Deacidification of Soybean Oil by Membrane Technology

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ABSTRACT: After extracting free fatty acids (FFA) from a model crude vegetable oil with methanol, FFA were separated from methanol by nanofiltration. Of the several commercially available membranes that were evaluated, the best resulted in FFA rejection of >90% and flux of >25 $\mathrm{Lm^{-2}\,h^{-1}}$. A combination of high-rejection and low-rejection membranes resulted in a retentate stream of 35% FFA and a permeate stream with less than 0.04% FFA, which can be recycled to the extractor. No alkali is required, no soapstock is formed, and almost all streams within the membrane process are recycled with little discharged as effluent.

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KEY WORDS: Free fatty acids, membrane technology, methanol, refining, vegetable oils.

After extraction from oilseeds, crude vegetable oil is refined to remove undesirable components, such as free fatty acids (FFA). In alkali-refining, the FFA form soaps, which are removed by centrifuging. The deacidification process has a significant economic impact (1), and several drawbacks with alkali-refining have been noted (2): (i) oil losses due to saponification and by occlusion in soapstock (3); (ii) soapstock has little value even though FFA in their native state find many uses; and (iii) large amounts of water are used to wash the oil after caustic treatment, which leads to contaminated discharges and high disposal costs. With soybean and cottonseed oils, total batch refining losses can be as high as three times the FFA content (4).

This paper describes a novel process for deacidification of vegetable oils that can ameliorate some of the problems with caustic refining. It combines solvent extraction and membrane technology to separate the triglycerides in the crude oil from the FFA. A membrane is a semipermeable barrier that separates different species of a solution by allowing restricted or regulated passage of some of the components of the mixture. Membrane processing is remarkably simple, involving pumping a fluid through a membrane of appropriate chemical nature and physical configuration while maintaining a transmembrane pressure differential (5). Vegetable oil processing is a relatively new application for membrane technology (6–10). The basic principles and potential of membrane technology in the vegetable oil industry recently have been reviewed (2,11).

Principle of the method. Fatty acids are about one-third the molecular weight of triglycerides. The difference in their molecular weights is too small if membranes alone are used in their separation (2). However, if the FFA were extracted from the crude oil by a solvent that selectively dissolves the FFA, then this extractant (containing the solvent + FFA) can be processed through the appropriate membrane to separate the solvent from the FFA. A conceptual diagram of the membrane refining process is shown in Figure 1. The crude vegetable oil, containing triglycerides and FFA, is mixed with the solvent under appropriate conditions. After extracting FFA, the mixture may go through a phase separator, which separates the triglycerides from the extractant. The extractant is pressurized through the membrane system, which separates it into two streams. Ideally, the permeate is FFA-free solvent and can be recycled to the extractor. The retentate is enriched in FFA, which can be further processed in an evaporator, by membrane technology, or separated into individual fatty acids. Two key elements of this process are (i) a solvent with a high extraction ratio for FFA and negligible extraction ratio for triglycerides; and (ii) a membrane that is stable to the solvent and has a high "rejection" of FFA (i.e., retaining the FFA and allowing the solvent to easily pass through) and a high flux (i.e., high rate of passage of filtrate through the membrane).

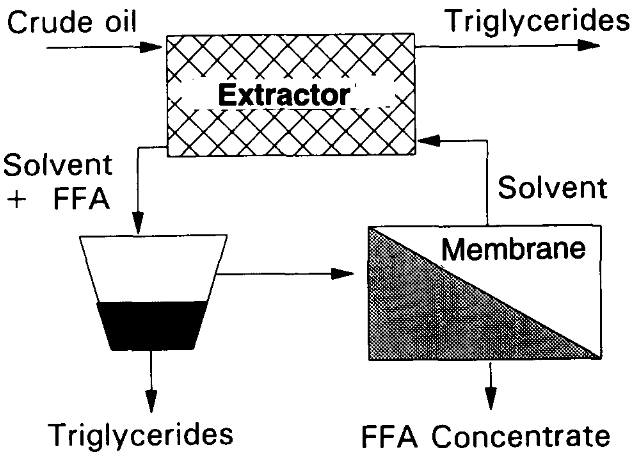

FIG. 1. Process for membrane deacidification of vegetable oils; FFA, free fatty acids.

