Deacidification of Soybean Oil Using Supercritical Fluid and Membrane Technology

W.E. Artz[a,*], T. Kinyanjui[b], and M. Cheryan[a]

[a]Department of Food Science and Human Nutrition, University of Illinois, Urbana, Illinois, and
[b]Department of Chemistry, Egerton University, Nkuru, Kenya

ABSTRACT: Membrane processing has been used for oil purification, but low flux and membrane instability are major impediments. A technique that combines membrane processing and supercritical CO_2 was investigated. A specialized, high-pressure, dead-end membrane cell was designed, fabricated, and connected to two ISCO (Lincoln, NE) supercritical fluid extraction (SFE) systems. The cell has a base with a grooved bottom for permeate removal, plus a porous metal disc for membrane support; a cell body with threaded connections; and a cap with an inlet assembly. One SFE pump provided the appropriate pressure on the feed stream, the second maintained pressure on the permeate at a slightly lower pressure. The sample consisted of 50% TAG and 50% FFA. For example, for separations at 45°C and a transmembrane pressure of 7 atm, the β (selectivity factor) values (TAG, FFA) for the SE and BW membranes were 0.56, 3.63 and 0.60, 2.63, respectively, whereas the β values (TAG, FFA) for the DK and NF90 membranes were 0.58, 1.37 and 0.70, 1.28, respectively.

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The worldwide annual production of vegetable oil is estimated to have exceeded 100 million tons in the harvest year 2003–2004 (1). The method selected to refine crude oil/fat depends on the crude oil quality, oil acidity, and environmental restrictions within which the processing is done. Physical refining can be applied to almost any oil, but chemical refining has the advantage of assisting in the removal of a wide range of undesirable, but sometimes valuable, components (2).

Supercritical CO_2 (SC-CO_2), at relatively moderate densities and temperatures, is an excellent solvent for nonpolar solutes, including fats and oils. Most importantly, it has a viscosity that is almost two orders of magnitude less than fats, oils, or solvents, suggesting that through dilution of the lipid mixture, an improvement in solute flux through the membrane can be attained (3). The advantages of using supercritical solvents include the ability to easily control the solvating capacity of the supercritical fluid with changes in the system pressure and/or temperature. SC-CO_2 also has several other characteristics that make it very useful for food processing: It is nontoxic, inert, relatively inexpensive, and readily available (4).

*To whom correspondence should be addressed at Dept. FSHN, 382 Agr. Eng. Sci. Bldg., 1304 W. Pennsylvania Ave., University of Illinois, Urbana, IL 61801. E-mail: wartz@uiuc.edu

One of the primary limiting factors in the application of membrane technology to oil purification has been the low flux (or membrane throughput), which is partially due to viscosity of the oil/solvent mixture. In spite of the substantial viscosity limitations, there are several publications on membrane separations of fat and oil components. Using gas separation membranes, Snape and Nakajima (5) separated FFA and sunflower oil TAG. Similar work by Raman *et al*. (6) on vegetable oil showed a reduction in FFA concentration from 2.0% in the feed to 1.6% in the retentate. Membranes have been used for hexane recovery from a soybean oil/solvent mixture, as well as for refining oil and recovery of FFA from soybean and rice bran oil (7,8). Membrane technology has been used for fat/oil refining and for processing enzymatically modified fats and oils (5) and degumming of vegetable oil (9). Membrane processing of vegetable oil provides the possibility of energy savings and improved oil quality (10).

Sarrade *et al*. (11) used membrane processing with SC-CO_2 for separating a highly unsaturated fraction from less saturated TAG in fish oil, and for separating β-carotene from carrot seed oil. SC-CO_2 also has been used for reducing the viscosity and hence improving the flux rates of viscous organic liquids across membranes during regeneration of used industrial oil (petroleum-based) (12–14).

In this report, the results from a combined supercritical fluid/membrane separation technique for the deacidification of vegetable oil are presented. The first objective was to design and fabricate a high-pressure membrane cell, designed to withstand the pressures required for supercritical conditions (50°C and 100–400 atm). There are very few, if any, of these cells available commercially, since the membrane cells manufactured for research purposes are designed for use with solvents at much lower pressures (up to approximately 20 atm). The second objective was to measure the flux of the supercritical fluid through the membranes to determine the efficacy of the process in terms of flux. The third objective was to evaluate the membranes for their relative selectivity and durability during the separation process. Deacidification was used as the purification model method for the evaluation, although this process could apply, with the appropriate membranes and operating conditions, to degumming or any other oil refining steps. The fourth objective was to process an oil–supercritical carbon dioxide mixture through selected membranes and determine the extent of separation (i.e., rejection) of TAG and selected FFA.

