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Extraction of sesame seed oil using supercritical CO_2 and mathematical modeling

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ABSTRACT

In this work, extraction of sesame oil from sesame seeds using supercritical CO_2 was carried out. The effect of operating parameters such as pressure, temperature, and supercritical CO_2 flow rate and particle size on extraction yield were investigated. An increase in the pressure and the supercritical CO_2 flow rate improved the extraction yield and also shortened the extraction time. The extraction yield increased as the particle size decreased depending on decreasing intraparticle diffusion resistance. The maximum extraction yield obtained was about 85% (relative to Soxhlet extraction by hexane) at 50 °C, 350 bar, 2 mL CO_2/min, 300–600 μm of particle size. Some extraction curves were modeled with two mathematical approaches as shrinking core model and broken and intact core model. The evaluation of model parameters showed that shrinking core model, however, is better than broken and intact cell model.

1. Introduction

Supercritical fluid extraction (SFE) eliminates the disadvantages of conventional solvent extraction (CSE) which leads to degradation of heat sensitive compounds and leaves traces of toxic solvents in the solute. This is a concern for food and medicinal extracts. By changing the operating pressure and/or temperature, the low solubility of oil in supercritical fluids (SCFs) can be increased and also improves the extraction rates. Therefore, new functional and/or nutritional characteristics for use in creating new formulated foods can be improved using SFE. Extraction of oils from different seeds with supercritical CO_2 ($scCO_2$) is widely reported (Özkal et al., 2005; Roy et al., 1996).

Sesame oil has a mild odor and a pleasant taste and, as such, is a natural salad oil requiring little or no winterization. It is used as a cooking oil, in shortening and margarine, as a soap fat, in pharmaceuticals and as a synergist for insecticides. Sesame oil is very popular as cooking oil in many countries, and more expensive than other vegetable oils (Hai and Wang, 2006; Budowsk and Markely, 1951). An analysis of the operating cost of SFE indicated that use both of CO_2 and entrainer is much less expensive than CSE (Salgın et al., 2004).

Odabaşı and Balaban (2002) investigated the conditions which would give maximum oil yield from raw sesame seeds by $scCO_2$ extraction. They examined the effect of three parameters including pressure, temperature and co-solvent concentration on extraction yield and also used Response Surface Methodology to analyze the experimental data. They reported that the presence of 10 vol.% ethanol gave maximum yield of 89.40% at 276 bar and 70 °C relative to yield obtained by Soxhlet extraction using hexane.

The mathematical modeling of experimental data obtained in SFE has the objective of determining parameters for process design, such as equipment dimensions, solvent flow rate, particle size, and the characterization of SFE to enable the prediction of the viability of SFE processes on an industrial scale, through the simulation of overall extraction curves (Machmudah et al., 2006). The distribution of the natural materials within the solid structure affects the selection of models. Extractable materials easily accessible on the surface of the solid matrix, adsorbed on the outer surface, located within pores, or probably distributed within plant cell homogeneously. There are many mathematical models used for extraction of solutes from natural matrices in the literature to correlate overall extraction curves (Hortaçsu, 2000). The authors are aware, there are no investigation reported in the literature mathematical modeling of sesame oil extraction from raw seeds.

In this study, the extraction rate and extraction yield of sesame oil was investigated as a function of four parameters including pressure, temperature, $scCO_2$ flow rate and particle size. $scCO_2$ extraction process for various experimental conditions was also modeled using both shrinking core model (SCM) and broken and intact cell model (BICM) (Özkal et al., 2005; Döker et al., 2004; Sovová, 2005).

2. Experimental

2.1. Materials

The sesame seeds used were obtained from the region of Antalya (Turkey). The seeds were milled and then sieved. Sesame seed