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A variety of solvents can be used, e.g., ethyl alcohol, isopropyl alcohol, methanol. For this research, methyl alcohol was selected as the solvent, based on a review of the literature (12–15). Methanol has high selectivity for FFA and should have a high flux due to its small molecular size (molecular weight = 32).

To retain such small molecules as FFA, nanofiltration or reverse osmosis (RO) membranes are needed. Although molecular size is the primary factor that affects separation with these membranes, other interactions, such as membrane-solvent, membrane-solute, and solute-solvent interactions are important (16,17). Several commercially available and prototype membranes were screened for key properties (high FFA rejection, high flux of methanol, and stability of the membrane during processing).

EXPERIMENTAL PROCEDURES

Equipment. Figure 2 shows a schematic of the experimental set up, which consisted of a membrane test cell, a magnetic stirrer, and a nitrogen cylinder to provide the driving force (pressure) for permeation. The test cell was the Sepa ST model (Osmonics Inc., Minnetonka, MN), 8 cm diameter × 25 cm long, capable of withstanding pressures of up to 6.9 MPa (1000 psi). The cell's capacity was 300–800 mL, depending on the fittings used. A flat sheet membrane with a diameter of 5 cm (effective membrane area of 17.35 cm^2) was placed at the bottom of the vessel and was supported by a porous disc mounted on a circular base plate. The plate, in turn, was attached to the test cell by a coupling. The nitrogen cylinder was connected to the top of the test cell. A conduit also was provided in the bottom plate of the test cell to collect the permeate. Turbulence, to minimize concentration polarization, was created by a magnetic stirrer bar turning just above the membrane. A tube placed just above the membrane surface allowed sampling the retentate from inside the test cell while the experiment was in progress.

Membranes. Based on our experience and after consultation with membrane manufacturers, the following membranes were selected for screening: MS-10, ST10, MX07, BQ01 and B*02 (Osmonics Inc.); NF-40 and FT-30 (Film Tec/Dow, Midland, MI); CA, TLC, and PZ (Fluid Systems, San Diego, CA); NTR-729 and NTR-759 (Nitto Denko, Osaka, Japan); and Desal-5 (Desalination Systems, Inc., Escondido, CA).

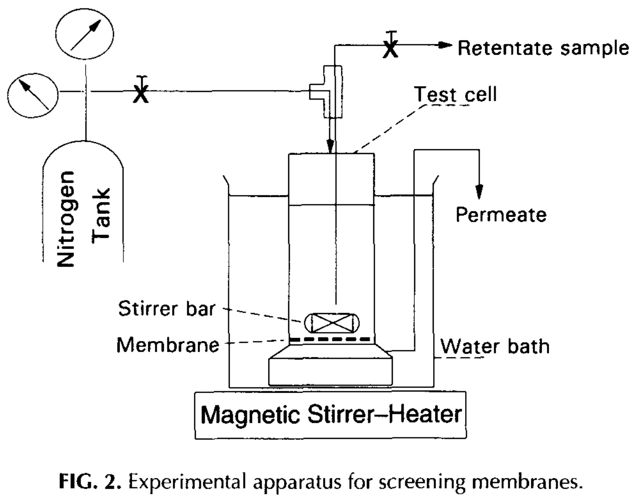

FIG. 2. Experimental apparatus for screening membranes.

Membrane stability and permeability. The stabilities of the selected membranes in methanol were evaluated by soaking the membrane discs in various concentrations of methanol [high-pressure liquid chromatography (HPLC) grade; Fisher Scientific, Fair Lawn, NJ]. Membrane discs (5-cm diameter) were cut from larger flat sheets of the membrane, washed in deionized water several times to remove any preservatives, and then immersed overnight in methanol. The membrane was placed in the test cell, which was then charged with pure methanol. The cell was pressurized, and the permeate flow was measured as a function of applied pressure. Membranes that exhibited instability, e.g., swelling of the membrane (as evidenced by large fluxes) or shrinking of the membrane matrix (resulting in negligible solvent permeation), were not considered for further experiments. For comparative purposes, the water flux of these membranes also was recorded in the same manner. Flux is expressed as liters of permeate per square meter of membrane area per hour (LMH).

