Separation of Oil Constituents in Organic Solvents Using Polymeric Membranes

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ABSTRACT: Different types of commercial nonporous (reverse osmosis and gas separation) polymeric membranes were screened for their abilities to separate FFA, MG, DG, and TG from a lipase hydrolysate of high-oleic sunflower oil after diluting it with organic solvents (ethanol and hexane). Cellulose acetate (CA) (NTR-1698) membrane gave the largest difference in rejection between FFA and glycerides and high flux in oil/ethanol mixtures. In the hexane system, the values of permeate flux and rejection were generally lower than those in the ethanol system. The silicone–polyimide composite membrane (NTGS-2100) gave the highest flux and rejections of solutes (70.2% for FFA, 94.4% for TG) in oil/hexane mixtures. In the ethanol system with the CA membrane, TG had the highest rejection (98%) followed by DG (90%) and MG and FFA (50–70%) when the oil concentration was varied from 6.3 to 45.8%. A discontinuous diafiltration process (16 batches) using the CA membrane with ethanol changed the composition of the oil from 31:28:9:32 TG/DG/MG/FFA to 65:30:1:4. The results of this study showed that oil constituents can be separated in suitable solvents using appropriate nonporous membranes.

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KEY WORDS: Diafiltration, ethanol, free fatty acids (FFA), glycerides, hexane, nonporous polymeric membranes, oil constituents, permeate flux, rejection, selectivity.

The crude oil that is extracted from oilseeds is a mixture of FFA; MG, DG, and TG; phosphatides; sterols and tocopherols; and pigments (1). The most important component is the TG fraction, which is used primarily as an edible oil. MG and FA can be used as flavors and emulsifying agents, and lecithin is widely used as a food ingredient, especially as an emulsifier (1). The deacidification step in the conventional chemical process removes FFA, and the deodorization step removes MG and DG along with other odor-causing compounds during deodorization.

Membrane processing offers several advantages over conventional chemical and physical refining processes. Many German, Japanese, and American researchers have used micelle-enhanced ultrafiltration to degum hexane–oil miscella (2). Keurentjes *et al.* (3,4) attempted to remove FFA first with a combination of hydrophobic and hydrophilic membranes and later by using membrane extraction with 1,2-butanediol as an extractant. There are reports of FFA removal from crude rice bran oil by alcohol extraction of FFA followed by separation using a nanofiltration membrane (5). Snape *et al.* (Snape, J.B., C.K. Reddy, and M. Nakajima, unpublished results) compared cellulose acetate (CA), polyimide (PI), and polyamide (PA) composite membranes, as well as commercial composite membranes of unknown composition, to separate oleic acid and triolein in methanol, ethanol, isopropanol, and *n*-hexane. They reported on the possibility of combining membrane separation with liquid–liquid extraction to simultaneously separate and concentrate different oil fractions. Sahashi *et al.* (6) used an ethanol solution (75%) to extract FFA such as eicosapentaenoic acid and docosahexaenoic acid without TG from fish-oil hydrolysate and achieved phase separation with a hydrophilic PI ultrafiltration membrane (MWCO 20,000 Da). Kuk *et al.* (7) observed differences in rejection between TG of different FA compositions while attempting to separate cottonseed oil from ethanol using a PA reverse osmosis (RO) membrane and attributed it to differences in viscosity and diffusivity. Koseoglu *et al.* (8) attempted to separate cottonseed oil from hexane, ethanol, and isopropanol using RO/nanofiltration and ultrafiltration membranes.

We have carried out extensive studies on membrane processing of vegetable oils without any pretreatment or addition of solvents using denser nonporous membranes (2,9). In the studies on screw-pressed groundnut oil (2), tocopherols and FFA permeated preferentially compared to TG, increasing their relative amounts in the permeates. In a TG–oleic acid model system, total permeate flux increased with oleic acid concentration in the feed, mainly due to the increase in the permeation rate of oleic acid (10). The membranes used in the study had a reasonably long life (9). Although the membranes from the NTGS series (Nitto Denko, Kusatsu, Japan) exhibited selectivity among the liquid oil constituents (TG and FFA) in the solvent-free system, the permeate flux as well as selectivity need improvements for industrial adoption.