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Nomenclature

a	model constant for shrinking core model ($a = \upsilon R^2/D_L L$)
b	model constant for shrinking core mode ($b = C_{sat}/q_0$)
c	model constant for shrinking core mode ($c = D_L/D_e$)
Bi	biot number ($Bi = k_f R/D_e$)
C^b	oil concentration in the fluid phase (kg/m^3)
C^p	solute concentration in the pore volume (kg/m^3)
C^p_{sat}	solubility of sesame oil in the solvent (kg/m^3)
$C^p_{r_c}$	solute concentration in the pore volume at the critical radius of the core (kg/m^3)
D_e	effective diffusivity (m^2/s)
D_L	axial dispersion coefficient (m^2/s)
E	mass of extract (kg)
G	grinding efficiency, fraction of the total pil released ($0 \leqslant G \leqslant 1$)
h	dimensionless height of packed bed ($0 \leqslant h \leqslant 1$)
h_k	dimensionless coordinate of the division between the fast and slow extraction period
J	mass transfer rate per volume of packed bed (kg/m^{3}s)
k_f	film mass transfer coefficient (m/s)
$k_f a$	mass transfer coefficient for fluid phase (1/s)
$k_a a$	mass transfer coefficient in the solid phase (1/s)
L	bed length (m)
Pe	Peclet number ($Pe = 2R\upsilon/D_L$)
q	solid phase concentration (kg/m^3)
q_{avg}	average solid phase concentration (kg/m^3)
q_o	initial solid phase concentration (kg/m^3)
Q	mass flow rate of solvent (kg/s)
r	radial coordinate in particle (m)
r_c	critical radius of the core (m)
R	initial radial coordinate of the solid phase (m)
Re	Reynolds number ($Re = 2R\upsilon\rho/\mu$)
Sc	Schmidt number ($Sc = \mu/\rho D_e$)
Sh	Sherwood number ($Sh = 2Rk_f/D_e$)
t	time (s)
x	solid phase concentration (kg/kg)
x^b	dimensionless concentration in the bulk phase ($x^b = C^b/C_{sat}$)
x^p	dimensionless concentration in the solid ($x^p = C^p/C_{sar}$)
x^+	solid phase concentration at interfacial boundary (kg/kg)
x_0	initial oil content of sesame seed (kg/kg)
X	parameter of the fast extraction period ($X = Nk_f a\rho/Q(1-\upsilon)\rho_s$)
y	solvent phase concentration (kg/kg)
y	dimensionless solid phase concentration ($y = q/q_o$)
Y	parameter of the slow extraction period ($Y = Nk_s a x_0/Q(1-\epsilon)C_{sat}$)
υ	interstitial velocity of solvent in bed (m/s)
z	axial distance (m)
Z	dimensionless axial distance ($Z = \{z/L\}$

Greek symbols

ε	void fraction in bed
ε_p	porosity of the solid
μ	solvent viscosity (kg/m s)
θ	dimensionless time ($\theta = D_L t/R^2$)
ρ	solvent density (kg/m^3)
ρ_s	solid phase density (kg/m^3)
ξ	dimensionless radial coordinate in particle ($\xi = r/R$}
ξ_c	dimensionless critical radius of the core ($\xi_c = r_c/R$)
ψ	dimensionless time ($\psi = tQC_{sat}/Nx_0$)
ψ_k	dimensionless time when the released oil in the bed is totally extracted

particles were sorted by certified test sieves (Endecotts Ltd., London, England). The sieving operation using the sieve aperture sizes of 300, 600 and 1180 μm was carried out by a sieve shaker (Octagon 2000 Model, Endecotts Ltd., London, England). Therefore, the fractions were separated to three different particle size (d_p) ranges such as 300 μm < d_p < 600 μm (d_{p1}), 600 μm < d_p < 1180 μm (d_{p2}) and d_p > 1180 μm (d_{p3}). Each collected fraction was stored in a glass bottles under a vacuum desiccator until used for extraction experiments. Moisture content of seeds was determined as 2.4 wt.% according to the AOCS methods Ca-2c-25 (Anonymous, 2002–2003). The oil content of the sesame seeds was determined to be 50.6 wt.% by Soxhlet extraction with hexane, which would be referred as total oil content. All solvents used in the analysis were of analytical grade.

2.2. Supercritical fluid extraction system and experimental procedure

Extraction of sesame seed oil was carried out using a supercritical fluid extraction system (SFX™ System 220, Isco Inc., Lincoln, NE, USA), whose description has been previously detailed (Salgın, 2007). In each experiment, a known mass of dry seeds of about 4 g was put in extraction column (inner diameter of 5.2 mm, length of 55.8 mm). The extract was collected in collection vials which contained glass wool. In order to obtain extraction profiles with time, the extracts were collected in four consecutive time periods: in every 5 min for the first period of 30 min, in every 10 min for a second period of 30 min, in every 15 for the third half hour and in every 30 min for the fourth period. After that, the mass of extracted oil was determined gravimetrically. Each experimental condition was repeated at least three times. The extraction yield was defined according to the weight of the extracted sesame oil divided by the weight of the dry seed (g oil/g dry seed). In this study, the effects of pressure (250, 300 and 350 bar), temperature (50, 60 and 70 °C) and supercritical CO_2 flow rate (1, 2 and 3 mL/min) and particle size (300 < d_p < 600 μm; 600 < d_p < 1180 μm and d_p > 1180 μm) on the extraction yield were investigated.