Model FFA solutions. Performance characteristics of model fatty acid solutions were studied in batch mode with selected membranes that were stable in methanol. The model fatty acid was oleic acid (approximately 70% pure, clear, NF/FCC, class IIIB) purchased from Fisher Scientific. Permeate samples were collected at various times and stored in sealed screw-cap test tubes under refrigeration. The feed, permeate, and retentate were analyzed for oleic acid by HPLC. The experiments were repeated at least two times for each membrane.

A model solution of mixed fatty acids in methanol also was studied. Soybean fatty acids (Emery 610 Soya Fatty acid; Emery Group, Cincinnati, OH) were made up to 20 gL^{-1} solution in methanol, resulting in 11 gL^{-1} linoleic acid and 4 gL^{-1} oleic acid. The experiment was repeated 3–4 times for each membrane (NTR-759 and Desal-5 membranes were used in this experiment).

Vegetable oil. A model crude (unrefined) vegetable oil was simulated by adding oleic acid or mixed fatty acids to commercial soybean oil, purchased at a local grocery store. Our model crude vegetable oil contained 20 gL^{-1} added fatty acids. It was vigorously mixed with an equal volume of methanol for 30 min at room temperature to extract the fatty acids. This mixture was then transferred to a separator funnel and allowed to separate overnight into two layers of liquid, a bottom layer of oil, and a top layer of methanol containing the FFA. The oil layer was removed through the bottom stopcock, and the methanol phase was charged into the test cell. Experiments were repeated 3–5 times and data reported are means.

Analytical methods. Fatty acids were determined by HPLC with the fatty acid analysis column of Water's Inc. (Milford, MA), operated at room temperature (23 ± 1°C). The mobile phase was acetonitrile, tetrahydrofuran, water, and acetic acid in the ratio of 45:20:35:1, respectively. Flow rate was 1.0 mL min^{-1}. The samples were detected by refractive index (SP8340; SpectraPhysics, Fremont, CA).

Total oil (triglycerides + FFA) was measured gravimetrically by evaporating the sample at 75°C. The total FFA concentration was measured by titrating the sample against 0.1N NaOH with phenolphthalein as the indicator. The triglyceride content was obtained by subtracting the FFA concentration from the total oil concentration.

RESULTS AND DISCUSSION

Membrane properties. Most membranes are designed to operate in aqueous solutions. In the absence of water, many membranes lose their structural integrity. Of the different membranes evaluated, only six (MS10, PZ, FT-30, NTR-729, NTR-759, and Desal-5) were stable in methanol. Pure methanol fluxes of these membranes are shown in Figure 3 as a function of applied pressure. The slopes of the lines are the permeability coefficients. High methanol permeabilities were observed for NTR-759 and Desal-5 membranes (27.6 LMH/MPa) and the lowest for the NTR-729 membrane (10.5 LMH/MPa). In contrast, the pure water permeabilities of the membranes showed a different trend (Table 1), indicating the presence of solvent-membrane interactions. For example, the NTR-759 had the lowest water permeability coefficient (4.9 LMH/MPa) of the different membranes tested but the highest methanol permeability coefficient (27.6 LMH/MPa), giving it a relative permeability of 5.5. The NTR-729 membrane exhibited the opposite trend, with a relative permeability of 0.33, the lowest of all the membranes tested. This could indicate that the interstitial space in the matrix of the NTR-759 expands in the presence of methanol but shrinks in the NTR-729 membrane. In contrast, this phenomenon was not as dramatic with Desal-5 and MS10 membranes.

