

Modeling the Supercritical Fluid Extraction of Hazelnut and Walnut Oils

M. Gabriela Bernardo-Gil

Centre for Biological and Chemical Engineering, DEQB, IST, 1049-001 Lisbon, Portugal

Miguel Casquilho

Centre of Chemical Processes, DEQB, IST, 1049-001 Lisbon, Portugal

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Data from supercritical fluid extraction of hazelnut and walnut oils were modeled using the Sovová's mass transfer model. The extractions were carried out at temperature ranging from 308–321 K and pressure 18–23.4 MPa. For the hazelnut oil, the influence of superficial velocity of the fluid (CO_2) was studied in the range $(4.42\text{--}7.10) \times 10^{-4} \text{ ms}^{-1}$, for ground hazelnut with $D_p = 0.7 \text{ mm}$. For the walnut oil, the influence of particle size was studied, in the range 0.01–0.5 mm, for $6.8 \times 10^{-4} \text{ ms}^{-1}$ of superficial velocity of the fluid. The overall mass transfer coefficients in the solvent phase and in the solid phase, the fraction of the solute directly exposed to the solvent, and the void fraction in the bed were selected as adjustable parameters. For hazelnut oil, values of these parameters were: $\varepsilon = 0.273$; $f_k = 0.668$; $K_f = (1.29\text{--}3.65) \times 10^{-2} \text{ s}^{-1}$; and $K_s = (8.97\text{--}28.1) \times 10^{-5} \text{ s}^{-1}$. The K_f calculated by the Sherwood equations varied from 1.61×10^{-2} to $2.62 \times 10^{-2} \text{ s}^{-1}$, agreeing very well with values determined by the Sovová's model. For the walnut oil, ε varied from 0.142 to 0.225; $f_k = (0.339\text{--}0.581)$; $K_f = (1.04\text{--}3.62) \times 10^{-2} \text{ s}^{-1}$; and $K_s = (5.17\text{--}16.0) \times 10^{-5} \text{ s}^{-1}$. The K_f calculated by the Sherwood equations varied from 1.49×10^{-2} to $5.46 \times 10^{-2} \text{ s}^{-1}$, agreeing well with those obtained by Sovová's model. © 2007 American Institute of Chemical Engineers *AIChE J*, 53: 2980–2985, 2007

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Introduction

Hazelnuts (from *Corylus avellana* L.) and walnuts (from *Juglans regia* L.) are important vegetable products from trees found in European countries and elsewhere. This type of product includes almonds, peanuts, pine nuts, pumpkin seeds, and other kernels, which are valued for their remarkable nutritional properties leading to a high economical value. They have high oil contents, which contribute to their use as

a source of energy in the Mediterranean diet and exhibit high levels of mono- and poly-unsaturated fatty acids. Hazelnut oil has about 80% of oleic acid, and linoleic acid in the range 6–9%¹; walnut oil has about 20% of oleic acid, 55% of linoleic acid, and linolenic acid in the range 13–14%². These fatty acids, as well as sterols and tocopherols also present, play a preventive role in many diseases, especially cardiovascular ones, as they contribute to lower the “low density lipoprotein” cholesterol.^{3,4}

The oils can be obtained by supercritical fluid extraction (SFE), which is considered to compare favorably with conventional extraction (*n*-hexane). The modeling of SFE of oils from ground vegetable substrates addresses the mass transfer

Correspondence concerning this article should be addressed to M. Gabriela Bernardo-Gil at gbernardo.gil@ist.utl.pt.

interaction between the ground solid and the fluid, namely supercritical carbon dioxide (SCCO₂). Due to the technological difficulties encountered with the use of high pressures for these processes, knowledge of the thermodynamic behavior (solubility, selectivity, etc), and mass transfer rates is important. However, information about mass transfer in SFE is still scarce, which is aggravated by the variety of current and foreseeable extractable substances, which are normally composed of a high number of components. There are also difficulties in establishing the interactions between the extract (and its components), the solvent, and the solid phase.

