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Performance of Nanofiltration Membranes for Solvent Purification in the Oil Industry

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Abstract The extraction stage of edible oil in the oil industry is commonly performed by using toxic solvents (e.g. hexane) and processes with high energy consumption (e.g. distillation, evaporation) to recover the solvent, which represents around 70–75 wt% in the oil–solvent mixture. In this paper, a membrane-based extraction method using nanofiltration (NF) membranes is presented. Commercial nanofiltration membranes made of different polymers (Desal-DK-polyamide NF from GE-osmonics®, NF30 polyethersulfone NF from Nadir®, STARMEM^{TM}122 polyimide from MET® and SOLSEP NF030306 silicone base polymer SOLESP®) were selected and tested to recover the solvent from soybean oil/solvent (10–20–30% w/w oil) mixtures at various separation pressures and constant temperature in a dead-end filtration set up. The selection of the solvent was made in order to compare solvents obtainable from renewable resources, such as ethanol, iso-propanol and acetone, with solvents traditionally used in the industry (i.e. cyclohexane and n-hexane). The structural stability of the membranes towards the different solvents used in this work was verified visually, by the variation of the membrane area and by means of permeate flux assessments. Desal-DK and NF30 showed poor filtration performance and even visible defects after exposure to acetone but a good performance was obtained for the nanofiltration membranes STARMEM^{TM}122 and SOLSEP NF030306 with ethanol, iso-propanol and acetone. For example, considering a mixture with 30% edible oil in acetone, STARMEM^{TM}122 shows a flux and oil rejection of 16.8 L m^{-2} h and 70%, respectively. For the same conditions, SOLSEP NF030306 exhibited a flux of 4.8 L m^{-2} h with 78% rejection, which shows the potential application of nanofiltration membranes in the oil industry.

Keywords Organic solvent nanofiltration · Oil industry · Solvent recovery · Permeability

Introduction

Nanofiltration (NF) has been applied in water treatment since the late 1980s. One decade later, the increasing competition for optimal production processes has led to the introduction of solvent resistant nanofiltration (SRNF) as a novel technique for separation and purification of organic compounds and solvent streams recycling [1]. Since then, several applications were developed using solvent resistant membranes for solvent extraction, such as the removal of phospholipids from miscella (oil + solvent mixtures) known as the dewaxing process [2, 3] and deacidification of vegetable oil [4, 5]. The vegetable oil industry is an important branch of the food industry where organic solvents are used in processing [6]. Vegetable oil is extracted from vegetable seeds, such as sunflowers or soybean plants, by solvent extraction or combinations of solvent extraction and mechanical procedures [7]. The discharged mixture of oil and solvent (miscella) from the extractor contains approximately 25% oil (triglycerides) that needs separation from other compounds present in the crude oil for further processing and solvent recycling (typically n-hexane) to the system. Conventional processes for solvent recovery consist of passing the miscella through a series of distillation columns, evaporators, stripping columns and condensers. This

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separation step consumes around 50% of the total energy in the edible oil processing [8]. In addition, during solvent extraction, air and vapors are released from the plant. Losses of about 3 L of solvent per ton of produced oil are typically produced even in efficient plants [9]. Thus, one of the challenges in solvent extraction is to recover as much oil as possible while minimizing solvent losses.

Typically, non-polar solvents are used for oil extraction since triglyceride-based oils are often miscible with these solvents. The most common solvents used for solvent extraction from oil are light paraffins, such as n-hexane and n-heptane, and cyclic hydrocarbons, such as cyclohexane [8]. Mainly, n-hexane has been used over several decades due to its availability, oil solubility, hydrophobic properties (water mixing behavior) and low boiling point (low heat of vaporization). This solvent can be emitted during extraction and recovery and it has been identified as an air pollutant since it can react with other pollutants to produce ozone and photochemical oxidants [10, 11]. Edible oil producers are more interested in alternative solvents less dependent on petroleum sources [12], such as ethanol [13, 14], iso-propanol [15–17] and acetone [18].

