%.

Samples of permeate were periodically collected in long test tubes (10 cm long x 1 cm diameter) immersed in an ice bath and immediately stoppered after sampling to minimize the evaporation of n-hexane. Samples were then weighed in an analytical balance (Shimadzu, model AY220). The permeate flux was calculated by dividing the mass of permeate by the time required for sample collection and the membrane area.

The concentrations of the feed and permeate streams were estimated by measuring the densities of the mixtures in a digital densimeter (model DMA4500, Anton Paar, Ashland, VA, USA) at 25 °C and converting the density results to n-hexane concentration using a calibration curve (%n-hexane= -401,1*density of the mixture+366.5; r^2=0.992). The rejection coefficient was calculated according to Equation (1):

$$R = \left(1 - \frac{C_P}{C_F}\right).100 \tag{1}$$

where C_p is the concentration of oil in the permeate and C_F is the concentration of oil in the feed stream.

Module Integrity Test

The integrity of the module assembly was assessed periodically to check for damage to the hollow fibers, using a procedure recommended by the supplier. The solvent was removed from the shell and lumen side of the module and it was connected to a nitrogen gas line. The lumen side was sealed, as well as the retentate exit, and the nitrogen was forced through the feed inlet on the shell side until a trasmembrane pressure of 0.5 bar was reached. The nitrogen supply was then closed and the pressure was monitored for 5 min. If the feed pressure drop was higher than 0.1 bar, the module was not suitable for further use and then discarded.
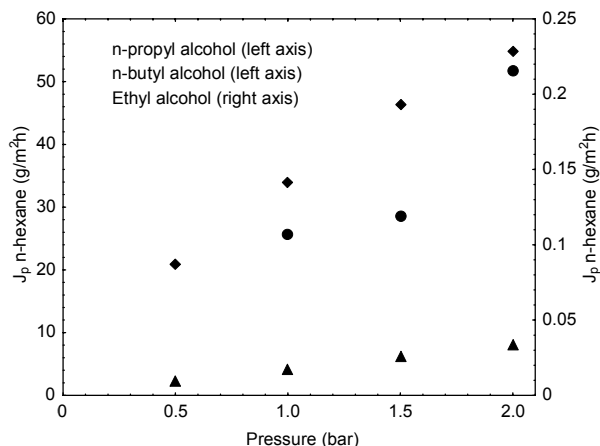
RESULTS AND DISCUSSION

Membrane Conditioning

The determination of the pure water flux of the new membranes at different transmembrane pressures allowed the calculation of the water permeability, yielding a value of 120 kg/(m^2.h.bar), which is similar to that reported by the manufacturer (111 kg/(m^2.h.bar)). The alcohol and n-hexane fluxes obtained during and after membrane conditioning are presented in Figs. 2 and 3, respectively. It can be observed that the alcohol permeability is inversely proportional to the alcohol chain length. Two effects may explain this fact. The increase in viscosity with the increase in the number of carbons of the alcohol (viscosities of ethyl, n-propyl and n-butyl alcohol at 20 °C are 1.26, 1.94, and 3.0 cP, respectively (Lide, 1999) may cause a decrease in permeability, since this