2.3. Fatty acid analysis of sesame oil

Fatty acid methyl esters were prepared using IUPAC method 2.301 (Anonymous, 1987). Fatty acids were identified by comparison of retention times with a standard (Fluka, FAME). Fatty acid composition of sesame oils extracted with $scCO_2$ and hexane by Soxhlet were analyzed with a gas chromatography system (GC-2010 Model, Shimadzu Co., Kyoto, Japan) which equipped with a flame ionization detector (FID) and a TR-CN100 poly(bicyanopropyl)siloxane capillary column (60 m × 0.25 mm I.D., 0.20 μm film thickness, Teknokroma Co., Barcelona, Spain). The carrier gas was nitrogen (80.1 mL/min). The temperature of detector and injector was set to 300 °C. The oven temperature was held at 90 °C for 7 min then it was raised with a rate of 5 °C/min to the final temperature of 240 °C where it was held for 15 min. One microlitre sample was introduced using split injection (split ratio, 1:100). Each analysis was repeated three times and the standard error of the analysis was given in Table 1.

Table 1
Fatty acid composition of sesame oil in supercritical and Soxhlet extracted samples.

Operating conditions				Fatty acid composition (wt.%)				
Pressure (bar)	Temperature (°C)	Flow rate (mL/min)	Particle size* (μm)	C16:0	C18:0	C18:1	C18:2	C18:3n2
Supercritical fluid extraction								
250–350	50–70	2	d_{p1}	9.10 ± 0.53	4.90 ± 0.29	41.79 ± 0.42	43.23 ± 0.39	0.52 ± 0.02
350	50	1–3	d_{p1}	8.90 ± 0.10	4.97 ± 0.12	41.91 ± 0.23	43.21 ± 0.28	0.52 ± 0.01
350	50	2	$d_{p1} - d_{p3}$	8.89 ± 0.10	4.99 ± 0.15	41.97 ± 0.24	43.12 ± 0.34	0.52 ± 0.01
350	70	2	d_{p1}	8.79 ± 0.01	5.14 ± 0.02	42.47 ± 0.09	42.52 ± 0.11	0.54 ± 0.01
Soxhlet extraction								
			$d_{p1} - d_{p3}$	8.82 ± 0.12	5.19 ± 0.03	42.44 ± 1.30	42.49 ± 0.73	0.53 ± 0.04

d_{p2}: 600 μm < d_p < 1180 μm.
d_{p3}: d_p > 1180 μm.
* d_{p1}: 300 μm < d_p < 600 μm.

3. Description of mathematical models

3.1. Shrinking core model

Shrinking core model (SCM) describes the situation of the irreversible desorption followed by diffusion in the porous solid through the pores. When the mass transfer rate of the solute in the non-extracted inner part is much slower than that in outer part where most of the solute has been extracted, or solute concentration is much higher than the solubility of the solute in the solvent phase, a shape boundary may exit between outer and inner region. A core of inner region shrinks with the progress of the extraction. The following criteria are assumed:

i. the extraction system is isothermal and isobaric,
ii. the matrix is a porous material where sesame oil are uniformly distributed throughout the particle,
iii. the physical properties of the supercritical fluid are constant during the extraction,
iv. the radial dispersion is neglected,
v. the extraction is irreversible desorption.

Based on these assumptions, material balances in a volume element of packed bed column for fluid and solid phase are described as (Döker et al., 2004);

Fluid phase:

$$\frac{\partial C^b}{\partial t} + \upsilon \frac{\partial C^b}{\partial z} = D_L \frac{\partial^2 C^b}{\partial z^2} - \frac{(1-\varepsilon)}{\varepsilon} \frac{3k_f}{R} [C^b - C^p_{r_c}] \tag{1}$$

Solid phase:

$$\varepsilon_p \frac{\partial C^p}{\partial t} + (1-\varepsilon_p) \frac{\partial q}{\partial t} = \frac{D_e}{r^2} \frac{\partial}{\partial r} \left[r^2 \frac{\partial C^p}{\partial r} \right] \tag{2}$$

Diffusion in outer region is given by Eq. (3).

$$\frac{D_e}{r^2} \frac{\partial}{\partial r} \left[r^2 \frac{\partial C^p}{\partial r} \right] = 0 \tag{3}$$

Solid phase solute exists within the core.

$$\frac{q_{avg}}{q} = \left(\frac{r_c}{R} \right)^3 \tag{4}$$

Boundary conditions are given as follows. At the core boundary, the concentration in the fluid phase is at its saturated value.

$$C^p = C^p_{sat} \quad \text{at} \quad r = r_c \tag{5}$$

Diffusion flux at the outer surface of a particle is equal to mass transfer through external film.

$$D_e \left(\frac{\partial C^p}{\partial r} \right)_{r=R} = k_f [C^b - C^p(R)] \tag{6}$$

