REVIEW

Processing Vegetable Oils Using Nonporous Denser Polymeric Composite Membranes

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ABSTRACT: Membrane processing offers several advantages over conventional processes for edible oil refining. In recent years, processing solvent-extracted, screw-pressed, and used frying oils using nonporous denser polymeric composite membranes without pretreatment and addition of chemicals has been extensively investigated. In the present review, results obtained with real and model systems have been summarized and a comprehensive explanation is provided on the mechanism of rejection and differential permeation of oil constituents. Phospholipid-TG and pigment-TG systems are construed as conventional solute–solvent systems, and tocopherol-TG and FFA-TG systems are treated as liquid mixtures exhibiting differential permeability. Dense membrane theory appears more applicable than the reverse osmosis theory in qualitatively explaining the differential permeability of liquid constituents of the oil. Membrane processing of oils appears to have the potential to be a one-step process, especially for screw-pressed oils, in producing a premium-quality product. However, the development of suitable membranes that enable higher fluxes is necessary for industrial adoption of this technology.

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Oilseeds are the major source for the production of edible oils. In terms of volume production, the most important vegetable oil sources are soybean, palm, rapeseed, sunflower, cottonseed, and groundnut (= peanut). Prepressing followed by solvent extraction is the most widely followed method of handling a variety of oilseeds, namely, groundnut, coconut, palm kernel, sunflower, cottonseed, and rapeseed (1), which contribute nearly 50% of the total vegetable oil production worldwide. The oil obtained from screw pressing amounts to 75% of the oil in the oilseed and is superior in quality compared to the oil obtained by solvent extraction. The major vegetable oil producers often blend screw-pressed oil and solvent-extracted oil before refining.

The main objective of refining is to remove, as much as possible, those contaminants that otherwise adversely affect the quality of the end product. The principal impurities in these oils are water, FFA, partial glycerides, phosphatides, oxidation products, pigments, and trace elements such as copper, iron, sulfur, and halogens (1). These impurities are removed at various steps in conventional chemical refining, namely, the degumming, neutralizing, washing, drying, bleaching, filtering, and deodorizing processes. This chemical process has many drawbacks, such as high energy demand, loss of neutral oil, need for large amounts of water and chemicals, loss of nutrients, and disposal of highly polluted effluents.

In conventional physical refining, FFA are distilled off, and this process offers many advantages over the chemical method such as improved product yield, elimination of soapstock, and reduced effluent quantity. However, quality requirements of the pretreated crude oils are much more stringent, the most important being that the phosphorus and iron levels are low.

By contrast, a membrane process is remarkably simpler and offers many advantages over conventional processes, namely, low energy consumption, ambient temperature operation, no addition of chemicals, and retention of all of the nutrients as well as other desirable components in the oil (2). Pressure-driven membrane processes are classified as reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), and microfiltration (MF) depending on the nature of particles or molecular sizes of solutes to be separated. Many researchers have used micelle-enhanced ultrafiltration (MEUF) to degum hexane–oil miscella (3–5). Keurentjes *et al.* (6,7) attempted to remove FFA with a combination of hydrophobic and hydrophilic membranes, and later by membrane extraction using 1,2-butanediol as an extractant. There are reports on removing FFA from model vegetable oils and crude rice bran oil by alcohol extraction of FFA followed by membrane separation (8–10). Lin *et al.* (11) optimized a bench-scale degumming process for hexane–oil miscella by using modified, commercially available UF membranes. Pioch *et al.* (12) reported simultaneous reduction of phosphorus, FFA, and water concentrations in crude vegetable oils by a solvent-free single MF step with the addition of sodium hydroxide. Zhang *et al.* (13) screened 36 laboratory-made UF membranes for refining vegetable oils without added solvent, and one of the membranes achieved 93% separation of phospholipids. Kondal Reddy *et al.* (14) reported that nonporous membranes were effective in reducing color compounds in undiluted oils as well as in hexane–oil miscella.

Edible oil processing has become one of the prime opportunities for membrane applications owing to potential energy savings as well as the potential for improved oil quality. However, only a few commercial processes are available in the edible

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TABLE 1
Nonporous Denser Composite Polymeric Membranes[a] (hydrophobic)

Experiment details	Designation	Membrane material: Active layer	Membrane material: Support layer
Solvent-extracted soybean and rapeseed oils	NTGS[b]-1100	Silicon	Polysulfone
	NTGS-2100	Silicon	Polyimide
Screw-pressed groundnut and sunflower oils	NTGS-1100	Silicon	Polysulfone
	NTGS-AX	Silicon	Polysulfone
	NTGS-BX	Silicon	Polysulfone
	NTGS-CX	Silicon	Polysulfone
	NTGS-2200	Silicon	Polyimide
Used frying oils	NTGS-AX	Silicon	Polysulfone
	NTGS-BX	Silicon	Polysulfone
	NTGS-CX	Silicon	Polysulfone
	NTGS-2200	Silicon	Polyimide
Permeation/rejection mechanism	NTGS-2200	Silicon	Polyimide

[a] Supplied by Nitto Denko, Kusatsu, Japan.
[b] NTGS, membrane series.

oil industries despite considerable research efforts. In recent years, Subramanian *et al.* (15–17) extensively investigated processing solvent-extracted oils, screw-pressed oils (18), and used frying oils (19) with nonporous denser polymeric composite membranes. Studies were also carried out to understand the rejection mechanism of phospholipids (20) and pigments (21), as well as differential permeation of liquid constituents, namely, TG, FFA, and tocopherols (22,23). In this review, attempts are made to explain the results obtained in these studies with real and model systems in a batch membrane cell, focusing on the mechanism of rejection or differential permeation of oil constituents during processing using nonporous denser polymeric composite membranes (Table 1).

