

Degumming of rapeseed and sunflower oils

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Abstract

Crude extracted or pressed rapeseed and sunflower oils contain phospholipids, which must be removed from oil during refining process. For removing phospholipids following methods were used: water, acid, and TOP degumming process (TOP is a Dutch acronym derived from “Totaal Ontslimings Process” meaning total degumming process). After the water degumming, the amount of phosphorus was reduced to 70.4 mg kg⁻¹ in extracted rapeseed oil and to 60.9 mg kg⁻¹ in pressed one. The residual amount of phosphorus in extracted and pressed sunflower oils was 56.9 mg kg⁻¹ and 50.1 mg kg⁻¹ respectively. However, acid degumming process reduced the amount of phosphorus below to 11.8 mg kg⁻¹ in extracted and pressed sunflower oils and below to 21.4 mg kg⁻¹ in extracted and pressed rapeseed oils. The most effective degumming process was TOP degumming, that allowed to decrease the amount of phosphorus in pressed rapeseed oil to 9.6 mg kg⁻¹ and in pressed sunflower oil to 4.5 mg kg⁻¹. In extracted oils the results were for rapeseed oil 15.1 mg P per kg and 10.6 mg P per kg of sunflower oil. However, TOP degumming process can not reduce the amount of P, Mg and Ca under 15.1 mg kg⁻¹, 15.6 mg kg⁻¹ and 3.2 mg kg⁻¹ in extracted rapeseed oil, because of the high content of these elements in initial crude oil.

Keywords: degumming, phospholipids, rapeseed oil, sunflower oil, refining

Introduction

The oil obtained by mechanical expelling or solvent extraction is termed “crude” oil, as it contains a number of impurities. Some of the impurities, such as seed fragments and meal fines, are oil insoluble and thus can be readily removed by filtration. Others, including free fatty acids, hydrocarbons, ketones, tocopherols, glycolipids, phytosterols, phospholipids,

proteins, pigments, and resins, are soluble or form stable colloidal suspensions in the oil. Most of these have unfavorable effects on the flavor, odor, appearance, and shelf life of the oil, and therefore have to be removed from the vegetable oils by chemical or physical refining processes (Verleyen et al. 2002). The common oilseeds as soybean, cottonseed, sunflower and rapeseed are rich sources of phospholipids (Indira et al. 2000; Willem et al. 2008). Phospholipids pose many problems for the storage and processing of the crude oil and are removed from oil during refining by a process known as degumming (Brekke 1975).

There are two types of phospholipids: hydratable (HPL) and nonhydratable (NHPL), and they are removed from oil by the degumming process. Most of the phospholipids in crude sunflower and rapeseed oils are hydratable and can be removed by water degumming (Carelli et al. 1997). NHPL are not hydratable with water, can not swell and form gels or precipitate from oil (Szydłowska-Czerniak 2007). Removing of NHPL requires more complex process at increased temperature with the use of phosphoric acid, citric acid or other degumming substances.

The phosphatidyl choline and phosphatidyl inositol are completely hydratable. Phosphatidyl ethanolamine is only partly and phosphatidic acid is not hydratable, when they form salt with divalent cation (mainly calcium and magnesium) or when they are not in dissociated form. The simplified chemistry is the following: the phosphatide/metal complexes are decomposed by addition of acid or complexing agent, then follows hydration of phospholipids by water. Partial neutralisation of acid is applied to avoid migration of phosphatides back to the oil phase (Kovari 2004).

However, for physical refining of vegetable oils, water degumming is not sufficient, so degumming process plays a critical role at physical refining of edible oils. Traditional degumming processes, including water degumming, superdegumming, TOP degumming, acid treatment and other ones, cannot guarantee the achievement of low phosphorus contents required for physical refining, and they are not always optimally suited for all oil qualities because of the high content of NHPL (Copeland et al. 2005).

