J Am Oil Chem Soc (2011) 88:1053–1060
DOI 10.1007/s11746-011-1760-9

ORIGINAL PAPER

Separation of FFA from Partially Hydrogenated Soybean Oil Hydrolysate by Means of Membrane Processing

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Received: 1 June 2010 / Revised: 4 January 2011 / Accepted: 5 January 2011 / Published online: 12 February 2011

Abstract Different types of commercial porous and non-porous polymeric membranes have been investigated for their capabilities to separate free fatty acids (FFA) from hydrolysate of partially hydrogenated soybean oil. A regenerated cellulose (RC, PLAC) membrane exhibited the most prominent difference in rejection between FFA and glycerides and the highest flux (27 kg h^{-1} m^{-2}) in hydrolysate ethanol solution. The results also showed that, besides the pore size of membrane, the membrane flux depended largely on the property matching between membrane and solvent, as observed (40 kg h^{-1} m^{-2}) flux was achieved with methanol but no flux detected with hexane for PLAC. The polyvinyl alcohol (PVA, NTR-729 HF) and Polyamide (PA, NTR-759HR) membranes gave the second and third highest flux (10.1 and 5.7 kg h^{-1} m^{-2}, respectively), where solute rejections for NTR-759HR were 95.9% for triacylglycerols (TG), 83.3% for diacylglycerols (DG); 87.7% for monoacylglycerols (MG) and 22.9% for FFA, respectively. A discontinuous membrane filtration using an RC membrane with ethanol changed the composition of hydrolysate from 32.2:34.2:7.9:25.7 TG/DG/MG/FFA to 47.8:36.0:10.2:6.0. The results from this work proved that FFA can be efficiently separated from a hydrolysis mixture of oil using an RC membrane in methanol and ethanol.

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Keywords Partially hydrogenated soybean oil (PHSO) · Hydrolysates · Membrane separation · *Trans* fatty acids (TFA) · Ultra filtration

Introduction

Recently the applications of membrane technology have been extended into industrial aspects, such as petrochemicals, food, biotechnology, pharmaceuticals, as well as processing of oils and fats [1]. Membrane technology has several advantages, namely improving the production by shortening the process, lowering energy consumption, allowing operation at ambient or relatively low temperature, and a better product quality [2, 3]. The main applications of membrane technology in oil and fat processes include recovery of solvent from micelles, waste water treatment, separation in degumming, refining and bleaching, condensate return, catalyst recovery [2–4], separation processing in hydrolysis of oils and fats [5, 6] and in a membrane reactor for the synthesis of glycerides [7].

The chemical and physical deacidification processes used for removing free fatty acids (FFA) have some drawbacks [8, 9], e.g., a complicated process for recovery of FFA, generating wastes and cost of silica, etc. Membrane technology provides an opportunity to develop eco-friendly alternative processes. In previous reports, nanofiltration (NF) membranes were employed for simultaneously de-solventizing and removing FFA from soybean oil [9–11], however, NF in combination with solvent extraction [4] seems to be a slightly better option. Membrane refining was firstly applied to model oils (soybean oil) obtained by adding FFA to refined oils [12, 13] and later on was applied to a few real systems, such as rice bran oil [14–17]. Artz et al. [18] investigated the combination of the membrane processing

with super critical CO_2 for the deacidification of soybean oil. They examined both SE (a thin film composite polyamide membrane with a polysulfone base and a 100-MW cut off) and BW (a reverse osmosis membrane which was made of polyamide amine with a <100-MW cut off). The findings from their study revealed that the BW membrane had good selectivity for FFA and TG and withstood the high pressure without breakage whereas the SE membrane had the best selectivity for TG/FFA mixture but ruptured more frequently at higher pressures. In another report Jos et al. [19] conducted extraction and fractionation of FFA from vegetable oil by ultra membrane filtration (UF). In all, substantial research efforts have been made in this area; however, most work has focused on the separation of FFA from TGs, and thus, further improvements in the case of membrane flux, selectivity, and longevity, and applications to more complicated glyceride mixture systems, are needed to produce a membrane-based approach suitable for a successful technology.

TFAs exist in variable amounts in a wide range of foods, including those foods made with partially hydrogenated soybean oils (PHSO) such as baked, fried foods, and some margarine products. Natural soybean oils are liquid, but the oils lack the stability and shortening properties. Hence partial hydrogenation process was developed to modify liquid oils so that the hydrogenated product could be suitable as a substitute for plastic fats. The partial hydrogenation TFA are formed typically in the range of 15–25% [20]. Recent researches claimed that the technology of hydrogenation of oils has been improved in order to produce hydrogenated fats with low levels of *trans* fatty acids, by optimizing the physical parameters of the process and use of new types of catalysts of hydrogenation reaction [21, 22]. However, the formation of TFA is still in the range of 11–18%, thus the development of technology and process to remove TFA is needed.

