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Effect of degumming process on physicochemical properties of sunflower oil

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ABSTRACT

The effect of different degumming processes on physicochemical properties of crude sunflower oil was studied by means phosphorous content, acid value, peroxide value, phospholipids, iron, moisture, unsaponifiable matter, viscosity, density and color value. Three different degumming processes were evaluated: phospholipase A1 degumming process, phospholipase A2 degumming process and water degumming process. The enzymatic degumming trials were performed at 50 °C, pH 5 and an enzyme dosage of 200 U/kg of oil during 180 min with both enzymes. The water degummed treatment was carried out at the same time with 3% water/oil ratio, and 65 °C of temperature. The phosphorus content decreased from 544.51 to 3.02 mg/kg and 5.81 mg/kg using phospholipase A1 and A2 respectively. These results indicated the high efficiency of the treatments to achieve good quality oil suitable for physical refining. The residual phosphorus content value obtained for water degummed treatment suggests that it was not enough for physical refining process. Phospholipids content showed a drastic decrease with the enzymatic degumming process. The iron content was reduced with all degumming processes, being more significantly after the enzymatic treatment. The unsaponifiable matter decreased in all treated samples compared with crude sunflower oil. Impurities that enhance the viscosity of oil and some pigments were removed during the process, being more noticeably in the enzymatic treatment. The results obtained revealed that the enzyme-mediated degumming oils had better physicochemical parameters than the crude and water degummed oils.

1. Introduction

Crude sunflower oil obtained by oilseed processing has to be refined before the consumption in order to remove undesirable compounds. The most important of these minor substances are free fatty acids, color pigments, phospholipids, metals and waxes. The objective of refining is to eliminate these impurities with the least possible effect on desirable components present in the crude vegetable oils in order to obtain an odorless, bland and oxidative stable refined vegetable oil that is acceptable to consumers (Medina-Juarez et al., 2000). Presence of compounds such as odiferous volatiles, pigments, waxes and metal traces, affect negatively the taste, smell, appearance and storage stability of the refined oil. They must be removed to yield a stable product with a bland or pleasant taste (Aluyor et al., 2009). The presence of phospholipids can cause the oil discoloration, serve as a precursor of off-flavors and contribute to the losses of neutral lipids during neutralization (Jiang et al., 2015). In addition, phospholipids are naturally occurring emulsifiers, which bind oil molecules together leading to increased viscosity, and refining and/or flow losses (Iwuoha et al., 1996). In the food industry, viscosity is one of the most important parameters required in the design of technological process. On the other side, viscosity is also an important factor that determines the overall quality and stability of a food system (Abramovic and Klofutar, 1998). Therefore, the removal of phospholipids is essential for the production of high-quality finished oil (Subramanian et al., 1999). Degumming is an important step in the refining process of vegetables oils, and it removes phospholipids and mucilaginous gums. Traditional degumming that include water, super, total, acid degumming and ultrafiltration processes cannot guarantee the low phosphorus levels that are required for physical refining (Jiang et al., 2015). These techniques are not suitable for oils with high levels of non-hydratable phospholipids (Zufarov et al., 2008). Enzyme-mediated degumming is a unique process quite distinct from the well-known acid degumming variations, since both hydratable and nonhydratable phospholipids present in the oil are hydrolysed to the corresponding

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lysophospholipids (Clausen, 2001).

Currently, the most commonly utilized phospholipases in enzymatic degumming are phospholipase A1 (PLA1) and phospholipase A2 (PLA2), which remove the fatty acid from positions 1 and 2 with respect to glycerol, respectively (Galhardo et al., 2010). Other enzymes are commercially available for vegetable oils processing, such as phospholipase B (PLB), phospholipase C (PLC) and the lipid acyltransferase (LAT). PLB eliminates both fatty acids from the glycerol group (Jiang et al., 2011), PLC catalyses the hydrolysis of phosphate-glycerol bond in phosphatidylcholine and phosphatidylethanolamine and LAT, transfers a fatty acid to a sterol present in the oil in order to convert it into a sterol ester (Dijkstra, 2011).

There are several studies about the effect of enzymatic degumming on the phosphorus content (Jiang et al., 2011; Manjula et al., 2011), the quantitative and qualitative analysis of phospholipids (Sampaio et al., 2015) and the acid value achieved (Jahani et al., 2008). However, just few studies have been undertaken to determine the changes in physical and chemical characteristics of sunflower oil during the enzymatic degumming process. The aim of this work was to evaluate the effect of the different degumming process on physical and chemical parameters of crude sunflower oil.