parameter is known to be inversely proportional to solvent viscosity, according to Darcy's law. Although viscous flow is the governing mechanism in MF and UF membranes, another very important factor affecting solvent permeation through membranes is the polarity of the solvents, which decreases with the alcohol chain length, thus decreasing permeate flux for membranes with predominantly hydrophilic characteristics (Bhanushali *et al.* 2001). Although ethyl alcohol permeability was the highest of the alcohol series, the n-hexane fluxes were higher when the membrane was pretreated with n-propyl alcohol. The base polymers of commercial polymeric membranes are usually aromatic polyamides, polysulfone and cellulose acetate, among others. These polymers have both hydrophilic and hydrophobic sites in their structures, which increase the complexity of membrane behavior with organic solvents. Modification of the polarity of the membrane surface caused by the alcohol permeation can explain the effects observed in this study. n-Propyl alcohol is slightly less polar than ethyl alcohol (dielectric constants: ethyl alcohol 24.3, n-propyl alcohol 21.8; n-butyl alcohol 17.8 (Lide, 1999) and immersion in less polar solvents may cause agglomeration of hydrophobic and hydrophilic sites at the membrane surface (van der Bruggen *et al.*, 2002). Consequently, membranes may have their hydrophilicity reduced and the hexane flux should be increased. However, the use of a less polar solvent like n-butyl alcohol does not seem to cause a further increase in the membrane flux of n-hexane, showing the complexity of the interfacial phenomena involved in this process.
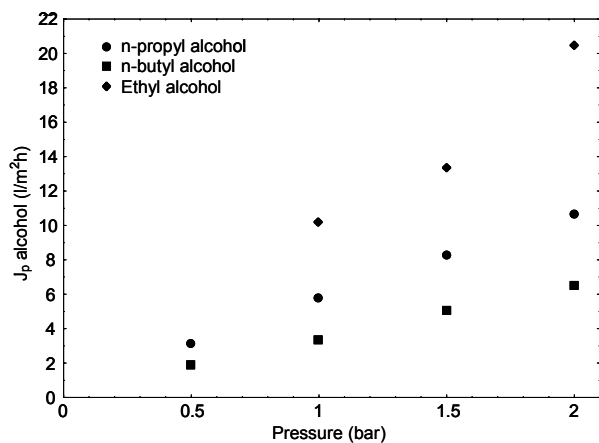
Figure 3: n-Hexane permeate fluxes obtained after conditioning with ethyl alcohol, n-propyl alcohol and n-butyl alcohol at 25 °C.

Some studies have shown that the permeation of organic solvents through polymeric membranes does not depend only on the viscosity or molecular diffusion, but also on additional parameters reflecting interactions between the solvent and the membrane, such as dielectric constant (polarity), surface tension, sorption and interfacial hydrophilicity or hydrophobicity (Araki *et al.*, 2010; Guizard *et al.*, 2002; Darvishmanesh *et al.*, 2009).

Permeation of Oil/n-Hexane Mixtures

The permeation fluxes under all studied conditions are presented in Fig. 4. In most cases, there was only a small variation of the flux with time. A small increase in flux with time was observed when the ratio of oil/hexane was 1:4. The base polymer in the membrane matrix, PES, is hydrophobic. As the permeation proceeds, the oil can penetrate the base polymer matrix, causing changes in membrane hydrophobicity and possibly in pore size, which can explain the observed increase in flux. This behavior was already observed in other studies (Tres *et al.*, 2010).

Araki *et al.* (2010) have shown that commercial poly(ether sulfone) membranes swell when in contact with n-hexane. Basso *et al.* (2009) also observed an increase in flux with time. Those authors attributed this effect to electrostatic interaction between the triacylglycerols, phospholipids and minor components of the oil (mono- and diglycerols, free fatty acids and others) and the membrane surface. The electrostatic interactions tend to cause a deposition of these molecules on the pore walls at the beginning of the

Figure 2: n-Propyl alcohol, n-butyl alcohol and ethanol volumetric permeate fluxes obtained in the membrane conditioning step.

process. After this initial adsorption, the surface of the membrane was thus covered with a layer of these components, probably decreasing the polar interactions with the same components in the feed stream, thereby resulting in elevation of the permeate flux.

An increase in flux was reported by Othman *et al.* (2010) as well. These authors investigated eight types of commercial nanofiltration membranes to separate methyl esters (biodiesel) from a liquid phase also containing of the homogeneous catalyst, free glycerine and methanol in excess after the transesterification process, employing transmembrane pressures between 6 and 30 bar at 40 °C. The authors attributed the increase in the flux to membrane degradation by alkaline attack of the mixture on the membrane, since upon neutralization to pH 8 no increase in the

flux with time was observed.

An assay in the transient regime, where the system was operated without recycling the permeate stream to the feed tank (concentration mode), was carried out at 1.1 bar and a 1:5 (w/w) oil to hexane feed. The expected drop in flux was then observed, due to the increase in feed concentration with time and the consequent stronger fouling phenomena (Fig. 4 (c)).

