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Supercritical carbon dioxide extraction of flaxseed oil: Effect of extraction parameters and mass transfer modeling

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ABSTRACT

Supercritical carbon dioxide (SC-CO_2) extraction of flaxseed oil was performed and effects of process parameters including particle size (mean particle diameter <0.85–0.92 mm), solvent flow rate (2–4 g/min), pressure (40–60 MPa) and temperature (50–70 °C) were investigated. The broken and intact cells (BIC) model was used for mass transfer modeling of the extraction of flaxseed oil with SC-CO_2 successfully. Extraction of flaxseed oil was divided into two periods as first (fast) and second (slow) extraction periods. Great part of the flaxseed oil was extracted in the first period and a very small amount was extracted in the second period. Decreasing the particle size increased the amount of released (free) oil. Increasing the pressure, temperature and flow rate also caused slight increases in the released oil amounts. Increase in the solvent flow rate, pressure and temperature increased the extraction rate in the first period within the range of experiments. The fluid phase mass transfer coefficient ($k_f a$) varied between 0.38 and 2.32 min^{-1} and the solid phase mass transfer coefficient ($k_s a$) varied between 0.5×10^{-3} and 6.7×10^{-3} min^{-1}.

1. Introduction

Flaxseed (*Linum usitatissimum*) is the mostly studied oilseed to date as a functional food [1] and it has a great economic importance especially for Canada, which produces about 40% of all the world's total flaxseed production [2]. Flaxseed oil is the richest source of an α-linolenic acid, and it also contains tocopherols and tocotrienols [3,4]. These compounds provide various health benefits in human body [5–8]. It has also been shown that flaxseed oil has a positive influence on some diseases like colon tumor [9] and mammary cancer [10].

Traditionally, flaxseed oil is extracted from seeds by pressing or by using a solvent such as hexane. Press extraction has a lower yield but the energy consumption is high. Solvent extraction causes losses in biological activity of extracted oil as flaxseed oil is thermally unstable, moreover solvent used needs to be separated from the oil after extraction and requires larger extraction time. Using larger amounts of solvents can be harmful to both human and environment and is not desirable [11]. These disadvantages are not seen in supercritical fluid extraction (SFE) which became a common method in recent years. In SFE method most commonly used solvent is carbon dioxide, which is defined as a "green", healthy and safe fluid [12]. Some applications include extraction of rapeseed [13], canola [14,15], walnut [16], apricot kernel [17], sesame [18,19], peach seed [20] and grape seed [21,22] oils.

Several models have been proposed in the literature for supercritical fluid extraction of solutes from packed beds of solid matrices. Detailed reviews about these models were published previously [23–25]. Amongst them the mostly used one is the broken and intact cells (BIC) model, proposed by Sovová [26], considers the physical structure of the solid matrix. Mass transfer resistances in fluid and solid phases are considered in this model [26,27] and it was successfully used for the SFE of various solutes, such as essential oil from chamomile [28], various seeds such as grape [21,22,29], sunflower, coriander, tomato and peanut [30] and apricot kernel [17].

Bozan and Temelli [3] studied the influence of pressure (21, 35 and 55 MPa) and temperature (50 and 70 °C) on oil yield and the solubility of the oil in SC-CO_2. Özkal [12] performed a response surface analysis to investigate the effects of pressure (30–50 MPa), temperature (50–70 °C) and SC-CO_2 flow rate (2–4 g/min) on flaxseed oil yield in SC-CO_2 extraction. Pradhan et al. [31] compared the chemical composition of the SC-CO_2 extracted flaxseed oil with oil extracted by screw press and solvent extraction. However, there was not any study about mass transfer modeling of SC-CO_2 extraction of flaxseed oil reported in literature. Therefore, the aims of this

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Table 1
Parameters of BIC model at different particle sizes (P = 50 MPa, T = 50 °C, Q = 3 g/min, ρ_f = 964 kg/m^3).

Particle size	Dp_m (mm)	y_r (g/g)	G	t_k (min)	w_k (g/g seed)	m_{50} (g/g initial oil)	k_fa (1/min)	k_sa (1/min)	AAD (%)
1	<0.85	0.0193	0.919	36	0.303	0.929	0.809	0.00091	1.8
2	0.92	0.0193	0.724	29	0.240	0.748	0.747	0.00048	4.3

study were to perform mass transfer modeling by using the broken and intact cells (BIC) model and to determine the effects of the extraction conditions on the oil yield, extraction rate, mass transfer coefficients and model parameters for the SC-CO_2 extraction of flaxseed oil.

2. Materials and methods

2.1. Materials

Flaxseed samples were obtained from local market and stored at +4 °C in sealed glass jars. A kitchen grinder (Braun MultiQuick 6550) was used for particle size reduction and after grinding particles were sieved and fractionated. Moisture content, oil content and density determinations, and fractionation according to particle sizes were performed as reported in literature [17]. The density of oil free particles, ρ_s, was calculated from the mass and the volume of the oil free particles. The volume of the oil free particles was measured by a nitrogen stereopycnometer (Quantachrome, Boynton Beach, FL). CO_2 was purchased from Habaş (Turkey).