TFA-selective lipase provides a technical possibility to produce TFA-free or low TFA oil by a three step process. Firstly, TFA from PHSO could be specifically released as FFA by a TFA-selective enzyme (e.g. *Candida antarctica* Lipase A, CAL A); secondly, FFA fraction rich in TFA (pure *trans* FFA if the enzyme 100% trans-selective) was separated from the glycerides fraction by a proper approach; lastly, the resulting glycerides were re-esterified with other sourced FFA having a desirable FA profile. As a part of this strategy, this work aimed at developing a membrane based technology to separate FFA from PHSO hydrolysate. Even though the membrane in this work cannot distinguish trans and non-trans, and a high TFA-selective enzyme is not available, the technology developed in this work is still of academic value and practical potential being a directly transferable process.

Materials and Methods

Materials

Partially hydrogenated soybean oil (PHSO) hydrolysate used in the study was prepared by *Candida antarctica* lipase A (CAL-A) catalyzed hydrolysis of PHSO in our laboratory. The weight fractions of Triglyceride (TG), Diglyceride (DG), Monoglyceride (MG), and free fatty acid (FFA) in PHSO hydrolysate were 0.322, 0.342, 0.079, and 0.257, respectively. UF membrane PLAC (PLAC is a trade name of a membrane, MW cut off 1,000) made from regenerated cellulose (RC) was kindly provided by Millipore Corp. (Copenhagen, Denmark). Dense membranes from the NTR series namely, NTR-729 HF, NTR-759 HR and NTR-7250 purchased from Nitto Denko, Kusatsu, Japan. All other UF membranes used in this study, namely, ETNA 01, ETNA 10 PP, FS 61PP, GR 70 PE, GR 70 PP, GR 61 PP, GR 81 PP and GR 95 PP were donated by Alfa Laval A/S (Nakskov, Denmark).

Method for the Preparation of PHSO Hydrolysate

The reactions were carried out at 30 °C in screw-capped glass tubes with magnetic stirring at 300 rpm. PHSO (200 g) was taken in 100 mM Tris–HCl buffer (pH 7.0, 200 ml) which contained 10 mM $CaCl_2$. The reaction was initiated by adding commercial CAL A enzyme (10 g, 5 wt% of oil weight). Aliquots were collected at various time intervals viz. 0.5, 1, 2, 3, 4, 5 h. After 3 h, the solution was centrifuged in order to separate the hydrolysate from the buffer solution and enzyme. And then the PHSO hydrolysate was diluted in ethanol or methanol or hexane solvents based on the experiments' requirements. Finally the solution was centrifuged prior to being used in the experiments in order to separate enzyme particle traces remaining in the PHSO hydrolysate solution. The fatty acid composition of the PHSO used was as follows, Palmitic, 13.6%; Stearic, 6.4%; TFA (*t*-18:1) 16.3%; CFA (*c*-18:1), 35.6%; TFA (*t*-18:2), 2.7%; CFA (*c*-18:2), 22.4%; TFA (*t*-18:3), 0.5% and CFA (*c*-18:3), 2.5%, where TFA, CFA indicates *trans* fatty acids and *cis* fatty acids, respectively.

Membrane Apparatus

A stirred dead-end UF cell with a magnetic stirrer (Millipore, Glostrup, Denmark) was used for the separation of FFA from the hydrolysate. Pressurized nitrogen gas was employed as the driving force for the permeation operation. A detailed description and schematic diagram of the experimental set up are given elsewhere [23]. The cell capacity of the membrane apparatus was 300 ml with

an effective membrane area of 40 cm^2. Membrane screening experiments were conducted at room temperature, RT (20 °C) and 50 °C and pressure was kept at 0.3 MPa (based on previous experience and the manufacturer's recommendation) unless otherwise stated. A few experiments were conducted at 500 rpm to test the effect of agitation on the membrane flux; however, a similar flux was observed as at 250 rpm. Thus, all the other experiments were done at a constant agitation rate of 250 rpm. Initial experiments were also performed by applying different pressures, viz. 0.1, 0.2, 0.3 and 0.4 MPa to examine the effect of pressure on the flux rate. Permeate was collected through a port beneath the membrane support. Membrane screening was conducted by charging the cell with 100 g feed (lipid\solvent mixture). Each trial was continued until 40 g permeate was collected.