An increase in transmembrane pressure led to an increase in the flux, as predicted by transport models (Baker, 2004). An increment in the oil concentration in the feed caused a reduction in permeate fluxes. A 70% reduction in flux was observed when the 1:5 feed ratio was compared with 1:1. This effect could be related to the lower hydrophilicity of the mixtures with higher concentrations of oil in the feed.
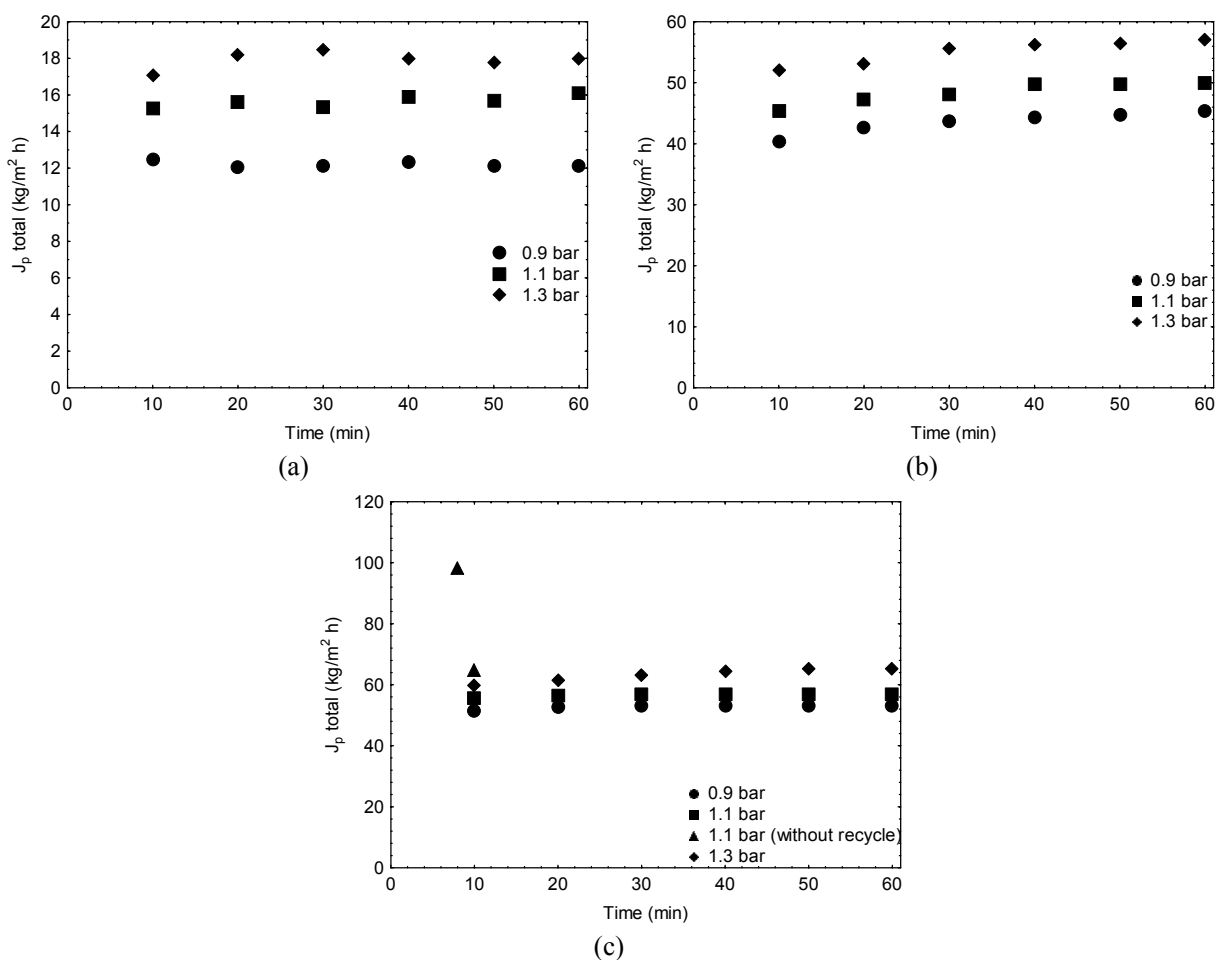
Figure 4: Total permeate fluxes at (a) 1:1, (b) 1:4 and (c) 1:5 oil to hexane ratios.