The “total degumming process,” known by its Dutch acronym TOP, is designed to further treat the oil that has already been water degummed. The process has two variations to cater to different needs (Dijkstra et al. 1987). In the first approach a dilute acid is finely dispersed into the oil. After a sufficient contact time a base is added and mixed into the acid-in-oil dispersion. Such a base can be NaOH, sodium carbonate or sodium silicate. During the process the acid initially decomposes metal/phosphatidic acid (PA) complexes into insoluble metal salts and PA (in acid form). Phosphatidic acid is then hydrated by partial neutralisation

with the base added, and removed from the oil by centrifugation. The second approach uses a combination of two centrifuges to remove the hydrated phospholipids with high efficiency and minimal losses. The first one removes the bulk of the gum phase. Clearly, the quality of the water-degummed oil is critical to TOP degumming. When the water-degummed oil has a higher Ca/Mg content, TOP process becomes less effective (Cleenewerck et al. 1992).

Removal of phospholipids from vegetable oils by using membrane techniques is the one of the modern technologies (Ochoa et al. 2001). The latest degumming processes are soft degumming and enzymatic degumming. Soft degumming process involves a complete elimination of phospholipids by a chelating agent, such as ethylenediaminetetraacetic acid (EDTA), in the presence of emulsifying agent. Different kind of crude oils were degummed by Soft degumming method; the content of phospholipids in the treated samples of the oils studied was lowered approximately to 5 mg kg^{-1} . However, the high cost of EDTA could not allow use this method in industry (Choukri et al. 2001). Nowadays, two kinds of enzymes, such as Lecitase 10L (pancreatic phospholipase A₂) and Lecitase Novo (microbial lipase), are used for oil degumming in the industry (Yang et al. 2006; Bo et al. 2006).

The aim of this article is the study of influence of water, acid and TOP degumming on the amount of P, Mg and Ca in rapeseed and sunflower oils respectively.

Experimental

Materials

Crude industrial rapeseed and sunflower oils were processed from Slovakian oilseed cultivars in Palma-Tumys Bratislava (Slovak Republic).

Methods

The acid value of the oils was determined according to AOCS Official Method Cd 3a - 63 (AOCS, 1997). The amount of phospholipids was determined as the total phosphorus of vegetable oil according to AOCS Official Method Ca 12-55 (AOCS, 1997). The absorbance was read at 650 nm using UV/VIS-1601 spectrophotometer (Shimadzu, Tokyo, Japan), and the phosphorus content was determined by means of standard curve using NaH_2PO_4 as a standard. The amount of calcium and magnesium were determined by inductively coupled plasma (ICP) optical emission spectroscopy (V Liberty 200, Victoria, Australia) by following AOCS official method Ca 17-01 (AOCS, 1997). Magnetic stirrer (IKA Werk, Staufen im

Breisgau, Germany), and centrifuge (MPW-340, CHEMARGO, Blachownia, Poland) operated at 1300 x g, were used during the all experiments. All measurements were repeated three times; the mean values and the respective standard deviations were reported.

Water degumming

Crude rapeseed and sunflower oils were degummed by heating the oils to 80 °C, mixed with water (to 5% vol.) and stirred for 15 min by magnetic stirrer. Then, the mixture was centrifuged for 20 minutes.

Acid degumming

Crude rapeseed and sunflower oils were heated to 80 °C and water solution of citric acid (30 %) was then added in amount of 2 % (by volume of the oil). The mixture was stirred for 20 minutes. The oil/acid mixture was kept at 80 °C up to 15 min, cooled down to 25 °C, mixed with water (1 %) and transferred to a holding vessel. After settling for 60 min the mixture was centrifuged for 20 min to separate acid degummed oil from its by-products.

TOP degumming

TOP degumming process consists of two-stage process: 1 - water degumming of crude oil; 2 - water-degummed oil was heated to 80 °C and was initially mixed intensively with a phosphoric acid (14 %) in amount of 0.1 % by weight of oil. After a short reaction time (for approximately 5 min), the acid is partially neutralized with NaOH (20 % water solution) in amount of 0.3 % by weight of oil. The total reaction times were 10 minutes. The phosphatides that are hydrated by this way are removed by centrifugation for 20 min to obtain oil with low content of phospholipids, Ca and Mg.