MATERIALS AND METHODS

Samples and reagents. Soybean oil samples were obtained from ADM (Decatur, IL). The β-carotene, oleic and linoleic acid samples were obtained from Fisher Scientific (Pittsburgh, PA). All samples were refrigerated in the dark prior to use. The carbon dioxide used as a supercritical fluid was ~99.99% pure. All other reagents used were analytical grade reagents, unless indicated otherwise. The sample was a mixture of 50% soybean oil TAG and 50% FFA (as either oleic or linoleic acid).

System design. The supercritical fluid extraction (SFE)/membrane system consisted of two 100DX syringe pumps (ISCO Inc., Lincoln, NE) and two supercritical fluid extractors (Fig. 1). The system components included (i) a pump and extractor unit for the production of supercritical conditions, preheating of the fluid, and control of both pressure and temperature parameters; (ii) a specially designed high-pressure cell and membrane immersed in a controlled temperature water bath; (iii) a second permeate stream pump and extractor unit to provide the required backpressure, or transmembrane pressure (P_T), on the downstream or permeate side of the membrane, as well as to maintain the permeate stream at supercritical conditions, and (iv) a modifier solvent pump (for hexane delivery) incorporated into the system. The backpressure supplied on the permeate stream was low enough to allow flux or flow through the cell membrane, but sufficient to prevent membrane rupture, which occurred rapidly without the appropriate backpressure.

The feed pump unit contained a syringe pump, **FP**, with a volume capacity of 100 mL (Fig. 1). The carbon dioxide was drawn from a tank of supercritical fluid chromatography-grade carbon dioxide, **T1**. Check valves were installed (**CV1**, **CV2**, and **CV3**) to prevent fluid backflow. The pressurized fluid was heated and maintained at the desired temperature by the use of supercritical fluid extractor heating chamber, and temperature/pressure controllers, **H1** and **H2**. A modifier pump (**MP**) (for the hexane cosolvent delivery) was connected to the feed side of the cell, and its pressure and fluid flow were manipulated with the same controller as the feed pump after the fluids were mixed at the junction between the check valves **CV1** and **CV2**.

The permeate pump unit (Fig. 1) was a duplicate of the feed pump unit and consisted of an extractor and a 100DX-syringe pump (**PP** and **H2**). The unit was coupled to the cell so that the pump (**PP**) *via* the extractor (**H2**) pressurized the permeate side of the membrane at a slightly lower pressure than the feed unit (**FP**). This also helped maintain the permeate stream in supercritical conditions so that the solute in the permeate stream did not precipitate. Connected to the extractor (**H2**) was a heated (to ~100°C to further reduce the possibility of solute solidification/precipitation) capillary tube (polyimide-coated, fused-silica glass tubing, 100 μm in diameter and approximately 50 cm in length), which was connected to a sample vial for sample collection. The permeate stream flowed through the membrane, out of the cell and back to the extractor (**H2**), and then to the sample vial through the capillary tubing.

A specialized, high-pressure membrane cell (Fig. 2) was designed and fabricated at the University of Illinois, then coupled to two ISCO, Inc. SFE systems. The cell consisted of four major components: (i) a cap (**A**) connected to the delivery line from the extractor, (ii) the main body of the cell (**B**) with threaded connections for the base and cap. On the top and bottom of the cell,

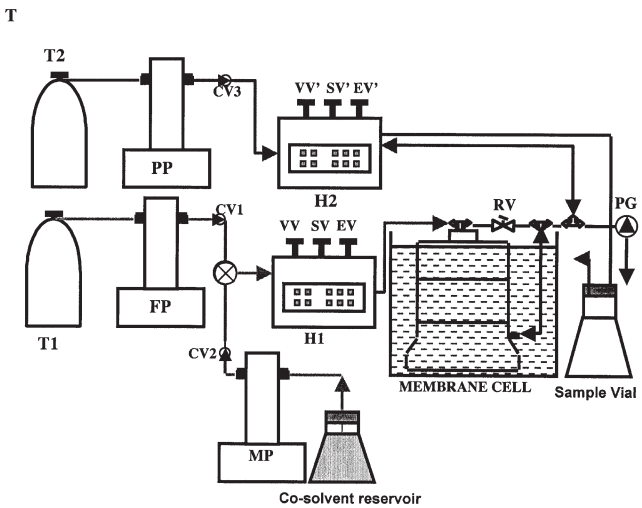

FIG. 1. The system diagram showing the fluid flow for the feed, retentate, and permeate streams. The components included (**T1, T2**) compressed carbon dioxide tanks, (**FP**) feed pump, (**PP**) permeate pump, (**H1, H2**) heated extractors, (**CV**) check valves, (**RV**) regulator valve, (**PG**) pressure gauge, (**SV**) supply valve, (**VV**) venting valve, (**EV**) extraction valves. Fluid flow starts at **FP**, then goes through **H1**, then the membrane cell, to **H2**, and finally the sample vial.

