LWT - Food Science and Technology 42 (2009) 1530–1537

Contents lists available at ScienceDirect

LWT - Food Science and Technology

journal homepage: www.elsevier.com/locate/lwt

Optimization of SC-CO_2 extraction of oil from almond pretreated with autoclaving

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ARTICLE INFO

Article history:
Received 29 August 2008
Received in revised form
5 May 2009
Accepted 5 May 2009

Keywords:
Optimization
Supercritical carbon dioxide extraction
Autoclaving
Almond oil
Composition

ABSTRACT

Supercritical carbon dioxide (SC-CO_2) extraction parameters affecting oil recovery from almond were optimized through response surface methodology (RSM). The optimum extraction conditions were as follows: extraction pressure, 44.1 MPa; extraction temperature, 43.8 °C; dynamic extraction time, 93.6 min; and CO_2 flow rate, 10.1 mL/min. Under these conditions, a mean value of 86.54 ± 0.66 g/100 g ($n = 3$) was observed, which is well matched with the predicted value of 87.32 g/100 g. Furthermore, the effects of autoclaving pretreatment for the almond particles on the oil recovery, fatty acids' composition, and almond particles' microstructure were also investigated by calculating the percentages of the oil yield, gas chromatograph fitted with a mass spectrometer (GC–MS), and scanning electron microscopy (SEM) analysis, respectively. The results showed that autoclaving pretreatment had minor modifications of the fatty acids' profile of the extracted oil, but greatly promoted the disturbing of almond cell walls, and increased the oil recovery by 6.44%.

1. Introduction

Almonds (*Prunus amygdalus*) are one of the most popular tree nuts on a worldwide basis and rank number one in tree nut production. It contains up to 25 g protein/100 g seed and provides all of the essential amino acids, except for methionine, in quantities equal to or greater than those recommended by the FAO guidelines (Esteban, López-Andréu, & Carpena, 1985; Sathe, Sze-Tao, Wolf, & Hamaker, 1997; Saura-Calixto, Bauza, Martinez de Toda, & Argamenteria, 1981). Apart from the high protein content, oil is also the main fraction in almond (50–65 g oil/100 g dried seed) (Martín-Carratalá, García-López, Berenguer-Navarro, & Grané-Teruel, 1998). The seed's high oil content, which is high in mono- and polyunsaturated fatty acids, with oleic and linoleic acids as the major constituents, justifies the interest of almond in human diet and cosmetics (Dourado, Barros, Morta, Coimbra, & Gama, 2004). Many human feeding studies proved that almonds could lower cholesterol, fight oxidative stress and maintain body weight. Davis and Iwahashi (2001) verified that almond consumption might prevent colon cancer. Owing to the benefits that almond offers, the interest in almond oil has greatly increased in recent years (Femenia, García-Marín, Simal, Rosselló, & Blasco, 2001; Marrone, Poletto, Reverchon, & Stassi, 1998; Martín-Carratalá, Llorens-Jordá, Berenguer-Navarro, & Grané-Teruel, 1999; Sharma & Gupta, 2006).

Vegetable oil from seeds is traditionally produced by hexane extraction from ground seeds. The process is very efficient, but its major problem is represented by hexane elimination after extraction. The possible thermal degradation of the oil and the incomplete hexane elimination (from 500 to 1000 mg/kg residue) are the drawbacks of this process (Reverchon & De Marco, 2006). Therefore, supercritical carbon dioxide has been the most frequently used extractant in food and pharmaceutical industries, being nontoxic, nonflammable, inexpensive, and easily separable from extracts (Xu, Gao, Liu, Wang, & Zhao, 2008).

Many studies have been reported in the case of almond oil extraction by SC-CO_2 (Femenia et al., 2001; Marrone et al., 1998), and these works are focused on the fundamental aspects of supercritical carbon dioxide extraction, i.e. either on the extraction modeling based on "broken" and "intact" cells or the main effects that SC-CO_2 extraction might produce on the cell wall matrix. It is clear that all the fundamental studies enhanced our understanding of the key aspects that regulate the mass transfer process taking place during SC-CO_2 extraction, and provided the basis on which to develop more accurate techniques for correlation and prediction that could be used with confidence in future investigations.

But there is a lack of optimization for the crucial parameters that affect the SC-CO_2 extraction efficiency. Moreover, the intricate honeycombed features of the pericarp and variability of the almond also affect the extraction yield and the varieties of fatty acids that

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0023-6438/$ – see front matter
doi:10.1016/j.lwt.2009.05.007

can be extracted (different molecular weight, polarity, link with the structure, etc.) (Marrone et al., 1998; Zaidul, Nik Norulaini, Mohd. Omar, Sato, & Smith, 2007). So it is necessary to do some suitable pretreatment on the almond before extracting the oil in order to improve the extraction efficiency. Kasai, Imashiro, and Morita (2003) reported an effective method for soybean oil extraction by the autoclaving treatment, which would solubilize and remove the adhesive substances such as glycine or hydroxyproline-rich protein or pectic polysaccharides between the cells of soybeans. As a result, the extraction efficiency was greatly improved. However, to the best of our knowledge, there is no prior report on the SC-CO_2 extraction oil from almond pretreated with autoclaving.

In this paper, SC-CO_2 extraction parameters such as extraction pressure, extraction temperature, CO_2 flow rate, and extraction time were optimized using response surface methodology (RSM), by employing a four-variable, three-level Box–Behnken design (BBD), in order to obtain the conditions with the high oil recovery from the autoclaved almond. Furthermore, we evaluated the effects of autoclaving pretreatment on the oil recovery, fatty acids' composition, and almond particles' microstructure by an electronic balance, gas chromatograph fitted with a mass spectrometer (GC–MS), and scanning electron microscopy (SEM) analysis, respectively.

