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Innovative Food Science and Emerging Technologies 6 (2005) 203–212

Innovative Food Science & Emerging Technologies

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# Membrane-based simultaneous degumming and deacidification of vegetable oils

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Received 20 January 2004; accepted 16 December 2004

**Abstract**

An efficient membrane based process for simultaneous degumming and deacidification of vegetable oil was investigated. Appropriate crude oil conditioning allow the formation of submicronic aggregates, composed with soaps molecules resulting from the neutralisation of FFA and PL, which are retained when microfiltrating. Initial flux for the 0.8 μm membranes (~560 l/h $m^2$) was about twice that of the 0.5 μm and about 10 times that of 0.2 μm membrane. The filtered oils showed good quality in the case of 0.2 and 0.5 μm membranes, but the use of 0.8 μm membranes has allowed some soaps to pass through. Two types of crude oils behaviour were noticed. Oppositely to some oils for which just simple neutralisation led to a satisfactory elimination of the phospholipids, others were very tough to refine. The operating pression seems not to affect the efficiency of the separation, whereas the stability of the vesicle-like aggregates is found to be greatly affected by the increase of the temperature above 25 °C. Beside the quasi-elimination of FFA, PL and water, minerals and pigments contents were also greatly lowered. When using an NaOH 20%, the lovibond yellow score lowered from around 28 to 10 in the case of sunflower oils and from ~34 to 6–20 in the case of soya and rapeseed oils. The monoglycerides were almost undetectable after membrane processing whatever the type of the conditioning used. After processing, the diglycerides contents, which ranges in the tested crude oils between 0.8% and 1.0%, showed almost no changes for two oils, whereas noticeable increases were obtained for the other oils. Total phytosterols contents were systematically reduced. The reductions vary from 3% to 44% upon the case. Neutralisation with an NaOH 20% lead to higher sterol losses in comparison to NaOH 40%. All the sterol components contents were found to be reduced in almost similar proportions.


*Keywords:* Vegetable oils; Degumming; Deacidification; Microfiltration; Minor components; Quality

*Industrial relevance:* Conventional oil recovery and purification processes are continuousely sought to be replaced by gentler processing conditions. Membrane based oil refining operating at low temperatures and without the generation of waste water offer an interesting and promising approach towards "greener" technologies.

## 1. Introduction

Excepting extra virgin olive oils and some speciality oils, vegetable oils must undergo refining operations to remove undesirable components granting them thus satisfactory purity and stability characteristics (acidity, colour, oxidative, and sensory). Classical edible oil refining processes include degumming, neutralisation, bleaching, and deodorisation. These series of operations aim mainly to remove phospholipids (PL), free fatty acids (FFA), pigments, hydroperoxides, and waxes. Such a processing can be operated according to two main schemes differing essentially in the manner the FFA are removed. In the so called chemical or alkali refining, they are turned to soaps by an alkali and, subsequently, removed from the neutral oil by centrifugations and washing steps, whereas in physical refining they are distilled during the deodorisation operation. The two processes are reputed to be very energy-consuming. In addition, all the refining operations subject oils to high temperatures; consequently, quantitative and qualitative

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doi:10.1016/j.ifset.2004.12.001

changes inevitably take place especially in components responsible of quality. High temperatures seem to be the most harmful parameter, which is responsible of hydrolytic, oxidative, and polymerisation alterations (Cert, Lanzon, Carelli, Albi, & Amelotti, 1994; Schulte, 1995). Structural changes are also related to the heating especially during bleaching (Schulte, 1995) and deodorisation (Cert et al., 1994). Devinant, Scamaroni, and Naudet (1980) and Jawad, Kocchar, and Hudson (1983) reported that, during physical refining, the stereoisomerisation and polymerisation depend on the time and the temperature. Some sterols can undergo a dehydration during bleaching (Schulte, 1995) and deodorisation (Cert et al., 1994) so β sitosterol can form the 3,5 stigmadiene. Total sterols are also reported to lower after neutralisation (Kochhar, 1983). Pasqualone and Catalano (2000) reported that neutralised oils showed losses up to 50% in total sterols. Catalano, De Leonardis, and Comes (1994) and Gomes (1992) have reported an increase of diglyceride amounts in refined olive oil. Most of these alterations are temperature-dependent.