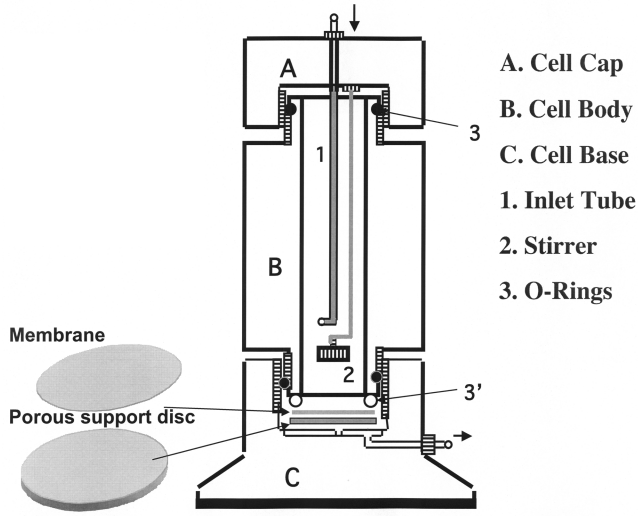

FIG. 2. The membrane cell cross-sectional view. The cell consisted of four major sections. The first was a cap (**A**) with a threaded connection for the delivery line from the extractor. The second was the main body of the cell (**B**), which was fitted with O-rings (**3** and **3′**) that were used to maintain the pressure inside the cell and hold the membrane in place under pressure. The third component was a base (**C**) with grooves across the bottom to allow the permeate to collect and flow along the grooves. The fourth component was a porous, stainless steel support disc that had been compressed to the appropriate pore size (10 mm), with a smooth fit within the cell diameter (4.75 cm and 0.14 cm thickness), which held and supported the membrane piece during processing.

O-rings (**3**) were used to maintain the pressure inside the cell. An additional O-ring (**3'**) was used in the bottom of the main body to hold the membrane in place and ensure that the oil/SC-CO_2 mixture flowed only through the membrane. The third component (iii) was a base (**C**) to hold the porous support disk and membrane. The base had small grooves cut across the bottom to allow the permeate to collect and then flow toward the exit line in the center. The base was connected to an exit line or tubing that carried the permeate out of the cell to the extractor, **H2**. The fourth component (iv) was a porous stainless steel support disc with an approximate pore size of 10 μm, a diameter of 4.75 cm, and a thickness of 1.4 mm, which held and supported the membrane during processing.

System operation. Previous work on oil component solubility indicated that good solubility for the oil components could be obtained at 306 atm pressure and a temperature of 45°C (15). In addition, experiments with 10% hexane (vol/vol) were used to determine whether this enhanced the selectivity of the membranes. Operational parameters were specified within the limitations of the available membranes in terms of pressure and temperature.

Samples of model oil were prepared by mixing commercial soybean oil with FFA (either oleic or linoleic acid) in the appropriate ratios. The membranes were cut and pretreated in 50% ethanol to condition them and remove the preservative used during shipment and storage. The membrane was then allowed to dry for a few minutes and then secured into the membrane cell (Fig. 2).

Flux across the membranes was evaluated by first passing pure supercritical fluid through the membranes for 1 h and observing the change of flux as a function of P_T and time. A dead-end cell mode was used. In this case the flow of the feed stream was perpendicular to the surface of the membrane as opposed to the cross-flow mode in which the feed stream runs parallel to the membrane surface.

The system was pressurized after filling the two pumps and allowing the cell to equilibrate in the heated water bath. Both the feed and permeate units were set to the same pressure. Valves **EV** and **RV** were opened to pressurize both sides of the membrane simultaneously with SC-CO_2 fluid from the feed unit. Then valve **RV** was closed and valve **EV'** on extractor **H2** opened. The pressure on both sides of the membrane was allowed to equilibrate. The feed stream unit was then set to a slightly greater pressure than the permeate pump unit, so that the target P_T was obtained. Valves **SV** and **EV** were closed and the feed unit depressurized *via* valve **VV** to access the extraction cell chamber. The sample was introduced into the extraction cell chamber of **H1**, and the relative percentages or amounts of SC-CO_2 and modifier or hexane co-solvent were set. The system was pressurized again and separation was completed.

