Latin American Applied Research 31:397-401 (2001)

MATHEMATICAL MODELING OF NUTMEG ESSENTIAL OIL EXTRACTION BY LIQUID CARBON DIOXIDE

C. B. SPRICIGO, A. BOLZAN and L. T. PINTO[*]

Departamento de Engenharia Química e Engenharia de Alimentos
Universidade Federal de Santa Catarina, 88040-900, Florianópolis, Santa Catarina, Brazil
phone: +55 48 331-9448; fax: +55 48 331-9687

Keywords: Essential Oil Extraction; Liquid Carbon Dioxide; Mathematical Modeling; Nutmeg

Abstract

A mathematical model based on the shrinking core approach was proposed to represent the nutmeg essential oil extraction with liquid carbon dioxide. The model assumes that the essential oil inside the nutmeg particle is located within a core that shrinks as the extraction is carried out. Concentration profiles along the bed were considered, as well as axial dispersion effects. The mass transfer coefficient and the axial dispersion coefficient were calculated by means of empirical relations, and the effective diffusion coefficient was used as fitting parameter. The model was validated with experimental data obtained for different particle sizes and solvent flow rates, and the values obtained for the effective diffusion coefficient varied from 1.5 x 10^{-12} to 2.5 x 10^{-11} $m^2.s^{-1}$.

1. Introduction

Different mathematical models have been proposed to describe the extraction of natural products from vegetable matrices by dense carbon dioxide. Mass transfer mechanisms involved in the extraction processes are closely related to the vegetable structure and to the location of the solute within the solid phase, and should be a guide to the choice of a suitable model. An extensive overview on mathematical modeling of supercritical fluid extraction (SFE) processes is given by Reverchon (1997).

The shrinking-core model has been proposed to represent the SFE of essential oils and lipids from seeds and roots. This model assumes that the solute inside the particle is located within a core that has its volume continually reduced as the solute is extracted. The solvent at the core interface is taken to be at equilibrium with the oil core. Fick´s law describes the porous region between the core and the particle surface, and the time profile of the average solute concentration in the solid phase equals the mass transfer through the fluid film that surrounds the particle.

King and Catchpole (1993) proposed the shrinking-core approach to model the SFE of vegetable oil from peanuts. A quasi-steady state solution was obtained with the assumptions that changes in the core radius during the residence time of the solvent in the extractor and changes along the bed were negligible at any given time. The equilibrium solubility and the mass transfer coefficient were predicted from empirical relations, and the effective diffusivity was used as a fitting parameter. The model represented well the experimental data with an effective diffusivity of 3.56 x 10^{-9} $m^2 s^{-1}$. Roy *et al.* (1996) proposed the use of the shrinking-core model to describe the SFE of ginger oil. The solute concentration profile in the fluid phase along the bed and axial dispersion effects were considered. Adjustable parameters were equilibrium solubility and effective diffusivity. The model produced a good fit of experimental data obtained with particles of 2.56 mm diameter, but it failed to describe the extraction from smaller particles (0.35 and 0.68 mm diameter).

The present work proposes the use of the shrinking-core model to describe the extraction of nutmeg essential oil by liquid carbon dioxide. The model was validated with experimental data obtained by Spricigo *et al.* (1999), and it was able to describe the extraction curves for all the particle sizes tested, using the effective diffusivity as fitting parameter.

2. Mathematical model

2.1 Fluid phase

The mathematical modeling of the fluid phase assumes the existence of a concentration profile along the bed and includes an axial dispersion term. The fixed bed is assumed to be composed of spherical particles, and the extraction term is described by the mass transfer through a fluid film at the particle surface. The equation for the fluid phase is written as:

$$\varepsilon \frac{\partial C}{\partial t} = D_L \varepsilon \frac{\partial^2 C}{\partial z^2} - v\varepsilon \frac{\partial C}{\partial z} - \left(1-\varepsilon\right)\frac{3k_f}{R}\left(C - C_p\big|_{r=R}\right) \tag{1}$$

---

[*] Author to whom correspondence should be addressed: E-Mail: leonel@enq.ufsc.br

where ε is the bed porosity, C is the solute concentration in the fluid phase (kg.m^{-3}), D_L is the axial dispersion coefficient (m^2.s^{-1}), k_f is the mass transfer coefficient (m.s^{-1}), R is the particle radius (m), t is time (s), v is the interstitial solvent velocity (m.s^{-1}) and z is the axial coordinate (m). The following boundary conditions apply:

$$
\begin{aligned}
&z = 0, \quad vC - D_L \frac{\partial C}{\partial z} = 0 \\
&z = L, \quad \frac{\partial C}{\partial z} = 0
\end{aligned}
\qquad (2)
$$

where L is the bed height (m).