Edible oils miscella consists of triglycerides, phospholipids, free fatty acids (FFA) and the solvent itself. Phospholipids can be retained by ultrafiltration (UF) membranes. The process results in a filtrate with triglycerides, FFA and solvent. FFA can be separated from the miscella by a second process such as liquid–liquid extraction or by SRNF. Finally, SRNF can be applied to separate triglycerides from the solvent. The concentrated oil should still be further purified by distillation or evaporation, but huge potential savings are obtained when membranes are used due to the reduction of chemicals and the improved quality of oil.

De Souza Araki et al. [19] evaluated UF polymeric membranes made of polyvinylidene fluoride (PVDF), polyethersulfone, polycarbonate and mixed cellulose esters to measure the permeability of water, ethanol and hexane. Tested membranes were hexane-resistant and suitable for use with n-hexane. Tres et al. [20] show a high potential NF membrane application for the separation of refined soybean oil from a mixture of this oil in liquid n-butane. Raman et al. [5] applied a commercial available NF membrane to recover n-hexane, observing that membrane technology can reduce 50% of the consumption energy compared to an evaporation unit. Schmidt et al. [21] and Stafie et al. [22] achieved over 90% oil rejections in n-hexane with a hydrophobic polydimethylsiloxane (PDMS) membrane.

To the best of our knowledge, solvent recovery by NF has been examined only in the system consisting of oil and n-hexane. The objective of this paper is to explore possible alternatives to hexane as solvent in the extraction of vegetable oils with SRNF as solvent recovery unit in the oil industry. The separation performance of NF polymeric membranes manufactured from different polymers was examined for three polar solvents (i.e. ethanol, iso-propanol, acetone) and compared with two solvents traditionally used in the oil industry (i.e. cyclohexane, n-hexane).

Materials and Methods

Chemicals

The solvents used in the experiments were ethanol, iso-propanol, acetone, cyclohexane and hexane. All solvents were purchased from Sigma-Aldrich, Germany (purity >99%).

Cooking oil (moisture contents <0.1%) was purchased from a local supermarket (Delhaize, Belgium). The characteristics of this oil were determined based on the method indicated by Nielsen [23] to calculate the average molecular weight. The saponification value (SV) and average molecular weight were 184.1 and 914.9, respectively. The following equation was used to calculate the average molecular weight from the saponification value:

$$M_{\mathrm{w}}(\text{oil}) = \frac{3 \times 56.11}{\text{SV}} \times 1000 \tag{1}$$

Membrane Properties

Table 1 shows relevant properties of the studied membranes. Four different types of polymeric membranes were considered. All membranes are reported as NF membranes, and were supplied in a "dry" form. In order to evaluate the hydrophilicity/hydrophobicity of membrane, contact angle measurements were performed with a Drop Shape Analysis System DSA 10 Mk2 (Krüss) in a three-phase system consisting of the membrane surface, air and water droplets of 2 μL. The sessile drop method was chosen and the contact angle was measured in an equilibrium mode.

Filtration Experiments

Experiments were performed in a dead-end mode with two Sterlitech HP4750 stirred cells, pressurized by nitrogen, as already reported elsewhere [24]. The active membrane area of the cell was 14.6 cm^2 and the capacity of the vessel was 300 mL.

The applied pressure varied from 4 to 20 bar (depending on the experiment). All experiments were performed in batch mode by charging the cell of pure solvent or miscella. Permeate samples were collected and weighed in order to determine the permeate flux and rejection values. For each series of experiments, two new membrane samples were cut in a disc of 49 mm diameter and immersed in pure solvent (the solvent to be used in the experiment) for

Table 1 Characteristics of commercial membranes used in this study according to the manufacture data sheets

Membrane	Manufacturer	Pore size, MWCO	Membrane class	Nature (contact angle of water)[e]
GE DK OSMONICS	GE Osmonics	150–300[a]	NF (Dense)	Hydrophilic (44 ± 3.1)
NF30	Filmtech	400[b]	NF (Dense)	Semi-hydrophilic (68 ± 2.2)
STARMEM[TM]122	(MET)	220[c]	NF (Dense)	Semi-hydrophobic (62 ± 1.8)
SOLSEP NF030306	SOLSEP	1000[d]	NF (Dense)	Hydrophobic (95 ± 2.7)

[a] Based on rejection of magnesium sulfate in water

[b] Based on rejection of lactose in water

[c] Based on rejection of normal alkanes dissolved in toluene

[d] Based on rejection of oil dissolved in ethanol and acetone

[e] Experimentally measured in this work

1 day prior to the permeation experiment. Then the experiments were conducted in duplicate by using the parallel set up to check the replication of the membrane performance at room temperature (21 °C) and stirred at 1,000 rpm [24]. Using a parallel set up gives the opportunity to apply the same conditions for both samples.