TABLE 1
Relative Permeabilities of Water and Methanol at 23°C for Several Membranes

Membrane	Water permeability (LMH/MPa)[a]	Methanol permeability (LMH/MPa)[a]	Relative permeability
NTR-759[b]	4.9	27.6	5.55
FT-30[c]	8.6	18.2	2.12
MS-10[d]	16.8	13.4	0.80
Desal-5[e]	28.9	27.6	0.96
NTR-729[f]	33.0	10.7	0.33
PZ[g]	50.7	23.8	0.47

[a] LMH = liters per square meter per hour; 1 MPa = 145 psi.
[b] Nitto Denko, Osaka, Japan.
[c] Film Tec/Dow, Midland, MI.
[d] Osmonics Inc., Minnetonka, MN.
[e] Desalination Systems, Inc., Escondido, CA.
[f] Nitto Denko.
[g] Fluid Systems, San Diego, CA.

Oleic acid model solutions. Flux and rejection of oleic acid–methanol solutions for two of the membranes are shown in Figures 4 and 5. Flux increased linearly with pressure and decreased with increasing concentration of oleic acid. The Desal-5 membrane showed little effect of pressure on rejec-

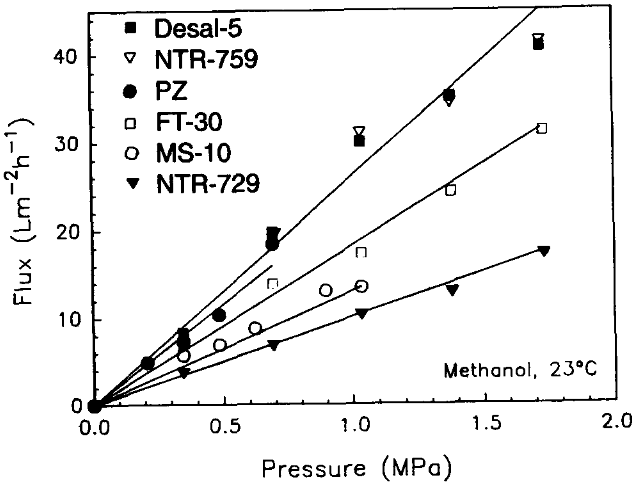

FIG. 3. Effect of transmembrane pressure on flux of methanol for selected membranes at 23°C (1 MPa = 145 psi); Desal-5 (Desalination Systems, Inc., Escondido, CA); NTR-759 (Nitto Denko, Osaka, Japan); PZ (Fluid Systems, San Diego, CA); FT-30 (Film Tec/Dow, Midland, MI); MS-10 (Osmonics Inc., Minnetonda, MN); NTR-729 (Nitto Denko).

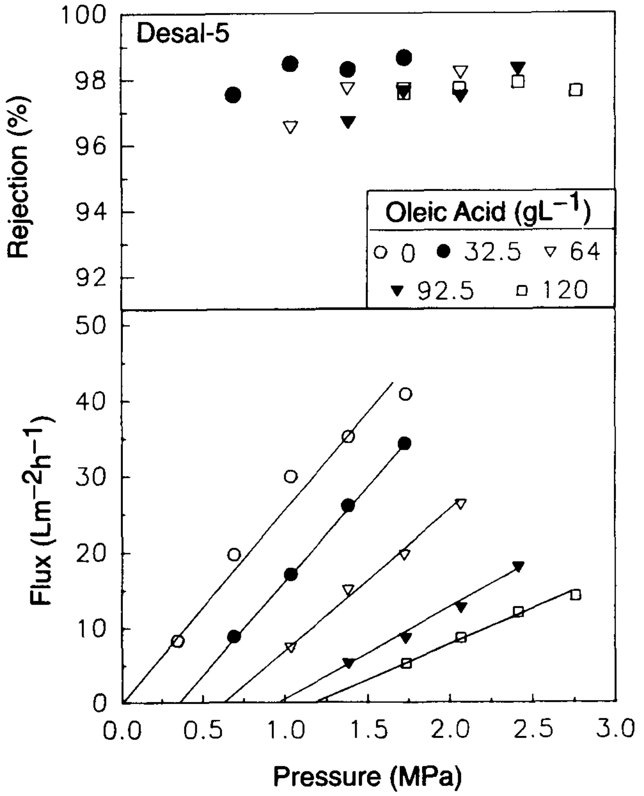

FIG. 4. Performance characteristics of the Desal-5 membrane with oleic acid–methanol solutions. Effect of pressure on flux (bottom graph) and rejection (top graph) at 25°C. The variable in the graph is concentration of oleic acid in solution (1 MPa = 145 psi). See Figure 3 for company source address.

