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Deacidification of Soybean Oil Using Membrane Processing and Subcritical Carbon Dioxide

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Abstract Vegetable oils have been deacidified using supercritical carbon dioxide and membrane processing. However, the pressures required are substantially greater than those used in industry. Therefore, the feasibility of using subcritical carbon dioxide (at much lower pressures) and membrane processing to separate free fatty acids (FFA) from triacylglycerols (TAGs) was examined. First, FFA/TAG solubility tests were completed (10–25 °C and 68–136 atm). The oil samples were separated using a FilmTec NF90 or a FilmTec BW30 membrane in a dead-end type cell. Within the range examined, the greatest solubility for oleic acid was at 25 °C and 136 atm. For soybean oil TAGs, the greatest solubility was at 20 °C and 136 atm. However, for the separation of the two components, 20 °C and 68 atm was best among the condition combinations examined. The solubility of oleic acid ranged from 0.294 to 0.455 mg/mL in subcritical carbon dioxide, while the solubility of triacylglycerols ranged from 0.066 to 0.139 mg/mL. The FilmTec BW30 membrane provided significantly better separation of FFAs from TAGs than did the NF90 membrane. Both membranes were selective for oleic acid, although the BW30 had greater selectivity for oleic acid ($\beta_{\text{oleic acid}} = 2.12$, $\beta_{\text{TAGs}} = 0.24$) than the NF90 membrane ($\beta_{\text{oleic acid}} = 1.26$, $\beta_{\text{TAGs}} = 0.81$).

Keywords Oil refining · Membrane technology · Supercritical fluids

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Introduction

In 2002 the world's yearly production of oils and fats was ~117 million tons and ~80% was used for human consumption [1]. In the United States, one of the two largest soybean oil producers in the world, chemical refining is the most common method used to produce a high quality product. There are four major steps in the chemical refining process; degumming, deacidification, deodorization, and bleaching. Refining is designed to remove free fatty acids (FFA), phospholipids, mono- and diacylglycerols, and pigments. The removal of these components increases the shelf stability, palatability, visual appeal, and marketability of the product.

There has been considerable interest in finding alternative methods to refine oil [2]. During chemical refining, caustic soda and phosphoric acid are used, and their disposal has environmental and safety issues. In addition to the organic solvents and strong chemicals used, high temperatures and moderate pressures are used, which present additional safety and cost challenges. As a result, both capital and energy costs are high. Finally, the large amounts of waste water produced during deacidification require expensive treatment.

One potential solution is the use of pressurized liquid carbon dioxide as a processing solvent. Supercritical (SC–CO_2) and subcritical carbon dioxide (sub-CO_2) are non-flammable and non-toxic solvents. Oil solubility in subcritical and supercritical carbon dioxide varies as a function of the density and temperature. Both SC–CO_2 and sub-CO_2 have a viscosity significantly lower than the oil and organic solvents [3] and they are less expensive than organic solvents.

Fats and oils could be selectively extracted using pressurized fluids, but the capital costs are very high,

which makes this process unattractive economically. Research done by Artz et al. [4, 5] on the use of supercritical carbon dioxide in combination with membrane technology indicated that the technology shows promise for the deacidification of crude vegetable oil. However, the processing conditions required for supercritical fluids greatly exceed those normally used for membrane processing, which presents some difficult technical challenges.

The processing or extraction of oils (essential oils and petroleum based products) with subcritical pressurized carbon dioxide has been explored [6], including membrane processing to isolate the extract [7–9]. Selective extraction with subcritical carbon dioxide is used commercially. The advantages of subcritical carbon dioxide include many of those associated with supercritical carbon dioxide, with the added benefit that reduced temperatures and pressures are required. However, under these conditions solute solubility, particularly of non-volatile or more polar solutes, can be much less than in supercritical fluids. In some cases, this selectivity is preferable, in that only the desired group of easily extracted compounds (e.g., essential oils) is removed. The reduced temperature and pressure conditions would also reduce the capital costs needed to employ the technology. So far, no work has been published investigating the use of subcritical carbon dioxide for vegetable oil refining.