Membrane retention ($R\%$) and selectivity factor (α) between FFA and glycerides were calculated by Eqs. 1 and 2 [23].

$$C_f/C_p \tag{1}$$

Where $R\%$ is membrane retention, C_p and C_f represent the concentration of a component in permeate and feed, respectively.

$$\alpha_{\frac{A}{B}} = \frac{C_p^A}{C_f^A} \Big/ \frac{C_p^B}{C_f^B} \tag{2}$$

Where, $C_P^A$and $C_P^B$are the concentration of components A and B in permeate, and C_f^A and C_f^B are the concentrations of components A and B in the feed, respectively.

Analyses

Samples of feed, retentate, and permeate were collected for quantifying the TG, DG, MG and FFA contents. The compositions of TG, DG, MG, and FFA in the hydrolysate samples were determined by the TLC–FID method of Tanaka et al. [24]. Weights of the initial (feed) and final retentate as well as permeate samples were measured before and after evaporation of the solvent. All the experimental runs were carried out in two replicates. The mean and standard deviations of the measurements of two replicate runs were used for result evaluation.

Statistical Analysis

Mean and standard deviations of the data were reported. The data sets were analyzed statistically at a significance level of $P < 0.05$ with SAS version 8.2 using the Generalized Linear Model procedures to determine if there were differences between treatments [25].

Mean Molecular Weight Calculation

The average MW of TG, DG, MG and FFA derived from PHSO were calculated by considering oleic acid (MW 282.46) as a representative fatty acid of PHSO. The MMW of each constituent present in PHSO hydrolysate was obtained as 282.46, 342.51, 606.96 and 871.41 for FFA, MG, DG and TG, respectively.

Performances of Polymeric Membranes with Undiluted Lipid Mixture

Preliminary experiments were conducted with undiluted lipid mixture, and the results demonstrated that none of the membranes examined exhibited flux >1 kg h^{-1} m^{-2} (data not shown). Higher temperatures (lower viscosity) would have helped but the membrane was not capable of running at higher temperatures. Therefore, further screening experiments of 12 different porous and dense hydrophobic and hydrophilic membranes were carried out at room temperature after diluting the lipid mixture with either a polar (methanol, ethanol) or a non-polar (hexane) solvent (Table 1).

Results and Discussion

Screening of Membranes with PHSO Hydrolysate Solution

The characteristics of the membranes employed for screening are depicted in Table 1. As indicated in Table 1, instead of the molecular weight cut-off of the membrane, the flux through a membrane was strongly dependent on properties of the solvent employed and the membrane material. For the hydrophilic membranes made of RC, PVA and PA, etc., the flux was extremely low when hydrophobic hexane was employed as a solvent; whereas for hydrophobic membranes made of polysulfone (PSf), polyethersulfone (PESf), polyvinylidene fluoride (PVDF) and polypropylene (PP) etc., hexane seems to be a efficient solvent to yield a flux rate >10 kg h^{-1} m^{-2}. In contrast, PHSO hydrolysate in ethanol or methanol yielded a flux in the range of 20–30 kg h^{-1} m^{-2} for almost all the membranes tested in the present study. In terms of selectivity of membranes for FFA/glycerides, the results are also summarized in Table 1.

For the membrane with an MW cutoff >2,000 Da, no selectivity was observed regardless of the solvents employed. For the systems with hexane as the solvent, neither flux nor selectivity was promising, therefore hexane was ruled out from further investigation. The polymeric membranes (NTR-729 HF and NTR 759 HR) and RC

Table 1 Membranes screened and their characteristics

Membrane designation	Material	Cut off (MW)	Solvent flux (kg h^{-1} m^{-2})		
			Hexane	Methanol	Ethanol
PLAC	R C	1,000	No flux	50 ± 0.25[a]	38 ± 1.90[b]
NTR 729 HF	PVA	Non porous	No flux	29 ± 1.45[a]	6 ± 0.00[b]
NTR-7250	PVA	Non porous	<1	20 ± 1.00[a]	1 ± 0.00[b]
NTR 759 HR	PA	Non porous	No flux	33 ± 1.65[a]	20 ± 1.00[b]
ETNA01PP	PVDF, PP	1,000	No flux	41 ± 2.05[a]	32 ± 1.60[b]
ETNA 10 PP	PVDF, PP	10,000	15 ± 0.75[c]	52 ± 2.60[a]	35 ± 1.75[b]
FS 61 PP	PVDF, PP	20,000	370 ± 18.5[a]	157 ± 7.85[b]	110 ± 5.50[c]
GR 70 PE	PSf, PET	20,000	24 ± 1.20[c]	203 ± 10.15[a]	167 ± 8.35[b]
GR 70 PP	PSf, PP	20,000	200 ± 10.01[ab]	217 ± 10.85[a]	189 ± 9.45[b]
GR 61 PP	PSf, PP	20,000	201 ± 10.11[b]	234 ± 11.70[a]	175 ± 8.75[c]
GR 81 PP	PESf, PP	10,000	10 ± 0.50[c]	135 ± 6.75[a]	90 ± 4.50[b]
GR 95 PP	PESf, PP	2,000	15 ± 0.75[c]	127 ± 6.35[a]	73 ± 3.65[b]

