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Soft purification of lampante olive oil by microfiltration

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Abstract

An efficient membrane-based process for deacidification of lampante olive oil was investigated. The neutralization of the free fatty acids with appropriate soda concentration allows the formation of submicronic particles which are subsequently removed by a microfiltration technique. A total or quasi-complete neutralisation of the acidity is necessary to achieve the complete retention of the soap molecules. Partial neutralization of the acidity leads to a lower membrane separation efficiency. The residual FFA causes permeation of soap molecules across the membrane. When filtered under suitable conditions, lampante olive oils show excellent quality characteristics, i.e., very low residual acidity as well as soap and water contents. The initial fluxes, obtained during crossflow filtration with membrane pore sizes 0.5 and 0.8 μm (147 and 212 l/h m^2, respectively) after neutralization with 20% NaOH are twice those obtained with 40% NaOH while there is only a slight improvement with the 0.2 μm membrane. The filtered oils show good quality (acidity and residual soaps) in the case of PS 0.2 and 0.5 μm, whereas the 0.8 μm membrane allows some soaps to pass through the membrane. The passage from the laboratory scale (1 kg) to a 50 kg unit shows the practical possibility of scaling up without meeting any particular problems or loss of efficiency.

Keywords: Lampante olive oil; Refining; Particles; Membrane technology; Microfiltration

1. Introduction

In recent years, research works concerning applications of membrane separation processes in the oils and fats industry have attracted a great deal of attention, owing to the numerous advantages that this technology offers, namely, energy saving, better product quality and environmental protection. Most works have focussed on hexane recovery from oil miscella (Koseoglu, Lawhon, & Lusas, 1990), phospholipid removal (Gupta, 1986; Subramanian & Nakajima, 1997) and vegetable oil deacidification using a solvent for extraction of the free fatty acids (Kale, Katikaneni, & Cheryan, 1999; Krishna Kumar & Bhowmick, 1996; Raman, Cheryan, & Rajagopalan, 1996; Zwijnnenberg, Krosse, Ebert, Peinemann, & Cuperus, 1999). Attempts have been made to use processing solvent-free glyceridic media as well. Under such conditions, the physicochemical properties of the medium are profoundly changed. The aggregates (micelles, lamellar phases) which may exist naturally or be induced, are expected to differ from those in miscella, at least in terms of their average size. In fact, in solvent free media, many works did show the suitability of microfiltration for the elimination of such particles from common seed oils (soya, rapeseed and sunflower oils), mainly when free fatty acids (FFA) are converted to salts by alkali treatment (Ajana, Pioch, & Graille, 1993; Pioch, Largueze, Graille, Ajana, & Rouviere, 1998; Pioch, Largueze, Hafidi, Ajana, & Graille, 1996; Van de Sande, 1989). The filtered oils are then

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completely freed from their phospholipids and FFA. Larguèze et al. demonstrated that phospholipid and soap molecules, in a solvent free glyceridic median can form onion-like vesicles which are constituted of almost concentric bilayers (Largueze, Pioch, & Gulik-Kryzwicki, 2002). These authors also found that both phospholipids and soaps are required to form the largest structures (Largueze et al., 2002).

Virgin olive oil (VOO), which is extracted from olive fruit by using only mechanical processes, including olive crushing, malaxation of the resulting paste and separation of the oily phase, essentially by pressure or centrifugation, can be consumed in the natural unrefined state, known as virgin oil, or as a refined product. According to the International Olive Oil Council and European regulations, virgin olive oil quality is differentiated on the basis of FFA content, organoleptic characteristics, peroxide values and UV absorption (EC regulation No. 2568, 1991). When the FFA content exceeds 3.3%, and/or the sensory panel test score is less than 3.5, the VOO is graded as "lampante virgin olive oil" (LVOO). This poor quality oil is recommended to be refined prior to human consumption and is marketed at prices lower than VOO. Usually, these oils are refined in the same manner as the common seed oils without any regard to their specificity. During this process, the oil is heated above 90 °C and even above 220 °C during deodorization. Consequently, qualitative and quantitative changes in composition take place during processing, such as the formation of trans fatty acids, conjugated dienes and the lost of useful components of olive oils for nutrition (Pérez-Camino, Ruiz-Méndez, Marquez-Ruiz, & Dobarganes, 1993; Ruiz-Mendez, Marquez-Ruiz, & Dobarganes, 1997).