2. Materials and methods

2.1. Materials

Molinos Río de la Plata (Rosario, Argentina) supplied the crude sunflower oil extracted by hexane utilized in this work (Table 1). The oil was stored in tightly sealed amber container at 5 °C for further use. All reagents were of analytical reagent grade. Citrate buffer (pH 5.0) was prepared by mixing citric acid solution (0.1 M) and sodium hydroxide solution (0.1 M), both made with double-distilled water, for stock solutions require to yield a desired pH value in each case. Lecitase® Ultra an acidic PLA1 (EC 3.1.1.32) from *Thermomyces lanuginosus* expressed in *Aspergillus oryzae* was acquired from Novozymes (Bagsvaerd, Denmark). This enzyme exhibits PLA1 activity at pH values from 4.5 to 6 at 50 °C according to the manufacture's instruction. MAXAPAL® A2, a liquid PLA2 (E. C. 3.1.1.4) obtained by submerged culture of a selected strain of *Aspergillus niger* was provided by DSM Food Specialties (Netherlands). This enzyme is active in the pH range 5.0–9.5 according to the manufacture's instruction.

Table 1
Characterization of crude hexane extracted sunflower oil.

Parameter	Crude Oil
Phosphorous content (mg/kg)	544.510 ± 19.830
Acid value (mg KOH/g)	2.290 ± 0.050
Moisture (g/100 g)	0.075 ± 0.010
Peroxide value, PV (meq/kg)	3.660 ± 0.160
Unsaponifiable matter (g/kg)	8.760 ± 0.500
Phospholipids (g/100 g)	0.944 ± 0.110
Iron content (mg/kg)	9.410 ± 0.410
Viscosity (mPa*s)	46.710 ± 2.120
Density (kg/m 3)	921.800 ± 3.020
Color	
L*	58.860 ± 2.800
a*	5.850 ± 0.370
b*	33.800 ± 2.600

Results are mean values ± standard deviation analyzed by triplicate.

2.2. Oil degumming assay system

The assay system consisted of a jacketed reactor fitted with lid, a propeller and a thermometer. The reactor was connected to a water bath with water pump and flexible tube.

For enzymatic degumming, the most influential factors include temperature, pH, buffer/substrate ratio and enzyme dosage. Their values were set based on preliminary assays and literature data (Lamas et al., 2014; Yu et al., 2014). Crude sunflower oil (*approximately 1000 g*) was loaded in the reactor, which was kept at 50 °C of temperature. The assay was performed at pH 5 by the addition of 2% buffer/substrate ratio. Followed by the addition of 200 U/kg of oil enzyme solution for both enzymes, the mixture was stirred with automatic mixer to provide a safe large surface area through emulsification. The process was performed during 180 min. The stop reaction was carried out during 30 min at 100 °C to inactivate the enzyme. To recover oil and water phases a centrifuged step was applied (10 min at 2400*xg*).

For water degumming, the experiment was carried out in the same reactor. When the heating temperature of sunflower oil (*1000 g*) reached 65 °C, 3% of distilled water was added. The mixture allowed under stirring during the process. Finally, the oil was centrifuged (10 min at 2400*xg*) to separate the gums to yield water degummed oil.

2.3. Analytical methodology

2.3.1. Efficiency

To evaluate the efficiency of enzymatic degumming processes, the phosphorus content determination in crude and degummed oil samples was used. The phosphorous content was determined by ashing the sample in the presence of zinc oxide, followed by the spectrometric measurement of phosphorous as a blue phosphomolybdic acid complex according to AOCS Official Method Ca 12-55 (Firestone, 2009). The absorbance was measured at 650 nm by using a Shimadzu 160 UV–vis spectrophotometer equipped with a computer-assisted system for data acquisition (Shimadzu 160 Japan). The efficiency of each degumming process was estimated based on its ability to reduce the phosphorus content using the following equation:

$$\text{Efficiency} = (\text{Pi} - \text{Pr})/\text{Pi} \quad (1)$$

where Pi is the total phosphorus content of the crude oil (mg/kg) and Pr is the residual phosphorus content in degummed oils (mg/kg).

2.3.2. Physicochemical indexes

Acidity was measured by titration with a standardized ethanolic solution of potassium hydroxide and phenolphthalein as indicator. The analysis was determined according to AOCS Official Method Cd 3d − 63 (Firestone, 2009). An acetic acid–chloroform AOCS Official Method Cd 8-53 (Firestone, 2009) for peroxide value was employed to measure peroxides and other similar compounds that oxidize potassium iodide as primary oxidation products.

Quantitative determination of phospholipids was carried out by enrichment using diol solid phase extraction cartridges (J.T. Baker Inc., Phillipsburg, NJ) and subsequent analysis by high-performance liquid chromatography according to AOCS Official Method