PROCESSING REAL OIL SYSTEMS

Processing solvent-extracted soybean and rapeseed oils. During membrane processing of crude soybean and rapeseed oils, phospholipids were rejected between 97.4 and 99.9% (15). Some of these results obtained with soybean oil are presented in Table 2 (15,17). The near-complete removal of phospholipids indicates that nonporous denser membranes reject not only hydratable but also nonhydratable phospholipids (NHP). Higher rejection of NHP (97.7%) in water-degummed soybean oil confirms that NHP also are effectively rejected by these membranes (16). NTGS-1100 and NTGS-2100 membranes reduced pigments by 74 and 80%, respectively, in soybean oil (17). A major advantage of membrane processing is that mild operating conditions prevent oxidative changes. In fact, membranes rejected oxidation products (expressed as Totox values—the sum of anisidine value plus twice the PV), from 59 to 91% and 67 to 73% in soybean and rapeseed oils, respectively. The formation of conjugated dienes and trienes predisposes the oil to further oxidative changes. Dienes and trienes were found to be rejected in the range of 22 to 26% and 34 to 37%, respectively, in soybean oil. Increased tocopherol content in the permeates of soybean and rapeseed oils ranged from 12 to 15% and from 18 to 26%, respectively. The NTGS-2100 and NTGS-1100 membranes gave an average permeate flux of 0.22 and 0.75 kg/(m^2·h) in the case of soybean oil.

Processing screw-pressed groundnut and sunflower oils. Prepressed oil contains lesser amounts of phospholipids as less soluble impurities are removed during prepressing. Solvent-extracted oil generally contains greater amounts of phospholipids since the majority of phospholipids are extracted in the final stages of solvent extraction. The phospholipid contents in the screw-pressed groundnut and sunflower oils were 690 and 120 mg/kg, respectively (18). From the study on characterization of the phospholipids in model and crude oils (20), the content could be inferred to be below the critical micelle concentration (CMC). The phospholipid contents of membrane permeates of groundnut and sunflower oils were lower than 360 mg/kg, which is far superior to oils obtained by any of the industrially known degumming processes (18). During membrane processing, FFA preferentially permeated compared to TG, resulting in negative rejection. In sunflower oil, the rejection was

TABLE 2
Membrane Processing of Crude (solvent-extracted) Soybean Oil[a] (15,17)

Sample description	Phospholipids (mg/kg)	Color pigments: Ar 340–800 nm	Oxidation products (Totox)	Tocopherols (mg/kg)
Crude	5370	760	3.3	1250
Permeate	27	152	0.4	1440
PR (%)	99.5	80	88	+15
R_o (%)	99.6	85	91	–24

[a] Ar, area; Totox = *p*-anisidine value + 2 × PV; PR, percentage reduction; R_o, rejection.

TABLE 3
Membrane Processing of Crude (screw-pressed) Groundnut Oil (18)

Sample description	Phospholipid (mg/kg)	Color		FFA (%)
		Yellow	Red	
Crude	690	4.5	0.6	0.99
NTGS-AX				
Permeate	180	2.5	0.5	1.12
PR (%)	74	44	17	+13
NTGS-2200				
Permeate	0	1.1	0.3	—[a]
PR (%)	100	76	50	

[a]—, not determined. For abbreviation see Table 2.

−8 to −27%. The maximum reductions in Lovibond yellow and red color values were 75.6 and 50.0% in groundnut oil and 77.9 and 77.8% in sunflower oil, respectively, using NTGS-2200 membranes. Some of the results obtained with groundnut oil are presented in Table 3 (18). Oxidation products were rejected by NTGS-AX and NTGS-2200 membranes by 27 to 40%. Conjugated dienes and trienes were not formed and, in fact, the dienes and trienes present in the crude oil were rejected during the membrane process. Tocopherols in groundnut and sunflower oils preferentially permeated compared to TG, increasing the relative amount of tocopherol in permeates to 72%. The performances obtained with solvent-extracted and screw-pressed oils during membrane processing were similar in terms of rejection as well as relative permeation, even though the phospholipid content of one system was above the CMC and another system was below the CMC. The study of these two different systems contributed significantly to understanding edible oil processing using nonporous denser membranes.