Membrane technology is a process that involves the use of a selective barrier, a membrane, to separate components [10]. Lin et al. [11] reported on a bench-scale membrane process for the degumming of crude vegetable oil. They achieved a 99.6% rejection of phospholipids with a flux of 26.8 liters per square meter per hour (LMH) at 300 psi (20.4 atm) and 40 °C using hexane. In this study, phospholipids were retained and the degummed oil comprised predominantly of triacylglycerols permeated or passed through the membrane.

Membrane technology has some technical limitations, such as membrane fouling. Another limitation is the flux reduction that occurs with fluids with a high viscosity, such as vegetable oils [12]. Supercritical or subcritical CO_2 can be used as a solvent to reduce the oil/solvent viscosity so that mass transfer rates are enhanced. Research has shown that supercritical CO_2 can increase the mass transfer rate by an order of magnitude [13]. Sarrade et al. [14, 15] examined and reviewed the use of nanofiltration and ultrafiltration with SC–CO_2 and found that SC–CO_2 improves viscous liquid permeation through the membrane.

In this report, the results from a combined subcritical fluid/membrane separation technique for the deacidification of vegetable oil are presented. The first objective was to evaluate the solubility of soybean oil components in subcritical carbon dioxide over a narrow range of temperatures and pressures to determine if sufficient TAG and FFA solubility exists. Next, the best combination of pressure and temperature to deacidify the soybean oil using membrane processing was determined. The final objective was to use subcritical carbon dioxide in combination with membrane technology to separate FFAs from TAGs, by comparing the FFA flux through selected membranes (BW30 and NF90) using subcritical carbon dioxide as the solvent.

Experimental Procedure

Samples and reagents. Generic soybean oil samples were obtained from a local supermarket. The oleic acid samples were obtained from Fisher Scientific (Pittsburgh, PA). All samples were held in the dark at room temperature (~25 °C). The carbon dioxide used as a subcritical fluid was ~99.99% pure from S. J. Smith (Urbana, IL). All other reagents used were analytical grade, unless indicated otherwise. The sample or model oil was a mixture of 60% soybean oil TAGs and 40% FFAs (oleic acid). A sample with a high percentage of FFAs was used to facilitate quantitative component analysis and to examine a "worst case" scenario.

System design. The system diagram is shown in Fig. 1. The system has been described in detail previously [4, 5] and the same equipment set-up was used with slight modifications, e.g., a co-solvent pump was not used in this experiment. A supercritical extractor SFX-210 and a 100DX syringe pump with 100 mL capacity (ISCO Inc., Lincoln, NE) and with temperature control and monitoring systems were used for the solubility and membrane studies. A stainless steel extraction cartridge with a volume of 10 mL was used (ISCO Inc., Lincoln, NE) was used. The solubility test set-up included a Brinkmann Lauda RM6

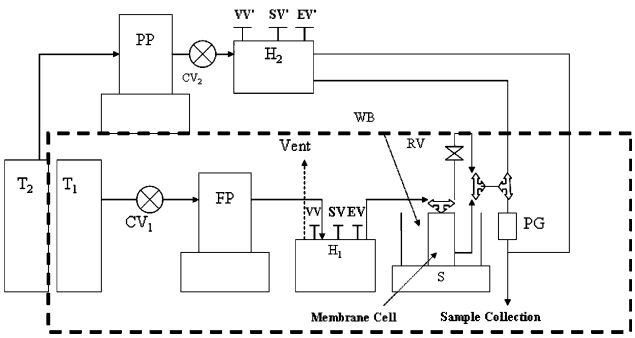

Fig. 1 Experimental setup diagram of the fluid flow for the feed, retentate, and permeate streams and solubility test setup (within the *dotted box*) [components included: carbon dioxide tanks (T_1, T_2), syringe pumps (*PP*, *FP*), check valve (CV_1, CV_2), extraction units (H_1, H_2), refrigerated bath (*WB*), magnetic stirrer (*S*), retentate-side valve (*RV*), pressure gauge (*PG*), and the extraction units and valves (VV', SV', EV'—H_2) and (VV, SV, EV—H_1)]

Super refrigerated water bath (Brinkmann, Westbury, NY) and membrane cell modified to hold the extraction cartridge/sample cell during the solubility test (Fig. 2a). The temperature was monitored with thermocouples.

