Acetone-Stable Nanofiltration Membranes in Deacidifying Vegetable Oil

H.J. Zwijnenberg[a,*], A.M. Krosse[a], K. Ebert[b], K.-V. Peinemann[b], and F.P. Cuperus[a]

[a]Agrotechnological Research Institute ATO-DLO, 6700AA Wageningen, The Netherlands, and [b]GKSS Forschungszentrum, Institut für Chemie, D-21494 Geesthacht, Germany

ABSTRACT: The separation of different vegetable oil/solvent mixtures with two types of nanofiltration membranes was studied. One type had a PEBAX [poly(amide-b-ether) copolymer] top layer, and the other had a cellulose-type top layer. These membranes were stable in acetone, ethanol, 2-propanol, and hexane, all important to the oleochemical industry. Permeabilities were highest for acetone, ±140 L/m^2 · h · MPa, and lowest for hexane, which had negligible flux at 2 MPa. Permeabilities decreased with increasing triglyceride or free fatty acid (FFA) concentration. Rejection of triglycerides was constant over the concentration range tested, about 80–95% ± 5%, depending on the type of membrane used. These properties make membranes applicable for separating triglycerides from acetone by enhancing acetone recovery. Deacidification of triglycerides and FFA mixtures was possible (e.g., fatty acids were retained less than triglycerides). The permeate consisted almost entirely of fatty acids in acetone, and only small traces of triglycerides were found. This makes it feasible to selectively remove the fatty acids and reduce loss of triglycerides normally associated with deacidification.

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KEY WORDS: Acetone, deacidification, ethanol, extraction, fatty acid, fractionation, nanofiltration, recovery, solvent stability, vegetable oil.

In the fats and oils industry, deacidification of vegetable oils is important for consumer acceptance (1). Alkali refining, which is normally used to remove free fatty acids (FFA), yields a low-value soapstock and results in the loss of about 8% of the triglycerides (2). The alternative of steam stripping of physical refining is energy intensive (3). Several investigations have been published on the deacidification of vegetable oils by using membranes (3–8). It is expected that membrane technology will be able to decrease both energy consumption and triglyceride loss.

The major problem involved in the separation of FFA from triglycerides is the combination of high solvent stability and high selectivity in the separation between the two components (9). Lakshminarayanan *et al.* (6) used direct separation of the hexane miscella which resulted in a decrease from an initial FFA concentration of 10% (w/w), relative to triglycerides, to an ending concentration of about 5%. One disadvantage of these membranes was the loss of rejection above 40% (w/w) triglycerides in solvent. In a different process (3), a four-stage extraction of the miscella with methanol was proposed to separate FFA from triglycerides and recirculate the extracting solvent by membrane recovery. A disadvantage of this reverse osmosis membrane process is that the separation between fatty acids and triglycerides is not determined by the membrane but by solvent properties. Therefore not only FFA but also triglycerides are extracted, resulting in a loss of the latter component. This can only be overcome by an additional or more complex recovery system.

A combination of both processes is possible with a membrane that separates fatty acids from triglycerides. The miscella containing a high FFA concentration could be separated into a triglyceride/solvent stream and an FFA/solvent stream. From both streams the solvent could be recovered by distillation or reverse osmosis. As the latter is already shown to be feasible on lab scale (3), investigations were done to examine the possibility of direct deacidification of a triglyceride extract by solvent-stable nanofiltration.

EXPERIMENTAL PROCEDURES

Setup. To determine the permeability and retention of nanofiltration membranes, two setups were used, one with a dead-end module and a second with a cross-flow module.

The dead-end setup consisted of a Varian 8500 plunger pump (Varian Nederland B.V., Houten, The Netherlands) and delivered pressures up to 3 MPa. The mixture was circulated in the system by an Ismatec P121 gear pump (Ismatec SA, Glattburg-Zlejrich, Switzerland). The setup was always used in concentration mode (i.e., without recycling of the permeate and retentate to the feed). During the permeation experiment samples of permeate and retentate were taken. The effective membrane size for the module was 37 cm^2.