Many efforts have been made addressing the modeling of mass transfer kinetics for SFE from solid substrates, appropriate models being expected to facilitate the scale-up from laboratory data to industrial design. Several models in the literature have been proposed for SFE of packed beds of solid matrices. Some of them are empirical, and their only advantages are their simplicity and capacity to describe the evolution of the extraction process,⁵⁻⁷ and they are thus not adequate for scaling-up. Other more theoretical models consider only the fluid phase resistance.⁸⁻¹¹ Yet, whenever the major mass transfer resistance is within the solid phase, the models must also consider solute transport within the solid particles.¹²⁻¹⁶ Del Valle and de la Fuente¹⁷ present a review of kinetic models, starting from a general model that includes desorption, shrinking core, and diffusion, but they indicate several limitations of the model, mentioning subsequent simplifications.

One convenient model is that developed by Sovová,¹⁴ who extended Lack's plug flow model for application to SFE, which has proved to describe very well the SFE of several products, such as grape oil,¹⁸ black pepper,^{19,20} aniseed oil,²¹ and apricot kernel oil.²² Sovová's mass transfer model takes into account the solute solubility in the solvent phase and the mass transfer coefficient both in the fluid and in the solid phases, neglecting the accumulation of the solute in the fluid phase. The model assumes pseudo-steady state and plug flow, with temperature, pressure, and solvent velocity being kept constant throughout the operation. The model also assumes that the bed is homogeneous regarding the particle size distribution and the initial solute distribution in the bed. Axial dispersion and solute accumulation in the fluid phase are assumed to be negligible.

In this work, Sovová's model was applied to data of the supercritical fluid extraction of hazelnut oil¹ and of walnut oil.²

Mass Transfer Model

The extraction curves of SFE operations involving oils from vegetable stuff (fruits, seeds) with high fat content can be divided into three periods:

- Constant extraction rate (CER) period: Mass transfer is controlled by the resistance in the solvent phase, as the external surface of the particles is covered with easily accessible solute.
- Decreasing extraction rate (DER) period: The availability of the easily accessible solute decreases within the extractor in the direction of the flow, until its exhaustion, allowing the start of the rise of the diffusion mechanism.
- Final extraction rate (FER) period: Mass transfer is diffusion-controlled in the bed and inside the solid particles, and only the less accessible oil is extracted.

When the solvent flows axially through a bed of milled plant material in a cylindrical extractor vessel, homogeneous with respect to both particle size and the initial distribution of solute, with superficial velocity (V_s), the model assumes that a fraction of the solute (f_k), is directly exposed to the solvent, the remaining fraction, $(1 - f_k)$, being less accessible.

$$1 - f_k = \frac{x_k}{x_0} \quad (1)$$

The initial specific concentration of solute in bed (x_0), expressed as the mass of solute per mass of solute-free feed, is the sum of the accessible specific solute concentration (x_p), resulting from the milling of the plant stuff, and the specific concentration of the inaccessible solute inside the particles (x_k).

The accessible oil is extracted first, mass transfer being influenced by diffusion resistance in the solvent (k_f). In this work, however, the quantity of available oil is quite high, so the solubility limit could be attained, which would possibly be a limiting factor.

When all the accessible oil is extracted, mass transfer is retarded by the diffusion in the solid phase, and a solid phase coefficient (k_s) must be applied.

The amount of solute (e), expressed as kg (solute)/kg (solute-free seed), extracted during the first, the second, and the third extraction periods mentioned is given by the Sovová's model, which accounts for both the solubility- and diffusion-controlled regimes of the extraction:

$$e = \begin{cases} qy_r[1 - \exp(-Z)] & q < q_m \\ y_r[q - q_m \exp(z_w - Z)] & q_m \leq q < q_n \\ x_0 - \frac{y_r}{W} \ln \left\{ 1 + \left[\exp\left(\frac{Wx_0}{y_r}\right) - 1 \right] \exp[W(q_m - q)] (1 - f_k) \right\} & q_n \leq q \end{cases} \quad (2)$$

where q is the specific mass of solvent passed through the extractor ($q = Q/N$), Q being the mass of solvent, and N the mass of solute-free solid phase. The boundary values of q are as follows:

q_m , the specific mass of solvent, when the extraction from the inside of particles starts (the end of the CER period):

$$q_m = \frac{x_0 f_k}{y_r Z} \quad (3)$$

q_n , the specific mass of solvent at the end of the DER period:

$$q_n = q_m + \frac{1}{W} \ln \left[(1 - f_k) + f_k \exp\left(\frac{Wx_0}{y_r}\right) \right] \quad (4)$$

where z_w is the dimensionless axial coordinate of the boundary between fast and slow extraction:

$$\frac{z_w}{Z} = \frac{y_r}{Wx_0} \ln \frac{\exp[W(q - q_m)] - (1 - f_k)}{f_k} \quad (5)$$