Initial conditions are given as follows:

$$C^b = 0 \quad \text{at} \quad t = 0 \tag{7}$$

$$r_c = R \quad \text{at} \quad t = 0 \tag{8}$$

$$q = q_0 \quad \text{at} \quad t = 0 \tag{9}$$

Danckwerts' boundary conditions at the inlet and exit of extractor are given by

$$\upsilon C^b - D_L \frac{\partial C^b}{\partial z} = 0 \quad \text{at} \quad z = 0 \tag{10}$$

$$\frac{\partial C^b}{\partial z} = 0 \quad \text{at} \quad z = L \tag{11}$$

Eqs. (1)–(11) were arranged using dimensional groups as $a = \upsilon R^2/D_L L$, $b = C_{sat}/q_0$, $Bi = k_f R/D_e$, $c = D_L/D_e$, $\mathrm{Pe} = L\upsilon/D_L$, $x^b = C^b/C_{sat}$, $x^p = C^p/C_{sat}$, $y = q/q_o$, $Z = z/L$, $\theta = D_L t/R^2$, $\xi = r/R$ and $\xi_c = r_c/R$. Hence, dimensional material balances for fluid and solid phase were derived to following equations.

$$\frac{\partial x^b}{\partial \theta} + a \frac{\partial x^b}{\partial Z} = \frac{a}{\mathrm{Pe}} \frac{\partial^2 x^b}{\partial Z^2} - \frac{(1-\varepsilon)}{\varepsilon} 3Bi \frac{(x^b - 1)}{(1 - Bi(1 - 1/\xi_c))} \tag{12}$$

$$\frac{\partial \xi_c}{\partial \theta} = \frac{cBi(1 - x^b)}{\varepsilon_p Bi(x^b - 1) + (1-\varepsilon_p) b \xi_c (\xi_c + Bi(1 - \xi_c))} \tag{13}$$

3.2. Broken and intact cell model

The following criteria are assumed in broken and intact cell model (BICM) based on differential mass balance equation.

i. extraction system is isothermal and isobaric,
ii. the physical properties of the supercritical fluid are constant during the extraction,
iii. the initial oil concentration and particle size distributions are uniform in the packed bed,
iv. bed void fraction are constant during the extraction in the packed bed,
v. the solute accumulation in the solvent is negligible,
vi. axial dispersion is neglected because of assuming plug flow.

Based on these assumptions, material balances in a volume element of packed bed column for fluid and solid phase are described as (Astová et al., 1996; Özkal et al., 2005);

Fluid phase:

$$-\rho_s(1-\varepsilon)\frac{\partial x}{\partial t} = J(x,y) \tag{14}$$

Solid phase:

$$-\rho_s(1-\varepsilon)\frac{Q}{N}\frac{\partial y}{\partial h} = J(x,y) \tag{15}$$

Boundary conditions are:

$$x = x_0 \quad \text{at} \quad t = 0 \quad \text{and} \quad h = h \tag{16}$$

$$y = 0 \quad \text{at} \quad t = t \quad \text{and} \quad h = 0 \tag{17}$$

Model also assumes that, sesame oil is deposited in the oil cells of the seed matrix and protected by cell walls. Some of the cells are broken up during grinding and some part of the oil is released from the cells and directly proposed to the solvent on the surface of the particles. The rest remains unreleased in the intact cells. The mass of oil free solid phase is constant during the supercritical fluid extraction.

Concentration of the released oil (g released oil/g solid) in the bed is Gx_0 at the beginning of the extraction. The grinding efficiency, G ($0 \leqslant G \leqslant 1$), shows the fraction of the total oil released in the bed. Extraction occurs in two periods as fast and slow extraction periods. The released oil is extracted in the fast extraction period with a rate controlled by its diffusion and convection in the solvent,

$$J(x,y) = k_f a \rho (C_{sat} - y) \quad \text{for} \quad x > (1-G)x_o \tag{18}$$

When the released oil is removed, the unreleased oil in the intact cells is extracted in the slow extraction period with a rate controlled by the diffusion of the oil from the interior of the particles to the surface. Instead of taking into account the complex nature of the vegetable matrix, the mass transfer is expressed with mass transfer coefficient in the solid phase, $k_s a$,

$$J(x,y) = k_s a \rho_s (x - x^+) \quad \text{for} \quad x \leqslant (1-G)x_o \tag{19}$$

Approximate solution for these conditions gives the oil recovery as (g oil extracted/g oil initially present in the bed). The mass of the sesame oil (E) was described as below;

$$\frac{E}{Nx_o} = \begin{cases} \psi[1-\exp(-X)] & \text{for} \quad \psi = \frac{G}{X} \\ \psi - \frac{G}{X}\exp[Z(h_k-1)] & \text{for} \quad \frac{G}{X} \leqslant \psi \leqslant \psi_k \\ 1 - \frac{1}{Y}\ln[1+[\exp(Y)-1]\exp[Y(\frac{G}{X}-\psi)](1-G)] & \text{for} \quad \psi \geqslant \psi_k \end{cases} \tag{20}$$