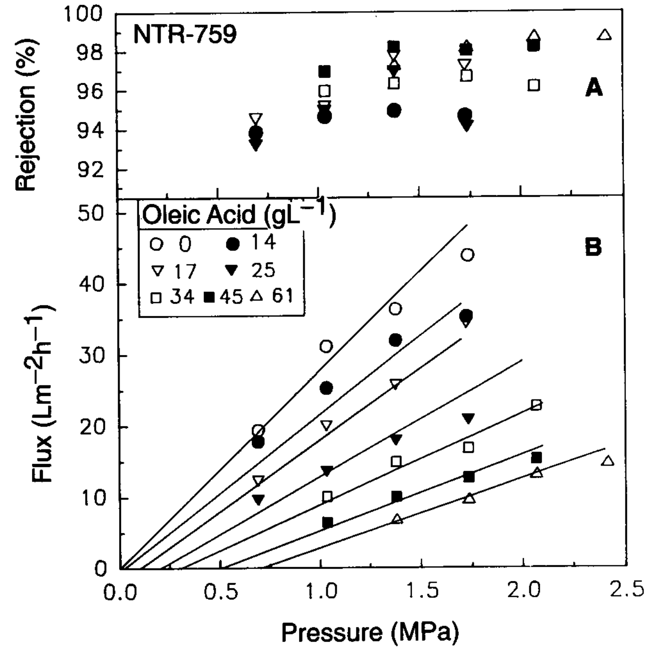

FIG. 5. Performance characteristics of the NTR-759 membrane with oleic acid–methanol solutions. Effect of pressure on flux (B) and rejection (A) at 25°C. The variable in the graph is concentration of oleic acid in solution. See Figure 3 for company source address.

tion, and the NTR-759 membrane showed a slight increase in rejection of oleic acid with pressure. Figure 6 shows the effect of oleic acid concentration on rejection. The Desal-5 and NTR-759 membranes had high rejections (HR) (>90%), and the MS10 had the lowest (~60%) of all membranes tested. In addition, rejection increased with oleic acid concentration. This increase in rejection could have been due to the formation of a fouling layer or dynamic secondary membrane (e.g., due to concentration polarization), which hindered the passage of solute (5). These phenomena are not unexpected, based on RO theory (17).

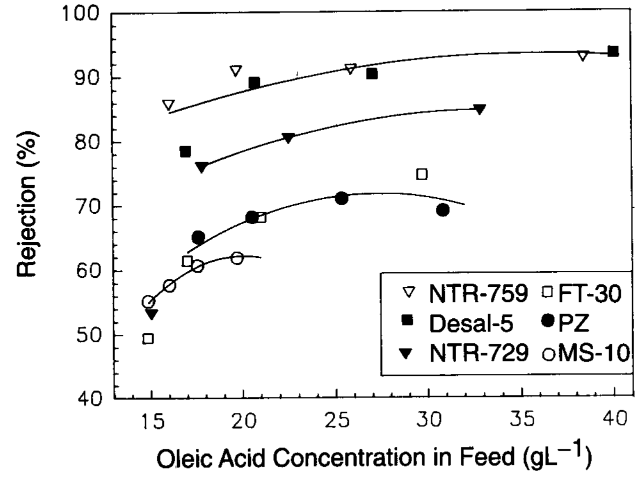

FIG. 6. Effect of oleic acid concentration on rejection of oleic acid for several membranes. The feeds were model solutions fo oleic acid in methanol at 25°C; pressure = 1.73 MPa (250 psi). See Figure 3 for company source addresses.