The rejections of oil for all the conditions studied are presented in Fig. 5. As in the results for permeate fluxes, there is only a small variation of rejection with time. The decrease in rejection with increasing concentration can be related to the effect of plasticization or swelling of the membrane by the oil and solvent, as commented earlier in this paper, causing it to lose its selective properties.

When the system was operated without recycling the permeate stream, an increase in rejection was observed. In this operation mode, the concentration in the feed continuously rises, what can increase the effects of membrane fouling, as reported elsewhere (Kong *et al*., 2006; Ribeiro *et al*., 2006; Tres *et al*., 2009; White and Nitsch, 2000). These authors report that an increase in retention is often observed, due to the increase in the polarization layer and membrane fouling, which increase the resistance to permeation (Cheryan, 2005). In the present study, polarization phenomena may be a minor issue relative to fouling,

as described previously (Tres *et al*., 2010).

Soybean oil rejection for all tests ranged from 10.0 to 28.7% and the total permeate flux was between 12.2 and 65.3 kg/m^2 h. The ratio of oil/n-hexane of 1:4 (w/w) showed the highest oil rejection compared to the other mass ratios (~30%). The flux results obtained in the present study are comparable to those reported for flat sheet and inorganic commercial ultrafiltration and nanofiltration membranes (Ribeiro *et al*., 2006 and Carvalho *et al*., 2006).

Actually the intention here is not to replace completely the distillation of the oil/hexane mixture by the membrane process, but rather to minimize the energy requirements of the process by the use of hybrid technology. Membrane concentration of the oil could be the first step before distillation, thus decreasing the energy demands of the solvent recovery process. A cascade system can be used to increase the performance of the membrane system.
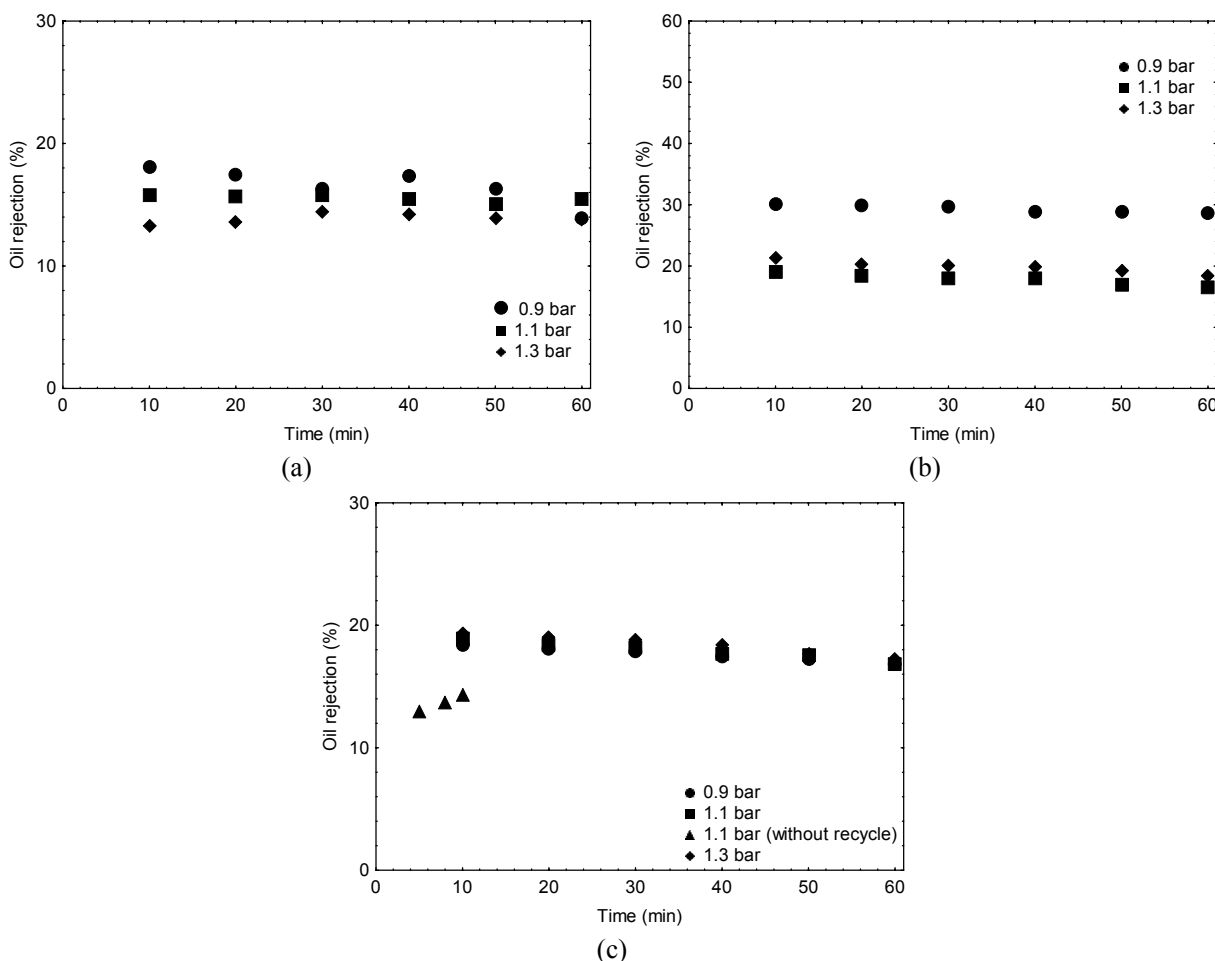