The process we have already tested for seed oils operates at relatively low temperature and is expected to avoid oil damage and to preserve the sensitive and bioactive components (Ajana et al., 1993; Pioch et al., 1998, 1996). These interesting features are particularly suitable for processing lampante virgin olive oils. In this paper, attempts are made to adapt this soft process to the purification of lampante olive oil.

2. Materials and methods

2.1. Oil conditioning and microfiltration

The LVOO samples were purchased locally. They were neutralized at 20–24 °C by adding slowly (with a pipette) an aqueous sodium hydroxide solution (20% or 40% w/v) under magnetic stirring (600 rpm) and then filtered. The "neutralisation 50% + 50%" consists of neutralisation of one half of the acidity, followed by filtration; the remaining acidity (theoretically the other half) was neutralised in a subsequent step. The oil was microfiltered again. For dead-end filtration experiments, a stainless steel Gelman module was used (200 ml volume; 200 kPa pressure; Whatman cellulose filter (PS 2.5 μm): area 16 cm^2). Crossflow filtration experiments were performed at 25 °C with a laboratory stainless steel apparatus (1 kg oil sample; tubular alumina membrane 200 mm length, 40 cm^2 area) under continuous recycling of permeate, 3.5 m/s as tangential velocity and 200 kPa as transmembrane pressure. Flows were measured using graduated cylinders.

Pilot assays were conducted under identical conditions with a 50 kg capacity unit fitted with a multichannel alumina membrane (19 channels, 1 m height, 0.25 m^2 area) and a backflush system (a volume of the permeate is injected backward in the membrane; 700 kPa back-pressure every 10 min). All membranes were provided by Exekia, Baset, France and the pilot filtration unit originated from TIA, Bolène France.

2.2. Analytical methods

In order to check the chemical composition of both starting and refined oils, the following procedures were applied: Free fatty acids NF T 60–204; soaps NF T 60–217; water NF T 60–225 (AFNOR, 1984) .

3. Results and discussion

3.1. Partial neutralization

Free fatty acids in oils result from alteration of triacylglycerols by chemical or enzymatic hydrolysis. This phenomenon is of particular importance in water-containing lipidic matrices, such as olive oil, during storage and processing. Many works have outlined the pro-oxidant effect of FFA, contributing thus to reducing shelf life (Frega, Mozzon, & Lercker, 1999; Kiristakis & Tsipeli, 1992). Common steps of the chemical refining include water degumming, acid and alkali treatment, bleaching and deodorization along with heating, cooling, filtration and centrifugation and this process is best used with low-to medium-FFA oils, like most LVOOs. The high temperatures (90–250 °C) used during these operations are quality-harmful, especially in the case of olive oils, whereas, in most cases, just a slight lowering of the original acidity of the LVOOs below 3.3% would confer acceptable quality.

As shown in Table 1, the neutralization of one half the acidity allowed us in all cases, to reach proportions under the limiting value of 3.3%. So, regarding this sole quality parameter, these oils cannot any more be considered as lampante. In all cases, the residual acidity was smaller than the theoretical expected values. Some FFAs must have been retained within the

Table 1
Lampante virgin olive oil acidity (%) after partial or total neutralization of FFA and dead-end filtration

Olive oils	Acidity (%)			
	Crude	Neutralized		
		50% SA	50% SA + 50% SA	SA
LVOO 1	3.76	1.31	0.11	0.16
LVOO 2	3.97	1.16	0.08	0.03
LVOO 3	5.06	1.77	0.07	0.07
LVOO 4	6.13	2.65	0.04	0.08
LVOO 5	8.04	3.20	0.06	0.10

SA, Stoichiometric amount of soda.
50% SA + 50% SA, Neutralization with one half the stoichiometric amount applied to the oil already subjected to the same treatment.

Table 2
Residual soap content (ppm) in the neutralized, then dead end filtered olive oils

Olive oils	50% SA	50% SA + 50% SA	SA
LVOO 1	4347	14	163
LVOO 2	1095	13	30
LVOO 3	1943	13	12
LVOO 4	5392	14	14
LVOO 5	7565	14	28

aggregates of soaps during filtration. Molecular interactions between soaps and FFAs were observed as early as 1823, when Chevreul demonstrated that some sediments from a partially hydrolyzed oil had a composition intermediate between those of fully un-ionized fatty acids and ionized soaps (Cistola, Atkinson, Hamilton, & Small, 1986). The subsequent neutralization of the remaining acidity in the half-deacidified oils and filtration resulted in a residual acidity generally below 0.1%.