Dimensionless parameters for the Eq. (18) are defined as below:

$$\psi = \frac{tQC_{sat}}{Nx_0} \tag{21}$$

$$\psi_k = \frac{G}{X} + \frac{1}{Y}\ln(1 - G[1-\exp(Y)]) \tag{22}$$

$$h_k = \frac{1}{Y}\ln\left[1 + \frac{[\exp[Y(\psi - G/X)] - 1]}{G}\right] \quad \text{for} \quad \frac{G}{X} \leqslant \psi \leqslant \psi_k \tag{23}$$

$$X = \frac{Nk_f a\rho}{Q(1-\varepsilon)\rho_s} \tag{24}$$

$$Y = \frac{Nk_s a x_0}{Q(1-\varepsilon)C_{sat}} \tag{25}$$

Therefore, the model has four adjustable parameters (G, ψ_k, X and Y) that were determined by minimizing the errors between experimental and calculated yield values.

4. Results and discussion

4.1. Supercritical fluid extraction

4.1.1. Effect of pressure

The effect of pressure on the extraction yield at different temperature conditions for d_{p1} (300 μm < d_p < 600 μm) and 2 mL/min is shown in Fig. 1a–c. According to the figures, extraction yield increased by increasing pressure at a constant temperature. A number of research groups have reported that the solubility of seed oil in SCFs increases with the increasing of operating pressure. Similar results were also found in our previous studies (Salgın, 2007; Salgın et al., 2004, 2006).

As seen in Fig. 1a, extraction yield at 50 °C increased from 0.359 to 0.427 g oil/g dry seed when the pressure was increased from 250 to 350 bar. Furthermore, the time required to reach maximum

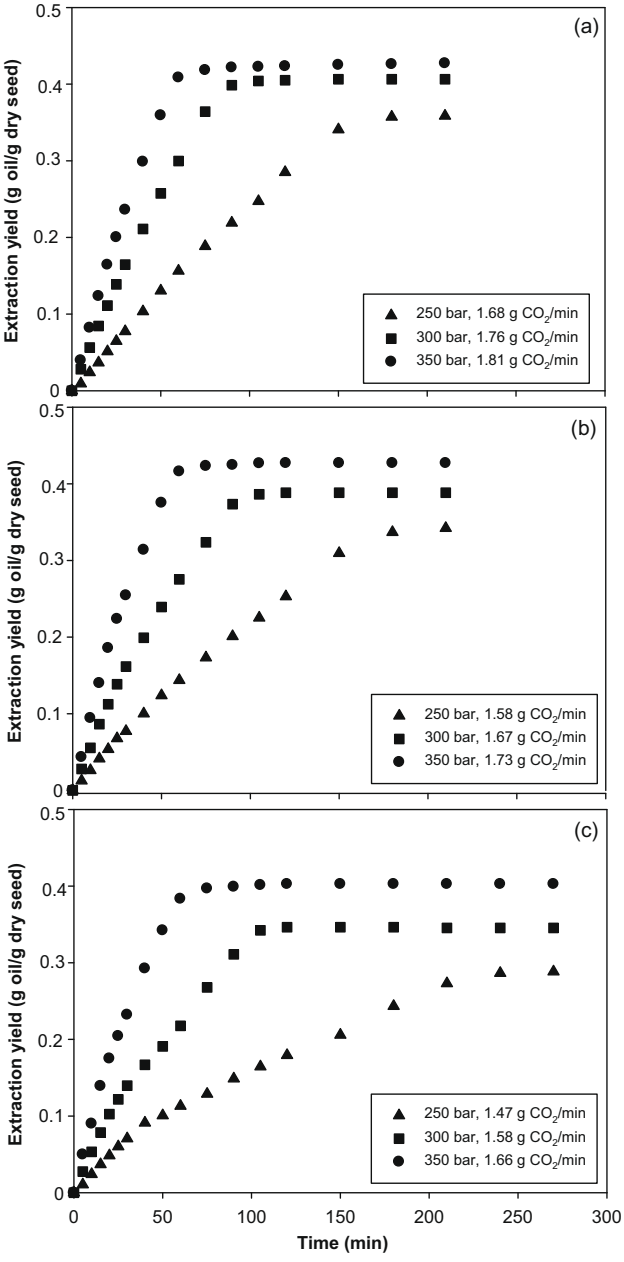

Fig. 1. Effect of pressure on the extraction yield of sesame oil with time at 300 μm < d_p < 600 μm (d_{p1}). (a) 50 °C, (b) 60 °C and (c) 70 °C.

yield was shortened with increasing pressure. 50 °C and 350 bar provided the best initial extraction rate and solubility of sesame seeds in the d_{p1} fraction. As seen in Fig. 1b and c, at 60 and 70 °C the extraction yield was also increased with increasing pressure. These results are consistent with those presented in other studies (Özkal et al., 2005; Louli et al., 2004; Bharath et al., 1992).