In the present study, attempts were made to separate oil constituents, namely, MG, DG, TG, and FFA, in a solvent system (ethanol and hexane) using nonporous hydrophilic (RO) as well as hydrophobic (gas separation) membranes. The study evaluates the potential of membrane processing, which may be useful for value-added separations in the oilseed industry.

EXPERIMENTAL PROCEDURES

Materials. Lipase hydrolysate of high-oleic sunflower oil prepared in our laboratory was used as the lipid mixture in the

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*To whom correspondence should be addressed at Reaction and Separation Engineering Laboratory, National Food Research Institute, Tsukuba 305-8642, Japan. E-mail: mnaka@nfri.affrc.go.jp study. The weight fractions of TG, DG, MG, and FFA in high-oleic sunflower oil were 0.31, 0.28, 0.09, and 0.32, respectively. Oleic acid content was greater than 80% of the FA composition of high-oleic sunflower oil. The polymeric membranes used in the study are listed in Table 1.

Membrane apparatus. Experiments were done using a stirred-batch membrane cell. A detailed description and schematic diagram of the experimental setup are given elsewhere (9). The membranes were cut into circular discs (7.5 cm diameter and 32 cm^2 effective area) and fitted into the test cell along with a porous Teflon support sheet. A Teflon O-ring was used on the membrane surface. In the preliminary experiments conducted without dilution of feed, pressure and temperature were maintained at 6 MPa and 40°C, respectively. The operating pressure was reduced to 4 MPa for experiments conducted with solvent-diluted feed. Membrane screening experiments were conducted at room temperature (20–25°C), and further experiments were conducted at 30°C. The cell was charged with 100 mL of feed (oil or oil/solvent mixture). The permeate was collected through a port beneath the membrane support; flux was recorded by using a personal computer that was interfaced with an electronic balance.

Analyses. The compositions of TG, DG, MG, and FFA in the oil samples were determined by TLC–FID generally following the method of Tanaka *et al.* (11). Weights of initial (feed) and final retentates as well as permeate samples were measured before and after evaporation of solvent. Mass balance was obtained after each solute was corrected by partitioning according to Equations 1 and 2:

$$R_S = \left(\frac{F_{S,\exp}}{R_{S,\exp} + P_{S,\exp}} \right) \times R_{S,\exp} \quad [1]$$

$$P_S = \left(\frac{F_{S,\exp}}{R_{S,\exp} + P_{S,\exp}} \right) \times P_{S,\exp} \quad [2]$$

where R_S and P_S are corrected weights of each solute in the final retentate and permeate and $F_{S,\exp}$, $R_{S,\exp}$, and $P_{S,\exp}$ are experimental weights of each solute in the initial and final retentates and in the permeate, respectively.

Percentage observed rejection. The percentage observed rejection of solutes for each permeate collected was determined by assuming it was constant during each experimental batch, from Equation 3 (12):

$$R_{o,S} = \frac{100\left[\ln\left(C_{S,f}/C_{S,o}\right)\right]}{\ln\left(W_o/W_f\right)} \quad [3]$$

where $C_{S,o}$ and $C_{S,f}$ are the initial and final concentrations of each solute in the retentate (kg/kg), and W_o and W_f are the initial and final weights of retentate (kg), respectively.

All the experimental runs were carried out in duplicate with a new membrane for each experimental run and practically no differences were observed (±0.5%).

TABLE 1
Polymeric Membranes Used in the Study

Material	Manufacturer[a]	Type	Rejection of NaCl[b] (%)
Cellulose acetate	Nitto Denko	NTR-1698	98
	Toray	SC-3000	96
	Daicen	DRC-97	97
Polyvinyl alcohol	Nitto Denko	NTR-729HF	93
	Nitto Denko	NTR-7250	60
Polyamide	Nitto Denko	NTR-759HR	99.5
Aramid	Toray	UTC-70T	99.4
Polyether	Toray	PEC-1000	99.7
Silicone–polyimide composite	Nitto Denko	NTGS-2100	—

[a] Nitto Denko, Kusatsu, Japan; Toray, Ohtsu, Japan; Daicen, Tokyo, Japan.
[b] Information provided by the membrane manufacturers.