2. Materials and methods

2.1. Materials

The following reagents and chemicals were used: methanol (Tianjin Chemicals Co., Ltd, China); sodium hydroxide (Xi'an Chemical Industry, China); hydrochloric acid (Kaifeng Chemicals Co., Ltd, China); acetone (Tianjin Chemicals Co., Ltd, China). All the reagents and chemicals used in the study were of analytical grade. Milli-Q water (obtained through a Millipore filter system, Millipore Co., USA) was used throughout.

2.2. Sample preparation

Almonds were obtained from the local market in the Yulin city, Shaanxi province, China. The seeds were ground using a cyclone mill. In general, decreasing particle size in SC-CO_2 extraction creates more surface area and benefits extraction, but it also may hinder extraction if the analytes re-adsorb on matrix surfaces. So particles with the mean diameters of 0.75 mm sorted by passing it through a series of mesh sieves (Φ 200 type, Xinxiang Kangda New Machine Co., Ltd., China) were collected for future use. The autoclaving for the almond powder was done according to the method described by Kasai et al. (2003) with some modifications. After being dipped in 5 parts of water at 4 °C overnight, the dipped powder was filtered through the Whatman No. 1 paper, and then autoclaved at 121 °C for 10 min and immediately taken out for air drying. The autoclaved dried almond powder was collected and stored at low temperature for future use.

2.3. Soxhlet extraction

Soxhlet extraction was carried out in triplicate for each experimental run, for which 15 g almond powder was used and refluxed with 250 mL hexane for 8 h. After the hexane being removed using a rotary vacuum evaporator, the oil was then dried in an oven at 85 °C to constant mass (Luque-García & Luque de Castro, 2004). The results showed that soxhlet extraction gave a yield of 54.80 g oil/100 g almond seeds, which was taken as 100% while calculating the oil recovery by SC-CO_2 extraction.

2.4. SC-CO_2 extraction

Supercritical CO_2 extractions were performed using the Model SFT-100XW extraction system (Supercritical Fluid Technologies, Inc., USA), equipped with a 100 cm^3 extraction vessel in which 10.00 g of almond particles packed with the Whatman No. 1 paper was loaded for each experimental run. The vessel was placed in a temperature-controlled oven, and liquid CO_2 (99.995% pure) was pressurized by a reciprocating pump, heated and then pumped to the extractor. Methanol (1 mL/100 mL) was used as the modifier. Each sample was first held in static extraction for 15 min, followed by a different dynamic extraction time. At the end of the extraction, the supercritical fluid was depressurized across a flow control valve to atmospheric pressure, and the oil was collected in a pre-weighted collection vial. The oil yield was calculated by the weight increased, and oil recovery was calculated as percentages of the oil yield extracted by soxhlet.

2.5. Experimental design and statistical analysis

A four-variable, three-level Box–Behnken design (BBD) (Guan & Yao, 2008; Hu, Wang, & Xu, 2008; Özkal, Yener, & Bayindirli, 2005; Wanasundara & Shahidi, 1996; Wang, Sun, Cao, Tian, & Li, 2008) was applied to optimize the extraction conditions with the high oil recovery from the autoclaved almond powder. Four independent variables studied were extraction pressure (MPa, X_1), extraction temperature (°C, X_2), dynamic extraction time (min, X_3), and CO_2 flow rate (mL/min, X_4) (Table 1) for uncoded variable levels. These independent variables and their levels were selected based on the preliminary experiments in our laboratory (data not shown). Response (Y), i.e. the oil recovery at each design point was recorded. Triplicate extractions were carried out at all the design points.

The generalized second order polynomial model used in the response surface analysis was:

$$Y = \beta_0 + \sum_{i=1}^{4}\beta_i x_i + \sum_{i=1}^{4}\beta_{ii}x_i^2 + \sum_{i=1}^{3}\sum_{j=i+1}^{4}\beta_{ij}x_i x_j \tag{1}$$

where, β_0, β_i, β_{ii}, and β_{ij} are regression coefficient for intercept, linear, quadratic, and interaction terms, respectively; x_i and x_j are the independent variables.

The responses obtained from the experimental design set (Table 2) were subjected to multiple nonlinear regression using the software Design-Expert 7.1.3 Trial (State-Ease, Inc., Minneapolis, MN, USA), to obtain the coefficients of the quadratic polynomial model. The quality of the fitted model was expressed by the coefficient of determination R^2, and its statistical significance was checked by an F-test.

2.6. Fatty acid methyl esters (FAMEs)

The FAMEs were obtained according to the *Métodos Oficiales de Análisis* (1993), with some modifications. The preparation of the

Table 1
Variable levels used in the response surface methodology.

Variable	Symbol	Coded variable levels[a]		
		−1	0	+1
Extraction pressure (MPa)	X_1	25	35	45
Extraction temperature (°C)	X_2	35	45	55
Dynamic extraction time (min)	X_3	60	90	120
CO_2 flow rate (mL/min)	X_4	5	10	15

[a] Coded variable (X_i) levels can be uncoded (x_i) by using equations: $x_1 = 10X_1 + 35$; $x_2 = 10X_2 + 45$; $x_3 = 30X_3 + 90$; and $x_4 = 5X_4 + 10$.