Membrane processing of used frying oils. The major quantity of vegetable oils produced is used for frying foods. To maintain consistency in the quality of the frying oils, both insoluble particulates and soluble components have to be removed, thereby decreasing the rate of degradation. Studies have been conducted with used frying oils and five different types of polymeric membranes to decrease soluble degradation products. Some of the results obtained are presented in Table 4. Two of the nonporous denser membranes having higher active surface thickness, namely, NTGS-AX and NTGS-2200, selectively rejected polar compounds and oxidation products by 25 and 32, and 25 and 30%, respectively (19). In addition, the NTGS-AX membrane reduced the oil viscosity by 22%, value close to that of fresh frying oil, indicating that polymerized products were almost completely rejected by the membrane.

TABLE 4
Membrane Processing of Used Frying Oil (19)

Sample description	TPM[a] (%)	Color (5R + Y)	Viscosity (mPa·s)
Used frying oil	12.4	24	55.2
Permeate of NTGS-AX	9.7	4	43.3
PR (%)	22	83	22
Permeate of NTGS-2200	9.0	3	—
PR (%)	27	88	

[a]TPM, total polar materials; for other abbreviations see Tables 2 and 3.

The color of used frying oil is due to complex reaction products (mainly melanoidines) formed during frying (24). The reduction in Lovibond color values (5R + Y) was 83 and 88% using NTGS-AX and NTGS-2200 membranes, respectively. The reduction in viscosity of the used frying oils reduces oil absorption in the fried products. Having less color compounds increases the organoleptic acceptability of the oil. The results suggest that a membrane process can be used to extend the life of frying oils.

MECHANISM OF REJECTION OF CONSTITUENTS/DIFFERENTIAL PERMEATION OF LIQUID CONSTITUENTS

TG make up over 95% of crude vegetable oils. Oleic, linoleic, and palmitic acids are the major FA present in the common vegetable oils (25). The minor constituents, such as phospholipids (600 to 800 Da), carotenoids (537 to 569 Da), FFA (256 to 282 Da), and tocopherols (402 to 472 Da), have lower molecular sizes than the TG (>800 Da). Chlorophyll (892 Da) has a slightly higher molecular size. Membrane processing produces permeate and retentate fractions containing TG, as well as other oil constituents. The decreasing order of relative preferential permeation in the nonporous denser membranes is expected to be FFA, tocopherols, TG, aldehydes, peroxides, pigments, and phospholipids. During membrane processing, phospholipids and pigments are rejected to a greater extent. Therefore, phospholipids–TG and pigments–TG could be construed as conventional solute–solvent systems. Tocopherols and FFA preferentially permeated compared to TG. Hence, tocopherols, FFA, TG, and lipid oxidation products could be treated as a liquid mixture system exhibiting differential permeability in a nonporous denser membrane.

Transport across nonporous membranes. The transport behavior observed in processing oil systems using nonporous denser polymeric composite membranes probably can be understood better by considering the theory of permeation through denser membranes, as well as RO theory.

(i) Denser membranes. Transport in nonporous denser membranes is completely controlled by the solution–diffusion mechanism in applications such as gas separation, liquid separation, pervaporation, and vapor permeation (26). Permeability, P_m, is equal to

$$P_m = D \cdot S \tag{1}$$

where D is the diffusion coefficient and S the solubility (27). The flux equation will take the following form:

$$J = D \cdot S \cdot \left(\frac{\Delta P}{\Delta x}\right) = P_m \cdot \left(\frac{\Delta P}{\Delta x}\right) \tag{2}$$

where J is the permeate flux, ΔP the transmembrane pressure, and Δx the membrane thickness. Solubility values of various oil constituents, namely, TG, β-carotene, α-tocopherol, and oleic acid, were predicted based on the group-contribution lattice-fluid equation of state (GCLF-EOS) model proposed by

Lee and Danner (28). This model provides excellent predictions of solvent activity coefficients in polymers both at infinite dilution and finite concentrations with only input of molecular structures in terms of their functional groups. Polydimethylsiloxane (PDMS), which is identical to silicon rubber, was chosen as the polymer for solubility predictions (from the database of the above model). The solubility of PC and chlorophyll in PDMS could not be predicted using the GCLF-EOS model since its database does not include functional groups containing phosphorus, nitrogen, and magnesium atoms. Predicted solubility values suggested that the order of solubility at any given value of activity is oleic acid > β-carotene ~ α-tocopherol > TG.

Diffusion coefficients are dependent on the sizes of the penetrants: The lower the M.W., the greater the diffusivity. Therefore, by virtue of their M.W., the diffusion coefficients occur in the following order: oleic acid > tocopherols > carotenoids > phospholipids > TG > chlorophyll.

(ii) RO membrane. The permeate flux in an RO membrane (29) is given by

$$J = A(\Delta P - \sigma \cdot \Delta\pi) \quad [3]$$

where J is the permeate flux, A the pure solvent permeability coefficient, ΔP the transmembrane pressure, σ the reflection coefficient, and $\Delta\pi$ the osmotic pressure difference across the membrane. The value of the permeability coefficient is a function of the distribution coefficient (solubility) and the diffusion coefficient (26):

$$A = \frac{D \cdot c \cdot V}{R \cdot T \cdot \Delta x} \quad [4]$$

where R is the universal gas constant, T the absolute temperature, Δx the membrane thickness, D the diffusion coefficient, c the distribution coefficient, and V the molar volume of the permeating component. From the above equations, it can be seen that the flux depends on solubility as well as diffusivity and also on convective flow.