Inside the cell, a stainless steel inlet tube (**1**) delivered the sample to a position immediately above the magnetic stirrer (**2**). The stirrer was used to reduce concentration polarization. Permeate was collected through a capillary tube connected to the extractor (**H2**) *via* valve **EV'**. The driving force for permeate production was the pressure difference between the two units.

The effective flux determination. The effective flux through each membrane was measured using the combined supercritical fluid/membrane system. To measure the effective flux, the flow rate of the permeate was measured, and the effective flux was calculated by dividing the flow rate of the permeate by the area of the membrane surface exposed to the feed. The effective flux measurements were made in duplicate for each membrane. The effective flux was measured in the first 5 min (a pseudo initial flux method). This avoided the effect of compaction of the membrane surface due to the high pressures applied (up to 374 atm). The membranes used in these experiments are generally used for liquid applications at much lower pressures. A few custom-made membranes are available for supercritical work, but they are manufactured for specific purposes and equipment designs and were not appropriate for these experiments.

The extent of separation after membrane processing was determined using high-performance size exclusion chromatography (HPSEC) (16). The HPSEC system consisted of an HP drive module (Rainin Instruments Co., Woburn, MA) and an autosampler, model 728 (Alcott Chromatography, Norcross, GA). Five HPSEC Phenogel columns (Phenomenex, Torrance, CA) were connected in series to an ELSD (ELSD II A; Varex Corp., Burtonsville, MD). The detector was operated at the following conditions: adjusted temperature at 100°C, heater temperature at 99°C, exhaust temperature at 50°C; ultra-high purity nitrogen (99.99%) gas was used at a ball flow meter set at 39 mm, pressure at 10.5 psi, range 20 and time constant at 0.5. The mobile phase was THF, which was filtered through a 0.45 μm HV disc (Millipore Corp., Bedford, MA) and degassed by sonication. The flow rate was 1.0 mL/min, and each run was 55 min.

Standard curves were generated for the FFA and the TAG. The relative amounts of FFA and TAG in the retentate and permeate were then obtained by identification of the peaks using the relative retention times and the standard curves.

The samples were accurately weighed and then diluted to a concentration of approximately 2 mg oil/mL of THF. The samples were filtered through 0.22 μm HV discs before injection.

Crude degummed soybean oil (ADM, Decatur, IL) was winterized and then decanted. The oil was then processed through the membrane and the level of deacidification determined.

β-Carotene (400 ppm) was added to the oil and processed through the membranes. A small amount of hexane was used to dissolve the carotene prior to oil addition. The samples were then membrane processed using the same methods as the TAG and FFA samples. The concentration of β-carotene in the permeate stream and the retentate was determined based on the absorbance at 436 nm and a standard curve.

Experimental design and statistical analysis. The results represent the means of duplicate values collected in duplicate experiments. The data sets were analyzed statistically using Statistical Analysis System software (SAS Institute, Cary, NC) using the Generalized Linear Model procedures to determine if there were differences between treatments.

RESULTS AND DISCUSSION

Several nanofiltration (NF) and reverse osmosis (RO) membranes were screened for stability and performance. Some of the membranes provided promising results in terms of withstanding the pressure without collapse or rupture. These included DK, a thin film polyamide membrane with a M.W. cutoff (MWCO) of 200–300 Daltons, and SE (MWCO ≈ 100), a thin film composite polyamide membrane with a polysulfone base (Osmonics, Inc., Vista, CA). Other membranes with good results included NF90 (MWCO ≈ 200) and BW (RO with MWCO < 100), which were made of polyamide amine (FilmTec, Inc., Minneapolis, MN). MWCO is defined as the smallest M.W. species for which the membrane has more than 90% rejection (10).

Figures 3 and 4 show the SC-CO_2 flux through each membrane. The DK membrane had a significantly greater flux than the other membranes ($P < 0.05$). This was expected since it had the highest MWCO of approximately 250 Da. The NF90 membrane had a comparable MWCO, but the flux was lower than the DK especially at low P_T (3–9 atm). Both membranes (DK and NF90) had an increase of flux with an increase in the P_T. The rate of flux is greater at lower P_T than at higher values, which could be due to compaction of the membrane and concentration polarization as the pressure increased at the surface of the membrane. This is especially a problem with the dead-end cell membrane design (17).