Z is the dimensionless mass transfer parameter in the solvent phase:

$$Z = K_f \rho / [\dot{q}(1 - \varepsilon) \rho_s] \quad (6)$$

W is the dimensionless mass transfer parameter in the solid phase:

$$W = K_s / [\dot{q}(1 - \varepsilon)] \quad (7)$$

The overall mass transfer coefficient in the fluid phase is $K_f = k_f a_0$, with k_f being the solvent-phase mass transfer coefficient and a_0 the specific interfacial area. The global mass transfer coefficient in the solid phase is $K_s = k_s a_0$, with k_s being the solid-phase mass transfer coefficient. The void fraction in the bed (ε) was calculated from the solid density (ρ_s), and apparent (bulk) density (ρ_a): $\varepsilon = 1 - \rho_a / \rho_s$. $\dot{q}$ is the mass flow rate of solvent related to N [kg (solvent)/s per kg (solute-free feed)].

The solubility of the oils in the solvent at the temperature and pressure conditions investigated (y_r) was calculated assuming that the solubility of vegetable oils in supercritical carbon dioxide is proportionally dependent on the composition in fatty acids. Chrastil's equation²³ was used to estimate the solubility of the main fatty acids of hazelnut oil and walnut oil in SCCO₂. At phase equilibrium, this author assumed a linear relationship between the logarithm of solute solubility and the natural logarithm of SCCO₂ density, which can be expressed as:

$$\ln y = (k - 1) \ln \rho + \left(\frac{a}{T} + b \right) \quad (8)$$

where y is the solubility (kg/kg CO₂), ρ is the density of SCCO₂ (kg/m³), and T is the temperature (K). The parameter k represents the number of solvent molecules associated with one molecule of solute in the solvate complex, a is related to the heat of solvation and the heat of vaporization of the solute, whereas b depends on the molecular mass and melting points of solvent and solute. The values of these parameters for fatty acids were obtained from Vasconcellos and Cabral.²⁴

The yield, Y , expressed as the mass of extract per mass of substratum, is related to e :

$$Y = \frac{e}{1 + x_0} \quad (9)$$

The mass transfer coefficients are dependent on several variables, namely flow rate, density, diffusivity, viscosity of the solvent, particle size, and porosity of the bed. They are often related to the relevant dimensionless groups of Sherwood ($Sh = k_f D_p / D_{12}$), Reynolds ($Re = V_s \rho D_p / \mu$), and Schmidt [$Sc = \mu / (\rho D_{12})$], as the general correlation:

$$Sh = C_1 Re^{C_2} Sc^{1/3} \quad (10)$$

where C_1 and C_2 are constants determined from experimental data and generally depend on the range of the Reynolds number under study.²⁵ The characteristic length introduced in

the Reynolds and Sherwood groups is usually related to the particle size as the equivalent particle diameter (D_p). Also, the Reynolds number is frequently defined using the superficial velocity (V_s), and ρ and μ , which are the solvent density and viscosity respectively. The diffusion coefficient, D_{12} , was estimated by using the Stokes-Einstein equation²⁶: $D_{12} = kT / (6\pi r \mu)$, where k is the Boltzman constant and r is the solute molecular radius.

As the product $Z\dot{q}$ is directly proportional to the overall mass transfer coefficient in the supercritical phase, it must change with the superficial velocity of CO₂ (V_s) according to:

$$Z\dot{q} = C_3 V_s^{C_4} \quad (11)$$

Evaluation of the Model Parameters

To evaluate the parameters, the model equation was fitted to the various sets of experimental data by minimizing the discrepancies through the minimum sum of squares criterion. Minimization was done by the sequential simplex (Nelder-Mead) algorithm, which was purposely programmed, allowing to easily set constant selected parameters, since Eq. 2, with its unyielding functions, was expected to pose considerable convergence difficulties.