Permeation experiments for separation and purification of oil were started by measuring the permeability of each pure solvent (ethanol, acetone, iso-propanol, n-hexane and cyclohexane) for all membranes mentioned in Table 1.

Then, the mixture containing oil and solvent were poured in two parallel dead-end filtration cells, and the samples were collected for 1 h. The concentrations of oil and solvent in the permeate and retentate were determined by the initial weight of those fractions followed by evaporation of solvent in a rotary evaporator (Rotavapor, Büchi RE 111, Switzerland). After that, the samples were kept in an oven at 100 °C for 2 h, to eliminate solvent residues. After cooling the samples in a desiccator, they were weighed again for the determination of the retention of oil.

The flux was assessed every 3 min for every pressure over 1 h. Thus, the permeate flux (L h^{-1} m^{-2}) was estimated on an average basis from 20 recorded assessments. The standard deviation of every experiment, denoted by S_N, is defined as follows:

$$S_N = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(x_i - \tilde{x})} \tag{2}$$

where x_i are the observed values of the sample items and $\tilde{x}$ is the mean value of these observations.

Results and Discussion

Permeability of Pure Solvents Through the Membranes: Effect of Applied Pressure

The effect of pressure on the permeation behavior of the polymeric NF membranes was tested to study their potential for edible oil extraction and purification. The effect of applied pressure on pure solvent fluxes was studied in the range of 8–20 bar at ambient temperature (23 °C) with different types of NF membranes. Figure 1 shows the permeation flux of different solvents, where the solvent flux was increased by increasing the applied pressure. No significant variation was observed for all membranes (standard variation was between (maximum standard variation was 4.8%). Based on Fig. 1, the STARMEM[TM]122 membrane yielded the highest permeates fluxes for polar solvent compared to other membranes. Only two membranes (STARMEM[TM]122 and Desal-DK) show an acceptable permeability for iso-propanol, due to the high viscosity of this solvent. No measurable flux was obtained through the other membranes that were tested. Desal-DK and NF30 were not stable in acetone, due to the lack of stability in the ketones of the polymer from which they are made (polyamide and polyethersulfone). Acetone flux is dramatically higher than for the other solvents for STARMEM[TM]122 and SOLSEP NF030306. One explanation for this high flux can be in the effect of swelling of the membrane structure. Due to this swelling macro voids are formed, and these increase the solvent permeability. In case of non-polar solvents (n-hexane and cyclohexane) only for SOLSEP NF030306 and Desal-DK measurable permeation was observed. No measurable flux was observed through the other tested membranes. This was thought to be due to hydrophilicity effects of the membranes on the non-polar solvents (cyclohexane, n-hexane). Non-linear behavior on the flux of membranes has been observed in some cases with increasing of applying pressure at constant operation temperature. Machado et al. [25] related the non-linear behavior of alcohol fluxes in the case of commercial PDMS membranes (MPF50 and MPF60) to the compaction of membranes under high pressure. Dijkstra et al. [26] also found the same non-linear behavior for alcohol fluxes through laboratory made PDMS membranes. Compaction of membranes, which occurs under high pressure, affects the permeability of solvents through the membrane. During compaction, the membrane's
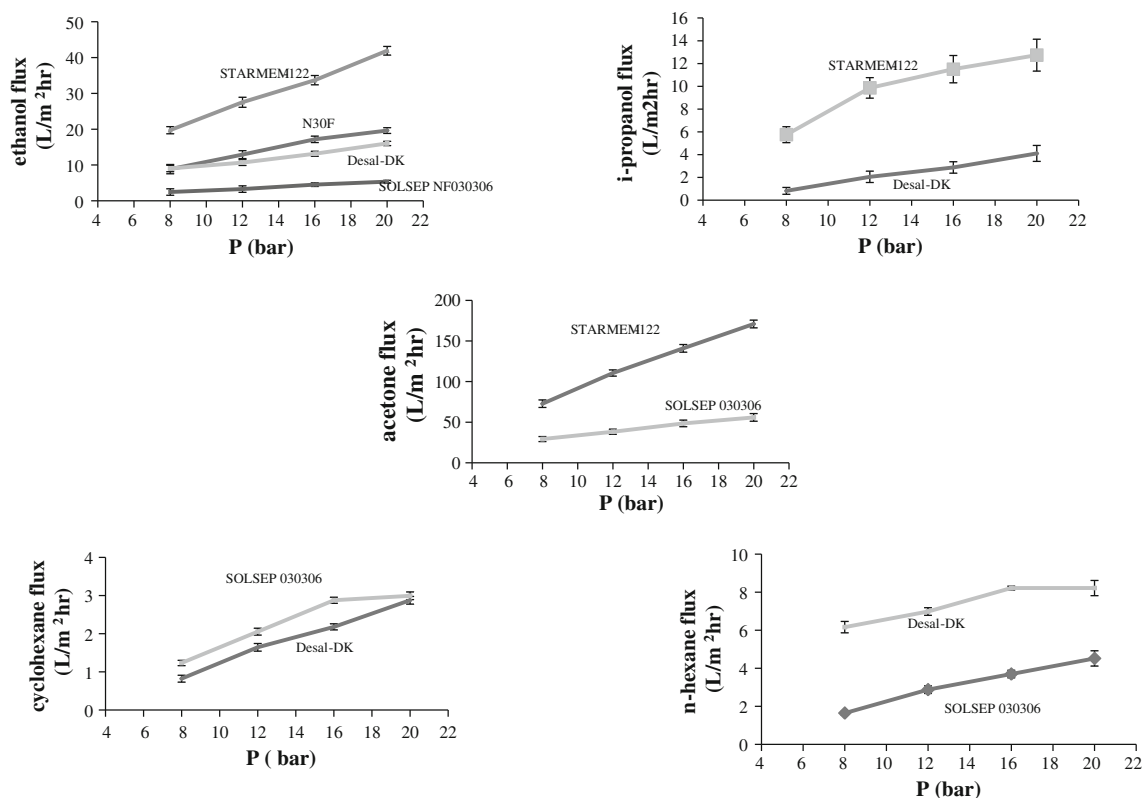
Fig. 1 Effect of pressure on solvent flux trough different membranes at ambient temperature (23 °C). Flux increases with increasing applied pressure