RESULTS AND DISCUSSION

Performance of the silicone–PI composite membrane with the undiluted lipid mixture. In preliminary experiments conducted with the undiluted lipid mixture, the silicone–PI composite membrane (NTGS-2100) exhibited some separation capability (Table 2). TG were concentrated in the retentate as the membrane rejected them, whereas FFA permeated preferentially through the membrane or, in other words, were negatively rejected, which resulted in an increased concentration of FFA in the permeate. MG and DG showed intermediate rejection behavior. Although the silicone–PI composite membrane was a hydrophobic membrane, the flux obtained was very low [0.13 L/(m^2·h)] in this solvent-free nonaqueous lipid mixture system. Therefore, further screening experiments were carried out with nine different nonporous hydrophobic or hydrophilic polymeric membranes after diluting the lipid mixture with either a polar (ethanol) or a nonpolar (hexane) solvent.

Screening membranes after diluting the lipid mixture. The polymeric membranes listed in Table 1 were tested for their separation ability with the ethanol/oil solution (6.3% w/w) and the hexane/oil solution (7.0% w/w). Permeate flux values and percentage observed rejections of TG, DG, MG, and FFA in ethanol and hexane systems are presented in Tables 3 and 4, respectively. NTR-1968, NTR-729HF, NTR-759HR, UTC-70T, and NTGS-2100 membranes showed appreciable selectivity and/or good permeability in both solvent systems. Other membranes showed appreciable selectivity and/or good permeability in only one of the two solvent systems studied.

In the oil/ethanol system, the permeate flux values ranged between 0.9 and 46.8 kg/(m^2·h). CA membranes gave higher flux followed by the aramid membrane. Polyvinyl alcohol

TABLE 2
Fractional Separation of Sunflower Oil Hydrolysate with the NTGS-2100 Membrane

Lipid fraction	Feed	Permeate	Retentate
FFA (%)	40.0	59.4	34.7
MG (%)	6.2	4.5	6.6
DG (%)	12.9	8.2	14.4
TG (%)	40.9	27.9	44.3
Weight (g)	60.0	12.8	47.2

TABLE 3
Permeate Flux and Rejection in the Ethanol System[a]

Type of membrane	Rejection (%) TG	DG	MG	FFA	Flux [kg/(m^2·h)]
SC-3000	100	97	80	78	46.8
NTR-1698	100	92	53	54	33.3
DRC-97	100	92	65	59	24.3
UTC-70T	71	64	46	79	18.0
NTR-729HF	82	82	80	80	8.6
NTR-759HR	82	86	88	88	4.5
NTGS-2100	18	23	18	14	4.3
PEC-1000	98	98	98	97	0.9

[a] See Table 1 for membrane suppliers.

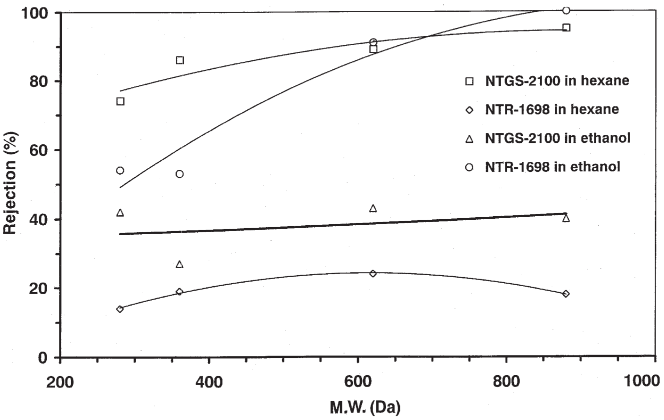

FIG. 1. Comparative rejection of solutes of various M.W. in the ethanol and hexane systems. NTGS-2100 and NTR-1698 were supplied by Nitto Denko, Kusatsu, Japan.

(PVA), PA, and silicone–PI composite membranes exhibited low flux, and the polyether membrane gave the lowest flux [<1 kg/(m^2·h)]. CA and aramid membranes had good selectivities among the four solutes. Though PVA, PA, and polyether membranes exhibited very high rejection values, selectivities were rather poor. The silicone–PI composite membrane (NTGS-2100) had a very low rejection as well as low selectivity between solutes. All three CA membranes performed better than the other membranes in terms of selectivity as well as permeate flux. The rejection values of solutes were generally in the order of their M.W. (TG > DG > MG > FFA).

