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Changes in quality and composition of sunflower oil during enzymatic degumming process

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ABSTRACT

The objective of this study was to examine the effect of the enzymatic degumming process on composition of crude sunflower oil.

To analyze the crude and degummed oils, different parameters were determined. Phosphorous content, metal traces, phospholipids, acid value, peroxide value, anisidine value, moisture, color and stability oxidative, were measured.

The degumming assays were performed in a batch system with continuous stirring using a phospholipase A1 (Lecitase® Ultra) and an acyltransferase (LysoMax® Oil). The assays were carried out at 50 °C, pH 5 and an enzyme dosage of 200 U/kg of oil during 60 min.

The degumming process with both enzymes decreased the phosphorus content in crude sunflower oil below 3 mg/kg.

Phospholipid content showed a drastic decrease with the enzymatic degumming process. The calcium and magnesium content in crude sunflower oil was extremely high, and it was reduced noticeably with the enzymatic treatment. Induction time for oxidative stability of the crude oil was 17.25 h. In the degummed oil samples with phospholipase A1 and acyltransferase, the oxidative stability index was found to be 4.18 h and 4.33 h respectively. These results indicate that the enzymatic degumming process affected several quality and stability characteristics of crude sunflower oil.

1. Introduction

Crude vegetable oils are traditionally refined by physical or chemical processes. Degumming is the first step in the refining process of vegetable oils, and it removes phospholipids and mucilaginous gums that affect quality and storability. Some enzymatic degumming processes have been suggested for laboratory and pilot plant scales (Clausen, 2001; Dayton, Staller, & Berkshire, 2010; J.G. Yang, Wang, Yang, Mainda, & Guo, 2006; Yang, Zhou, Yang, Wang, & Wang, 2008), and have led to the process on an industrial scale (Autino, 2009). This technique improves the quality and the oil yield (Dijkstra, 2010).

The different enzymes that are commercially available for processing vegetable oils vary in the way they act on phospholipids, but all of them increase the yield of the oily phase recovered by the degumming process (Galhardo & Hitchman, 2011). There are several types of enzymes of interest for the treatment of vegetable oils, such as phospholipase A1 (PLA1) and phospholipase A2 (PLA2) that remove the fatty acid from positions 1 and 2 respectively with respect to glycerol (Dijkstra, 2010; Galhardo et al., 2010). The phospholipase B (PLB) eliminates both fatty acids from the glycerol group (Galhardo et al., 2010). The phospholipase C (PLC) catalyzes the hydrolysis of the phosphate-glycerol bond in phosphatidylcholine and phosphatidylethanolamine (Dijkstra, 2010). There are another group of microbial enzymes, the acyltransferases, which transfer a fatty acid to a sterol present in the oil, in order to convert it into a fatty acid ester (Dijkstra, 2011). All enzymes cause less oil to be retained by the gums by decreasing the amount of gums and their oil retention, which also contributes to an improved oil yield (Dijkstra, 2010).

The oil refining objective is to remove impurities with the least possible effect on desirable components present in the crude vegetable oils in order to obtain an odorless, bland and oxidatively stable refined vegetable oil (Medina Juarez, Gamez, Ortega, Noriega, & Angulo, 2000). Quality and stability are the main factors in the production acceptance and marketing of the vegetable oil product (Brevedan, Carelli, & Crapiste, 2000). These properties depend on seed quality, seed treatment, extraction method and

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processing conditions. They are influenced by the presence of minor components such as free fatty acids, phospholipids, trace metals and waxes, which have pro-oxidant or antioxidant properties (Autino, 2009).

Metallic particles have a catalytic effect on the oxidation reaction of oil, as they promote the formation and decomposition of hydroperoxides. These compounds are decomposed into aldehydes, ketones, organic acids, alcohols, and volatile compounds, which are called secondary oxidation products (Villa Salinas, 2009). The presence of trace metals is an important factor as far as the quality of edible oil is concerned (Pehlivan, Arsian, Gode, Altun, & Ozcan, 2008).