Within the range of 5 to 10 atm of pressure differential, the DK membrane showed a flux increase of about 30%, whereas the NF90 had an increase of approximately 50% (Fig. 3). The fluxes obtained for the DK and NF90 membranes were greater than the fluxes obtained with liquid hexane at similar P_T, but without supercritical conditions (6). The relatively greater flux observed with supercritical fluids, as compared with normal solvents, is most likely due to the much lower viscosity of the supercritical fluids. The average flux for the four membranes was approximately 85 liters per meter squared per hour (LMH).

Reverse osmosis of edible vegetable oil by Sridhar and coworkers (18) required much higher feed pressures (70 atm) to produce a flux comparable with that attained (70 LMH) for pure water. As a comparison, since the permeate pressure is atmospheric pressure, the feed pressure for nonsupercritical membrane systems would be the same as the P_T reported in these experiments.

Comparison of data in this field (membrane processing/SC-CO_2) can be difficult, since the methodologies and equipment used by various researchers differ substantially and there are few data sets available for comparison. Even when available, the equipment used often differs and can be much larger (pilot or industrial) than that used in the laboratory.

There was a reduction in flux with time for all four membranes tested (Figs. 5, 6). At the lower P_T (7 vs. 14 atm) there was a drop in flux for the DK and NF90 membranes of approximately 50% after 1 h. The SE and BW membranes showed a decrease in flux of approximately 42% (Fig. 5). There were significant differences in the initial flux, especially for the DK membrane relative to the other three membranes ($P < 0.05$). The flux dropped rapidly with time, and all four membranes had a much lower flux after 1 h. The final values ranged from 20 (BW) to 45 LMH (DK). Several factors can contribute to the decay in flux with time, including fouling, compaction, and the formation of a concentration gradient (17). A greater P_T should ideally increase the flux, but in these experiments it did not.

An additional reason for the drop in flux could be membrane compaction caused by the high pressures used. An increase in the P_T resulted in an increase in the flux decay rate (Fig. 6). All four membranes showed more rapid decreases in flux at 14 atm of P_T than at 7 atm of pressure, suggesting membrane compaction. An average flux reduction of 65% for the four membranes was observed over a period of 1 h. Others have made similar observations regarding the drop in flux with time

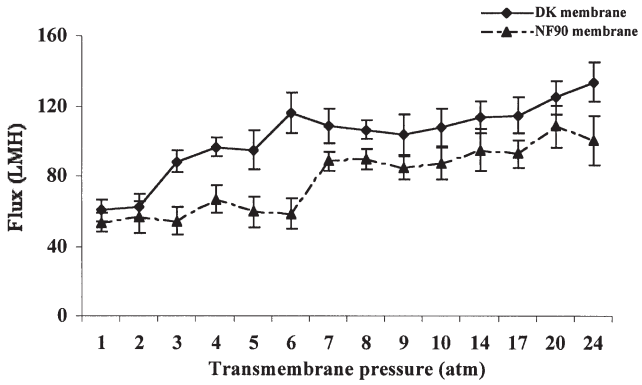

FIG. 3. Effect of transmembrane pressure on the flux (liters per square meter per hour, LMH) for the DK and NF90 membranes (M.W. cutoff between 150 and 300) at a temperature of 45°C. Each data point and error bar represents the average ± the SD. NF90, a nanofiltration membrane having a M.W. cutoff of 200 Daltons (FilmTec, Minneapolis, MN); DK, a thin film polyamide membrane with a M.W. cutoff of 200–300 Daltons (Osmonics, Inc., Vista, CA).

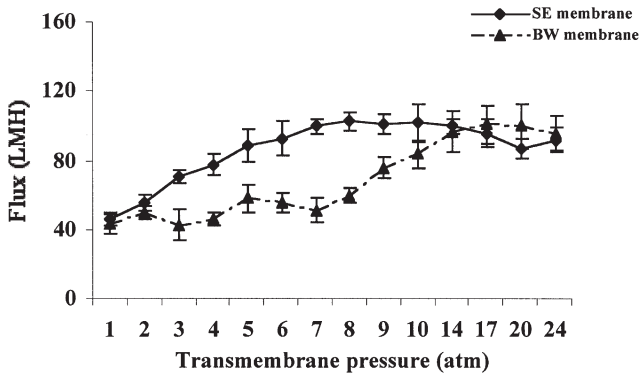

FIG. 4. Effect of transmembrane pressure on the flux for SE and BW membranes (M.W. cutoff ≤ 100) at a temperature of 45°C. Each data point and error bars represents the average ± SD. SE (M.W. cutoff ≈ 100), a thin film composite polyamide membrane with a polysulfone base (Osmonics, Inc., Vista, CA); BW, reverse osmosis (RO) membrane with M.W. cutoff < 100, which was made of polyamide amine (FilmTec, Inc., Minneapolis, MN). For other abbreviation see Figure 3.