Modeling was made in two steps: in the first one K_f , K_s , and f_k were estimated as adjusted parameters; in the second step f_k was kept constant and equal to the average of the f_k values obtained in the first step, K_f and K_s being fitted to experimental data.

Experimental Data

The hazelnut oil SFE experiments were carried out for $D_p = 0.7$ mm, with $x_0 = 1.96$ kg oil/kg oil-free hazelnut (66 %), V_s varying in the range $(4.42\text{--}7.10) \times 10^{-4}$ m s⁻¹, pressure of (18–23.4) MPa, and temperature of (308–321) K. The oil solubility, which is influenced by the concentration in fatty acids, varied in the range $(4.68\text{--}9.40) \times 10^{-3}$ kg hazelnut oil/kg SCCO₂, depending on the conditions of pressure and temperature of extraction.

The walnut oil SFE experiments were carried out at superficial velocity of about 6.8×10^{-4} m s⁻¹, at 18–23.4 MPa, and 308–321 K, with $x_0 = 2.45$ kg oil/kg oil-free walnut (71%), D_p varying within the range 0.01–0.5 mm. The calculated walnut oil solubilities varied from 7 to 15 g walnut oil/kg SCCO₂, depending on the conditions of pressure and temperature of extraction.

Results and Discussion

For the hazelnut oil extraction, the values of the model parameters f_k , K_f , and K_s , which were estimated in two steps from the SFE experimental values, are presented in Table 1. The value of the fraction of solute directly exposed to the solvent (f_k), taken as the average of the values obtained in the first step of the calculation, was 0.668. It is evident from Figure 1 that the Sovová's model represents very well the SFE results obtained for the hazelnut oil at 18 MPa.

Table 1. Parameters Found by Using the Extraction Curves of Hazelnut Oil (for $f_k = 0.668$, and $D_p = 0.7$ mm)

P (MPa)	T (K)	$V_s \times 10^4$ (m s ⁻¹)	$K_f \times 10^2$ (s ⁻¹)	$K_s \times 10^5$ (s ⁻¹)	q_m	q_n	Z	$W \times 10^3$
18	308	6.4	3.65	16.7	267	598	0.901	4.04
18	308	4.4	2.19	8.97	353	672	0.797	3.75
18	318	6.4	1.68	12.7	492	740	0.513	3.63
18	318	4.7	1.29	10.3	469	721	0.441	4.07
20	313	7.1	2.86	18.2	272	489	0.643	4.50
20	321	5.4	1.33	14.5	398	567	0.361	4.45
23.4	313	5.3	2.71	19.6	170	338	0.812	6.10
20	313	5.4	2.48	18.0	244	468	0.735	5.71
20	313	5.4	2.17	12.7	281	494	0.637	4.00
22	308	6.2	3.71	28.1	126	376	0.946	5.27
22	308	4.2	3.08	20.2	127	379	1.191	7.11
22	318	6.4	2.09	27.6	252	413	0.513	5.31
22	318	4.4	1.39	11.0	259	409	0.499	4.28

The values of K_f were calculated by using Eq. 10 with $C_1 = 0.206$ and $C_2 = 0.8$ from the literature,²⁷ varying in the range $(1.61\text{--}2.62) \times 10^{-2}$ s⁻¹, which is in good agreement with the values of Table 1, determined by Sovová's model.

Using the values of Table 1, the following relation was found:

$$Z\dot{q} = 4.10 V_s^{0.66} \quad (12)$$

In this equation, the coefficient and the exponent are of the same order of magnitude as the various values reported by Brunner,²⁸ in the extraction of rape seed; Sovová et al.,¹⁸ in the extraction of grape oil; and Esquivel et al.,⁵ in the extraction of olive husk oil.