effective thickness increases due to the penetration of the top-layer polymer into the support pores.

In real applications of membrane processes, the observed flux and rejection are those after compaction. In this study, compaction was measured during the first hour of pure solvent permeation and the time needed to reach the stable flux was measured for different solvents and membranes. Figure 2 shows the compaction of the membrane in the presence of different solvents, where the compaction factor, α, is defined as a function of the initial and final membrane permeability:

$$\alpha = \frac{L_{\text{final}}}{L_{\text{initial}}} \tag{3}$$

Values of α are between 0 and 1. The membrane with the highest resistance to the applied pressure (least compaction) has an α value that is the closest to 1.

Except for STARMEM[TM]122 compaction for all membranes was solvent dependent. However, STARMEM[TM]122 shows a similar compaction factor in all cases. The flux of ethanol and iso-propanol reached its final value after 10 min of the experiment for Desal-DK and SOLSEP NF030306, while the flux dropped dramatically in the presence of *n*-hexane and cyclohexane. The N30F

membrane, which shows an acceptable performance only in the presence of ethanol, had the highest compaction value (α = 0.93).

The permeability of pure oil was also tested through all membranes. No flux was observed in any case under different operating pressures (8–20 bar).

Separation Performance of Membranes

Oil rejection in solvents was tested with a mixture containing 10 wt% oil in one of the following solvents: ethanol, iso-propanol, acetone, cyclohexane and *n*-hexane. In order to achieve the best possible result, the membrane with the highest permeability reported above was selected for each solvent. Table 2 includes the membranes that were tested for the rejection of oil in each solvent. The operating pressure was 20 bar. All experiments were run at room temperature. The flux and rejections are also presented in Table 2.