Although denser membranes are nonporous membranes, pores on a molecular level exist in such membranes. The structures of the RO membranes are not as dense as those of other nonporous membranes used for applications such as gas separation and pervaporation (26). The denser the membrane, the higher the contribution of solution–diffusion mechanism.

(iii) Polarity. The nonporous denser membranes used in these studies were hydrophobic in nature. Therefore, the relative polarity of the oil constituents also would play a major role in the permeabilities of these constituents. TG are nonpolar whereas other oil constituents are relatively more polar in nature than TG.

REJECTION OF PHOSPHOLIPIDS

Model studies. From the experiments conducted with model systems (TG–PC), PC contents in the feed and permeate and percentage rejection are presented in Table 5 (22). The PC contents of the permeates ranged between 6 and 92 mg/kg (phosphorus content 0.2 to 3.6 mg/kg), and rejection of PC was well above 98% in all cases. Further, the rejection did not differ significantly with either feed concentration or operating conditions (temperature and pressure). The near-complete removal of PC during membrane processing indicated that a nonporous denser membrane was very effective in rejecting PC. The rejection performance observed with the model system was similar to the performance with crude oils.

TABLE 5
High-Oleic Sunflower Oil and a PC Model System (22)

Experiment description	Pressure (MPa)	Temperature (°C)	PC[a] (mg/kg) Feed	PC[a] (mg/kg) Permeate	R_o (%)
PC concentration	4	40	1740	7	99.6
	4	40	4720	6	99.9
	4	40	8240	10	99.9
Temperature	4	30	4720	34	99.3
	4	40	4720	6	99.9
	4	50	4720	8	99.8
Pressure	3	40	4720	45	99.1
	4	40	4720	6	99.9
	6	40	4720	92	98.1

[a] PC, phosphatidylcholine; for other abbreviation see Table 2.

Mechanism of rejection. The rejection of phospholipids could have been due to the formation of phospholipid reverse micelles, swollen in the presence of small quantities of water and having an affinity for some of the other impurities, such as color compounds, which were then rejected by size exclusion. Another possibility for the observed behavior of these membranes could have been a solution–diffusion effect, that is, interactions between individual solutes as well as their interactions with the silicon active layer of the membrane. To understand the rejection phenomenon, studies were conducted to determine the CMC of phospholipids in vegetable oils and the size of their reverse micelles.

Characterization of phospholipid reverse micelles. The CMC values of PC in triolein and phospholipids in crude soybean oil were determined to be 440 and 1020 mg/kg, respectively, by using the TCNQ (7,7,8,8-tetracyano-quinodimethane) solubilization technique of Kanamoto *et al.* (30). The surface tension measurements of these samples gave CMC values similar to that of the TCNQ technique for PC and mixed phospholipids. The crude vegetable oils contain mixed phospholipids, and their PC contents are generally low. Therefore, the CMC values of mixed phospholipids in these crude oils would be much higher than the CMC value of PC and closer to the CMC value obtained with the crude soybean oil. From small-angle X-ray scattering (SAXS) analysis based on the spherical model (31), the size of the PC micelles was in the range of 3.56 to 4.70 nm (Table 6).

From the results of the characterization studies, the phospholipid contents in the solvent-extracted crude soybean and rapeseed oils could be inferred to be above the CMC, whereas the phospholipid contents in screw-pressed sunflower and groundnut oils were below the CMC. In both systems, nonporous denser membranes were effective in rejecting phospholipids (Tables 2 and 3). This suggested that the mechanism of transport was the solution–diffusion effect and the rejection of

TABLE 6
SAXS Analysis of Triolein Samples Containing PC and Water[a] (20)

Additive	Concentration PC (%)	Concentration Water (mg/kg)	Diameter of micelles (nm)
PC	0.89	700	3.56
	1.77	700	3.70
	4.52	600	4.22
	9.13	600	4.70
PC and water	0.89	1000	4.60
	1.77	1200	4.74
	4.52	1800	4.80
	9.12	2600	4.80

[a] SAXS, small-angle X-ray scattering; for abbreviation see Table 5.

phospholipids was attributed to low solubility in the membrane material. Generally, the phospholipid content is well above the CMC in crude solvent-extracted oils. In such systems, size exclusion may provide a synergistic effect in the rejection. This analysis suggests that hydrophobic NF membranes with 4-nm pore size would be the ideal choice for separating phospholipids (above the CMC) from crude oils so as to exploit size exclusion as a predominant separation factor and at the same time to achieve higher permeate flux.

REJECTION OF CAROTENOIDS

Studies with crude soybean oil showed that the nonporous denser membranes rejected color compounds by 80 to 85% (17). The following systems were studied to understand the rejection phenomenon of carotenoids (21).