4.1.2. Effect of temperature

Because of decreasing solubility, the extraction yield decreased by increasing the extraction temperature at a constant pressure (Fig. 1a–c). While the vapor pressure of solute increases by increasing the extraction temperature, the density of CO_2 decreases. Similar solubility behavior has been reported for other vegetable oils and seed oils obtained via SFE (Louli et al., 2004; Bharath et al., 1992; Gomez and Ossa, 2002; Kriamiti et al., 2002).

4.1.3. Effect of particle size

These experiments were performed using three particle fraction ranges at 50 °C, 350 bar and 1.81 g CO_2/min (2 mL CO_2/min) and results shown in Fig. 2. As seen in the figure, the equilibrium or final yield was not yet reached for the larger particles within the time allotted for measurement. Certainly, the rate of extraction increased as the seed size decreased. In addition, the experimental yield was increased with decreasing the particle size from 0.175 to 0.426 g oil/g dry seed.

Intraparticle diffusion resistance becomes smaller for small particle sizes because of the shorter diffusion path. Effect of intraparticle diffusion seems to gain importance for large particles causing appreciable decrease in the extraction. In that case, part of the oil was not extracted due to the very long diffusion times of the solvent in the vegetable seed particles. It means that the rate of extraction is also increased because with grinding more of the oil is freed from the cells and therefore more accessible. This effect may be stronger with smaller particle sizes. Hence, extraction yield increased with decreasing of the particle size, as noted in the literature (Salgın et al., 2006; Özkal et al., 2005; Louli et al., 2004; Bharath et al., 1992; Gomez and Ossa, 2002; Kriamiti et al., 2002; Gomez et al., 1996).

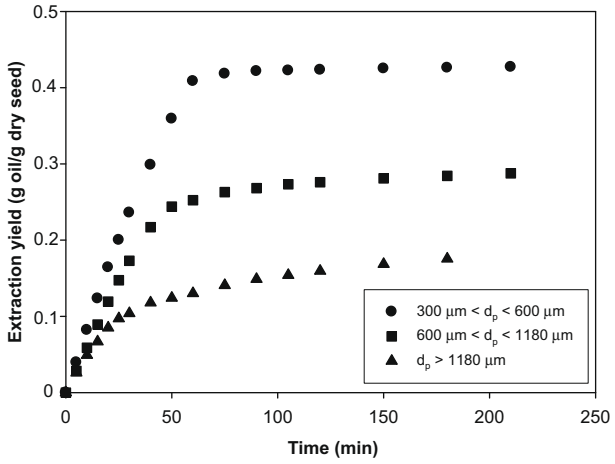

Fig. 2. Effect of particle size on the extraction yield of sesame oil with time at 50 °C, 350 bar and 1.81 g CO_2/min.

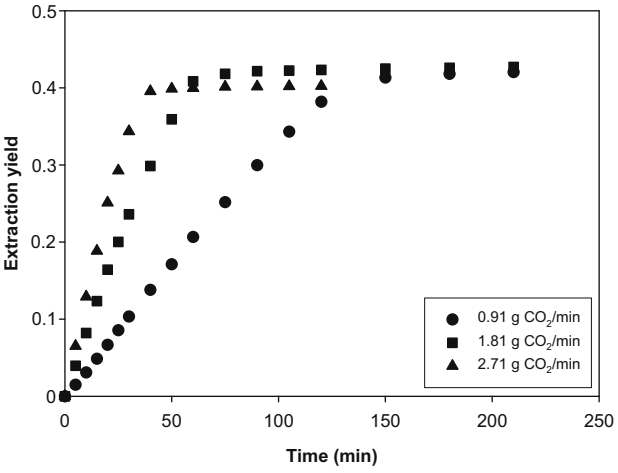

Fig. 3. Effect of $scCO_2$ mass flow rate on the extraction yield of sesame oil with time at 50 °C, 350 bar and 300 < d_p < 600 μm.