In the oil–hexane system, the values for permeate flux and rejection were generally lower than those in the ethanol system. The CA, PA, PVA, and aramid membranes showed very low flux [<13 kg/(m^2·h)]. However, the silicone–PI composite membrane (NTGS-2100) had not only higher flux [72 kg/(m^2·h)] but also relatively higher rejection as well as selectivity among the solutes. The rejection values of solutes were in the same order (TG > DG > MG > FFA) as that of the ethanol system. The silicone–PI composite membrane rejected TG and FFA to the extent of 95 and 74%, respectively, whereas the rejections of DG and MG were between these two values.

Performance of CA and silicone–PI composite membranes in solvent systems. The rejection performances of CA (NTR-1698) and silicone–PI composite (NTGS-2100) membranes in ethanol and hexane systems against the M.W. of solutes are depicted in Figure 1, and representative selectivities of the membranes are provided in Table 5. The CA membrane in hexane and the silicone–PI composite membrane in ethanol exhibited very low rejections as well as poor flux. Ethanol is more polar than hexane and, therefore, the ethanol/oil flux was very poor in the silicone–PI composite membrane (active surface, silicone), which is hydrophobic. The CA membrane is more hydrophilic and hence exhibited poor flux in the hexane/oil system. The CA membrane in the ethanol system exhibited good separation characteristics. The silicone–PI composite membrane also exhibited good separation characteristics in the hexane system, accompanied by higher permeate flux (Table 4 and Fig. 1). Pure hexane permeate flux in the silicone–PI composite membrane and pure ethanol permeate flux in the CA membrane were in the range of 115–144 and 77–133 kg/(m^2·h), respectively. The separation capability demonstrated by the CA membrane in the ethanol system was much better than for the silicone–PI composite membrane in the hexane system (Table 5). Therefore, further studies were conducted with the CA membrane (NTR-1698) in the ethanol system.

Effects of oil concentration on rejection and flux. The performance of the CA membrane (NTR-1698) with oil concentration is presented in Figure 2. Permeate flux declined when oil concentration increased from 6.3 to 45.8% (w/w). This system can be considered to be a nonaqueous liquid mixture

TABLE 4
Permeate Flux and Rejection in the Hexane System[a]

Type of membrane	Rejection (%) TG	DG	MG	FFA	Flux [kg/(m^2·h)]
NTGS-2100	95	90	88	74	72.0
UTC-70T	70	47	38	44	12.6
NTR-7250	39	26	25	21	9.7
NTR-729HF	53	33	22	34	5.4
NTR-759HR	74	61	61	62	2.2
NTR-1698	40	42	26	40	1.1

[a] See Table 1 for membrane suppliers.

TABLE 5
Representative Selectivity of NTR-1698 and NTGS-2100 for Oil Constituents in the Ethanol and Hexane Systems[a]

	Selectivity TG/FFA	TG/MG	TG/DG	DG/FFA	DG/MG	MG/FFA
Hexane						
NTGS-2100	1.28	1.10	1.07	1.20	1.03	1.16
NTR-1698	1.29	0.95	0.75	1.71	1.26	1.36
Ethanol						
NTGS-2100	0.95	1.48	0.93	1.02	1.59	0.64
NTR-1698	1.85	1.89	1.10	1.69	1.72	0.98

[a] See Table 1 for membrane suppliers.

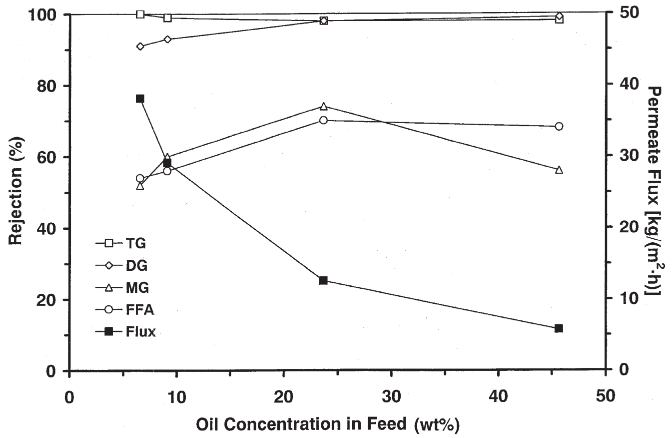

FIG. 2. Effect of oil concentration on permeate flux and rejection values in the ethanol system (NTR-1698). For supplier see Figure 1.

consisting of ethanol, TG, DG, MG, and FFA. The phase separation of the mixture was not observed even at high oil concentrations probably owing to the presence of MG and DG, which increased the solubility of the mixture. Agitation provided in the membrane cell also could have helped prevent phase separation. The relative permeation rates of the individual constituents were in the order of ethanol > FFA > MG > DG > TG. For convenience, TG, DG, MG, and FFA can be considered solutes dissolved in ethanol solvent, and membrane performance can be expressed as rejection values of solutes.