(a)

(b)

(c)

Figure 5: Soybean oil rejections at (a) 1:1, (b) 1:4 and (c) 1:5 oil to hexane ratios

Simple mass balance simulations of a two-effect cascade membrane system were run, using the data obtained in this work and the feed concentration of oil typically found in the soybean oil industry (approximately 17 wt % in oil). The results of the simulation showed that it is possible to obtain a concentrated stream with 34 wt% in oil, which represents a 2-fold concentration of the oil stream. An energy balance of the process, as well as an economic evaluation should then be carried out to confirm the potential gains of the use of the membrane process in the solvent recovery step in vegetable oil production.

Module Integrity Test

At the end of each assay, a standard integrity test was carried out to check for damages to the membrane, possibly caused by the solvent and oil. The membrane was cleaned with the solvent n-hexane, which removed the oil residues. The shell side of the module was pressurized with gaseous nitrogen at 0.7 bar, while the permeate (fiber lumen side) was closed. The permeate valve was then opened and the pressure on the shell side was monitored. If the pressure drop was not significant within 5 minutes of monitoring, it was an indication that the fiber assembly had not suffered any degradation. In our case, the module integrity was not affected by the permeation experiments.

CONCLUSIONS

In this work, the separation of refined soybean oil/n-hexane mixtures using a hollow fiber ultrafiltration membrane (50 kDa) was investigated. Due to the low permeate flux of n-hexane compared to the nominal water flux, membrane conditioning was needed to improve the membrane hydrophobic character. Three alcohols with different chain lengths were tested for membrane conditioning. The pre-treatment with n-propyl alcohol presented the highest n-hexane permeate flux. Both flux and rejection showed a slight increase with time. This behavior was related to membrane swelling and/or plasticization by the oil and solvent. Rejections up to 30% and permeate fluxes up to 65.3 kg/m^2 h were observed. With increasing oil/n-hexane mass ratio and transmembrane pressure, there was an increase in rejection and total permeate flux for most assays. No degradation was observed in the membrane module during the operation, as confirmed by integrity tests.

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