Improving the quality of the processed oils by reducing side effects and diminishing the energy consumption has been among the most active research areas throughout the past half-century. Due to its characteristics as non-polluting and energy saving technology, membrane processing has recently emerged as a promising alternative. Potential applications covering various aspects such as solvent removing (Bhanushali, Kloos, & Bhattacharyya, 2002; Koseoglu, Lawhon, & Lusas, 1990; White & Nitsch, 2000), edible oil degumming (Kim, Jong-Ho Kim, Lee, & Tak, 2002; Koseoglu, Rhee, & Lusas, 1990; Subramanian & Nakajima, 1997), deacidification and free fatty acids recovering (Kale, Katikaneni, & Cheryan, 1999; Raman, Cheryan, & Rajagopalan, 1996; Zwijnenberg, Krosse, Ebert, Peinemeann, & Cuperus, 1999), dewaxing (De, Das, Dutta, & Bhattacharyya, 1998), and triacylglycerols partitioning (Bornaz, Fanni, & Parmentier, 1995a, 1995b) were reported. In the very first works from the last century, Sen Gupta, a pioneer, demonstrated the efficiency of degumming the oil miscellas using ultrafiltration techniques (Gupta, 1977, 1986). Ajana, Pioch, and Graille (1993) demonstrated the possibility of a complete degumming and deacidification of crude vegetable oils subsequently to appropriate conditioning using membrane separation techniques. The neutralisation of the free fatty acids with appropriate soda concentration and under adequate conditions allow the formation of submicronic particles with onion-like structures as revealed by scanning electron microscopy (Largueze, Pioch, & Gulik-Kryzwicki, 2002). These structures are believed to be formed not only by fatty acid salts but also with phospholipids and water molecules. Due to their relatively important sizes, these aggregates can be easily removed by a microfiltration technique. Such structures are thought to be formed of hundreds of fatty acid salts and phospholipid bilayer stacks. Both oil conditioning and filtration can be operated at low temperature (20–25 °C). These mild conditions which contrast with the conditions in industrial practices are expected to preserve the sensitive and bioactive components in edible oils.

In the present paper, we report an assessment of the efficiency of such a processing by testing different crude oils and comparing their suitability for our membrane-based purification process. The effects of some physico-chemical parameters on the stability of the aggregates and therefore on the efficiency of the separation were studied. The impact of our simultaneous degumming and neutralisation process on some minor components of the oils was also investigated.

## 2. Materials and methods

### 2.1. Oil samples

Soya, sunflower, and rapeseed crude oils were obtained from CEREOL, sète, France. The crude oils were neutralised at room temperature (20–25 °C) (unless otherwise stated) by pouring slowly with a pipette an aqueous sodium hydroxide solution (20% or 40% w/v) under magnetic stirring (600 rpm) and then filtered as described in previous works (Hafidi, Pioch, & Ajana, 2004; Pioch, Largueze, Graille, Ajana, & Rouviere, 1998; Pioch et al., 1996). In the cases of acid conditioning, 0.1% or 0.3% (w/w) of the acid phosphoric 85% (Sigma) were added at room temperature (20–25 °C) to the crude oils under vigorous mixing during 20 min before neutralisation of the whole acidity with an appropriate NaOH solution.

### 2.2. Microfiltrations

Dead end filtration experiments were performed with a stainless steel Gelman module (200 ml volume, 200 kPa pressure; Whatman cellulose filter (pore size: 2.5 μm, filtration area 16 $cm^2$)). Crossflow filtration experiments were carried out at 25 °C with a laboratory stainless steel apparatus (1 kg oil samples, tubular alumina membrane 200 mm length, 40 $cm^2$ area) under: continuous permeate recycling, 3.5 m/s as a tangential velocity and 200 kPa transmembrane pressure. Fluxes were estimated by direct measurements using an appropriate graduated cylinder.

### 2.3. Analytical methods

In order to check the chemical composition of both starting and refined oils, French standard procedures (AFNOR, 1984) were applied: phosphorus NF T 60-227, soaps NF T 60-217, free fatty acids NF T 60-204, water NF T 60-367, and peroxide value NF T 60-220. Cations (Na, Ca, Mg, Fe, Cu) were analyzed after mineralisation following the ISO 6884: 1985 (ISO standards methods, 1985) standard method, comprising mineralisation and atomic emission spectrophotometry analysis (inductive