2.2. Supercritical fluid extraction

SC-CO_2 extractions of the flaxseed oil were done by using a Supercritical Fluid Extraction System (SFX System 5100, Isco Inc., Lincoln, NE, USA). System has an extractor (SFX 3560) and two syringe pumps (Model 100DX). A 10 ml aluminum sample cartridge was used as an extractor and SC-CO_2 flows downward in the extractor. During the extractions cooling temperature of the CO_2 pump was 5 °C. The volumetric flow rate was measured as liquid CO_2 at this pump temperature.

For the extraction experiments 5 g of flaxseed particles were used. During the extraction, the SC-CO_2 and the extracted oil was passed through the adjustable restrictor which was coaxially heated to 110 °C to inhibit fouling due to the solidification of oil on the inside surface of the restrictor as a result of temperature decrease occurred during expansion of the SC-CO_2. The oil was collected in test tubes containing glass wool at selected time periods. The oil yield was determined gravimetrically. Extraction was ended after the amount of oil collected decreased to an insignificant level.

Different particle sizes (sizes 1 and 2 (Table 1)), solvent flow rates (2, 3 and 4 g/min), pressures (40, 50 and 60 MPa) and temperatures (50, 60 and 70 °C) were tested. Particle size 1, 50 MPa, 50 °C and 3 g/min flow rate were selected as standard conditions and one of these conditions was changed at a time while the others were fixed during the experiments. To determine the solubility of the flaxseed oil in the SC-CO_2, extractions at lower solvent flow rates (0.5 and 1.0 g/min) were performed and slopes of the initial linear parts of these extraction curves were used for solubility calculation.

3. Mass transfer model

Experimental oil yields were fitted to the BIC model. Details of the model were reported previously [17,24]. Adjustable parameters of the model were calculated by minimizing the errors between

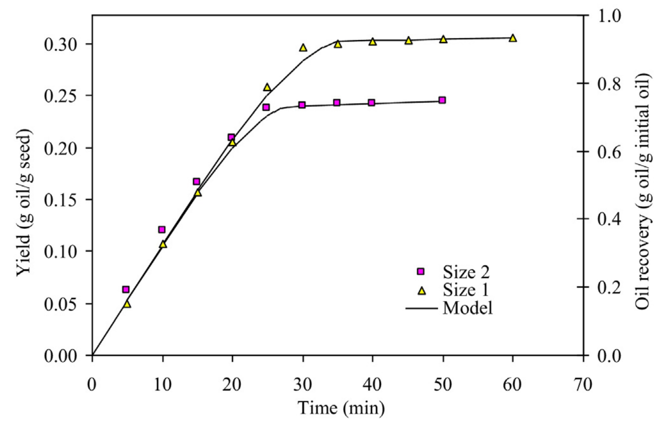

Fig. 1. Extraction curves of flaxseed oil for different particle sizes (P = 50 MPa, T = 50 °C, Q = 3 g/min, ρ_f = 964 kg/m^3).

the experimental and the calculated yield values. Average absolute deviation (AAD) was used for error estimation,

$$\mathrm{AAD}\,(\%) = \frac{1}{n}\sum_{i=1}^{n}\left|\frac{y_{\mathrm{exp}} - y_{\mathrm{calc}}}{y_{\mathrm{exp}}}\right|_i \times 100 \quad (1)$$

where n is the number of data, y_{exp} and y_{calc} are the values obtained from experiments and model estimations, respectively at the ith condition. Grinding efficiency (G), the duration of the first (fast) period (t_k), oil yield at the end of the first period (w_k), fluid phase mass transfer coefficient (k_fa) and solid phase mass transfer coefficient (k_sa) were determined from these parameters [17].

4. Results and discussion

Flaxseed particles contained 3.4 and 32.74% moisture and oil, respectively. The density of oil free particles, ρ_s, was measured as 1.97 g/cm^3.

4.1. Effect of particle size

To investigate the effect of particle size, two different particle sizes of size 1 (<0.85 mm) and size 2 (0.92 mm) were used (Table 1). First one represents the particles passed through a sieve mesh of 0.85 mm and the second one represents the particles left between the sieves having meshes of 0.85 mm and 1.0 mm. Extraction curves for these particle sizes at constant extraction conditions of 50 MPa pressure, 50 °C temperature and 3 g/min flow rate are given in Fig. 1 and estimated model parameters are given in Table 1. First (fast) and second (slow) extraction periods can be clearly distinguished for both particle sizes. The extraction rate was high in the first period however it was low in the second period. This is due to the fact that grinding releases oil from the broken cells and in the first period this released (free) oil is extracted but in the second period the unreleased (tied) oil is extracted, and the extraction of released oil is easier than the extraction of unreleased oil that requires first the SC-CO_2 to enter into the solid matrices than solve oil and exit the solid matrices. Duration of the first period, t_k, of the sample having particle size 1 (36 min) was larger than t_k of the sample having particle size 2 (29 min) because the released oil amount, w_k,