There are studies on the changes in chemical composition that affect the quality and stability of vegetable oils obtained by solvent extraction. These characteristics are primarily dependent on extraction solvents, extraction temperature and pretreatment of seeds (Jung, Yoon, & Min, 1989; Yoon & Min, 1986). Tasan, Gecgel, and Demirci (2011) reported the influence of industrial oilseed extraction methods (pre-pressed, solvent-extracted, full-pressed and mixed oil) on the quality and stability of crude sunflower oil. The effect of pressing conditions on nonrefining sunflower oil has been presented by Turkulov, Dimic, Karlovic, and Vuksa (1998). The influence of water degummed oil in the phosphatide content was discussed by Crapiste, Brevedan, and Carelli (1998). The changes in composition and quality of sunflower oils during extraction and water degumming were described by Brevedan et al. (2000).

Furthermore, there are several studies about the effect of enzymatic degumming on the phosphorus content (Chakrabarti et al., 2009; Jahani, Alizadeh, Pirozifard, & Qudsevali, 2008; Jiang et al., 2011; Soe & Brown, 2011; B. Yang, Wang, & Yang, 2006; J.G. Yang et al., 2006), the quantitative and qualitative analysis of phospholipids (Clausen, 2001; Galhardo et al., 2010) and the acid value achieved (B. Yang et al., 2006). However, there are just few studies reported in the literature concerning changes in physical and chemical characteristics of sunflower oil during the enzymatic degumming process.

The aim of this work was to investigate and analyze the effect of the enzymatic degumming process on composition, quality and oxidative stability of sunflower oil.

2. Materials and methods

2.1. Materials

Crude sunflower oil extracted by hexane, provided by a local Company was used. The oil was stored under refrigeration and protected from light until it was used.

Lecitase® Ultra, an acidic phospholipase A1 (EC 3.1.1.32) from *Thermomyces lanuginosus* expressed in *Aspergillus oryzae* was acquired from Novozymes (Bagsvaerd, Denmark). This enzyme exhibits phospholipase A1 activity at pH values from 4.5 to 6 at 50 °C according to indicated by the manufacturer.

LysoMax® Oil, a microbial lipid acyltransferase (EC 2.3.1.43) with phospholipase A2 activity, was provided by Danisco & Genencor (Arroyito, Córdoba, Argentina). This enzyme exhibits activity at pH values from 5 to 10 at temperature range from 45 to 80 °C according to indicated by the manufacturer.

All reagents were of analytical grade. Citrate buffer pH 4.94 was prepared by mixing sodium citrate solution (0.1 mol/L) and sodium hydroxide solution (0.1 mol/L). Both reagents were made with twice-distilled water, in the amount in which the stock solutions required, in order to yield a desired pH value in each case.

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 (Fig. 1).

The assay was performed in a batch system with continuous stirring, at pH 5. One Liter of sunflower oil was loaded in the reactor which was kept at about 50 °C. Followed by the addition of 2 mL/100 mL buffer/substrate ratio and 200 U/kg of oil enzyme dosage solution, the mixture was stirred with a mechanical mixer to provide a safe large surface area through emulsification. Aliquots of the reaction mixture were taken at 10, 20, 30, 40, and 60 min and heated for 30 min at 100 °C to stop the enzymatic reaction. Then, they were centrifuged (10 min at 2400 × *g*) to recover oil and water phases. The processed samples were stored until analysis at 5 °C, protected from light.

2.3. Analytical methodology

To analyze the crude and degummed oils, different parameters were determined by standard official methods.

2.3.1. Phosphorus content analysis

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 (Ca-12 55,AOCS, 2009).The absorbance was measured at 650 nm by using a Shimadzu 160 UV-VIS spectrophotometer (Shimadzu 160 Japan, equipped with a computer assisted system for data acquisition).

Fig. 1. Reactor used for the enzymatic degumming process of crude sunflower oil samples.