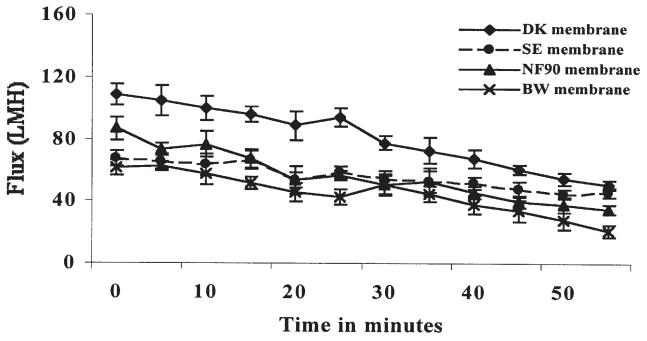

FIG. 5. The decay of the flux (LMH) with operation time for the four membranes (NF and RO) at 7 atm transmembrane pressure (PT) and 45°C. Each data point and error bars represent the average ± SD. For abbreviations see Figures 3 and 4.

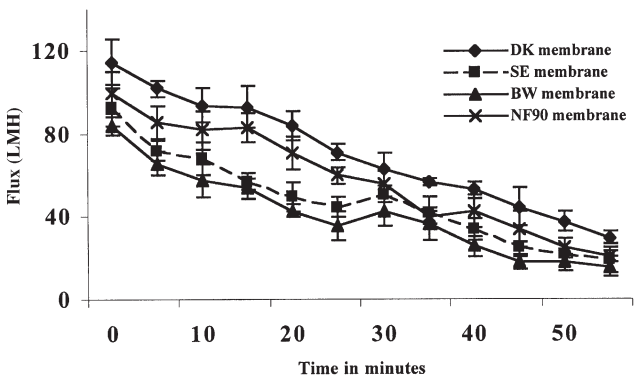

FIG. 6. The decay of the flux (LMH) with operation time for the four membranes (NF and RO) at 14 atm PT and 45°C. Each data point and error bars represent the average ± SD. For abbreviations see Figures 3–5.

(11,17,19,20). Luthra *et al*. (19) noted a drop in flux from 23 to 15 LMH in 120 min for pure toluene at 30 atm of pressure.

The membranes were evaluated for their effectiveness for separating TAG from FFA. An ideal membrane would be one that allows all of the FFA to pass through the membrane, while retaining or rejecting all of the TAG. A high retention for the TAG and a low retention for FFA would be desirable.

A selectivity factor (β), previously defined by Sarrade *et al*. (11), was used to compare the retentate and permeate compositions, where $\beta = \%X_P/\%X_R$ and $\%X_P$ is the mass percentage of the component X in the permeate and $\%X_R$ is the mass percentage of the component in the retentate. A β value that is less than one for a given component indicates that the membrane significantly retains the component, whereas a β value greater than one for a component indicates that it permeates more through the membrane. An ideal membrane in this case would be one with a low β value for TAG and a high β value for FFA. The SE and BW membranes had better TAG/FFA separation (selectivity) characteristics than the DK and NF90 membranes. For example, for separations at 45°C and a P_T of 7 atm, the β values (TAG, FFA) for the SE and BW membranes were 0.56, 3.63 and 0.60, 2.63, respectively, whereas the β values (TAG, FFA) for the DK and NF90 membranes were 0.58, 1.37 and 0.70, 1.28, respectively. Although the NF90 membrane had a comparatively low selectivity, similar to the DK membrane, one important factor was the membrane stability at high pressures. The NF90 and BW maintained their structural integrity better than the DK and SE membranes. Experiments completed at 7 and 14 atm P_T indicated that improved membrane integrity (less tearing and failure) was achieved at the lower P_T of 7 atm, rather than at the higher P_T.

Several sequential separations were completed to simulate one of the normal industrial modes of operation in which the retentate is recycled. The approximate retentate concentration ratio after each stage of processing was used as the feed concentration for the succeeding run. Multiple stage processes are typical in industry. The permeate stream would also need to be processed similarly to maximize TAG recovery and purity. Using this mode, it may be possible to reduce the FFA concentration in the retentate stream from 50% to ~1% with approximately seven successive runs (Table 1) for the NF90 membrane. A reduction of the FFA in the retentate stream from 50% to ~1% can be achieved in about five runs using the BW membrane (Table 2), which was a reverse osmosis membrane. The results indicate that a sequential separation could be effective for the removal of FFA from vegetable oil with the appropriate membrane under the appropriate combinations of temperature and pressure.