Statistical analysis

All measurements were performed in triplicate. The statistical analysis was carried out with the program Statgraphics Plus, Version 1.4 for Windows (Manugistic, Rockville, USA). The significance of differences between mean values of all measurements were determined at the $p = 0.05$ (5%) level, using a one way analysis of the variance and the t-test.

Results and Discussion

Degumming process removes impurities like phospholipids, gums, residual metals, Ca and Mg from crude vegetable oils. The present alkali metals, such Ca and Mg are bound on NHPL. These substances are thermally unstable, they are altered and decomposed at increased temperatures, and deteriorate the color and overall appearance of the oil. For demonstration of the efficiency of individual steps the amounts of phosphorus, Ca and Mg were determined after every degumming operation.

Water degumming

During the water degumming HPL react with water, form gels and are separated by centrifugation. After the water degumming the amount of total phospholipids (it is expressed as mg of phosphorus per kg of oil) decreased from 863.6 mg kg⁻¹ to 70.4 mg kg⁻¹ of P in rapeseed extracted oil and from 156.4 mg kg⁻¹ to 60.9 mg kg⁻¹ in pressed one (Table 1). In extracted and pressed sunflower oils, the amount of phosphorus also significantly decreased from 293.5 mg kg⁻¹ to 56.9 mg kg⁻¹ and from 95.7 mg kg⁻¹ to 50.1 mg kg⁻¹ respectively. In addition to, the amount of Ca and Mg was also reduced (Table 2 and Table 3).

Table 1. Influence of water, citric acid and TOP degumming on phosphorus removal from crude rapeseed and sunflower oils

Vegetable oils	Phosphorus in oils (mg kg ⁻¹)			
	Rapeseed oil		Sunflower oil	
	Extracted	Pressed	Extracted	Pressed
Crude oil	863.6 ± 9.3	156.4 ± 6.2	293.5 ± 7.8	95.7 ± 4.3
Water degummed	70.4 ± 1.2	60.9 ± 1.8	56.9 ± 1.7	50.1 ± 1.1
Acid degummed	21.4 ± 1.5	16.9 ± 1.2	11.8 ± 1.7	7.1 ± 1.1
TOP degummed	15.1 ± 1.1	9.6 ± 0.9	10.6 ± 1.3	4.5 ± 0.9

Despite lowered values of P, Mg and Ca in examined oils, these amounts are still unsuitable for physical refining, so these oils must be directed to the next technological steps before the final physical refining.

Acid degumming

The efficient degumming process should convert the NHPL into HPL, which can be removed from vegetable oils. Citric acid is used not only for decomposition of metal salt but also as a chelating agent to keep the metals in water-soluble complex (Katalin 2004).

In comparing with simple water degumming, the acid degumming has lowered the amount of phosphorus in rapeseed and sunflower oils (Table 1). After the acid degumming, the amounts of Ca and Mg were also reduced in both oils. Acid degummed, extracted and pressed rapeseed oils contained 19.9 mg kg⁻¹ and 9.7 mg kg⁻¹ of Ca in comparing with initial amount of 181.2 mg kg⁻¹ and 78.3 mg kg⁻¹ of Ca. The amount of Mg in rapeseed extracted and pressed oils are also decreased under to 10.3 mg kg⁻¹ from initial amount 92.2 mg kg⁻¹ and 25.6 mg kg⁻¹, respectively (Table 2 and Table 3). The amount of phosphorus in extracted and pressed sunflower oils decreased from 293.5 mg kg⁻¹ to 11.8 mg kg⁻¹ and from 95.7 mg kg⁻¹ to 7.1 mg kg⁻¹

Table 2. Influence of water, citric acid and TOP degumming on Ca removal from crude rapeseed and sunflower oils