Soap molecules resulting from the alkali treatment are retained when microfiltering, so they must have sizes somewhat above the membrane pore diameter (2.5 μm). Soap molecules are amphiphilic and consist of a polar headgroup and a nonpolar tail which causes their preference for self assembly with the hydrophobic groups on one side and the hydrophilic groups on the other side. Surfactants are normally believed to exist as monomers up to a certain concentration, above which they may self-assemble into a wide variety of aggregate to form micelles, liquid crystals or crystals. Another morphology of amphiphilic self-assembly has recently drawn considerable attention, when a lamellar phase is subjected to shear, it undergoes a dynamic transition into an array of close-packed multilayer vesicles, referred to as onion phases (Berghausen, Zipfel, Lindner, & Richtering, 1998; Diat, Roux, & Nallet, 1993). Using freeze-fracture electronic microscopy, Largueze et al. (2002) reported multilamellar close packed aggregates in seed oils when subjected to an alkali treatment. Most likely the soap molecules resulting from the neutralization of LVOOs self organize in to similar macrostructures, allowing their retention with microfiltration membranes. In the case of seed oils, PL molecules participate in the aggregates and were eliminated, together with the FFA salts. Because of the compression extraction mode, virgin olive oils contain only very small amounts of PLs (<10 ppm P) which do not allow an accurate determination of their retention after filtration. On the other hand, PL are supposed to play key roles in determining the average particle sizes. Smaller aggregates were reported in model oils made by adding FFA to refined oils, i.e., when phospholipids are not present (Largueze et al., 2002). These model oils are the closest to the LVOO, which naturally contain very small amounts of phospholipids.

Table 2 shows that the retention of soap molecules is only almost complete, in all cases after neutralizing the whole acidity; so all the resulting soap molecules are likely to participate to the aggregation phenomenon. Contrary to the above case, half neutralization allows huge amounts of soap to permeate through the membrane. However, the retention ratio, (initial soap–residual soap)/(initial soap), is close to or better than 80%. Thus, even if most of the soap molecules actually participate in aggregation, the residual FFAs seem to cause part of them not to self organize as large macrostructures and pass through the membrane, either as "monomers", dimers or as very small aggregates. This demonstrates the molecular interactions between soaps, FFAs and minor components, such as phospholipids, in the triacylglycerol medium. Jandacek (1991) showed that FFA causes calcium soaps to dissolve in the presence of triglycerides or in an organic solvent and that these fatty acid-calcium soap complexes organize as a bilayer structure. Such a phenomenon is likely to occur in the present case.

The residual soaps can be considerably lowered only when the residual FFAs are also significantly decreased. Table 3 shows that, for the LVOO 2, the neutralization of 70% of the initial acidity (~4%) allows the residual acidity to pass less than 1% and soaps in the filtered oil to be almost not detectable. In the case of LVOO 4 and 5 which have higher initial acidities (~6% and 8%, respectively), neutralization of 80% and 90%, respectively, was necessary to get the residual soaps under the detection limit. It appears that decreasing the acidity below 1% is necessary for avoiding detection of residual soaps in the oil. Thus, the particle sizes are likely to depend on the concentration of FFA or on the FFA to soap ratio; the size of the aggregates probably decreases when this ratio increases. It also appears that water contents in the filtred oils are directly linked to the residual soaps. Very low water contents (<0.1%) are abtained only when the soaps are completely eliminated from the oils (Table 3).

Table 3
Residual free fatty acid and soap contents in the neutralized then filtered olive oils

Olive oils	LVOO 2			LVOO 4			LVOO 5		
	Acidity (%)	Soap (ppm)	Water (%)	Acidity (%)	Soap (ppm)	Water (%)	Acidity (%)	Soap (ppm)	Water (%)
50% SA	1.90	1095	0.77	2.65	5392	1.25	3.20	7565	1.57
60% SA	1.01	95	0.12	1.63	1120	0.85	2.18	6213	1.30
70% SA	0.82	nd	0.08	1.20	367	0.23	1.15	163	0.15
80% SA	0.47	nd	0.06	0.90	nd	0.08	0.92	62	0.06
90% SA	0.20	nd	0.06	0.21	nd	0.06	0.52	nd	0.04
100% SA	0.03	nd	0.04	0.08	nd	0.06	0.10	nd	0.04

nd, not detectable.