In another experiment, a crude soybean oil sample with FFA was processed using two different membranes. A single run of the feed reduced the FFA concentration from 2.9 to 0.8%, and from 3.3 to 0.6% in the retentate for the membranes NF90 and BW, respectively. There was no observable enhancement in selectivity when hexane was used as a co-solvent. The use of hexane, however, enhanced the solubility of the oil in the supercritical fluid.

β-Carotene is a valuable co-product that one would like to remove and concentrate, if possible. Oil color is also an important quality parameter for finished vegetable oil products. Colored

TABLE 1
Separation of TAG/FFA with SC-CO_2 and NF90 Membranes Using Consecutive (multistage) Membrane Processing[a]

Feed concentration % (TAG/FFA)	Sample[b]	%TAG	%FFA
50:50	P[b]	38 ± 2	62 ± 2
	R	59 ± 1	42 ± 3
60:40	P	56 ± 3	44 ± 2
	R	72 ± 3	28 ± 2
70:70	P	63 ± 2	38 ± 1
	R	76 ± 3	24 ± 4
80:20	P	81 ± 1	19 ± 1
	R	91 ± 1	9 ± 1
90:10	P	86 ± 1	14 ± 2
	R	94 ± 2	6 ± 1
95:5	P	96 ± 1	4 ± 1
	R	99 ± 1	1 ± 1

[a]The temperature was 45°C and the transmembrane pressure (PT) used was 7 atm. The values represent averages ± SD.
[b]P and R refer to the permeate and retentate, respectively. SC-CO_2, supercritical carbon dioxide; NF90, a nanofiltration membrane having a M.W. cutoff of 200 Daltons (FilmTec, Minneapolis, MN).

TABLE 2
Separation of TAG/FFA with SC-CO_2 and BW Membranes Using Consecutive (multistage) Membrane Processing[a]

Feed concentration % (TAG/FFA)	Sample[b]	%TAG	%FFA
50:50	P	48 ± 3	53 ± 2
	R	80 ± 3	19 ± 4
80:20	P	71 ± 5	29 ± 3
	R	87 ± 4	13 ± 1
86:14	P	78 ± 4	22 ± 3
	R	91 ± 2	9 ± 4
90:10	P	88 ± 2	12 ± 3
	R	95 ± 2	5 ± 1
95:5	P	94 ± 1	6 ± 1
	R	99 ± 0	1 ± 0

[a,b]For footnotes, see Table 1; BW membrane, a reverse osmosis membrane with a M.W. cutoff < 100 Daltons (FilmTec, Minneapolis, MN).

materials, such as carotenoids, are removed to enhance oil appearance, generally by adding bleaching clay/earth to the oil and then filtering the oil. Carotenoids were concentrated slightly in the retentate stream and reduced in the permeate. The retentate and permeate concentrations were, respectively, 476 ± 19 and 371 ± 16 ppm for the membrane BW and 423 ± 9 and 382 ± 7 ppm for the membrane NF90. The relatively small changes in concentration indicate that it would be difficult to separate carotenoids from TAG using supercritical fluids and the membranes examined in this series of experiments. This was expected, since the M.W. of TAG and carotene are similar. However, the results do demonstrate that the procedure could be used to concentrate the β-carotene in the oil, given sufficient recycling, although the use of more selective membranes would be preferable.

The combination of supercritical fluids and membrane separation has the potential for oil purification with careful control of all the parameters and customization of the membranes for this particular application. The P_T must be carefully controlled to ensure membrane integrity when working at the high pressures associated with supercritical fluids. The results obtained suggest that the combined technique of supercritical fluid and membrane separation can be successfully used for deacidification of vegetable oil. A recycling mode can be particularly useful for purification of crude oil. Oil solubility is enhanced by the use of a co-solvent (modifier), but it did not increase the selectivity of the membranes for the oil components.

Membranes with the higher MWCO had greater fluxes (DK and NF90), but selectivity and resistance to rupture were the most important factors in determining the membrane efficacy. The reverse osmosis membrane (BW) had good selectivity for FFA and TAG and withstood the high pressures without breakage. The SE membrane had the best selectivity for the TAG/FFA mixture but ruptured more frequently at higher pressures, so it was not used for the multistage processing experiments.