Since the solvent was allowed to be in contact with the solid phase for some time before it started to flow out from the extractor (Spricigo, 1998), it is assumed that the fluid is initially in equilibrium with the solid phase. Therefore, when $t=0$:

$$C = C_{eq} \qquad (0 \le z \le L) \qquad (3)$$

where C_{eq} is the equilibrium solute concentration in the fluid phase (kg.m^{-3}).

2.2 Solid phase

The porous region between the oil core and the particle surface is modeled with base on single spherical particles, assuming transient diffusive transport in the radial direction. The transport coefficient is interpreted as an effective diffusion coefficient:

$$\frac{\partial C_p}{\partial t} = \frac{D_e}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial C_p}{\partial r}\right) \qquad (4)$$

where C_p is the solute concentration in the solvent within the particle pores (kg.m^{-3}), D_e is the effective diffusion coefficient (m^2.s^{-1}) and r is the radial coordinate in the particle (m).

With the assumption that the diffusive mass flux at the particle surface is equal to the mass flux to the fluid phase at the solid-fluid interface film, the following boundary condition is obtained:

$$r = R, \qquad \varepsilon_p D_e \frac{\partial C_p}{\partial r} = k_f \left(C - C_p\big|_{r=R}\right) \qquad (5)$$

where ε_p is the particle porosity and R is the particle radius (m).

At the core surface, the fluid is assumed to be saturated with essential oil, as proposed by Roy *et al.* (1996). However, in this work, in order to avoid numerical instabilities during model solving, the saturation condition is changed to a condition of symmetry when the oil core is exhausted:

$$
\begin{aligned}
&r = r_c, r_c \ne 0, \qquad C_p = C_{sat} \\
&r = r_c, r_c = 0, \qquad \frac{\partial C_p}{\partial r} = 0
\end{aligned}
\qquad (6)
$$

where C_{sat} is the saturation concentration of solute in the fluid phase (kg.m^{-3}) and r_c is the core radius (m).

A linear concentration profile is assumed as initial condition in the porous region limited by the core and the particle surface:

$$C_p = \frac{\left(1 - r/R\right)}{\left(1 - r_{c0}/R\right)}\left(C_{sat} - C_{eq}\right) + C_{eq} \qquad (t = 0) \qquad (7)$$

where r_{c0} is the initial core radius (m), that is calculated by a mass balance involving the particle porous region, the core and the fluid phase:

$$\int_{r_{c0}}^{R} \varepsilon_p n_p C_p 4\pi r^2 dr + \frac{4}{3}\pi r_{c0}^3 q_0 n_p + \frac{\pi d^2}{4} L\varepsilon C_{eq} = M.e \qquad (8)$$

where d is the bed diameter (m), d_p is the mean particle diameter (m), e is the maximum extractable solute content of the solid phase (g_{solute}/g_{solids}), M is the initial mass of solids in the bed (kg), n_p is the number of particles in the bed and q_0 is the initial solute concentration in the solid phase (kg/m^3). The values n_p and q_0 are calculated by Eqns. (9) and (10) respectively:

$$n_p = \frac{3}{2}\frac{d^2 L(1-\varepsilon)}{d_p^3} \qquad (9)$$

$$q_0 = e.\rho_s \qquad (10)$$

where ρ_s is the specific gravity of the porous particle (kg.m^{-3}). After substitution of Eqn. (7) in (8) and integration, the final expression is obtained for the calculus of the core radius at $t = 0$:

$$\pi\varepsilon_p n_p\left[\frac{4}{3}\frac{\left(R^3 - r_{c0}^3\right)}{\left(R - r_{c0}\right)}\left(RC_{sat} - r_{c0}C_{eq}\right) - \frac{\left(R^4 - r_{c0}^4\right)}{\left(R - r_{c0}\right)}\left(C_{sat} - C_{eq}\right)\right] + \frac{4}{3}\pi r_{c0}^3 q_0 n_p + \frac{\pi d^2}{4}L\varepsilon C_{eq} = M.e \qquad (11)$$

The core radius at any given time is calculated by a mass balance in the particle. The time variation of the mass of solute within the particle (core + porous region) is equal to the mass flux through the external fluid film at the particle surface:

$$\frac{dN}{dt}+\frac{dP}{dt}=k_f.4\pi R^2\left(C-C_p\big|_{r=R}\right) \tag{12}$$

where N is the mass of solute in the core (kg) and P is the mass of solute in the fluid within the porous region (kg). The mass of solute in the core is given by Eqn. (13):

$$N=\frac{4}{3}\pi r_c^3 q_0 \tag{13}$$

Equation (14) is obtained by time derivation of Eqn. (13).