3.2. Crossflow filtration

3.2.1. General

After the promising results obtained by dead-end filtration regarding the retention of soaps, FFA and water, crossflow filtration trials were performed. The tangential flow permit the transport of the particles away from the membrane surface and thus limits cake thickening. This brings a substantial advantage to the crossflow filtration over the dead-end mode and allows higher fluxes. However, if the particles formed in the oils during neutralization of FFA are considered to be soft matter, the shear caused by the tangential flow and by pumping can cut or even destroy these particles. For the following trials, the acidity was neutralized with an excess of 10% of soda (i.e., 1.1 stoichiometric equivalents).

3.2.2. Laboratory trials

As shown for LVOO1 in Figs. 1 and 2, fluxes were plotted against filtration time. The main feature is an initial short period of rapid flux decline, followed by an extended period of an endless but slow flux decline due to membrane fouling. When using a 40% NaOH solution (Fig. 2), the initial flux for PS 0.8 µm (~127 l/h m^2) is about twice those measured for the 0.2 and 0.5µm membranes. After 30 min of crossflow filtration, the fluxes are reduced to about one half the initial values in the case of the 0.2 and 0.5 µm membranes and to 30% of the initial flux in the case of PS 0.8 µm. After 60–90 min, a relative stabilization of the fluxes is observed. The slope is then in the range of 2–10 l/h m^2. Our previous studies on seed oils revealed similar behaviour and a relatively good repeatability (Hafidi, Pioch, & Ajana, 2003; Pioch et al., 1998, 1996).

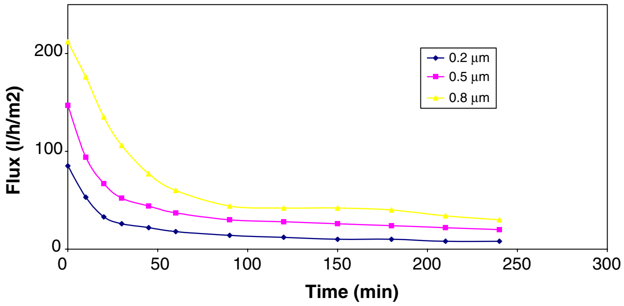

Fig. 1. Evolution of fluxes during crossflow filtration of LVOO1 neutralized with 20% NaOH.

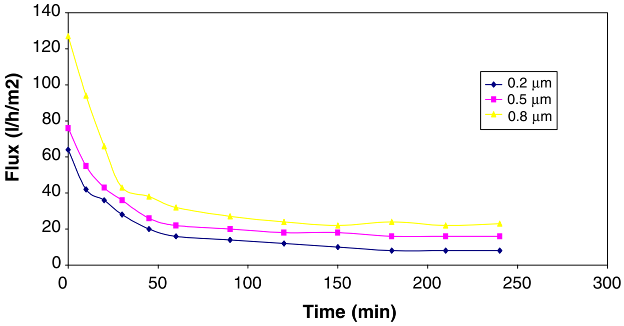

Fig. 2. Evolution of fluxes during crossflow filtration of LVOO1 neutralized with 40% NaOH.

When neutralizing with a less concentrated lye (20% NaOH), the initial fluxes are improved, probably because of greater sizes of the aggregates resulting from solubilisation of more important amounts of water. The initial flux for the 0.8 µm membrane (~220 l/h m^2) is about 70% greater than that obtained for PS 0.5 µm and three times that observed in the case of PS 0.2 µm. When comparing the influence of soda concentration the initial fluxes are improved; for PS 0.5 and 0.8 µm, the initial fluxes are twice those obtained with 40% NaOH but only a very slight improvement is noted in the case of PS 0.2 µm. However, the flux drops drastically: After 30 min of crossflow filtration, it is reduced to about one half the initial value in the case of 0.8 µm and down to 30% of the initial flux in the case of the 0.2 and 0.5 µm membranes. Nevertheless, after having filtered for 3 h, flow rates are still higher with the less concentrated soda solution, probably because of larger aggregates resulting from increased water absorption.