Among all four types of membranes, STARMEM[TM]122 and SOLSEP NF030306 show the best performance. This could be expected, since these membranes are specified as SRNF membranes. The performance of these two
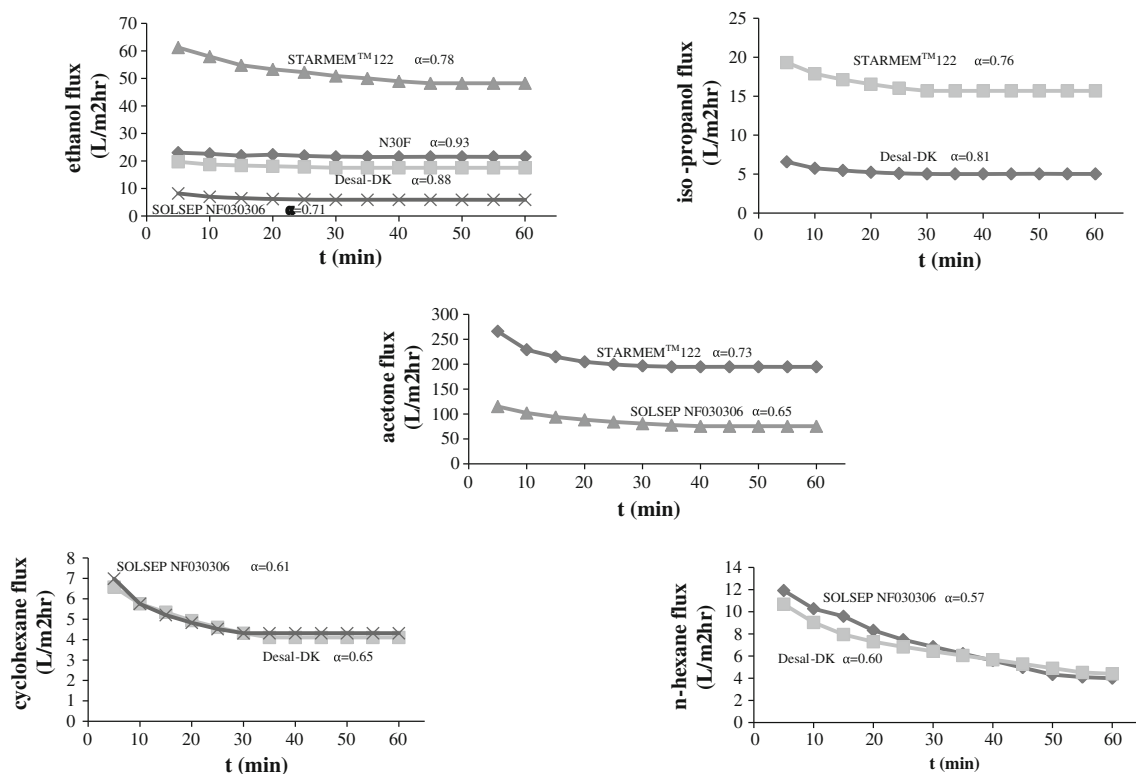
Fig. 2 Pressure decline versus time for different solvents and membranes. The α values present the compaction factor

Table 2 Overall flux and oil rejection in different studied systems

Solvent	Membrane	Overall flux (kg m^{-2}h^1)	Rejection (%)
Ethanol	STARMEM^{TM}122	17.4	96
	SOLSEP NF030306	4.89	78
Iso-propanol	STARMEM^{TM}122	4.48	79
Acetone	STARMEM^{TM}122	56.6	70
	SOLSEP NF030306	16.6	78
Cyclohexane	SOLSEP NF030306	0.54	64
Hexane	SOLSEP NF030306	0.55	38

membranes can be compared in terms of rejection of oil in ethanol and acetone. In case of ethanol, the STAR-MEM^{TM}122 membrane had a higher flux and a higher rejection compared to the SOLSEP NF030306 membrane. The rejection of oil in acetone by the SOLSEP NF030306 membrane was slightly higher than for the STAR-MEM^{TM}122 membrane while the overall flux for STAR-MEM^{TM}122 is three times higher than for the SOLSEP NF030306 membrane.