$$\frac{dN}{dt}=4\pi q_0 r_c^2\frac{dr_c}{dt} \tag{14}$$

The mass of solute within the porous region is given by:

$$P=\int_{V_c}^{V}C_p\varepsilon_p dV \tag{15}$$

where V is the volume of the particle (m^3) and V_c is the volume of the core (m^3). Time derivation of equation (15) is simplified if time variations of the volume of the core are neglected. That is a reasonable approach since the model equations are integrated in very small time intervals, so that one obtains:

$$\frac{dP}{dt}=\varepsilon_p\int_{V_c}^{V}\frac{dC_p}{dt}dV \tag{16}$$

Equation (16) is solved numerically in discrete radius intervals, from the core surface to the particle surface:

$$\frac{dP}{dt}=\varepsilon_p\sum_{i=1}^{n}\frac{1}{2}\left(\frac{dC_p}{dt}\bigg|_{i+1}+\frac{dC_p}{dt}\bigg|_{i}\right)\left(\frac{4}{3}\pi r_{i+1}^3-\frac{4}{3}\pi r_i^3\right) \tag{17}$$

where $i = 1$ indicates the core radius and $i = n + 1$ indicates the particle radius.

Substitution of Eqns. (14) and (17) in Eqn. (12) provides the mass balance for the calculus of the time variation of the core radius in each discrete axial position in the bed (Eqn. (18)).

The system formed by Eqns. (1), (4) and (18) was written in dimensionless form and solved numerically by the method of orthogonal collocation in finite elements. The solid phase equations were written in discrete form in the radial direction by means of finite difference approximation.

$$\varepsilon_p\sum\frac{1}{2}\left(\frac{dC_p}{dt}\bigg|_{i+1}+\frac{dC_p}{dt}\bigg|_{i}\right)\left(\frac{4}{3}\pi r_{i+1}^3-\frac{4}{3}\pi r_i^3\right)$$
$$+4\pi q_0 r_c^2\frac{dr_c}{dt}=k_f 4\pi R^2\left(C-C_p\big|_{r=R}\right) \tag{18}$$

3. Experimental data

The model was validated with experimental data (Spricigo *et al.*, 1999) for the extraction of essential oil and lipids from nutmeg with liquid carbon dioxide at 90 bar and 23 °C. The fixed bed of nutmeg particles was 0.10 m high and the extractor diameter was of 0.021 m. Although essential oil and lipids were co-extracted, only essential oil extraction curves were used as validation data for mathematical modeling. The essential oil was considered as a pseudo-single compound and its extraction was assumed to be independent of the extraction of lipids. Table 1 presents the extraction parameters associated with the experimental data. At the extraction temperature and pressure, the specific gravity of the CO_2 is 819 $kg.m^{-3}$ (Sovová *et al.*,1994), and the viscosity is 75.4 x 10^{-6} Pa.s (calculated with the correlation of Altunin and Sakhabetdinov, as referenced by Sovová and Procházka (1993)). Particle porosity was measured by mercury porosimetry (ε_p = 0.15), and specific gravity of the porous nutmeg particles was measured by a gravimetric technique (ρ_s = 1,050 $kg.m^{-3}$) (Spricigo, 1998). The value of C_{sat} = 0.0675 $g_{\text{essential oil}}/g_{CO_2}$ was estimated with base on solubility data of essential oils in liquid carbon dioxide published by Ferreira (1991) and by Germer and Petenate (1988).

The equilibrium concentration was obtained experimentally as the slope of the initial linear region of the extraction curves. It was observed that the equilibrium concentration was dependent on the solid phase external surface and on the volume of solvent in the bed. Fig. 1 relates equilibrium concentration and the ratio between the solid-fluid interfacial area and the total volume of CO_2 in the bed. A logarithmic function was used to fit the experimental data:

$$C_{eq}=-5.524x10^{-2}+2.41x10^{-2}\ln\left(0.01.A_i/V_{CO_2}\right) \tag{19}$$

where A_i is the solid-fluid interfacial area (m^2) and V_{CO_2} is the total volume of CO_2 in the bed (m^3). The initial equilibrium concentration of solute in the fluid phase for each experimental situation within the validity range of Fig. 1 was calculated with Eqn. (19).

As reported by Spricigo *et al.* (1999), the maximum essential oil yield is dependent on particle size, and the extractable oil content of the solid phase (*e*) is obtained from the experimental extraction curves for each particle diameter studied.