Mixed fatty acids model solutions. Figure 7 shows the behavior of a model solution of mixed fatty acids in methanol. Both membranes allowed less than 1 gL^{-1} of the fatty acids to permeate, equivalent to >95% rejection for both acids. Linoleic acid (MW = 281) and oleic acid (MW = 282) are structurally similar except for a double bond at the C_{12} position; thus their similar behavior was not unexpected and suggested that separation of FFA in methanol by a membrane appears to be a size-exclusion phenomenon.

Simulated crude vegetable oil. Fatty acid rejections are shown in Figure 8 for the model crude soybean oil, containing a single added FFA (oleic acid), and in Figure 9 for the mixed FFA (added linoleic and oleic acid). The membranes rejected >90% of the fatty acids. The methanol extract also

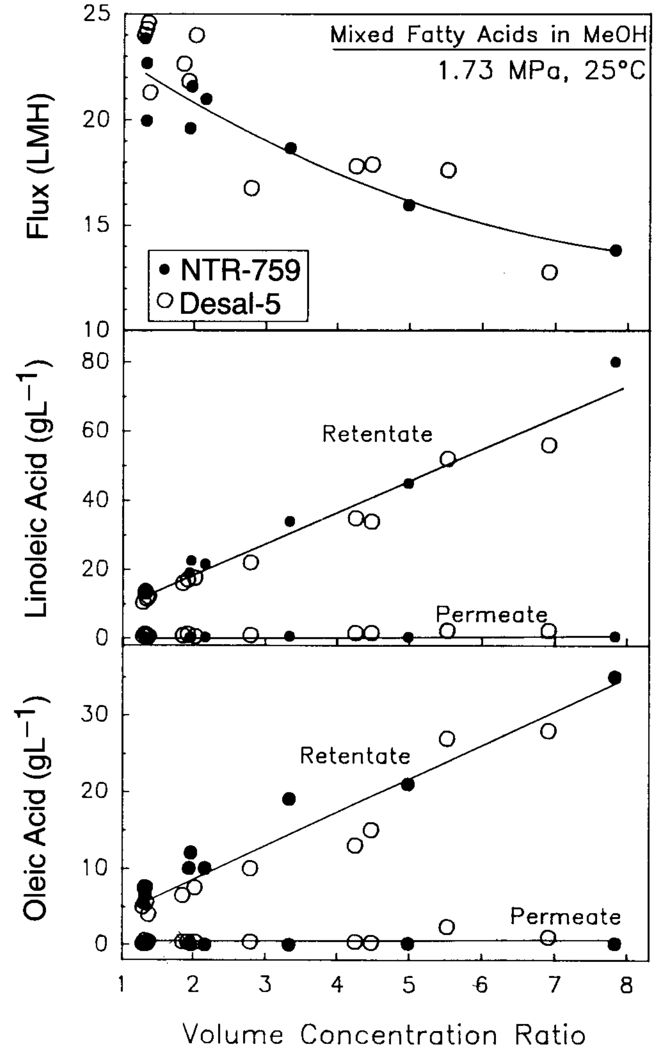

FIG. 7. Performance of Desal-5 and NTR-759 membranes with solutions of mixed fatty acids in methanol [data obtained at 1.73 MPa (250 psi) and 25°C; volume concentration ratio = initial volume/retentate volume]. See Figure 3 for company source addresses.

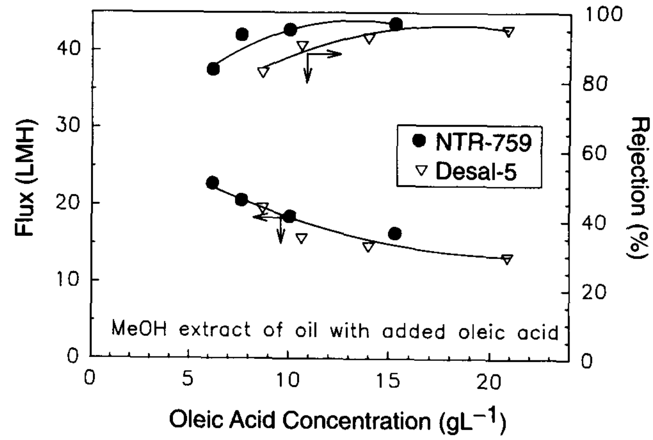

FIG. 8. Performance of Desal-5 and NTR-759 membranes with a methanol extract of simulated crude oil containing added oleic acid [data obtained at 1.73 MPa (250 psi) and 25°C]. See Figure 3 for company source addresses.