Operation conditions 0.3 MPa, 20 °C and agitation at 250 rpm. 10% of PHSO hydrolysate solution of different solvents was used as feeds for membrane property evaluation. Data used for evaluation were means ± standard deviations of two replicates. UF membrane PLAC (PLAC is a trade name of a membrane, MW cut off 1,000) made from regenerated cellulose (RC) was kindly provided by Millipore Corp. (Copenhagen, Denmark). Dense membranes from the NTR series namely, NTR-729 HF, NTR-759 HR and NTR-7250 were purchased from Nitto Denko, Kusatsu, Japan. All other UF membranes used in this study, namely, ETNA 01, ETNA 10 PP, FS 61PP, GR 70 PE, GR 70 PP, GR 61 PP, GR 81 PP and GR 95 PP were donated by Alfa Laval A/S (Nakskov, Denmark)

RC Regenerated Cellulose, *PVA* Polyvinyl alcohol, *PA* Polyamide, *PSf* polysulfone, *PESf* Polyethersulfone, *PVDF* Polyvinylidene fluoride, *PP* Polypropylene, *PET* polyethylene terephthalate, (−) no selectivity

[abcd] The same letters in each row show that the values are not significantly different ($P < 0.05$)

membrane (PLAC) showed a higher flux when methanol (or ethanol) was used as a solvent (e.g. for methanol flux at 29–50 kg h^{-1} m^{-2} and somewhat promising selectivity with the preliminary test (Table 1).

Within a 95% confidence interval, a linear increase as a function of time was observed for all the solvents, indicating that the permeating flow rate is stable and close to constant. The flux with different solvents decreases in the order methanol, ethanol and hexane, which may be ascribed to the decreasing molecular polarity and/or increasing molecular size (Fig. 1) [23]. This flux decreasing order obtained for hydrolysate solutions agreed well with the data obtained for pure solvent systems (Table 1). Methanol exhibited a higher flux than ethanol for all tested membranes (Table 1). However, for food applications, ethanol instead of methanol was selected for further evaluation and optimization of membrane operation.

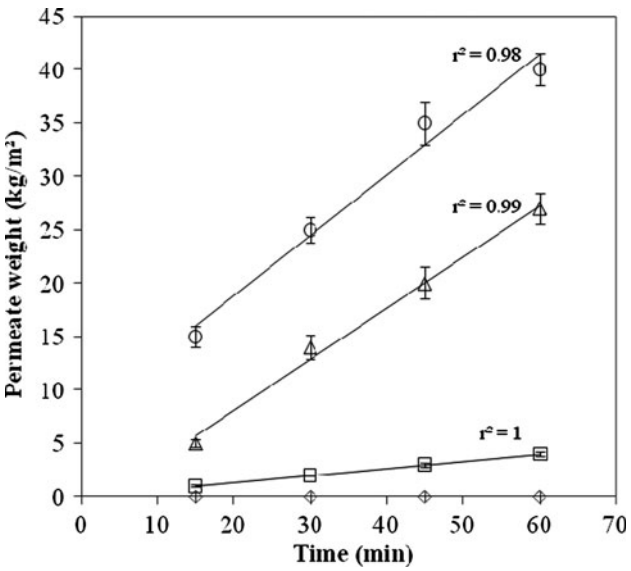

Fig. 1 Fluxes of different solvents with PLAC membrane. Operating conditions 0.3 MPa, 20 °C, and agitating at 250 rpm with 10% solute concentration. The mean ± standard deviations of two replicates were used for evaluation. *Open diamonds*, hexane; *filed squares*, 2-propanol; *open triangles*, ethanol; *filled circles*, methanol. The *solid line* was a linear regression of measured points with displayed r^2 values indicating correlation coefficients

Performances of RC, PVA and PA Membranes

PLAC, NTR-729 HF and NTR 759 HR membranes were selected for further investigation because they showed a higher selectivity and/or flux rate in both methanol and ethanol, whereas other membranes achieved a similar performance only in methanol (e.g., NTR-7250, Table 1). Composition of TG, DG, MG and FFA of permeate and of retentate are depicted in Table 2 with a feed of 10% hydrolysate ethanol solution. As presented in Table 2, FFA were concentrated in the permeate fraction at 84.1% from 25.7% in feed with only 6.0% left in the retentate, whereas

MG, DG and TG were retained more than the permeated. For example, 47.8% of retentate was TG with only (5.5% × 13.5) × (100)/(32.2% × 50) = 4.6% (of the total loaded TG) permeated through the PLAC membrane.