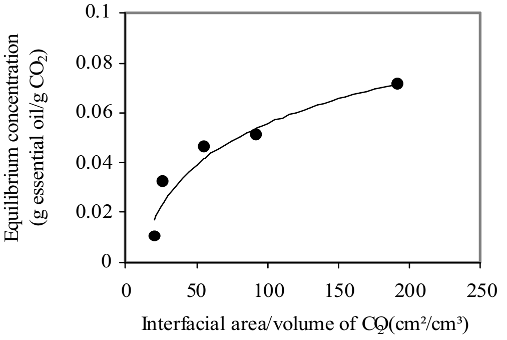

Figure 1. Equilibrium concentration related to interfacial area per total volume of CO_2 in the bed.

4. Evaluation of model parameters

The parameters k_f and D_L were estimated through the correlation of Wakao (Madras *et al.*, 1994) and of Tan and Liou (1989) respectively. The diffusion coefficient of the essential oil in the CO_2 at 90 bar and 23 °C ($D_{AB} = 8.21 \times 10^{-9}\ m^2.s^{-1}$) was calculated by the Wilke-Chang equation (Riazi and Whitson, 1993), and the molar volume of the essential oil as a pseudo-single compound ($V_B = 192.6 \times 10^{-3}\ m^3.kgmol^{-1}$) was calculated by the method of Le Bas (Reid *et al.*,1977). The effective diffusion coefficient (D_e) was used as fitting parameter.

5. Results and discussion

Figure 2 presents the comparisons between experimental extraction curves and mathematical modeling for different particle sizes and solvent flow rates. Table 2 presents the values of the model parameters corresponding to the calculated curves. It can be observed from Figure 2 that the mathematical model was able to describe the whole extraction curves for all the particle sizes tested. The change in the boundary condition when the oil core was exhausted allowed the model to keep stable until the extractable oil was exhausted. The model could be adjusted to the experimental data with values of D_e from 1.5×10^{-12} to $2.5 \times 10^{-11}\ m^2.s^{-1}$. Reverchon *et al.* (1993) obtained values of D_e from 1.5 to $2.8 \times 10^{-13}\ m^2.s^{-1}$ to the extraction of essential oils from leafs with supercritical carbon dioxide, and Roy *et al.* (1996) obtained D_e values of $2.5 \times 10^{-10}\ m^2.s^{-1}$ to the supercritical fluid extraction of ginger oil.

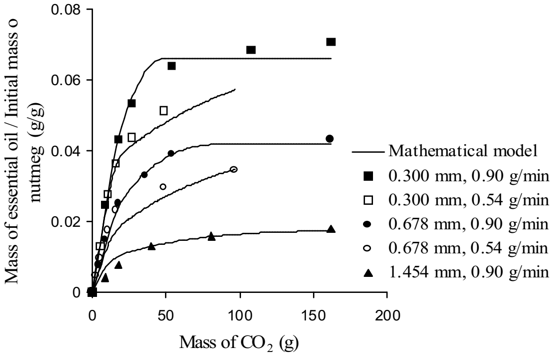

Figure 2. Comparison between experimental data and mathematical modeling for different particle sizes and solvent flow rates.

Table 1 – Parameters associated with experimental data (Spricigo, 1998).

Mean particle diameter (d_p) (mm)	Solvent mass flow rate ($g.min^{-1}$)	Interstitial solvent velocity (v) ($cm.s^{-1}$)	Initial mass of solids (M) (g)	Extractable oil content in the solid phase (e) (g oil/g solids)	Bed porosity (ε)	A_i/V_{CO_2} (cm²/cm³)
0.300	0.90	1.04×10^{-2}	17.8	0.069	0.51	56.28
0.300	0.54	6.11×10^{-3}	17.3	0.069	0.52	56.28
0.678	0.90	1.10×10^{-2}	18.8	0.043	0.48	26.97
0.678	0.54	7.22×10^{-3}	20.4	0.043	0.44	26.97
1.454	0.90	1.43×10^{-2}	24.2	0.018	0.37	21.36

Table 2 – Parameters of the mathematical model for different particle sizes and solvent flow rates.

d_p (mm)	CO_2 flow rate ($g.min^{-1}$)	D_L ($m^2.s^{-1}$)	k_f ($m.s^{-1}$)	D_e ($m^2.s^{-1}$)
0.300	0.90	2.34×10^{-7}	1.64×10^{-7}	1.5×10^{-11}
0.300	0.54	1.57×10^{-7}	1.46×10^{-8}	1.5×10^{-12}
0.678	0.90	4.45×10^{-7}	1.53×10^{-7}	2.5×10^{-11}
0.678	0.54	3.26×10^{-7}	2.86×10^{-8}	5.0×10^{-12}
1.454	0.90	9.52×10^{-7}	1.08×10^{-7}	2.5×10^{-11}

The experimental data presented in Fig. 2 shows that, for the same particle size, a decrease in solvent flow rate causes a reduction in solvent loading after the constant rate extraction period. In this case, the model only fitted

the experimental data with a reduction of the effective diffusion coefficient obtained for the same particle size and a larger solvent flow rate. This fact may indicate that the mass transfer within the porous particle is overestimated by the mathematical model, and this is probably due to the assumption of solvent saturation at the core interface.