High oleic sunflower (HOSF) oil along with β-carotene and lecithin model system. The reduction of carotenes was only 17% in the absence of added surfactants (Table 7). Experiments conducted with added lecithin to the model HOSF oil system did not improve the rejection of carotenes. Increasing the ratio of lecithin to β-carotene in the feed solution also did not improve the rejection by the membrane.

As discussed in the earlier section, the rejection/permeation of oil constituents in a nonporous denser membrane is primarily controlled by the solution–diffusion effect. Predicted solubility values based on the GCLF–EOS model suggested that the solubility of β-carotene is much higher than that of TG in PDMS at any given value of activity (~10- to 11-fold at unit activity). In the experimental model, β-carotene concentration was very low (<250 mg/kg). Therefore, the activity of carotene would be much lower than unity, and that of TG would be close to unity at the feed compositions used in the experiments. Furthermore, by virtue of lower M.W., the diffusivity of β-carotene would be greater than that of TG in membrane material.

Higher solubility and higher diffusivity of carotenes should have resulted in preferential permeation (negative rejection). However, a lower positive rejection of carotenes resulted. In a liquid system, solubility and diffusivity are strongly dependent on the feed composition, unlike gas systems where they are constant (26). Furthermore, in a ternary system (a binary mixture and a polymer), the interaction between the components of the binary mixture could alter the solubility and diffusivity of the individual components in the membrane material. Sorption plays a major role in determining the selectivity since the difference in diffusivity of components is generally smaller in liquid systems (27). Therefore, it can be construed that actual feed composition and thermodynamic interactions between the components in the ternary system resulted in lower positive rejection instead of preferential permeation of carotenes (21).

The model system with the addition of lecithin could be considered close to the real system. However, during membrane processing, the rejection of carotenes was not different from the system without any surfactant (Table 7). The reverse micelles formed with the addition of lecithin in the oil system did not seem to have the affinity for β-carotenes.

Crude soybean oil. In a control experiment, NTGS-2200 membrane reduced the carotenoids in crude soybean oil by 79% (Table 7). Earlier studies showed that nonporous denser membranes rejected color compounds by 80 to 85% in soybean oil (17). Hydrocarbon (β-carotene) and oxygenated (xanthophylls) carotenoids are the two groups of carotenoids present in oilseeds. Xanthophylls (predominantly lutein) were detected in mature soybean seeds, whereas no hydrocarbon carotenoids including β-carotene were detected (except for a trace amounts in some varieties) (32). Xanthophylls are the major carotenoids present in the oils extracted from soybean and rapeseed (21).

The greater rejection of carotenoids in vegetable oils is

TABLE 7
Percentage Reduction and Rejection of Carotenoids in a Membrane-Processed High-Oleic Sunflower (HOSF) Oil Model System and Crude Soybean Oil (21)

Type of system	Lecithin addition (%)	Carotenoids (mg/kg) Feed	Carotenoids (mg/kg) Permeate	PR (%)	R_o (%)
Real system					
Crude soybean oil	0.0	47	10	79	79
Model system[a]					
HOSF oil + β-carotene	0.0	258	213	17	18
	2.2	244	205	16	17
	5.4	216	175	19	20
HOSF oil + lutein	0.0	8.0	3.4	58	60
	8.1	9.6	3.2	67	69

[a] Added β-carotene/lutein. For abbreviations see Table 2.

considered to be mainly due to their association with the reverse micelles of mixed phospholipids formed in the crude oil system. But the greater reduction of color values observed in screw-pressed oils (18) revealed that the solution–diffusion effect was the predominant mechanism in rejecting pigments. It seems that the silicon layer of the membrane did not have higher permeability for xanthophylls, resulting in greater rejection in crude oils (21).

HOSF oil along with a lutein and lecithin model system. The nonporous denser membrane rejected lutein by 60% in the absence of added surfactants (Table 7), whereas the β-carotene rejection was only 18% under similar conditions. Lutein is an oxygenated carotenoid and contains two hydroxyl groups in its molecular structure. These hydroxyl groups make lutein more polar than β-carotene. This may explain the higher rejection of lutein in the model system, since the membrane used in the study was hydrophobic in nature. Experiments conducted with addition of lecithin to the model HOSF oil system showed a slight improvement in rejecting lutein (Table 7). It appeared that lutein has some affinity to phospholipid reverse micelles present in the oil system.

Rejection mechanism. Monma *et al.* (32) reported that there are few xanthophylls other than lutein present in some of the soybean seed varieties. HPLC analysis of crude soybean oil used in the study also revealed that there were few other xanthophylls, which are more polar than lutein (21). The membrane may reject these unidentified xanthophylls to a much greater extent. This could be a probable reason for the greater reduction in color observed in membrane-processed crude soybean oil.