As indicated in Table 1, PLAC is a porous membrane and NTR-729 HF and NTR 759 HR are dense membranes. The pore size and size distribution are basic parameters to determine separation performance of a porous membrane; however, for non-porous membranes the chemical nature and morphology of the polymeric membrane and the extent of interaction between the polymer and permeates are the important factors to consider. Therefore, transport of a solute molecule through non-porous membranes occurs by a solution-diffusion mechanism and separation is achieved by selective diffusion [26]. Separation of FFA from other glycerides has been obtained using two types of non-porous membrane, namely, NTR-729 HF concentrated FFA at 65.3% of permeate composition and NTR 759 HR with FFA amounted to 71.3% in permeate. In NTR 759 HR based retentate, TG concentrated to 46.3%, which is slightly lower than the 47.8%, achieved by PLAC. The reasons for this are not clear, however, this is not simply be ascribed to the affinity of glycerides to the non-porous membrane. It is clear that the permeation of glycerides through non-porous membranes is also related to molecular size and weight (Table 2). Because, according to the Wilke–Chang equation [27], the permeation rates (diffusivity) of the individual components in hydrolysate depend on their molecular sizes.

To quantitatively characterize the membrane selectivity, the selectivity factors (α) between different solutes were calculated, respectively, for three types of membrane separation performed with ethanol as the solvent (Table 3). For PLAC membranes, the α values of FFA versus TG, DG and MG were 19.3, 16.7 and 7.0, which agreed very well with the decreasing average MW of glycerides (871.41, 606.96 and 342.51). The α values of MG versus TG and MG versus DG were 2.8 and 2.4, respectively, which also reflected the dependency of membrane permeation on molecular sizes of solutes. For non-porous membranes NTR-729 HF and NTR 759 HR, the changes of selectivity factors of FFA versus TG, DG and MG (12.8, 3.6 and 4.9 for NTR-729 HF and 19.0, 4.6, 6.2 for NTR 759 HR) were not strictly dependent on the decrease in the average MW of glycerides. The actual reason is not clear, one possible explanation might be the different extents of the interactions between membrane and different glycerides as the principal mechanism of non-porous membrane separation [26].

Patterns of Permeate and Retentate

Figure 2 shows the glyceride composition in permeate (A) and retentate (B) against the molecular weights of

Table 2 Fractional separation of hydrolysate dissolved in ethanol with PLAC and non-porous membranes

Lipid fraction	Feed	Permeate			Retentate		
		PLAC	NTR 729 HF	NTR 759 HR	PLAC	NTR 729 HF	NTR 759 HR
FFA (%)	25.69	84.10 ± 2.10^{a}	65.31 ± 1.63^{b}	71.31 ± 1.78^{ab}	6.01 ± 0.15^{d}	15.69 ± 0.39^{c}	9.29 ± 0.23^{d}
MG (%)	7.91	3.70 ± 0.09^{c}	4.09 ± 0.10^{c}	3.49 ± 0.09^{c}	10.22 ± 0.26^{b}	13.41 ± 0.34^{a}	10.12 ± 0.25^{b}
DG (%)	34.18	6.71 ± 0.17^{d}	24.20 ± 0.61^{b}	20.52 ± 0.51^{c}	36.00 ± 0.90^{a}	27.54 ± 0.68^{ab}	34.31 ± 0.86^{a}
TG (%)	32.22	5.51 ± 0.14^{c}	6.40 ± 0.16^{c}	4.68 ± 0.12^{c}	47.77 ± 1.20^{a}	43.36 ± 1.09^{b}	46.26 ± 1.16^{a}
Weight (g)	50.00	13.50 ± 0.34^{b}	12.70 ± 0.32^{b}	13.90 ± 0.35^{b}	36.50 ± 0.91^{a}	37.30 ± 0.93^{a}	36.10 ± 0.90^{a}

Operation conditions 0.3 MPa, 20 °C and agitation at 250 rpm with 10% solute concentration; Data used for evaluation are means ± standard deviations of two replicates

^{abcd} Means with the same letters in each row are not significantly different ($P < 0.05$)

Table 3 Selectivity of PLAC, NTR 729 HF and NTR 759 HR membranes with ethanol as a solvent