Silica (SiO_2) based wet sample support (ISCO Inc., Lincoln, NE) was used to support the liquid oil/free fatty acid samples in the extraction cartridge to prevent pooling of the liquid in the bottom of the extraction cartridge/sample cell. This was done to avoid physically forcing the oil out of the extraction cartridge as a result of the pressure of the subcritical fluid, so only components soluble in the subcritical fluid were removed from the cell [4, 5].

The subcritical CO_2/membrane system (Fig. 1) consisted of two 100DX syringe pumps, two supercritical extractors (ISCO Inc., Lincoln, NE) and a Brinkmann Lauda RM6 Super refrigerated water bath (Brinkmann, Westbury, NY). Specifically, the system included (a) a pump, extractor unit, and a refrigerated water bath for the production of subcritical conditions, cooling the fluid and for control of both pressure and temperature parameters; (b) a high pressure cell containing the membrane immersed in a controlled temperature water bath; and (c) a second permeate stream pump and extractor unit to provide the required transmembrane pressure (P_T) on the permeate side of the membrane, as well as maintain the permeate stream in the selected subcritical conditions. The back pressure supplied by the permeate stream pump provided a pressure differential that was sufficient for good membrane flux, yet generally prevented membrane rupture and failure [4, 5]. If the membrane failed, the test data was considered invalid and that data was not used. When the membrane did survive, the experiment the data was used. The failure rate was not recorded so an estimate of the failure rate is unavailable.

The feed pump unit contained a 100DX syringe pump, FP, with a volume capacity of 100 mL (Fig. 1). The carbon dioxide was drawn from a tank of supercritical fluid chromatography (SFC) grade carbon dioxide, T_1. Check valves were installed (CV_1 and CV_2) to prevent fluid back flow.

The permeate pump unit (Fig. 1) consisted of an extractor and a 260D syringe pump (PP and H_2). This was coupled to the membrane cell so that a second pump, the permeate pump (PP) connected via the extractor (H_2), pressurized the permeate side of the membrane at a slightly lower pressure than the feed unit (FP). The permeate stream flowed through the membrane, out of the cell and back to the extractor (H_2) and then into the sample vial via a 1/16 inch (1.59 mm diameter) transfer tube.

A specialized, high-pressure, membrane cell (Fig. 2) designed and fabricated at the University of Illinois [4] was used with the two ISCO Inc., SFE systems. The cell consisted of four components; a cap connected to the delivery line from the extractor, and the main body of the cell with threaded connections for the base and cap. On the top and bottom of the cell, O-rings were used to maintain the pressure inside the cell. An additional O-ring was used in the bottom of the main body to hold the membrane in place and insure that the oil/SC–CO_2 mixture flowed only through the membrane. The third component was a base 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 towards the exit groove in the center. The base was connected to an exit line or tubing that carried the permeate out of the cell to the extractor. The fourth component was a porous stainless steel support disc with an approximate pore size of 10 μm, a diameter of