A larger cross-flow setup was used for measurements with a constant feed composition over several days by using it in total recycle mode (i.e., with recycling of the permeate and retentate to the feed). The membrane area of the cross-flow module was 440 cm^2. A diagram of the setup is given in Figure 1. The feed was stored in a feed tank with a cooling/heat-

*To whom correspondence should be addressed at Agrotechnological Research Institute ATO-DLO, P.O. Box 17, 6700AA Wageningen, The Netherlands. E-mail: F.P.Cuperus@ato.dlo.nl

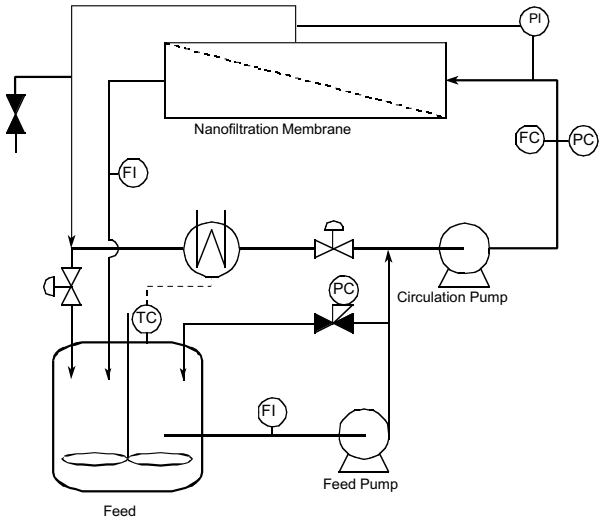

FIG. 1. The transversal flow setup. (TC, PC, and FC temperature, pressure, and flow controllers, respectively; FI and ΔPI are flow and pressure difference indicators, respectively.)

ing mantle, which was connected to a temperature-controlled water bath. The feed tank was closed to prevent evaporation of the solvent. The feed was pumped into the circulating system by a triplex piston pump with a maximal pressure of 7 MPa and a maximal flow of 15 L/min. A flow meter measured the feed flow capacity into the system. For safety reasons a back pressure relief valve was installed which opened at a preset value varying between 0.1 and 8 MPa. The circulation pump (Ismatec ISM506 gear pump) circulated the feed at 0.1–10.0 L/min, which was also measured by a flow meter. Both the pressure before the module and the pressure difference over the module were measured and used to regulate the feed pump to maintain a constant operating pressure. Behind the module the permeate flow was measured by a balance with a siphon vessel. The balance was coupled to the RS-232 port of a data acquisition computer to automatically log the data. Both permeate and retentate were recirculated to the storage tank to maintain constant feed composition. Approximately constant feed composition was achieved by maintaining the flow of the feed sufficiently larger (i.e., >50 times) than the permeate flow. To retain constant temperature of the circulation stream, a heat exchanger was installed in the circulation system.

Solvent mixtures and vegetable oils. Pro analysis-grade 2-propanol and ethanol and technical-grade acetone were used. The sunflower oil was food-grade and refined palm oil was the refined mid-fraction; both contained less than 0.5% FFA. The rapeseed oil was cold-pressed, unrefined, low-erucic rapeseed oil. This oil contained more impurities than the refined oils (e.g., FFA, waxes, phospholipids, and chlorophyll) in unknown concentrations. The Scandinavian tall oil consisted of FFA, mainly C_{18} fatty acids (92%). Tall oil FFA had an average molecular weight (MW) of about 280 Daltons; the MW of the triglycerides was approximately 890 Daltons.

Membrane treatment. Two types of membranes were used. Both were hydrophilic and had top layers of either PEBAX [poly(amide-b-ether) copolymers of Elf-Atochem, Amsterdam, The Netherlands] or a cellulose-type top layer. These membranes were developed with one of the partners in the Brite-Euram project, GKSS, Geesthacht, Germany, and are not yet produced on commercial scale. As a consequence, these membranes were not fully characterized with respect to their behavior under various conditions. During the experiments, one batch of the cellulose-type membranes and two batches of PEBAX membranes were used. The latter batches differed in absolute values for permeability and retention and are referred to as Batch 1 and Batch 2 PEBAX membranes.

For storage purposes, all membranes arrived impregnated with a mixture of glycerol and low MW poly(ethyleneglycol) of 200 g/mol. To remove the impregnation substances, the membranes were washed with deionized water overnight and then rinsed for 10 min with ethanol. Later this procedure was replaced by permeating at 2 MPa for 10 min after the permeate was clear before any data were collected. This procedure was as effective as the washing and reduced times.

Analysis. When possible, the determination of the permeate, retentate, and feed concentrations was done by means of a refractometer. For analyzing mixtures of FFA and triglycerides in solvent, a different method was used. First, the solvent concentration was determined refractometrically. This is possible because triglycerides and FFA have almost the same refractometric index, up to 50% w/w in acetone. Second, the solvent was evaporated at 60°C under nitrogen. The mixture of triglycerides and FFA was then titrated in methanol with a KOH solution and phenolphthalein as indicator to determine the FFA concentration.

The reproducibility of the tests was good in all cases. All tests were repeated at least two times. Differences in permeability for the same sample were less than 10%, and the differences in retention were less than 5%. However, between the separate samples from a batch, the maximal permeability difference found was 30% of the average value and the maximal difference in retention up to 7% of the average value. These larger differences are probably due to unhomogenic anomalies in the membrane structure and are commonly observed when working with relatively small membrane samples.