	Selectivity factor (α)					
	FFA/TG	MG/TG	DG/TG	FFA/DG	MG/DG	FFA/MG
PLAC	19.32 ± 0.39^{a}	2.81 ± 0.06^{ab}	1.21 ± 0.02^{b}	16.72 ± 0.33^{a}	2.37 ± 0.05^{a}	7.02 ± 0.14^{a}
NTR729 HF	12.78 ± 0.26^{c}	2.63 ± 0.05^{b}	3.64 ± 0.07^{ab}	3.61 ± 0.07^{b}	0.71 ± 0.01^{b}	4.93 ± 0.10^{b}
NTR 759 HR	19.01 ± 0.38^{b}	3.01 ± 0.06^{a}	4.12 ± 0.08^{a}	4.62 ± 0.09^{b}	0.69 ± 0.01^{b}	6.21 ± 0.12^{ab}

Operation conditions 0.3 MPa, 20 °C and agitation at 250 rpm with 10% solute concentration; Data used for evaluation are means ± standard deviations of two replicates

^{abcd} Means with the same letters in each column are not significantly different ($P < 0.05$)

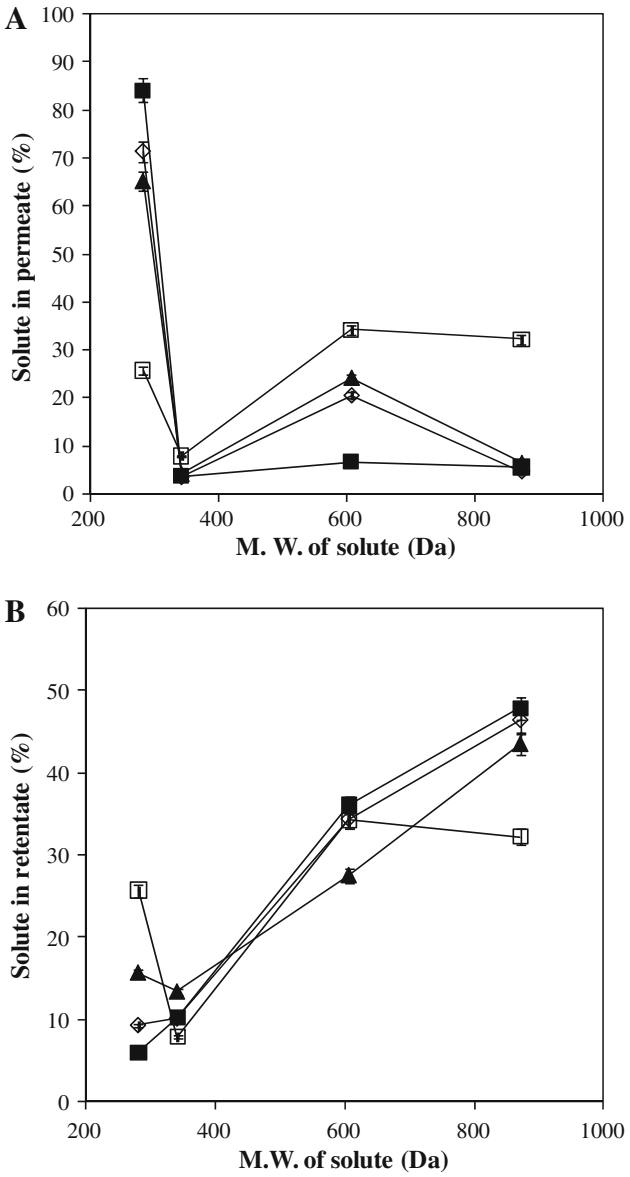

Fig. 2 Permeation (*A*) and retention (*B*) of solutes cut by different membranes. Solutes are glycerides and FFA, derived from PHSO (The average MW of TG, DG, MG and FFA were calculated by considering oleic acid (MW 282.46) as a representative fatty acid of PHSO) which correspond to free fatty acid (282.46), monoglyceride (342.51), diglyceride (606.96) and triglyceride (871.41). Operating conditions 0.3 MPa, 20 °C and agitation at 250 rpm with 10% solute concentration. The means ± standard deviations of two replicates were used for evaluation. *Open squares*, feed; *filled squares*, PLAC; *filled triangles*, NTR-729 HF; *open diamonds*, NTR-759 HR

glycerides after membrane separation operation. Compared to the content in the feed, the FFA content in the permeate was higher for all three membranes, while the TG content in the permeate was lower for all three membranes (Fig. 2a). The change of DG concentration depends on the individual membrane, a small amount of DG passed through PLAC and in the case of NTR-729 considerable DG permeated through (Fig. 2a). In the retentate, except for FFA, MG, DG and TG were concentrated for PLAC and NTR 759 HR to differing extents; whereas for NTR-729, the MG and TG contents in the resulting retentate were higher and DG lower in comparison with their corresponding contents in the feed (Fig. 2b).