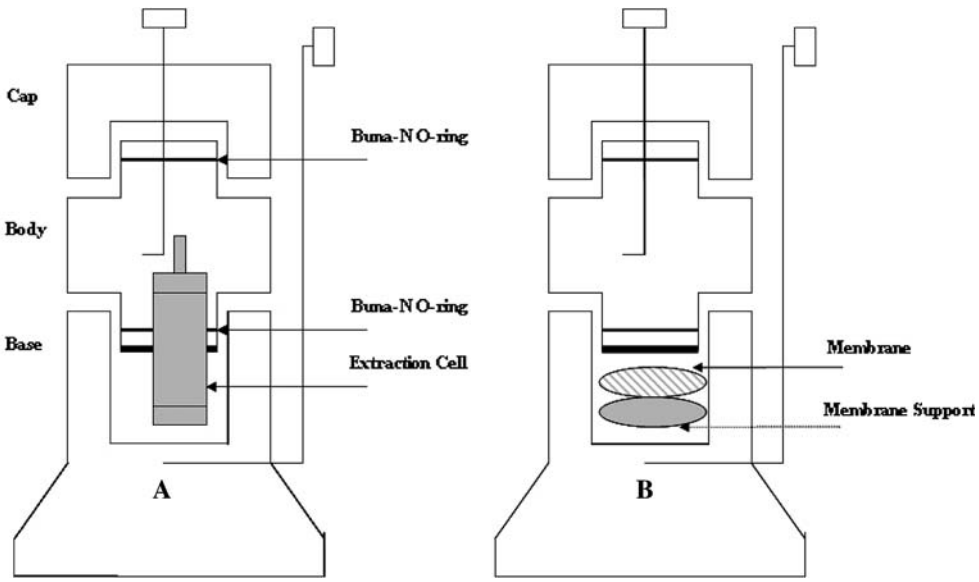

Fig. 2 Membrane cell with extraction cell (**a**) (which contained the silica-based, wet sample support and sample inside the cell), and membrane cell with membrane and membrane support (**b**)

4.75 cm and a thickness of 1.4 mm, which held and supported the membrane during the separation.

Procedures. The procedures used were similar to those published previously [4, 5] with slight modifications. The 10-mL extraction cartridge was filled approximately three fourths full with wet sample support matrix (ISCO). The particulate wet sample support increases the contact between the subcritical carbon dioxide and the sample components. It prevents the high-pressure carbon dioxide from simply forcing the liquid sample out of the extraction cartridge. Approximately 0.75 mL of the oil/fatty acid sample was transferred on top of the matrix of the support material via a pipette. The cartridge was assembled (cap and filters) and weighed. The cartridge was then loaded into the membrane cell and placed in a refrigerated water bath for 40 min to bring it to the selected temperature as determined by the thermocouple in the refrigerated water bath (WB). A dynamic flow mode was used for the solubility measurements in which the syringe pump delivered carbon dioxide continuously during the entire experiment. The cells were then filled with carbon dioxide to the desired pressure. The pressure was allowed to equilibrate for 10 min. After the pressure equilibrated, the test was started with a run time of 30 min. The cells were then depressurized and the sample cell was removed and allowed to warm (or cool, if the sample was at 25 °C) to room temperature ($\sim$22 °C) and then weighed. The difference in weight was equivalent to the amount of oil/fatty acid solubilized by the carbon dioxide. The conditions tested were combinations of temperature (10, 15, 20, and 25 °C) and pressure (68, 102, and 136 atm).

Acceptable oil component (TAG and FFA) solubility was obtained at 68 atm and 20 °C, so that separation experiments could be done within the pressure/temperature limitations of the best available membranes. The membranes used included FilmTEC BW30 membranes (ADM, Decatur, IL) and FilmTEC NF90 membranes (DOW Chemical Company, Midland, MI).

Oil samples were prepared by mixing commercial soybean oil obtained at a local grocery store with oleic acid (an arbitrarily selected, representative FFA) at a ratio of 60% soybean oil to 40% FFA. Fresh TAG/FFA oil samples were prepared at the same FFA/TAG ratio for each experiment. The membranes were cut and pretreated by a distilled water wash, a 23-h soak in 25% ethanol, and then a 23-h soak in 50% ethanol to remove the preservative used during shipment and storage. The ethanol on the membrane surface was allowed to evaporate and then the membrane was placed into the cell and secured [4].

The membrane flux (in LMH or liters per square meter per hour) was evaluated by first passing pure supercritical fluid through the membranes for 35 min and observing the change in flux as a function of a transmembrane pressure of 7 atm and time. A dead-end cell mode was used [4].