When different membrane sheets were used, the highest and lowest average values are presented in the tables. In cases where one sheet was used, the average value of the tests is presented.

TABLE 1
Solvent Permeabilities ($L/m^2 \cdot h \cdot MPa$) for the Membranes[a]

	Membranes	
Solvent	PEBAX (Batch 2)	Cellulose-type
Hexane	<0.1	<0.1
2-Propanol	1.3–1.6	4–7
Ethanol 96%	8.0–9.0	15–20
Acetone	25–44	63–146

[a]Measured at 2 MPa and 20°C; 1 MPa = 10 bar = 145 psi.

RESULTS AND DISCUSSION

Membrane separation characteristics. The permeabilities for several solvents were determined at 2 MPa and 20°C using the dead-end setup (Table 1). The cellulose-type membrane had the highest permeability with acetone. Compared to literature values for reverse osmosis membranes (8), the ethanol permeabilities of both types of membranes were substantially higher. Acetone permeabilities for nanofiltration membranes were not found in the literature, probably because membranes are often unstable when working with ketones. The permeability of hexane was negligible because the membrane materials for both types are hydrophilic. The high stability in acetone might open markets in oleochemical processes (10) such as the fractionation of triglycerides, which uses solutions of triglycerides in acetone. These processes could benefit from these membranes by using them to recover the solvent after separating the crystals.

Besides pure solvents, mixtures of solvents with triglycerides from refined sunflower oil were tested. First, the influence of pressure on rejection and permeability of the membranes was tested with a dead-end module (Fig. 2).

At higher pressures, both rejection and permeability decreased slightly. The permeability decrease was caused by compaction of the porous substructure of the membrane. Increased density of this layer increased the resistance for the permeate and, hence, decreased the permeability. The reason for the decreased rejection is unclear. A possible explanation of concentration polarization is not likely, as it did not occur in the same setup with solutions of biodiesel and triglycerides (Zwijnenberg, H.J., and F.P. Cuperus, unpublished data). Because the membranes were stored in the solutions for one night prior to the experiments, it is not likely that significant swelling of the membranes occurred during the measurements, which took about 3 h each.

To test the influence of the solute on the membrane properties, several tests were performed with different vegetable oil/acetone mixtures (Table 2) using the dead-end setup in concentration mode. The difference between the results of PEBAX and cellulose-type membranes was obvious. The rejection of the PEBAX was generally 10% lower than that of the cellulose-type, while permeability was about two times higher.

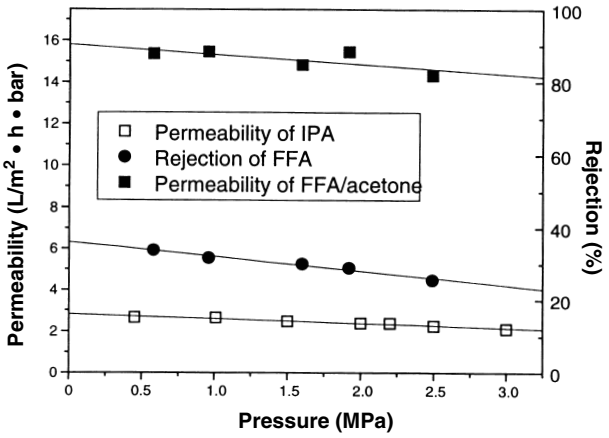

FIG. 2. Permeability of acetone and 2-propanol (IPA) and rejection of free fatty acids (FFA) in acetone for the PEBAX (Batch 1) membrane vs. pressure, measured at 20°C.

Initially, the composition and purity of the vegetable oil were expected to considerably influence separation characteristics of the membranes and fouling. However, the difference in performance of one membrane sheet between refined sunflower oil and cold-pressed unrefined rapeseed oil with a lot of impurities was smaller than the difference normally found between the different membrane samples. To check the influence of waxes or phospholipids, these components were added in large amounts. However, no significant influence of these components could be found. It was therefore concluded that the composition of the triglyceride mixture or unrefined oil does not have a significant influence on the permeability or the rejection of the membranes.