In the crude oils, carotenoids were rejected irrespective of the phospholipid content (either above or below the CMC). This implied that xanthophylls, the major carotenoids present in the crude oils, need not necessarily have affinity for the phospholipid reverse micelles present in the oil system for their rejection. The rejection seemed to be predominantly due to the solution–diffusion effect in which the silicon active layer of the membrane did not have higher permeability for xanthophylls. However, some of the xanthophylls, being more polar in nature, may have had affinity for reverse micelles (hydrophilic polar heads are inward in the reverse micelles), which may have further increased their rejection. The extent of rejection depended on the actual composition of xanthophylls present in the crude oil. The presence of phospholipid reverse micelles in the oil system could enhance the rejection of xanthophylls.

REJECTION OF CHLOROPHYLL

A TG and chlorophyll system is also a conventional solute–solvent system. In crude soybean oil, NTGS-1100 and NTGS-2100 reduced chlorophyll content by 69 and 78%, respectively. During the long-term studies, the rejection of chlorophyll by the nonporous denser membrane was much greater than that of total pigments and also was consistent irrespective of changes in the composition of retentate (17). The NTGS-2200 membrane rejected chlorophyll almost completely in the model studies as well (Table 8), showing that the silicon active layer of the membrane was not permeable to chlorophyll compounds as was the case for PC. Low sorption of chlorophyll in the membrane material appears to be the reason for high retention.

OLEIC ACID AND TG

As independent systems. TG and oleic acid were independently studied at various temperatures and pressures to examine the behaviors of the pure systems. The permeate flux of both increased with an increase in operating pressure as well as temperature. Pressure significantly affected permeation. Furthermore, the permeate flux at a given temperature showed a nonlinear relationship with operating pressure and the degree of nonlinearity was more for TG than for oleic acid. Owing to strong interactions between the liquid and the polymer (membrane), the system tended to be nonideal, and hence the sorption isotherms tended to be nonlinear, especially with increasing pressure (26). The permeate flux of oleic acid and TG showed a linear relationship with temperature at a given operating pressure.

Oleic acid–TG mixture system. Oleic acid contents in feed and permeate, viscosity of feed, total permeate flux, and relative permeation rates of TG and oleic acid are presented in Table 9. Oleic acid preferentially permeated when compared with TG. Total permeate flux increased with oleic acid concentration in the feed, mainly because of the increased permeation rate of oleic acid. Higher operating temperature increased the total permeate flux. A detailed analysis is presented elsewhere (22).

Relative permeation rates of oleic acid and TG. In the nonporous membrane, the relative permeation rates of liquid constituents depend on solubility as well as diffusivity in the membrane (26,33). In the separation of liquid mixtures, sorption in the membrane plays a major role in determining selectivity

TABLE 8
High-Oleic Sunflower Oil and Chlorophyll Model Systems (22)

Type of system	Chlorophyll (mg/kg) Feed	Chlorophyll (mg/kg) Permeate	Absorbance (670 nm) Feed	Absorbance (670 nm) Permeate	R_o (%)
Real system					
Crude soybean	—	—	0.225	0.028	90.7[a]
Model systems					
Oil + chlorophyll	54	0.5	—	—	99.2
Oil + PC[b] + chlorophyll	51	0.3	—	—	99.4

[a] Based on absorbance at 670 nm. For abbreviations see Tables 2 and 7.
[b] Addition, 0.4%.

TABLE 9
HOSF Oil and an Oleic Acid Model System^a (22)

Experiment description	Temperature (°C)	Oleic acid (%)		Feed viscosity (mPa·s)	Total flux [g/(m^2·h)]	Permeation rate [g/(m^2·h)]		R_o (%)
		Feed	Permeate			TG	Oleic acid	
Oleic acid concentration	40	1.9	2.9	36.0	90.6	88.0	2.7	–57
	40	5.2	8.4	35.7	105	96.3	8.9	–67
	40	10.0	16.7	34.4	125	104	20.8	–73
	40	21.2	37.1	31.5	151	95.1	56.1	–83
Temperature	30	5.3	8.9	50.7	84.0	76.5	7.5	–74
	40	5.2	8.4	35.7	105	96.3	8.9	–67
	50	5.3	8.4	7.8	168	154	14.2	–64

^{a}All experiments carried out at a pressure of 4 MPa. For abbreviation see Table 2.

(relative permeation) since the differences in diffusivity of the components are generally smaller (27). Predicted solubility values based on the GCLF-EOS model (28) suggested that the solubility of oleic acid was much higher than that of TG (27-fold at unit activity) in PDMS. By virtue of its lower M.W., the diffusivity of oleic acid was expected to be greater than that of TG in membrane material. The cumulative effect of higher solubility as well as diffusivity explained the higher relative permeability or preferential permeation of oleic acid over TG through the membrane.

Effect of feed composition. The total permeate flux increased from 90.6 to 151 g/(m^2·h) (66.7% increase) when the oleic acid content in the feed was increased from 1.9 to 21.2%. The solubility of constituents in the membrane material changed as their relative concentration in the mixture changed according to the GCLF-EOS model. The increased solubility of oleic acid was much higher than the decrease in the solubility of TG when the oleic acid content was increased in the feed from 1.9 to 21.2%. The increased solubility increased the penetrant's concentration in the membrane material and thereby increased its diffusivity as well. The concentration-dependent solubility as well as diffusivity explained the significant relative increase in the oleic acid permeation rate from 2.7 to 56.1 g/(m^2·h).