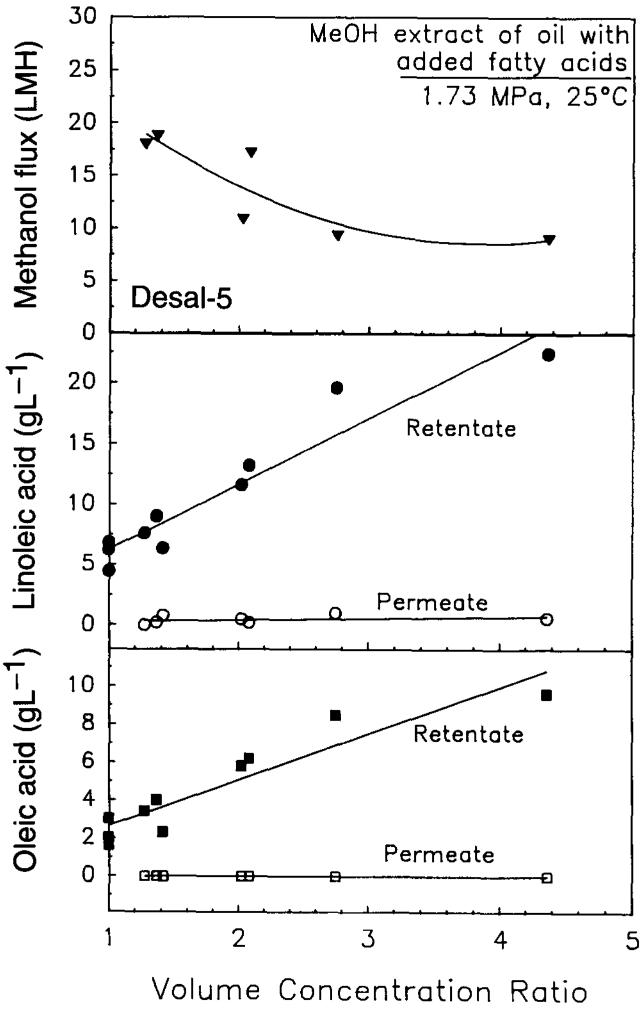

FIG. 9. Performance of Desal-5 membrane with a methanol extract of simulated crude oil containing added mixed fatty acids [data obtained at 1.73 MPa (250 psi) and 25°C]. See Figure 3 for company source address.

contained traces of triglycerides (4.5 gL^{-1}). However, the permeate contained only 0.15 gL^{-1} of triglycerides (18).

Process design. When flux vs. concentration data are plotted on a semilog scale (Fig. 10), a straight line can be fitted to the data, a relationship that is commonly observed in membrane separations (5,17). The limiting concentration depends on the rejection properties of the membrane. The NTR-759 and Desal-5 are HR membranes, rejecting >90% of the FFA. At 1.73 MPa (250 psi) pressure, they concentrated oleic acid to a maximum of 90 and 120 g/L oleic acid, respectively, before the flux reduced to zero. This decrease in flux was probably due to higher osmotic pressure with increased concentration. When the osmotic pressure of the retained solute equals the applied pressure, flux is zero (17). Higher flux and higher limiting concentrations can be obtained if the membranes are operated at higher pressures.

On the other hand, much higher concentrations can be obtained with low rejection membranes, e.g., MS10. Owing to the low rejection (~60%), the osmotic pressure difference across the membrane is lower, resulting in higher fluxes for the same feed concentration. Concentrations as high as 500 gL^{-1} were obtained before the flux became too low with the MS10 membrane. On the other hand, the FT-30 and PZ membranes displayed undesirable combinations of properties (low flux and low rejection of oleic acid) (18).