The influence of triglyceride concentration on the rejection and the permeability of the membrane was tested using the crossflow setup (Fig. 3). The data were collected by measuring the separation characteristics at varying feed concentrations using different batches for each data point. In the concentration mode, the feed is not refreshed, and buildup of minor components with high rejections and triglycerides occurs. However, the results of Table 2 did not show significant influence of

TABLE 2
Permeabilities and Retentions for the Different Membranes for Several Mixtures of Vegetable Oil in Acetone at 1 MPA and 20°C

Oil	Membrane	Solute concentration (% w/w)	Permeability ($L/m^2 \cdot h \cdot MPa$)	Rejection (%)
Palm	PEBAX (Batch 2)	9	33	86
Rapeseed	PEBAX (Batch 2)	10	42	81
Sunflower	PEBAX (Batch 1)	10	5	90
Palm	Cellulose	11	18	93
Rapeseed	Cellulose	10	20	>98
Sunflower	Cellulose	10	18	97
Sunflower + phospholipids (9:1)	Cellulose	10	16	93
Sunflower + beeswax (9:1)	Cellulose	9	15	92

TABLE 3
Separation Characteristics for PEBAX Membrane Sheets (Batch 1) at 25°C for Triglycerides, Free Fatty Acids (FFA), Methylated FFA, and a Mixture of FFA/Triglycerides in Acetone

Solute in acetone	Permeability ($L/m^2 \bullet h \bullet MPa$)	Triglyceride rejection (%)	Fatty acid rejection (%)
10% (w/w) Triglycerides	5.0	92–94	—
10% (w/w) FFA	3.5	—	45–56
10% (w/w) Methylated FFA	3.8	—	48–54
5% (w/w) Triglycerides + 5% (w/w) FFA	3.5	95–99.97	55–62

minor components. This suggests that the results of Figure 3 are comparable to an indicative run in concentration mode.

The acetone permeability was over 18 $L/m^2 \cdot h \cdot MPa$ for the PEBAX membrane, lower than the average of the other membranes. The influence of sunflower oil concentration on the permeability was significant, as the permeability of the mixture decreased rapidly with increasing oil concentration. Similar results were obtained with the cellulose-type membranes and by Koike *et al.* (4) and Lakshminarayanan *et al.* (6).

The rejection of the membrane toward triglycerides was 90% and almost constant over the entire concentration range. This means that with increasing feed concentration the permeate concentration increased at the same relative rate. The specific nature of the constant ratio between solvent and solute transport was not clear for this system, and both the solution diffusion and pore flow models (11) were not able to completely describe it. However, the constant rejection of the membrane was a strong indication that the membrane solute interaction was very low and the membrane was stable toward both triglycerides and acetone. This assumption was confirmed by experiments conducted over several months with the same membrane. During this period the permeability and rejection of the membrane remained constant.

Deacidification. The rejection of molecules with lower molecular weights than triglycerides was studied using a mixture of 10% FFA from tall oil in acetone and a mixture of 10% methylated FFA in acetone (Table 3) using the cross-flow setup in total recycle mode.

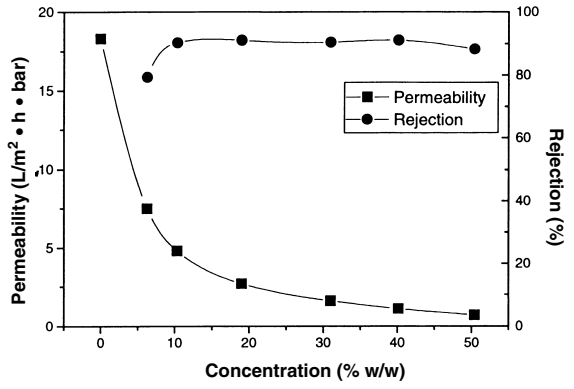

FIG. 3. Separation characteristics of the PEBAX (Batch 1) membrane for a mixture of triglycerides in acetone, measured at 2 MPa and 20°C.

Compared to the rejection toward 10% triglycerides from sunflower oil, the rejection of the smaller FFA and methylated FFA molecules was much lower. Both FFA and methylated FFA had similar separation characteristics. As the latter molecules differ significantly in polarity but not much in size, the difference in size between triglycerides and FFA is more important for the separation mechanism of the membrane than for the difference in polarity.

The test with a mixture of 5% (w/w) triglycerides and 5% (w/w) FFA in acetone showed that the rejection for triglycerides as well as FFA increased compared to that of the pure components. The FFA mixture was also less permeable compared to the triglyceride mixture, and this was attributed to swelling of the membrane by FFA which are known for their plasticizing effects on polymers (12). Increased rejection of the smaller components in a mixture with solutes of different sizes is also often found in ultrafiltration (13) and is attributed to hindered transport of FFA molecules by the larger triglyceride molecules.

As a result of this high rejection of triglycerides in the presence of FFA, the permeate contained only traces of triglycerides and gave almost 100% pure FFA after the removal of the acetone. Hence, it is technically possible to deacidify vegetable oil by using nanofiltration membranes and to considerably reduce loss of triglycerides.

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