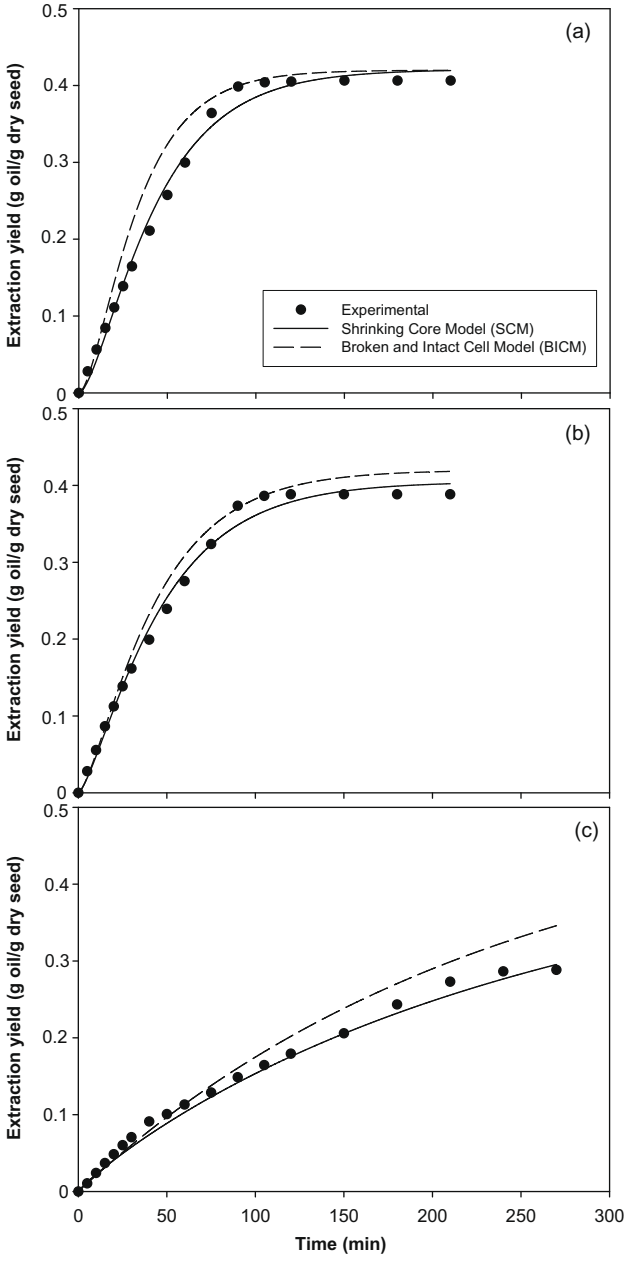

Fig. 4. Mathematical model results of extraction of sesame oil. (a) 50 °C, 300 bar, 1.67 g CO_2/min and 300 < d_p < 600 μm, (b) 60 °C, 350 bar, 1.74 g CO_2/min and 300 < d_p < 600 μm, (c)70 °C, 250 bar, 1.48 g CO_2/min and 300 < d_p < 600 μm.

Table 2
Parameters for the mass transfer models at 2 mL CO_2/min and d_{p1} (300 μm < d_p < 600 μm).

Temperature (°C)	Pressure (bar)	ρ (kg/m^3)	μ (Pa s)	D_e (m^2/s)	k_f (m/s)	D_L (m^2/s)	AAD (%)
Shrinking core model							
50	300	882	3.03×10^{-5}	5.57×10^{-10}	6.05×10^{-6}	2.69×10^{-11}	6.42
60	350	871	3.27×10^{-5}	5.30×10^{-10}	5.85×10^{-6}	3.06×10^{-11}	4.56
70	250	739	2.04×10^{-5}	4.43×10^{-10}	5.11×10^{-6}	2.79×10^{-11}	8.54

Temperature (°C)	Pressure (bar)	C_{sat} (kg/kg)	G	t_k (min)	ψ_k (kg/kg dry seed)	k_fa (1/s)	k_sa (1/s)	AAD (%)
Broken and intact cell model								
50	300	12.5×10^{-3}	0.805	120	0.406	11.517×10^{-3}	10.333×10^{-4}	14.60
60	350	12.6×10^{-3}	0.770	120	0.388	1.108×10^{-3}	5.933×10^{-4}	7.35
70	250	6.5×10^{-3}	0.541	270	0.238	1.221×10^{-3}	2.600×10^{-4}	9.60

ρ solvent density was estimated by Hankinson–Brobst–Thomson (HBT) method (Poling et al., 2001), μ solvent viscosity was calculated by Jossi–Stiel–Thodos method (Poling et al., 2001), D_e effective diffusivity (adjustable parameter for shrinking core model) K_f film mass transfer coefficient was calculated by Eq. (25), D_L axial dispersion coefficient was calculated by Eq. (26), C_{sat} solubility of sesame oil in the solvent was obtained using the data which were plotted as the mass of sesame oil extracted versus the mass of CO_2 utilized and then solubility was calculated from the slope of the line fitted to the experimental values up to 30 min, G Grinding efficiency (fraction of the total oil released, $0 \leqslant G \leqslant 1$), t_k duration of fast extraction time, ψ_k dimensionless time when the released oil in the bed is totally extracted, K_fa and K_sa are mass transfer coefficient for fluid phase and solid phase, respectively (adjustable parameter for broken and intact cell model) ϵ the value of bed void fraction, ϵ_p particle porosity, and density of oil free particles are 0.79, 0.13 and 1224 kg/m^3, respectively. The value of particle porosity was calculated by $(1 - \rho_p/\rho)$ (Roy et al., 1996).