Fig. 3 shows the effect of oil concentration on the solvent flux and oil rejection. It is observed a decrease in permeability as the concentration of oil increases, which may be assumed to be a normal behavior for SRNF membranes [27, 28]. As presented in Fig. 3, the retention of the membranes remained constant over entire range.

However, the permeation flux decreased dramatically with increasing oil fraction in the feed up to 30%.

Based on these observations, it can be concluded that STARMEM^{TM}122 membranes, which are made from polyimide, are better suited for the separation of oil in polar organic solvents such as ethanol, iso-propanol and acetone. This is due to the fact that polyimide membranes are slightly less hydrophilic, and they are less prone to compaction compared to polyamide (Desal-DK) or PES (NF30). SOLSEP NF030306 also shows a better performance in polar solvents compared to non-polar solvents. This membrane is the only membrane that shows an acceptable performance in cyclohexane and n-hexane.

Conclusions

In this study, four polymeric commercial NF membranes were used for the recovery of solvents from oil–solvent mixtures. The membranes were tested for permeation of several organic solvents and oil. Experimental results show that the new generation of SRNF membranes has a superior performance compared to the previously used NF membranes. Flux permeation and the rejection test of oil in ethanol, iso-propanol and acetone solution also confirmed the applicability of the new commercial SRNF membranes
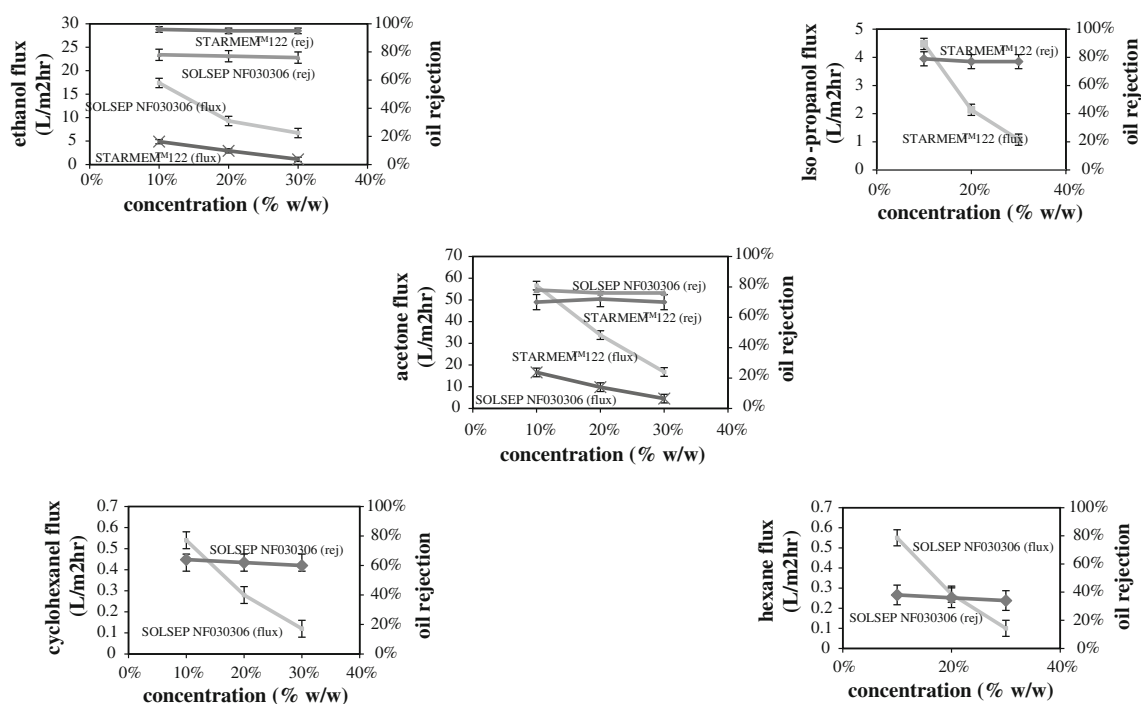
Fig. 3 Effect of oil concentration on solvent flux and oil rejection

for solvent recovery, promoting the use of these renewable solvents instead of the traditionally used *n*-hexane.

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