The values of $Z\dot{q}$ vary for the extraction of hazelnut oil with SCCO₂ in the range $(1.76\text{--}3.68) \times 10^{-2}$ s⁻¹, which is of the same order of magnitude of the values obtained by Louli et al.²⁹ for the extraction of parsley seeds $[(0.64\text{--}5.70) \times 10^{-2}$ s⁻¹], by Perakis et al.³⁰ for the extraction of black pepper $[(0.23\text{--}4.73) \times 10^{-2}$ s⁻¹], and by Esquivel et al.⁵ for the extraction of olive husk oil $[(1.50\text{--}25.7) \times 10^{-2}$ s⁻¹].

The values $W\dot{q}$ for the extraction of hazelnut oil vary in the range $(1.23\text{--}3.05) \times 10^{-4}$ s⁻¹, which compares very well with those for the extraction of olive husk oil $[(0.038\text{--}3.79) \times 10^{-4}$ s⁻¹]; parsley seeds $[(1.56\text{--}6.56) \times 10^{-5}$ s⁻¹];²⁹ and black pepper oil $[(0.21\text{--}1.47) \times 10^{-4}$ s⁻¹].³⁰

For the walnut oil extraction, Table 2 presents the values of f_k , ε , K_f , and K_s that were estimated in two steps as well as the other parameters calculated. In this case, in the first step of the regression, besides K_f , K_s , and f_k , ε was also used as an adjustable parameter. Values of this property can be found from bulk density, but it was decided to confirm them, and, as expected, it was seen that the ε values were very similar for each D_p value. So, as for the hazelnut oil, f_k and ε were kept constant and equal to the average value, depending only on D_p , while K_f and K_s were fitted to the experimental results.

The values of K_f and K_s estimated for the walnut oil are of the same order of magnitude as those obtained for the hazelnut oil. For the walnut oil, f_k and K_s values are slightly lower than for the hazelnut oil. Best-fit values of f_k were 0.339 for particles with $D_p = 0.01$ mm; 0.462 for $D_p = 0.05$ mm; 0.581 for $D_p = 0.1$ mm; and 0.563 for $D_p = 0.5$ mm.

Calculated values of ε were 0.225, 0.166, 0.151, and 0.142, for beds of particles with the same values of D_p , respectively. Some results are presented in Figure 2, and it becomes also evident that Sovová's model fitted fairly well the SFE experimental data for the walnut oil at 22 MPa.

The values of K_f calculated by using Eq. 10 for the extraction of walnut oil with SCCO₂ vary from 1.49×10^{-2} to 5.46×10^{-2} s⁻¹, agreeing fairly well with those obtained by Sovová's model (Table 2).

For both oils, hazelnut and walnut oil, the overall mass transfer coefficients obtained by Sovová's model for the supercritical fluid extraction are comparable to those obtained by several authors, a fact verifying the applicability of the model by Sovová et al.¹⁸ for the extraction of grape oil, $K_f = 0.04$ s⁻¹ and $K_s = (1.0\text{--}2.2) \times 10^{-5}$ s⁻¹; by Sovová et al.¹⁹ for the extraction of lipids from black pepper, $K_f = (2.7\text{--}3.3) \times 10^{-3}$ s⁻¹, and $K_s = (6.7\text{--}20.0) \times 10^{-5}$ s⁻¹; by Ozkal et al.²² for the extraction of apricot kernel oil, $K_f = (1.52\text{--}6.20) \times 10^{-2}$ s⁻¹ and $K_s = (3.83\text{--}8.07) \times 10^{-6}$ s⁻¹; and by Bernardo-Gil et al.³¹ for the extraction of acorn oil, $K_f = (1.34\text{--}6.02) \times 10^{-3}$ s⁻¹ and $K_s = (2.92\text{--}52.2) \times 10^{-5}$ s⁻¹.