As a matter of fact, due to the limited water content of the crude oil (0.16 g/100 g for LVOO1), the water available for participating in the aggregation of soap and phospholipids is almost entirely dependent on the concentration of the soda solution, ~1 and 2 g/100 g of oil for the same sample, respectively, for 40% and 20% NaOH. This amount of water provides a ratio of almost 5–10 water molecules per soap molecule and thus

Table 4
Free fatty acids and soap contents in the crossflow processed oils

	PS (µm)	FFA (%)		Soap (ppm)	
		20% NaOH	40% NaOH	20% NaOH	40% NaOH
Laboratory scale	0.2	0.12	0.37	nd	nd
	0.5	0.28	0.18	nd	nd
	0.8	0.22	0.25	65	47
Pilot plant trials	0.2	0.15	0.21	nd	nd
	0.5	0.12	0.28	23	nd

it makes sense that the soda concentration plays an important role in the properties of aggregates. However, the proportion of water allowed for an efficient retention is not expected to be very low; Pioch found that the number of water molecules per polar head may vary from at least 9 to 53 without impairing the complete elimination of soap (private communication).

Regarding the oil quality, the analysis showed a significant reduction of acidity and a complete retention of sodium soap in the cases of 0.2 and 0.5 µm (Table 4). From an applied point of view, two parameters could be used for lowering the residual FFA content: (i) a larger excess of caustic soda −1.1 stoichiometric equivalents in the present case-and (ii) a more efficient mixing device. The use of a 0.8 µm membrane allowed not only some FFA but also some soap to permeate across the membrane, whatever the soda concentration (20% or 40%). It is notable that, in the case of dead-end filtration, although the membrane PS was higher than those of the crossflow mineral membranes, no soap was found to permeate when neutralizing with a stoichiometric amount of base. This may be explained by the formation of a thick and compact cake, which most likely forms the actual filtration layer.

3.2.3. Pilot plant trials

Dealing with larger quantities of oils can reveal some specific problems and thus this is an important step for the validation of the laboratory results. Two trials were conducted under experimental conditions similar to those of the laboratory experiments, but with PS 0.2 and 0.5 µm only, and the FFA were neutralized with a 20% soda solution according to the best results noted in the above section. As illustrated in Fig. 3, flux evolution is similar to that noted during the laboratory trials. Initial and end fluxes are close to the laboratory results although slightly lower, possibly because of different cross-sections of membranes (multi channel and tubular for pilot and laboratory devices, respectively). In both cases, the quality of the processed oil estimated by residual FFA and soap analysis is acceptable (Table 4) although the oil processed with 0.5 µm contains traces of soap molecules.

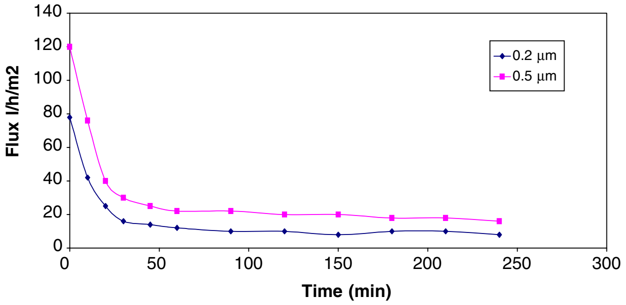

Fig. 3. Evolution of fluxes during pilot crossflow filtration experiments.

These results, which were obtained under conditions not yet optimized with a 50 kg load pilot unit, confirm the laboratory data and show that the process could be used for production.

4. Conclusion

The pioneering results show the efficiency and the potential interest of the use of membrane technology for olive oil deacidification. In a single step, oils were almost freed of their FFA and soap. At this stage, the process, which operates at ambient temperature does not generate any polluting effluent. It is expected to preserve most of the useful but often sensitive components present in the virgin oil and thus to meet consumer requirements and to avoid full refining of these still valuable oils.

Despite the promising results, a lot of research work must be done before bringing such a process to industrial production, namely, evaluation of the effect of the process on the whole oil composition, improvement of flow rate and reduction of fouling. This would allow upgrading of a substantial part of the olive oil produced in most of the Mediterranean countries at a time when the demand for quality olive oil is growing faster than production because of the agronomic peculiarities of the crop.

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References

AFNOR standard methods. (1984). *Recueil des normes françaises: Corps gras, graines oléagineuses et produits derives* (3rd ed.). AFNOR Ed.

Ajana, H., Pioch, D., & Graille, J. (1993). Raffinage d'huiles végétales ou animales par filtration. French patent application 93-02999.