The oleic acid content inversely affected the feed viscosity. The decrease in the viscosity of feed was 12.5% when the oleic acid content in feed was increased from 1.9 to 21.2%. The increase in total permeate flux (1.67-fold) was much higher, compared with the reduction of viscosity (1.14-fold), which indicated that viscosity did not play a significant role in the increased permeate flux.

Effect of temperature. When temperature was increased from 30 to 50°C at constant operating pressure and feed concentration, total permeate flux increased from 84.0 to 168 g/(m^2·h). The solubilities of oleic acid and TG increased with an increase in temperature. In general, diffusivity increased linearly with increasing temperature. The temperature also had a considerable inverse influence on viscosity. The increased permeation rates of TG and oleic acid were 101 and 89.0%, respectively. A similar trend was observed with studies on independent systems of TG and oleic acid. The extent of increase was greater for TG because the relative increase in solubility with temperature was higher for TG than for oleic acid. The increase in operating temperature resulted in a slightly higher relative permeation rate of TG, which in turn changed the relative selectivity of the membrane. This also implied that the effect of swelling was not significant in this nonaqueous system.

The reduction in viscosity was 84.6% in the feed when the temperature was increased from 30 to 50°C. The increase in total flux was only twofold, whereas the reduction in viscosity of feed was 6.5-fold. The reduction in the viscosity of feed solution did not play a proportional role in the permeation rate.

Effect of operating pressure. When the operating pressure was increased from 3 to 6 MPa at a constant temperature, total permeate flux and relative permeation rates of TG and of oleic acid increased. The detailed analysis is presented elsewhere (22).

The observed behavior of the TG–oleic acid mixture system suggested that solution–diffusion was the predominant mechanism in the transport of liquid mixtures through nonporous denser membranes.

TOCOPHEROLS AND TG

Effect of concentration of tocopherols in feed. The results from a model system of tocopherols and TG are presented in Table 10. Tocopherols preferentially permeated compared with TG, and the permeation rate of tocopherols increased with feed concentration, similar to the TG–oleic acid model system (22). However, the total permeate flux remained more or less constant between 98.1 and 104 g/(m^2·h) despite a large change in tocopherol concentration in the feed (0.144 to 60.7%). The selectivity showed a decreasing trend for tocopherols with increasing feed concentration.

In the nonporous denser membrane, the transport occurred mainly owing to solution–diffusion as just discussed. The predicted solubility values based on the GCLF-EOS model suggested that solubility of α-tocopherol was much higher than that of TG in PDMS at any given activity (~10-fold at unit activity). Owing to their lower M.W., the diffusivity of tocopherols was greater than that of TG in the membrane material. Therefore, the observed preferential permeation of tocopherols appeared to be due to the combined effects of its higher solubility and diffusivity. Increased concentration of tocopherols in the feed resulted in increased solubility as well as diffusivity

TABLE 10
HOSF Oil and an α-Tocopherol Model System[a] (23)

Experiment description	Temperature (°C)	Tocopherol (%)		Feed viscosity (mPa·s)	Total flux [g/(m^2·h)]	Permeation rate [g/(m^2·h)]		R_o (%)
		Feed	Permeate			TG	Tocopherol	
Tocopherol concentration	30–32	0.144	0.214	—	101.0	100.8	0.2	−51.8
	30–32	1.15	1.66	41.4	100.0	98.3	1.7	−47.2
	30–32	4.96	7.08	44.7	104.0	96.6	7.4	−45.4
	30–32	10.7	14.5	—	104.0	88.9	15.1	−37.6
	30–32	42.6	56.6	—	99.4	43.1	56.3	−34.8
	30–32	60.7	77.6	156	102.0	22.8	79.2	−29.4
Temperature	20	0.225	0.335	63.5[b]	64.4	64.2	0.2	−52.1
	30	0.225	0.333	41.5	95.3	95.0	0.3	−51.1
	40	0.225	0.332	18.9	152.0	151.5	0.5	−50.6
	50	0.225	0.329	9.43	246.0	245.2	0.8	−49.2

[a] Pressure, 4 MPa.
[b] Measured at 25°C. For abbreviations see Tables 2 and 3.

since they are both concentration dependent and, in turn, should have resulted in higher selectivity. However, selectivity showed a decreasing trend for tocopherols with increasing feed concentration. It appeared that the viscosities of the individual constituents of liquid mixtures also played some role in their permeation and therefore on selectivity. Solubility of TG in tocopherols was also probably playing a role besides higher viscosity of tocopherols. In another recent study (Bhosle, B.M., R. Subramanian, and K. Ebert, unpublished data) on the TG–oleic acid system, at higher concentrations of oleic acid in the feed, the membrane selectivity toward oleic acid showed a decreasing trend despite a decrease in the feed viscosity, which was attributed to the solubility of TG in oleic acid.