The membrane cell was placed on-line, and all valves were closed. Both syringe pumps were filled with carbon dioxide and the membrane cell, H_1 was pressurized to 68 atm (Fig. 1). If needed, the pump FP was refilled. The valve SV′ was then opened and the extractor H_2 was pressurized to 68 atm by pump PP and the pump continued to run to maintain the target pressure. The valves EV and RV were opened and both sides of the membrane were pressurized, by pump FP, to 68 atm. After the pressure equilibrated, the valve RV was closed and the pressure on the retentate side or high-pressure side was increased to 75 atm to provide the appropriate transmembrane pressure of 7 atm. The valve EV′ was opened to equilibrate at 68 atm. The valves EV and SV were closed and EV was depressurized via the valve VV. The extraction cell with the model oil sample was then placed into the membrane cell H_1 and the unit was pressurized to 75 atm. Then EV was opened at the retentate-side of the membrane and the pressure was brought to 75 atm. The separation was then done for 35 min.

After the separation, the pumps were stopped and the valves SV, SV′, and EV were closed. The membrane cell was then depressurized at a rate of $\leq$4 atm min^{-1}. This was to prevent rapid changes in pressure that could cause membrane rupture.

The sample collection vial was weighed before, as well as after, permeate collection. The extraction cell was weighed before and after the separation, as well. However, the retentate could not be collected quantitatively due to the limitations imposed by the system design, so the amount of sample solubilized or removed was based on the change in extraction cell weight [4, 5].

After depressurization and removal of the membrane, the system was cleaned. Isopropanol (20 mL) was placed in the membrane cell and the extraction units. The system was pressurized to 136 atm at 25 °C and a combination of pressurized CO_2 and isopropanol was flushed for $\sim$10 min through the system until all of the isopropanol had been removed. Pure CO_2 was flushed through the system for $\sim$10 min at 25 °C and 136 atm after the isopropanol had been removed.

Flux determination. To measure the flux for each membrane, the permeate flow rate was measured and divided by the area of the exposed membrane. The flux was measured (in LMH or liters per square meter per hour) during the first five min to avoid the effect of compaction of the membrane surface due to the relatively high pressures applied (68 atm). This was the same pseudo initial flux method reported by Artz et al. [4].

The extent of separation after membrane processing was determined using high performance size exclusion

chromatography (HPSEC) of the FFA and TAG components, using the same instrumentation, columns, detector settings, mobile phase, etc., as reported by Artz et al. [4, 5]. Standard curves were generated for the FFAs and the TAGs. The relative amounts of FFAs and TAGs in the permeate was determined using the standard curves. Peak identification was based on relative retention times.

Experimental design and statistical analysis. All of the solubility experiments were conducted in triplicate. The solubilities were compared statistically using the factorial method (proc glm), a form of ANOVA in the statistical program SAS [16].

For the membrane experiments, the statistical design and analysis were based on a complete random design and a 95% confidence level ($\alpha = 0.05$). A *t* test (LSD method) was used to compare means between replicates [16].

Results and Discussion

Temperatures used for the solubility tests were chosen to maintain the operating temperatures within a narrow range close to ambient temperature in subcritical conditions. The pressure range chosen was 68–136 atm. Current commercial membranes are designed to withstand pressures of ~70 atm, so the operating pressures selected were based roughly on the limits imposed by current membrane equipment design, but sufficiently high to allow appreciable component solubility. Oleic acid was more soluble than triacylglycerols (TAGs) in sub-CO_2 (Table 1). A similar trend was reported by Artz et al. [4] with an oleic acid solubility of 2.1 ± 0.32 mg/mL in SC–CO_2, as compared to a solubility in SC–CO_2 of 1.4 ± 0.29 mg/mL for TAGs. The data suggest that temperature (within the temperature range of 10–25 °C) had no significant effect on the solubility of TAGs in sub-CO_2. However, the solubility of TAGs was significantly less than the solubility of oleic acid in sub-CO_2 at the same conditions. There was an effect of temperature on the solubility of oleic acid. However, there was no significant difference in solubility for oleic acid within the temperature range of 15–25 °C. In addition, the solubility of oleic acid at 10 °C was not significantly different from its solubility at 20 °C (Table 1).