If a low rejection membrane is used to recover FFA in a membrane deacidification process, the permeate cannot be recycled to the extractor because of its high FFA content. On the other hand, high oleic acid concentrations cannot be obtained by using an HR membrane, but its permeate can be recycled to the extractor. A possible way to overcome both limitations is to use a combination of low rejection and HR membranes (Fig. 11).

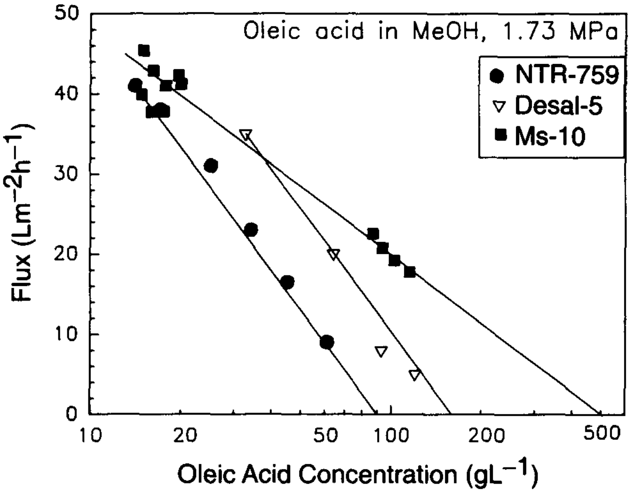

FIG. 10. Effect of fatty acid concentration on flux of model solutions with high-rejection membranes (Desal-5 and NTR-759) and a low-rejection membrane (MS-10) [data obtained at 1.73 MPa (250 psi) and 25°C]. See Figure 3 for company source addresses.

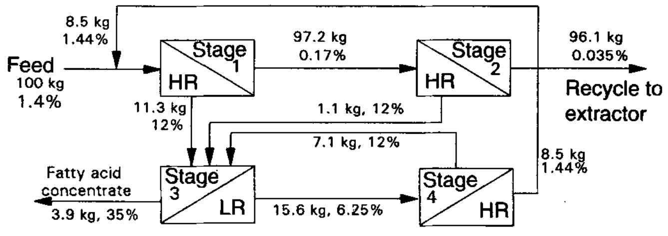

FIG. 11. Conceptual design of a membrane deacidification system for vegetable oils, incorporating high-rejection (HR) and low-rejection (LR) membranes.

Assuming the FFA concentration in the extractant (methanol) is 14 gL^{-1} for an oil containing 20 gL^{-1} FFA, a conceptual design of the membrane refining system would use a HR membrane (e.g., Desal-5 at ~3.5 MPa) in the first stage to concentrate the FFA from 14 to 120 gL^{-1}. The permeate from this stage is concentrated in a second stage (Stage 2) to 120 gL^{-1} by using an HR membrane. The permeate from Stage 2 has a low level of FFA (~0.35 gL^{-1}), which can be recycled to the extractor. The retentate streams from the HR membranes are now passed through an low rejection membrane (Stage 3 in Fig. 11). Permeate from the low rejection membrane is pressurized through another HR membrane, whose permeate is recycled to the feed stream of Stage 1, while its retentate is sent to Stage 3. The final products from this system are a concentrated FFA solution (350 gL^{-1}) and almost pure solvent. The net yield of FFA is estimated to be 97.5% of the FFA in the feed, and 96% of the solvent is recycled. The little solvent that goes out with the FFA concentrate can be evaporated and also recycled, if necessary.

In summary, there appears to be good potential for the use of membrane technology in deacidifying vegetable oils. An advantage of this concept is that it approaches a "zero discharge process." All the streams within the membrane process are recycled, and little is discharged as effluent. However, this was a bench-top feasibility study with a model crude vegetable oil, primarily for the purpose of screening membranes and evaluating the concept. Other trace components, normally found in crude vegetable oil (gums, color compounds, etc.), could affect the performance of the extraction and/or membrane systems. The dissolved methanol in the triglycerides fraction will have to be removed (e.g., by deodorization). In addition, there is a loss of triglycerides to the FFA stream, although this is less than with conventional refining. Pilot-scale experiments with actual crude vegetable oils will be needed to address these issues and to obtain design data to evaluate the economics of the process.

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