Transport in denser nonporous membranes is controlled by the solution–diffusion mechanism in applications such as gas separation, liquid separation, pervaporation, and vapor permeation (13). Convective flow also appears to exist in the denser nonporous membranes, as observed from the role of viscosity on permeation of liquid oil constituents (14). The denser the membrane, the higher will be the contribution of the solution–diffusion mechanism in transport. The structures of the RO membranes are not as dense as those of other nonporous membranes used for applications such as gas separation (13). Transport in the RO membrane is partly controlled by solution–diffusion and partly by convective flow. Viscosity inversely influences the convective flow. In the oil/ethanol mixture, viscosity increases with increased oil concentration, which could be the primary reason for the observed decline in total flux with the increase in oil concentration. Stirring provided in the membrane cell might reduce the effect of concentration polarization to some extent but cannot avoid it. Therefore, flux decline at higher concentrations was due to increased viscosity and osmotic pressure.

The CA membrane exhibited the highest rejection for TG among the four solutes, and the rejection was greater than 98% at all concentrations. The rejection of DG was 90% at low concentrations but increased to the level of TG rejection at solute concentrations above 23%. The rejection of MG and FFA was lower than that of DG and TG and varied in the range of 50 to 70%. Differential permeation rates of the individual constituents of the liquid mixture depend on the solubilities and diffusivities of these components in the membrane. Diffusivity is dependent on the size of the penetrant, and the lower the M.W., the greater the diffusivity according to the Wilke–Chang equation (15). Linoleic and oleic acids are the major FA present in sunflower oil (16). By virtue of their M.W., diffusivity values of oil constituents will be in the following order: FFA > MG > DG > TG. A similar pattern could be expected for permeation rates and an opposite pattern for rejection values. The coupling effect could also be playing a vital role in a multicomponent system.

Discontinuous diafiltration. Diafiltration was carried out at two different initial concentrations of oil/ethanol mixtures, 12.4 and 45.9% (w/w). The changes in permeate flux during diafiltration are represented in Figure 3. During diafiltration, the cell was charged with 100 g of oil/ethanol mixture and after nearly 35 g of feed had permeated through the membrane, the cell was depressurized and an equal weight of ethanol was added to the retentate before the unit was restarted. This step was repeated several times. Permeate flux decreased with increased oil concentration in the retentate during each batch run. As discussed earlier, flux decline was due to increased viscosity and osmotic pressure. After dilution with ethanol in the subsequent run, the permeate flux almost completely recovered. However, the flux gradually decreased with the number of batch operations, perhaps due to membrane fouling.

In another diafiltration experiment, an initial concentration of 9.1% (w/w) oil/ethanol mixture was used. During the experiment, 16 permeates were collected amounting to 504 g total permeate. The changes in the solute composition in the permeate and the retentate during diafiltration are presented in Figure 4. The solute fractions of MG and FFA in the retentate decreased gradually, whereas the TG fraction increased with every step in the diafiltration process. At the end of 16 batch operations, the solute composition (TG/DG/MG/FFA) had changed from 31:28:9:32 to 65:30:1:4. The following three conventional equations (Eqs. 4–6) were used to simulate the

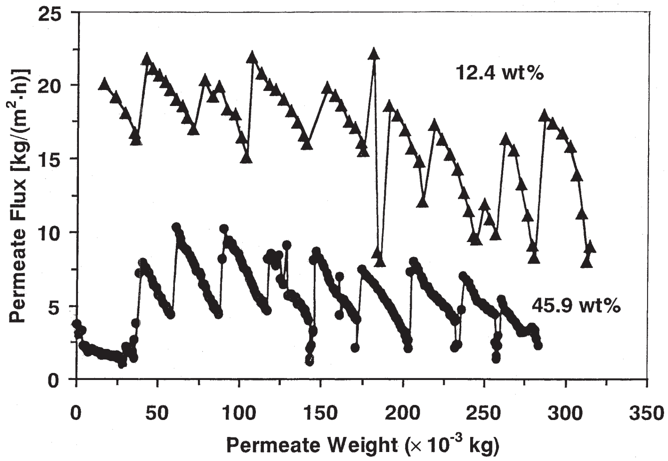

FIG. 3. Changes in permeate flux during discontinuous diafiltration (NTR-1698). For supplier see Figure 1.