Within the pressure/density and temperature range examined, the pressure/density and temperature did not have a significant effect of the solubility of TAGs. A significant difference in solubility between oleic acid and TAGs was found. In addition, there was a significant difference in oleic acid solubility as a function of pressure/density. With an increase in pressure/density at each temperature, there was an increase in oleic acid solubility (Table 2). This trend was reported in previous work [5, 17, 18].

Oleic acid is smaller and slightly more polar than TAGs containing long chain fatty acids. Within the temperature and pressure/density range examined, density rather than temperature was the most important factor regarding oleic acid solubility. The density appeared to be more important than temperature in terms of TAG solubility. The solubility of oleic acid and TAGs in subcritical carbon dioxide was less by approximately one order of magnitude than in supercritical carbon dioxide. However, the solubilities for the two components indicate there is sufficient TAG and oleic acid solubility to determine if the membrane separation of fatty acids and TAGs is feasible.

Table 1 Temperature (over a pressure range of 68–136 atm) effects on TAG/oleic acid solubility ($P < 0.05$)

Substance	Temperature (°C)	Solubility (mg oil/mL CO_2)	Density range* (g/cm^3)
Oleic acid	10	0.455 ± 0.129^a	0.89–0.93
	15	0.297 ± 0.217^b	0.84–0.90
	20	0.317 ± 0.147^{a,b}	0.80–0.88
	25	0.304 ± 0.296^b	0.76–0.85
TAG	10	0.089 ± 0.0432^c	0.89–0.93
	15	0.072 ± 0.0214^c	0.84–0.90
	20	0.132 ± 0.102^c	0.80–0.88
	25	0.092 ± 0.081^c	0.76–0.85

Means with the same letter are not significantly different

* Extrapolated from Gilgen et al. [19]

Table 2 Pressure (over a temperature range of 10–25 °C) effects on TAG/oleic acid solubility ($P < 0.05$)

Substance	Pressure (atm)	Solubility (mg oil/mL CO_2)	Density range* (g/cm^3)
Oleic Acid	68	0.281 ± 0.153^b	0.76–0.89
	102	0.294 ± 0.212^b	0.83–0.92
	136	0.455 ± 0.225^a	0.85–0.93
TAG	68	0.139 ± 0.091^c	0.76–0.89
	102	0.085 ± 0.062^c	0.83–0.92
	136	0.066 ± 0.017^c	0.85–0.93

Means with the same letter are not significantly different

* Extrapolated from Gilgen et al. [19]

Based on the results, the best set of conditions was 20 °C and 75 atm on the retentate side of the membrane and a permeate pressure of 68 atm. A retentate pressure of 75 atm was required to provide the appropriate transmembrane pressure (P_T) of 7 atm with a permeate pressure of 68 atm.

Pure CO_2 at the desired temperature/pressures was pumped though the membrane (NF90 or BW30) to determine the maximum theoretical flux possible. In both membranes, there was no difference in flux observed during the first 35 min. However, similar to the supercritical separation experiments [4], there was an observable reduction in flux after 35 min. A decrease in flux was expected and occurs with time due to membrane compaction. The NF90 membrane had a significantly greater flux than the other membrane ($P < 0.05$) shown in Fig. 3. This was expected since the NF90 membrane had the greater molecular weight cut-off (MWCO = 200 Da), which means a larger pore size. When considering both membranes, the flux observed using subcritical conditions was less than during supercritical conditions. Previous work done by Artz et al. [4] indicated a flux of ~70 LMH (liters per square meter per hour) at a pressure of 306 atm with the same membranes. This is more than double that observed in this study (~30 LMH). The viscosity of supercritical fluids is less than that of subcritical compressed liquids, which is probably the primary reason for the difference. Lin et al. [11] obtained a flux of 26.8 LMH using pure hexane during their studies on the degumming of vegetable oil using a DS-7 membrane (MWCO of 1000) at operating conditions of 40 °C and 20 atm. This is comparable to results reported in this experiment, although the DS-7 membrane pore size is substantially greater (hence less resistance to flow) than the pores in the membranes examined in these subcritical experiments.