Vegetable oils	Ca in oils (mg kg ⁻¹)			
	Rapeseed oil		Sunflower oil	
	Extracted	Pressed	Extracted	Pressed
Crude oil	181.2 ± 7.4	78.3 ± 4.6	74.9 ± 6.7	26.0 ± 2.2
Water degummed	69.3 ± 1.8	58.4 ± 2.9	34.4 ± 4.3	12.9 ± 1.8
Acid degummed	19.9 ± 1.2	9.7 ± 1.4	9.3 ± 2.1	4.1 ± 1.2
TOP degummed	15.6 ± 1.7	5.1 ± 1.1	4.1 ± 1.2	0.9 ± 0.2

Moreover, the residual content of Ca and Mg was lower than 9.3 mg kg⁻¹ in extracted and pressed sunflower oils. Sunflower oil degummed by citric acid can be directed to the next steps of refining process for improving oil color and removing of FFA (free fatty acids). However, extracted rapeseed oil can not be refined by physical refining process because of the relatively high content of P, Ca and Mg. This oil can cause complication at the further refining steps, as bleaching and deodorization.

TOP degumming

Rapeseed and sunflower oils after water treatment were mixed with phosphoric acid, which interact with phosphorus in NHPL. Then NaOH was added to the mixture and stirred, and whole mixture was directed to centrifugation process. Together with NHPL also Ca and Mg are partly removed from vegetable oils. According to the table 1, after TOP degumming the amount of phosphorus decreased to 15.1 mg kg⁻¹ in rapeseed extracted oil and to 9.1 mg kg⁻¹ in pressed one. Experiments showed that the TOP degumming process reduced the amount of phosphorus to 10.6 mg kg⁻¹ and to 4.5 mg kg⁻¹ in extracted and pressed sunflower oil.

Table 3. Influence of water, citric acid and TOP degumming on Mg removal from crude rapeseed and sunflower oils

Vegetable oils	Mg in oils (mg kg ⁻¹)			
	Rapeseed oil		Sunflower oil	
	Extracted	Pressed	Extracted	Pressed
Crude oil	92.2 ± 4.6	25.6 ± 2.3	80.6 ± 4.8	18.4 ± 1.7
Water degummed	41.4 ± 3.3	15.3 ± 1.3	29.0 ± 2.9	6.5 ± 1.2
Acid degummed	12.3 ± 1.4	9.7 ± 1.9	7.3 ± 1.1	2.3 ± 1.3
TOP degummed	3.2 ± 1.1	1.7 ± 0.8	1.6 ± 0.6	0.5 ± 0.1

After TOP degumming process, the amount of Ca and Mg in rapeseed pressed oil decreased to 4.2 mg kg⁻¹ and 1.1 mg kg⁻¹. The residual amount of Ca and Mg in extracted sunflower oil was 4.1 mg kg⁻¹ and 1.6 mg kg⁻¹ after the TOP degumming (Table 2 and Table 3). Pressed and extracted sunflower oils degummed by TOP degumming have the minimal amount of phosphorus, Ca and Mg, which allows to shift these oils to the next step of refining process. However, extracted rapeseed oil has still relatively high amount of P and Ca in comparison with the other ones. With a “good” water degummed oil as the starting material, the residual P level is low as 5 mg kg⁻¹ (for pressed sunflower oil) and can be achieved low Mg level (<3.2 mg kg⁻¹) as well. When the crude oil and water-degummed oil has a higher Ca/Mg content, TOP process becomes less effective (mainly for extracted rapeseed oil).

The goal of this paper was to analyze the effect of water, acid and TOP degumming on reducing of phospholipids from crude rapeseed and sunflower oils, both extracted and pressed. The acid and TOP degumming processes are more effective on pressed vegetable oils

and extracted sunflower oil. After TOP degumming process, the residual amount of P, Mg and Ca in extracted rapeseed oil was relatively high. The efficiency of degumming process is directly connected with obtaining methods of crude vegetable oils. For increasing the efficiency of degumming process, we suggest decreasing the amount of P, Mg and Ca in an extracted oil by its mixing with pressed one.

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