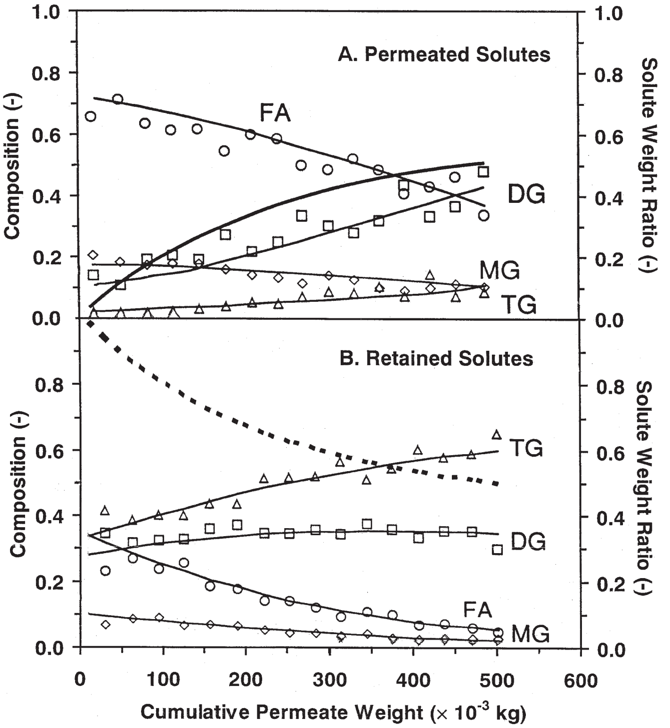

FIG. 4. Changes in the oil compositions of permeate and retentate during diafiltration (NTR-1698). For supplier see Figure 1.

changes during diafiltration and to estimate the solute composition as well as total solutes at every step of the process

$$F_i = F_{i-1}\sum_{S} X_{i-1}^{S}\left(\frac{W_o}{W_f}\right)^{R_{o,S}-1} \qquad [4]$$

$$X_i^S = \frac{F_{i-1}}{F_i} X_{i-1}^{S}\left(\frac{W_o}{W_f}\right)^{R_{o,S}-1} \qquad [5]$$

$$Y_i^S = \frac{F_{i-1}X_{i-1}^{S} - F_i X_i^S}{F_{i-1} - F_i} \qquad [6]$$

where F_i, X_i^S, and Y_i^S are the total solutes and composition of each solute in the retentate and permeate, respectively. $R_{o,S}$ is the observed rejection of each solute, and W_o and W_f are initial and final weights of retentates in the *i*th batch run.

The values estimated using the above equations are represented as solid lines in Figure 4, whereas the experimental values are indicated as markers. At the end of the diafiltration, the weights of the solutes in the retentate after evaporation were 45% of the original weight, which matched the estimated value from the above equations well. The predicted values of solute composition were also in good agreement with the experimental values in retentate as well as in the permeate fractions.

TG was retained to the extent of 94%. It was observed earlier that the rejection of DG was concentration dependent such that DG concentration decreased with decreases in the solute concentration in the retentate. During diafiltration the total solute concentration decreased with each batch run and ultimately the DG concentration did not change appreciably. In contrast, MG and FFA permeated preferentially compared to DG and TG and resulted in the permeation of 95 and 94% of their initial contents, respectively. Diafiltration showed that the CA membrane has the potential to separate different oil constituents dissolved in ethanol. Separation of FFA, MG, and DG from TG may find industrial application as it could replace or reduce the load on the deacidification and deodorization steps in the conventional refining process. The results of this study showed that oil constituents could be separated in suitable solvents using appropriate nonporous membranes. However, long-term stabilities of membranes need to be assessed under solvent conditions before commercial exploitation.

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