Table 4 presented the rejection values of individual glycerides obtained from different membrane separation operations. The percentage observed rejection of solutes for each permeates collected was determined by assuming that it was constant during each experimental batch [28]. Actually the rejection values of FFA by different membranes demonstrated the efficiency in separating FFA from other glycerides. The separation efficiency of FFA decreased following the increasing order of rejection values of FFA, PLAC < NTR 759 HR < NTR-729, as observed in Table 2. In the case of PLAC, the rejection values decreased in the decreasing order of their MW (TG > DG > MG > FFA) which agreed with the change of selection factors of FFA versus TG, FFA versus DG, and FFA versus MG (Table 3). For the three membranes, high level rejections of TG (≥95%) were obtained, and the rejections of DG also were up to ≥80%. The performance of PLAC was most preferable, not only due to its highest flux (27.0 kg h^{-1} m^{-2}, Table 4) and highest permeation for FFA (84.1%, Table 2) under identical conditions, but also due to its excellent rejection for TG (95.4%), DG (94.7%) and MG (87.4%). Although NTR 759 HR was able to achieve slightly better rejection for TG (95.7%) and MG (87.7%) (Table 4), its flux (5.7 kg h^{-1} m^{-2}) was only about one-fifth of that of PLAC (Table 4).

Effects of Applied Pressure on Membrane Flux

Figure 3 illustrates the flux rate change with applied pressures. In general, the flux rate increased with the increasing pressure applied but not evenly. For example, from 0.1 to 0.3 MPa the flux rate increased at about 180 kg h^{-1} m^{-2}/MPa, however, a further increase of the pressure from 0.3 to 0.4 MPa led to a flux increase of only 50 kg h^{-1} m^{-2}/MPa. This is because every membrane has a limiting flux (maximum flux) [26, 29]. The limiting flux depends not only on the property of the membrane but also on the concentration of the feed. The possible explanation for this phenomena can be the increase on the feed concentration leads to an increased polarization of concentration, the formation of a gel layer and fouling consolidation, leading to the permeate flux not responding more linearly with applied pressure levels. Pressure applied at 0.3 MPa resulted in a stable and optimum performance, thus was chosen as the optimum pressure for other parameter optimization such as feed concentration and solvent effect (Fig. 4).

Table 4 Permeate flux and rejection in the ethanol system

Type of membrane	Rejection (%)				Flux (kg h^{-1} $m^{-2)}$
	TG	DG	MG	FFA	
PLAC	95.41 ± 2.39[a]	94.70 ± 2.37[a]	87.42 ± 2.19[a]	11.64 ± 0.29[c]	27.04 ± 0.68[a]
NTR-729 HF	95.04 ± 2.38[a]	82.01 ± 2.05[b]	86.79 ± 2.17[a]	35.51 ± 0.89[a]	10.12 ± 0.25[b]
NTR-759 HR	95.91 ± 2.40[a]	83.32 ± 2.08[b]	87.71 ± 2.19[a]	22.89 ± 0.57[b]	5.67 ± 0.14[c]

Operation conditions 0.3 Mpa, 20 °C and agitation at 250 rpm with 10% solute concentration; The percentage observed rejection of solutes for each permeate collected was determined by assuming it was constant during each experimental batch [27]; Data used for evaluation are means ± standard deviations of two replicates

[abcd] Means with the same letters in each column are not significantly different ($P < 0.05$)

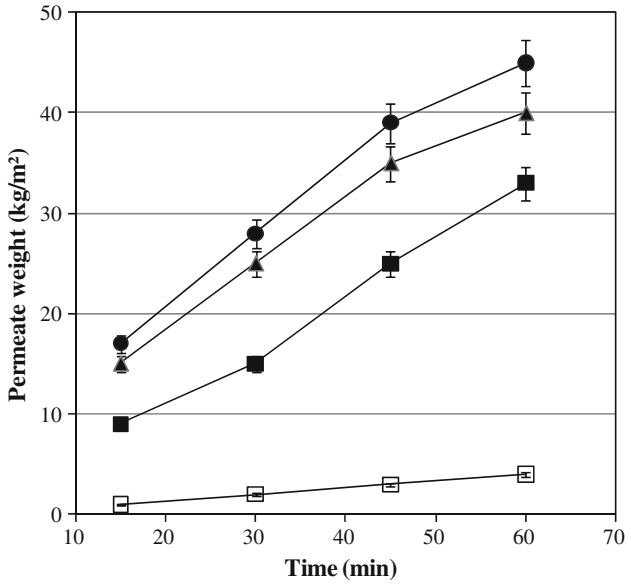

Fig. 3 Effects of pressures on membrane flux. The membrane applied is PLAC. Operating conditions 20 °C and agitation at 250 rpm with 10% solute concentration. The means ± standard deviations of two replicates were used for evaluation. *Open squares*, 0.1 MPa; *filled squares*, 0.2 MPa; *filled triangles*, 0.3 MPa; *filled circles*, 0.4 MPa