Berghausen, J., Zipfel, J., Lindner, P., & Richtering, W. (1998). Shear-induced orientations in a lyotropic defective lamellar phase. *Europhysics Letters, 43*, 683–689.

Cistola, D. P., Atkinson, D., Hamilton, J. A., & Small, D. M. (1986). Phase behavior and bilayer properties of fatty acids: Hydrated 1:1 acid-soaps. *Biochemistry, 25*, 2804–2812.

Diat, O., Roux, D., & Nallet, F. (1993). Effect of shear on lyotropic lamellar phase. *Journal de physique II, 3*, 1427–1452.

European commission regulation No. 2568. (1991). On the characteristics of olive oil and residue oil and on the relevant methods of analysis. *European Commission Official Journal*, L248, 09/05/91.

Frega, N., Mozzon, M., & Lercker, G. (1999). Effects of free fatty acids on oxidative stability of vegetable. *Journal of the Americal Oil Chemists Society, 76*, 325–329.

Gupta, A. K. S. (1986). Novel developments in refining of edible oils. *Fette Seifen Anstrichmittel, 88*, 79–86.

Hafidi, A., Pioch, D., & Ajana, H. (2003). Adsorptive fouling of inorganic membranes during vegetable oils microfiltration. *European Journal of Lipid Science and Technology, 105*, 138–148.

Jandacek, R. J. (1991). The solubilization of calcium soaps by fatty acids. *Lipids, 26*, 250–253.

Kale, V., Katikaneni, S. P. R., & Cheryan, M. (1999). Deacidifying rice bran oil by solvent extraction and membrane technology. *Journal of the American Oil Chemists Society, 76*, 723–727.

Kiristakis, A., & Tsipeli, A. (1992). Relationship of the acidity of olive oil to its resistance to oxidation. *La Rivista Italiana Della Sostanze Grasse, 69*, 513–515.

Koseoglu, S. S., Lawhon, J. T., & Lusas, E. W (1990). Membrane processing of crude vegetable oils: Pilot plant scale removal of solvent from oil miscellas. *Journal of the American Oil Chemists Society, 67*, 315–322.

Kumar, N. S., & Bhowmick, D. N. (1996). Krishna Separation of fatty acids/triacylglycerols by membranes. *Journal of the American Oil Chemists Society, 73*, 399–401.

Largueze, C., Pioch, D., & Gulik-Kryzwicki, T. (2002). Structure of clusters of phospholipids and soaps during refining of vegetable oils. In *Meeting of the euro fed lipids, Strasbourg, 25–28 November, 2002*.

Pérez-Camino, M. C., Ruiz-Méndez, M. V., Marquez-Ruiz, G., & Dobarganes, M. C. (1993). Virgin and refined olive oils: Differences in glyceridic minor components. *Grasas y Aceites, 44*, 91–95.

Pioch, D., Largueze, C., Graille, J., Ajana, H., & Rouviere, J. (1998). Towards an efficient membrane based process for vegetable oils refining. *Industrial Crops and Products, 7*, 83–89.

Pioch, D., Largueze, C., Hafidi, A., Ajana, H., & Graille, J. (1996). Membrane based vegetable oil refining process: Tangential filtration at laboratory and pilot scales. In *World conference and exhibition on oilseed and edible oils processing, Istambul, Turkey, 6–10th October*.

Raman, L. P., Cheryan, M., & Rajagopalan, N. (1996). Deacidification of soybean oil by membrane technology. *Journal of the American Oil Chemists Society, 73*, 219–224.

Ruiz-Mendez, M. V., Marquez-Ruiz, G., & Dobarganes, M. C. (1997). Relationships between quality of crude and refined edible oils based on quantitation of minor glyceridic compounds. *Food chemistry, 60*, 549–554.

Subramanian, R., & Nakajima, M. (1997). Membrane degumming of crude soybean and rapeseed oils. *Journal of the American Oil Chemists Society, 74*, 971–975.

Van de Sande, R. L. K. (1989). Method of refining glyceride oils. European patent 89201635.3.

Zwijnnenberg, H. J., Krosse, A. M., Ebert, K., Peinemann, K.-V., & Cuperus, F. P. (1999). Acetone-stable nanofiltration membranes in deacidifying vegetable oil. *Journal of the American Oil Chemists Society, 76*, 83–87.