It was observed experimentally that an increase in particle size was followed by a decrease in essential oil yield. As discussed by Spricigo *et al.* (1999), the extraction yield is related to the breakage of the cell walls and to the coextraction of lipids. The conception of the shrinking core model with the solvent saturated at the core interface imposes that the extraction only stops when the oil is exhausted, so that it was necessary to introduce in the model different contents of extractable oil (*e*) for each particle size studied. A proposition to solving of this problem could be the use of a variable effective diffusion coefficient along the particle radius, so as to increase internal mass transfer resistance as the oil is consumed.

6. Conclusions

The shrinking core model has shown to be a satisfactory approach to the mathematical representation of the extraction of essential nutmeg oil with liquid carbon dioxide. The seed is rich in essential oil, so that the conception of the oil core is reasonable. The proposed change in the boundary condition at the core interface when the oil is exhausted gave stability to the model for all the particle sizes tested. The model presented problems to describe the influence of the solvent flow rate in the extraction curves. Further studies are necessary to reevaluate the saturation condition at the core interface, in order to balance external and internal mass transfer phenomena.

Acknowledgements

This work was financially supported by CAPES (Brasília, DF, Brazil).

References

Ferreira S.R.S., “Extração com dióxido de carbono líquido subcrítico de óleo essencial de pimenta-do-reino”, M. Sc. Thesis, Universidade Estadual de Campinas, Brasil, 105 (1991).

Germer S.P.M., Petenate M.A.A.M., “Extração de óleo essencial de cravo-da-índia com dióxido de carbono líquido”, Proceedings of the 8th Congresso Brasileiro de Engenharia Química, São Paulo, Brazil, v. 2, 541-544, 1988.

King M.B. and Catchpole O.J., “Physicochemical data required for the design of near-critical fluid extraction process”, in: King M. B. and Bott T. R. (Eds.), Extraction of Natural Products Using Near-Critical Solvents, Blackie, Glasgow (1993).

Madras G., Thibaud C., Erkey C., Akgerman A., “Modeling of supercritical extraction of organics from solid matrices”, AIChE Journal, 40, 777-785 (1994).

Reid R.C., Prausnitz J.M. Sherwood T.K., The properties of gases and liquids, McGraw-Hill, New York (1977).

Reverchon E., “Supercritical fluid extraction and fractionation of essential oils and related products”, J. Supercrit. Fluids 10, 1-37 (1997).

Reverchon E., Donsi G., Osséo L.S., “Modeling of supercritical fluid extraction from herbaceous matrices”, Ind. Eng. Chem. Res., 32, 2721-2726 (1993).

Riazi M.R. and Whitson C.H., “Estimating diffusion coefficients of dense fluids”, Ind. Eng. Chem. Res., 32, 3081-3088 (1993).

Roy B.C., Goto M., Hirose T., “Extraction of ginger oil with supercritical carbon dioxide: experiments and modeling”, Ind. Eng. Chem. Res., 35, 607-612 (1996).

Sovová, H., Komers, R., Kucera, J., Jez, J., “Supercritical carbon dioxide extraction of caraway essential oil”, Chem. Eng. Sci., 49, 2499-2505 (1994).

Sovová, H. and Procházka, J., “Calculation of compressed carbon dioxide viscosities”, Ind. Eng. Chem. Res., 32, 3162-3169 (1993).

Spricigo C.B., “Extração de óleo essencial de noz moscada com dióxido de carbono a altas pressões”, M.Sc. Thesis, Universidade Federal de Santa Catarina, Florianópolis, Brazil, 17 (1998).

Spricigo C.B., Pinto L.T., Bolzan A., Novais A.F., “Extraction of essential oil and lipids from nutmeg by liquid carbon dioxide”, J. Supercrit. Fluids, 15, 253-259 (1999).

Tan C.S. and Liou D.C., “Axial dispersion of supercritical carbon dioxide in packed beds”, Ind. Eng. Chem. Res., 28, 1246-1250 (1989).

Received September 2, 1999.
Accepted for publication March 14, 2001.
Recommended by A. Bandoni.