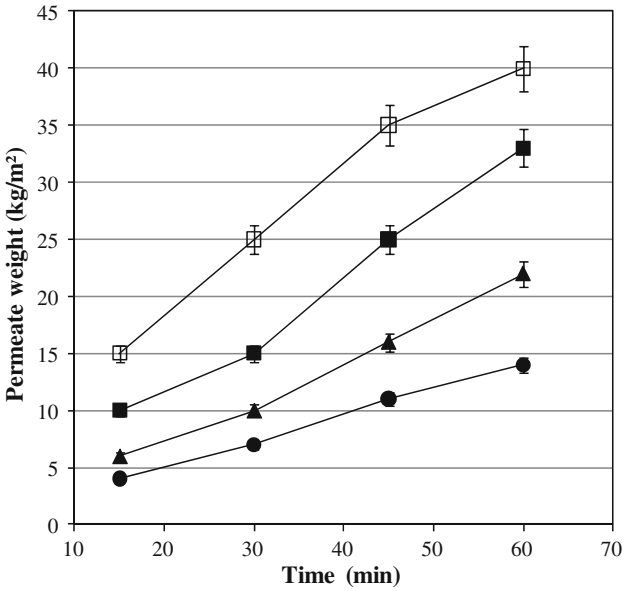

Fig. 4 Variation of Flux with different solute concentrations in case of the PLAC membrane. Operating conditions 0.3 MPa, 20 °C and agitation at 250 rpm. The means ± standard deviations of two replicates were used for evaluation. *Open squares*, 10%; *filled squares*, 20%; *filled triangles*, 30% and *filled circles*, 40%

Effect of Variation in Solute Concentration on Flux Rate

Flux rates declined with increases in solute concentrations, e.g., at 60 min filtration the flux for 10% feed was 40 kg h^{-1} m^{-2} and the flux for 40% feed was only 14 kg h^{-1} m^{-2}. Hence, a 10% feed solution proved to be the optimum concentration to bring about good separation.

PHSO contains not only oleic and linoleic acids as the major fatty acids, but also a substantial amount (~40%) of saturated and *trans* fatty acids (possessing dissimilar crystalline, solubility behavior compared to *cis* fatty acids); on the other hand, a typical vegetable oil, namely sunflower oil, possesses palmitic and stearic acids only up to 10%, and further unsaturated fatty acids namely oleic, linoleic and linolenic acids contribute around 90%. Because of unusual fatty acid composition of PHSO compared to a typical vegetable oil, the membrane processing of PHSO hydrolysate behaves differently from that of normal vegetable oil hydrolysate. As a result, even though in the past a few researchers reported about the deacidification of typical vegetable oils [12–15, 18, 19] there was no similarity observed with the present findings. The solubility effect might also be one of the reasons why most of the membranes tested in the current study exhibited lower fluxes at RT and higher fluxes at higher temperatures such as 50 °C [29]. A similar pattern could be expected for permeation rates and the opposite pattern for rejection values. The magnetic stirring rate is also important for keeping the solution homogeneous and preventing sedimentation of crystals on the surface of membrane with progressive concentration increases of MG, DG and TG in the

retentate. No obvious sediments on the surface of the membrane were observed with continuous magnetic agitation, while at a later stage of UF, a thin layer of sediments could be observed after stopping agitation for 10 min. However, the crystals can be easily removed after separation by increasing incubation temperature or washing with fresh solvent.

Conclusion

The basic aim of this work was to examine the possibility of using membrane technology to separate glycerides and FFA from hydrolysate of PHSO. Among the commercial membranes evaluated with ethanol as a solvent, the PLAC membrane was able to achieve up to 27 kg h^{-1} m^{-2} flux rate and high selectivity factor of FFA versus other glycerides (FFA vs. TG, 19.3; FFA vs. DG, 16.7; and FFA vs. MG, 7.0). Two types of dense membranes also achieved a good separation of FFA from other glycerides of PHSO hydrolysate, for instance, the selectivity factor of FFA versus TG for NTR-729 HF and NTR-759-HR amounted to 12.78 and 19.01, respectively. However, in spite of encouraging results from the present study, there are still some key issues to be resolved for membrane development, such as high selectivity to separate FFA from MG, DG and TG with low molecular weight difference, a good compromise between achieving high selectivity and keeping high permeate flux, and long term stabilities promising for scale-up operation under solvent conditions.

Acknowledgments Technical assistance from Flemming Lund Sorensen (Department of Molecular Biology, Aarhus University) is acknowledged.

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