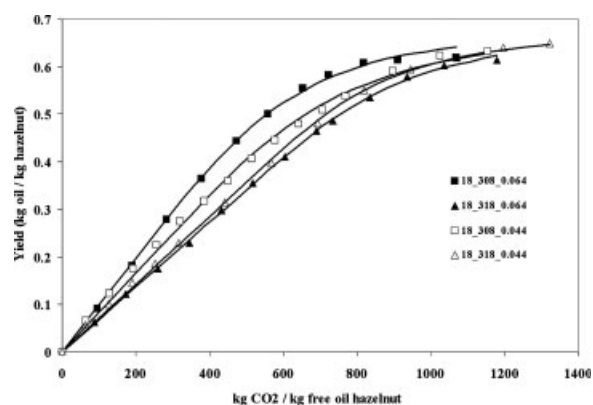


Figure 1. Comparison between the experimental extraction curves of hazelnut oil at 18 MPa [Pressure (MPa)_Temperature (K)_Superficial velocity (cm s⁻¹)] and those obtained by Sovová's model (lines).

Table 2. Parameters Found by Using the Extraction Curves of Walnut Oil (for $V_s = 6.8 \times 10^{-4} \text{ m s}^{-1}$)

P (MPa)	T (K)	D_p (mm)	$K_f \times 10^2$ (s^{-1})	$K_s \times 10^5$ (s^{-1})	f_k	q_m	q_n	Z	$W \times 10^3$	ε
18	308	0.01	1.84	6.74	0.339	332	469	0.353	1.37	0.225
18	308	0.1	3.07	8.39	0.581	368	591	0.545	1.58	0.151
18	318	0.01	1.07	5.49	0.339	483	591	0.202	1.19	0.225
18	318	0.1	1.42	7.26	0.581	690	871	0.246	1.41	0.151
20	313	0.5	2.07	5.17	0.563	353	489	0.367	1.01	0.142
20	321	0.05	1.16	8.77	0.462	425	520	0.206	1.76	0.166
23.4	313	0.05	1.88	13.3	0.462	234	320	0.331	2.42	0.166
20	313	0.05	1.73	7.19	0.462	348	463	0.306	1.37	0.166
20	313	0.05	1.71	10.2	0.462	349	468	0.305	2.01	0.166
22	308	0.01	1.97	12.1	0.339	205	299	0.384	2.41	0.225
22	308	0.1	3.62	16.0	0.581	213	365	0.634	2.87	0.151
22	318	0.01	1.04	9.26	0.339	260	321	0.212	2.04	0.225
22	318	0.1	1.49	9.96	0.581	358	458	0.264	1.91	0.151

Conclusions

Lack's plug flow model as extended by Sovová for supercritical fluid extraction was applied to represent the extraction behavior of hazelnut and walnut oils. Using supercritical carbon dioxide as the solvent, the oils were extracted at pressures ranging from 18 to 32.4 MPa and temperatures from 308 to 321 K. The adjustable parameters chosen were the overall mass transfer coefficient in the solvent phase (K_f), the overall mass transfer coefficient in the solid phase (K_s), the fraction of solute directly exposed to the solvent (f_k), and void fraction in the extraction bed (ε). These parameters were estimated in a two-step procedure, based on a Nelder-Mead minimization technique.

The predicted extraction curves agreed well with the experimental data for all conditions studied, and the fitted parameters are consistent with those published by several authors, for the oils in grape, black pepper, apricot kernel, and acorn. The results showed a free oil content for hazelnut of 66.8% and for walnut f_k in the range 0.339 to 0.581 depending on the particle size.

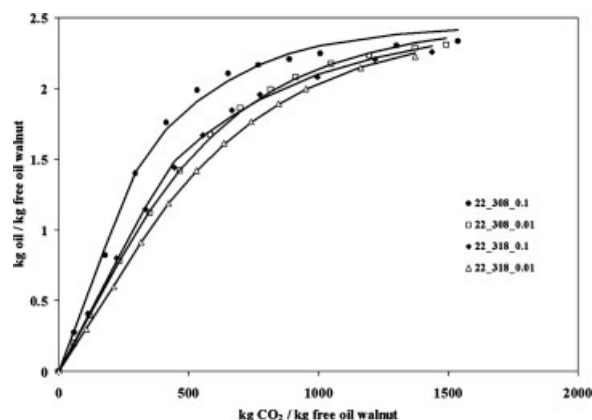


Figure 2. Comparison between the experimental extraction curves of walnut oil at 22 MPa [Pressure (MPa)_Temperature (K)_Medium particle diameter (mm)] and those obtained by Sovová's model (lines).

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