As discussed earlier, the solubilities of the constituents in the membrane material changed as their relative concentrations in the mixture changed. The increase in solubility of tocopherols was much higher than the decrease in the solubility of TG when the tocopherol content was increased in the feed (23). The increased solubility and resultant increased diffusivity should have resulted in an increased tocopherol permeation rate as well as total permeate flux. However, the total permeate flux remained nearly constant. The coupling effect that has an influence in the transport of liquid mixtures appeared to be negative in the TG–tocopherol mixture system. Another reason could be increased viscosity with an increase in tocopherol content in the feed (Table 10). Despite a large increase in feed viscosity (3.8-fold) as the tocopherol content increased from 0.355 to 60.7%, the total permeate flux remained more or less constant. Although concentration-dependent solubility and diffusivity are expected to increase the permeation rate of tocopherols at higher concentrations in the feed and thereby total flux, the magnitude of increase might not be large enough to compensate for the effect of viscosity. Therefore, it is unlikely that viscosity could cause any proportional effect on the permeation.

Effect of temperature. When the temperature was increased from 20 to 50°C at a constant operating pressure and feed concentration, total permeate flux increased from 64.4 to 246 g/(m^2·h) (Table 10). These flux values were comparable with the total flux values obtained in the TG–oleic acid system. The increase in total permeate flux may have been due to the cumulative effect of increased solubility and diffusivity with increased temperature.

Temperature has considerable inverse influence on viscosity. The reduction in viscosity was as much as 6.7-fold in the feed when the temperature increased from 25 to 50°C. The observed increase in permeate flux is 3.8-fold, which was affected by an increase in the solution–diffusion effect as well as convective flow. Therefore, it appeared that the effect of viscosity was not proportional in the permeation rate, which lends support to our earlier discussion on the effect of tocopherol concentration in feed.

Tocopherol content in the permeate remained nearly constant (Table 10), indicating that the relative rates of permeation of TG and tocopherols, or in other words membrane selectivity, remained more or less the same. As a function of temperature, diffusivity was expected to increase at the same rate for both components with increased temperature. The relative increases in solubility with temperature for TG and α-tocopherol were nearly the same between 25 and 65°C (23). Hence, the relative increase in the permeation rates of these two components remained the same in the temperature range studied. This also implied that swelling effects were not significant in the TG and tocopherol system, as was the case in the TG and oleic acid system discussed earlier.

The effect of viscosity (temperature) on permeation suggested that convective flow existed in these membranes, but the extent observed was not significant. Thus, solution–diffusion appeared to be the predominant mechanism of transport of oil constituents through nonporous denser membranes.

PERMEATE FLUX

The average permeate fluxes of nonporous denser polymeric composite membranes NTGS-1100, NTGS-2100, and NTGS-2200 were 0.75, 0.22, and 0.15 kg/(m^2·h), respectively (15,23). Lin *et al.* (11) reported 96.6% rejection of phospholipids and a permeate flux (hexane–oil miscella) of 26.8 L/(m^2·h) with commercial, hexane-resistant, nonaqueous, UF membranes. The corresponding oil flux was ~6 kg/(m^2·h). Thus, oil flux obtained with hexane–oil miscella was about eightfold greater than the flux obtained with NTGS-1100 membrane without added solvents. However, membrane life is another factor that affects the economics of the process. NTGS membranes were stable even up to 100 d in a long-term study (15). The useful life of the hexane-resistant UF membranes used by other researchers is yet to be established. Development of suitable nonporous denser polymeric membranes is necessary for the commercial adoption of a membrane process in the edible oil industry.

Potential of NF membranes. The characterization of reverse micelles formed in the oil system (20) enhanced understanding of the possible rejection phenomenon of phospholipids by the nonporous denser membranes used in studies on vegetable oils. This analysis suggests that hydrophobic NF membranes with 4-nm pore size would be ideal for separating phospholipids (above CMC) from crude oils and at the same time achieving higher permeate flux. Development of suitable NF membranes could replace the degumming step in conventional chemical refining as well as the pretreatment step in physical refining.

FEATURES OF NONPOROUS DENSER POLYMERIC COMPOSITE MEMBRANES

These nonporous denser membranes exhibited excellent selectivities for the phospholipids, xanthophylls, and chlorophyll present in the crude oil mainly because of their low solubilites in the membrane material. FFA and tocopherols preferentially permeated compared to TG owing to higher solubility as well as diffusivity. Dense membrane theory appeared to be more applicable than RO theory in qualitatively explaining differential permeation of oil constituents. The polarities of the compounds also seemed to be playing a major role as was evident from the difference in the rejection performance in systems containing β-carotene and xanthophylls. The decreasing order of relative preferential permeation in the nonporous denser membranes was found to be FFA/tocopherols, TG, aldehydes, peroxides, xanthophylls, chlorophyll, and phospholipids. Research efforts on membrane processing of oils have indicated its potential to be a single-step process for vegetable oils, more specifically for screw-pressed oils to produce a premium-quality product, without the use of solvents and chemicals. However, development of suitable membranes that enable achieving higher fluxes is necessary for industrial adoption of this technology. The nonporous denser membranes may find potential applications in the separation/concentration of various constituents in other nonaqueous systems.

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