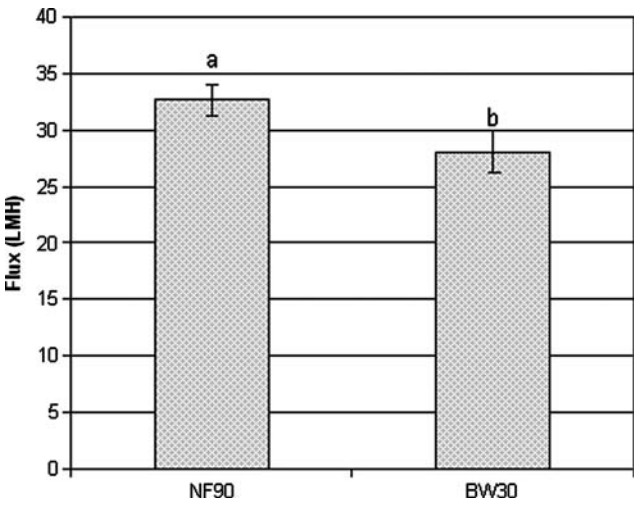

Fig. 3 Comparison of average flux ($P < 0.05$ with CO_2 Pressures at 68–136 atm; CO_2 Temperatures at 10–25 °C; and Model Oil FFA/TAG ratio at 40:60) for both membranes (means with the same letter are not significantly different and *error bars* represent standard deviation)

The membranes were evaluated for their effectiveness for separating TAGs from FFAs at subcritical conditions. An ideal membrane would allow all the FFAs to pass through the membrane, while retaining all of the TAGs, i.e., a high retention rate for the TAGs and a low retention rate for the FFAs. Membranes and conditions were selected so that TAGs would be retained and FFAs would permeate through the membrane, based on previous work with supercritical carbon dioxide as the solvent [4].

A selectivity factor (β) previously defined by Sarrade et al. [15] was used to compare membrane selectivity. The factor is based on the retentate and permeate compositions, where $\beta = \%X_P/\%X_R$, and $\%X_P$ is the mass percentage of component X in the permeate and $\%X_R$ is the mass percentage of component X in the retentate. If the selectivity factor was greater than one, then component X will permeate or pass through the membrane readily. If β was less than one, component X was significantly retained or rejected by the membrane.

A high ratio of oleic acid (40%) to TAG (60%) was chosen for the model oils to facilitate the HPSEC analyses. The FFA concentrations in most crude vegetable oils are generally small e.g., 1–3%, although some crude tropical oils can contain several percent FFA. Samples with high percentages of FFA were used in this study specifically to minimize the analytical errors that would occur with small volumes and small percentages of FFA. The objective was to determine feasibility, rather than optimize the separation of crude vegetable oil samples with relatively low percentages of FFA.

There was no significant difference between the composition of the model oil and the retentate, which was expected. Due to the experimental procedures used only a small percentage of the sample passed through the membrane (permeate), so little change in the retentate composition occurred. Therefore, the results were based on the permeate composition.

The permeate composition for the BW30 membrane was significantly different ($P < 0.05$) than the composition of the model oil, indicating the membrane was selective for FFAs relative to TAGs (Fig. 4). Statistically, the permeate composition for the NF90 membrane was not significantly different from the composition of the starting model oil.