REFERENCES

1. Gunstone, F.D., Early Forecasts for World Supplies of Oilseeds and Vegetable Oil in 2003–04, *inform 14*:668 (2003).
2. De Greyt, W., and M. Kellens, Refining Practice, in *Edible Oil Processing,* edited by H. Wolf and R.J. Hamilton*,* CRC Press, Boca Raton, Florida, 2000, pp. 190–199.
3. Verkerk, A.W., E.L.V. Goetheer, L.J.P. van den Broeke, and J.T.F. Keurentjes, Permeation of Carbon Dioxide Through a Microporous Silica Membrane at Subcritical and Supercritical Conditions, *Langmuir. 18*:6807–6812 (2002).
4. Jimmy, S.L., K. Liong, S. Gugdial, and N. Foster, Solubility of Cholesterol in Supercritical Carbon Dioxide, *Ind. Eng. Chem. Res*. *30*:2476–2482 (1991).
5. Snape, J.B., and M. Nakajima, Processing of Agricultural Fats Using Membrane Technology, *J. Food Eng. 30*:1–15 (1996).
6. Raman, L.P., M. Cheryan, and N. Rajagopalan, De-acidification of Soybean Oil by Membrane Technology. *J. Am. Oil Chem. Soc. 73*:219–224 (1996).
7. Raman, L.P., M. Cheryan, and N. Rajagopalan, Solvent Recovery and Partial De-Acidification of Vegetable Oils by Membrane Technology, *Fett/Lipid 98*:10–14 (1996).
8. Kale, V., S.P.R. Katikanen, and M. Cheryan, De-acidifying Rice Bran Oil by Solvent Extraction and Membrane Technology, *J. Am. Oil Chem. Soc. 76*:723–727 (1999).
9. Subramanian, R., S. Ichikawa, M. Nakajima, T. Kimura, and T. Maekawa, Characterization of Phospholipids Reverse Micelles in Relation to Membrane Processing of Vegetable Oils, *Eur. J. Lipid Sci. Technol. 103*:93–97 (2001).
10. Lin, L., K.C. Rhee, and S.S. Koseoglu, Bench-Scale Membrane Degumming of Crude Vegetable Oil: Process Optimization, *J. Membrane Sci. 134*:101–108 (1997).
11. Sarrade, S.J., G.M. Rios, and M. Carles, Supercritical CO_2 Extraction Coupled with Nanofiltration Separation Applications to Natural Products, *Sep. Purif. Technol. 14*:19–25 (1998).
12. Sarrade, S.J., L. Schrive, D. Gourgouillon, and G.M. Rios, Enhanced Filtration of Organic Viscous Liquids by Supercritical CO_2 Addition and Fluidification. Application to Used Oil Regeneration, *Ibid. 25*:315–321 (2001).
13. Ohya, H., T. Higashijima, Y. Negishi, Y. Tsuchiya, and H. Tokunaga, Separation of Supercritical CO_2 and Iso-octane Mixtures with an Asymmetric Polyimide Membrane, *J. Membrane Sci. 84*:185–189 (1993).
14. Ohya, H., T. Higashijima, Y. Negishi, Y. Tsuchiya, H. Tokunaga, and M. Aihara, Separation of Supercritical Fluid Mixtures of CO_2 and Petroleum Components with an Asymmetric Polyimide Membrane, *Ibid. 93*:165–173 (1994).
15. Artz, W.E., T. Kinyanjui, and M. Cheryan, Solubility Optimization of Oil Components in Supercritical Carbon Dioxide, *J. Food Lipids 12*:91–102 (2005).
16. Artz, W.E., S.L. Hansen, and M.R. Myers, Heated, Fat-Based, Oil Substitutes, Oleic and Linoleic Acid Esterified Propoxylated Glycerol, *J. Am. Oil Chem. Soc. 74*:367–374 (1997).
17. Cheryan, M., *Ultrafiltration and Microfiltration Handbook*, Technomic Publishing, Lancaster, Pennsylvania, 1998, pp. 1–29.
18. Sridhar, S., A. Kale, and A.A. Khan, Reverse Osmosis of Edible Vegetable Oil Industry Effluent, *J. Membrane Sci. 205:*83–90 (2002).
19. Luthra, S.S., Y. Xiaojin, L.M. Freitas dos Santos, L.S. White, and A.G. Livingston, Homogeneous Phase Transfer Catalyst Recovery and Re-use Using Solvent Resistant Membranes, *Ibid. 201*:65–75 (2002).
20. Cheryan, M., *Ultrafiltration and Microfiltration Handbook*. Technomic Publishing, Lancaster, Pennsylvania, 1998, pp. 406–412.

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