4.1.4. Effect of $scCO_2$ flow rate

The effect of $scCO_2$ flow rate on extraction yield at 350 bar and 50 °C is shown in Fig. 3. The extraction rate was also affected significantly by increase in $scCO_2$ flow rates at the beginning of extraction period (fast extraction period). Hence, the extraction rate increased with increasing $scCO_2$ flow rate. The duration of the fast extraction period, decreased from 180 to 50 min as the $scCO_2$ flow rate increased from 0.91 g CO_2/min (1 mL CO_2/min) to 2.71 g CO_2/min (3 mL CO_2/min).

Mass transfer coefficients were determined as 6.40×10^{-6}, 8.39×10^{-6} and 10.01×10^{-6} m/s for 0.91, 1.81 and 2.71 g CO_2/min, respectively (at 50 °C, 350 bar). Mass transfer coefficient increased with $scCO_2$ flow rate. This was due to the decrease in mass transfer resistance, because of increase in convection. Increase in mass transfer coefficient with flow rate was also reported for the extraction of apricot kernel oil (Özkal et al., 2005) and sunflower oil (Salgın et al., 2006).

However, at the end of the extraction period the extracted oil was reached 0.427 g/g dry seed which is close to organic solvent yield of 0.506 g/g dry seed.

4.2. Analysis of extracted sesame oil

The fatty acid composition of sesame oil obtained at various SFE operation conditions were not significantly different than oil extracted with hexane using Soxhlet extraction (Table 1) indicating that sesame oil was not fractionated during extractions. Odabaşı and Balaban (2002) were also reported similar results.

4.3. Results of models and discussion

In this study, two mathematical models known as the SCM and BICM were compared with each other. Some of the modeling results are shown in Fig. 4a–c. According to Fig. 4a–c, each model described satisfactorily the experimental data for each condition. For comparison of the models to the experimental data, SCM had good agreement with experimental data, but BICM could not describe experimental data well at giving conditions. This might be due to the use of more than one fitting parameters in broken and intact cell model. As can be seen in Table 2, the average absolute deviation (AAD) of shrinking core model is smaller than broken and intact cell model for each experimental condition.

The errors were quantified by defining average AAD as below.

$$\mathrm{AAD}(\%) = \frac{1}{n}\sum_{i=1}^{n}\left|\frac{y_{\mathrm{experimental}} - y_{\mathrm{calculated}}}{y_{\mathrm{experimental}}}\right|_i \times 100 \qquad (26)$$

where n is the number of data $y_{\mathrm{experimental}}$ and $y_{\mathrm{calculated}}$ are the data obtained from experiments and model equations, respectively at ith condition.

Differential equations were solved numerically by Crank–Nicholson's method at MATLAB 6.0 (Chapra and Canale, 1998). In SCM, the mass transfer coefficient (k_f) in a packed bed and axial dispersion coefficient (D_L) in the supercritical phase were estimated with using empirical correlations (Goodarznia and Eikani, 1997; Tan and Liou, 1989).

$$\mathrm{Sh} = 2 + 1.1\mathrm{Sc}^{1/3}\mathrm{Re}^{0.6} \qquad (27)$$

$$\mathrm{Pe} = 0.187\mathrm{Re}^{0.265}\mathrm{Sc}^{-0.919} \qquad (28)$$

Using the best fit of the effective diffusivity (D_e), the experimental data was well correlated by the mathematical model (SCM). This fact can be observed in Fig. 4.

BCIM has four adjustable parameters (G, ψ_k, X and Y) that were determined by minimizing the errors between experimental and calculated yield values.

Some difficulties were encountered in providing initial guess values of the parameters. Thus, it is important to minimize the fitting parameter. Besides that, the initial concentration of sesame oil in the solid, x_o, should be based on maximum yield of experimental result for giving conditions. Phenomenological models of a supercritical extraction process consist of mass balance equations for solute in solid phase and in fluid phase. By integration of these differential equations time-dependent concentration profiles in both phases are obtained and the extraction curve is calculated from fluid phase concentration at the extractor outlet. As can be seen in Table 2, the value of k_fa was 2 or 12-fold greater than the value of k_sa related to operating pressure and temperature.

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