However, based on the selectivity factor or β (Table 3) both membranes were selective for oleic acid, although the BW30 had much great selectivity for oleic acid ($\beta_{\text{oleic acid}} = 2.12$, $\beta_{\text{TAGs}} = 0.24$) than the NF90 membrane ($\beta_{\text{oleic acid}} = 1.26$, $\beta_{\text{TAGs}} = 0.81$). Artz et al. [4] also found that the BW30 membrane ($\beta_{\text{oleic acid}} = 2.63$, $\beta_{\text{TAGs}} = 0.69$) provided a better TAG/FFA separation than the NF90

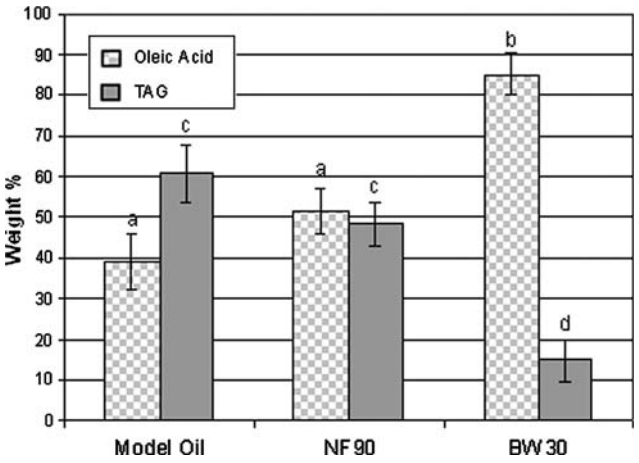

Fig. 4 Permeate compositions ($P < 0.05$ with CO_2 Pressures at 68–136 atm; CO_2 Temperatures at 10–25 °C; and Model Oil FFA/TAG ratio at 40:60) of both membranes compared to the model oil (means with the same letter are not significantly different and *error bars* represent standard deviation)

Table 3 Selectivity factor (β) for TAG and oleic acid (OA) for both NF90 and BW30 ($P < 0.0001$)

Membrane	β (OA)	β (TAG)
NF90	1.26 ± 0.09	0.81 ± 0.09
BW30	2.12 ± 0.13	0.24 ± 0.13

Experimental conditions: CO_2 pressures 68–136 atm; CO_2 temperatures 10–25 °C; Model Oil FFA/TAG ratio 40:60

membrane ($\beta_{\text{oleic acid}} = 1.28$, $\beta_{\text{TAGs}} = 0.70$). The selectivity factors for the NF90 membrane for both supercritical and subcritical carbon dioxide were not significantly different ($P < 0.0001$). For the BW30 membrane, the selectivity factors determined using supercritical carbon dioxide was significantly greater for both oleic acid and the TAGs. Under subcritical conditions, there was a lower rejection of TAG and a lower permeation of FFA ($P < 0.0001$). The selectivity of BW30 for FFA was significantly greater than for the NF90 membrane in both studies.

Thus, the combined use of subcritical carbon dioxide and membrane technology appears to have potential for vegetable oil deacidification, although additional work is needed. Although the TAG and oleic solubility was substantially lower in subcritical CO_2 than in supercritical carbon dioxide, the solubility of triacylglycerols and oleic acid was sufficient for successful membrane separation. Within the temperature range (10–25 °C) and pressure range (68–136 atm) examined, the solubility of oleic acid was greatest at 25 °C and 136 atm. For the TAGs, the greatest solubility was observed at 20 °C and 68 atm. The solubility of oleic acid was not significantly less at 20 °C and 68 atm than at 25 °C and 136 atm, so 20 °C and 68 atm were chosen for the membrane separation. These are conditions (lowest pressure examined and a temperature range nearest to ambient) that should be easiest to attain commercially.

The NF90 membrane had a lower average flux than the BW30 membrane when using pure subcritical CO_2. For both membranes, the flux did not vary with time for the short time period examined. The flux of supercritical CO_2 was greater than the flux for subcritical CO_2.

The selectivity factors for oleic acid were greater than 1 for both the BW30 and the NF90 membranes. Likewise, the selectivity factors for TAGs were less than 1 for both the BW30 and the NF90 membranes. However, the selectivity factor for oleic acid was much greater for the BW30 membrane than the NF90 membrane, indicating that the BW30 membrane would probably provide a better separation. It appears feasible to use reverse osmosis and nanofiltration membranes with subcritical carbon dioxide for the deacidification of soybean oil.

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