CHEMICAL ENGINEERING TRANSACTIONS

VOL. 43, 2015

A publication of AIDIC

The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Chief Editors: Sauro Pierucci, Jiří J. Klemeš
Copyright © 2015, AIDIC Servizi S.r.l.,
ISBN 978-88-95608-34-1; **ISSN** 2283-9216

DOI: 10.3303/CET1543176

Supercritical Fluid Extraction of Vegetable Oils: Different Approaches to Modeling the Mass Transfer Kinetics

Kurabachew S. Duba, Luca Fiori*

Department of Civil, Environmental and Mechanical Engineering, University of Trento, via Mesiano 77, 38123 Trento (TN), Italy
luca.fiori@unitn.it

Supercritical fluid extraction (SFE) of vegetable oils is an alternative method to organic solvent (namely hexane) and mechanical extraction. To exploit the SFE technology at industrial scale, the process has to be optimized. An effective way to perform optimization is to resort to models that are capable to describe and simulate the SFE process. Plenty of models are available in the literature concerning the SFE of vegetable oils. Modeling the process in a semi-continuous extraction column (the bed of matrix to be extracted is stationary, the supercritical fluid moves continuously through it) requires an equipment model, the column model, and a particle model accounting for mass transfer mechanisms. Column models are quite established. Thus, to achieve a satisfactory description of the process, having a very effective particle model seems the key-point. In this work the SFE kinetics of seed oil (namely: grape seed oil) was modeled using different particle models: the broken and intact cells (BIC) and the shrinking core (SC) models, and the results were compared with literature values obtained utilizing the combined BIC-SC model. The three models not only allowed to fit satisfactorily the experimental data, but also resemble the real physical structure of the vegetable matrix and the actual elementary steps (mass transfer phenomena) which are expected to occur at the micro-scale level. As a whole, the present analysis provides an insight of interest for the audience concerned with modeling the SFE process.

1. Introduction

Supercritical CO_2 (SCO_2) extraction is believed to be an alternative to conventional extraction techniques because CO_2 is non-toxic, non-reactive, non-flammable, non-corrosive, highly selective, can be operated at moderate temperature, is ease to separate from the product, has a liquid like solvent power and gas like transport properties (Reverchon and Marrone, 1997). The traditional oil extraction with organic solvents (i.e. *n*-hexane) requires a subsequent thermal treatment for the evaporation of the solvent that can result in a loss or degradation of active components (Dos et al., 2013). Conversely, the separation of SCO_2 from the extracted oil occurs by simple depressurization. The oil yield obtained with SCO_2 extraction is comparable to that obtained with *n*-hexane extraction, and the oil quality is comparable to that achievable with mechanical extraction (Fiori et al., 2014). SCO_2 is a promising industrial solvent for the future. Owning to the clear advantages, in the past few decades there has been an increase in research interest in the field of SCO_2 extraction from a wide range of solid substrates, and vegetable seeds in particular.
The extraction process involves a solid-SCO_2 operation where mechanically pretreated (milled) solid materials are kept in vertical cylindrical column(s) with SCO_2 flowing down the bed. The operation consists of static and dynamic extraction periods. During static period there is no product collection; usually this phase lasts the time needed for reaching the extraction conditions. During the dynamic phase, occurring at constant temperature and pressure, the extraction products are collected; this phase ends with the end of the extraction process.

2. Extraction kinetics models

In the literature there are several kinetics models developed for the SCO_2 extraction (Oliveira et al., 2011). These models can be broadly classified into two general categories. The first category accounts for the

Please cite this article as: Duba K.S., Fiori L., 2015, Supercritical fluid extraction of vegetable oils: different approach to modeling the mass transfer kinetics, Chemical Engineering Transactions, 43, 1051-1056 DOI: 10.3303/CET1543176

empirical models and for the models describing the mass transfer resorting to analogies with other physical systems and transfer phenomena. Among them, it is worth citing the Crank (1975) hot ball diffusion model (HBD), the Naik et al. (1989) empirical model, the Tan and Liou (1989) desorption model, and the Martìnez et al. (2003) logistic model. In the second category, models where the solute mass flux is defined by the concentration gradient as driving force can be clustered. Under this category, the Sovovà (1994) broken and intact cell (BIC) model, the Goto et al. (1996) shrinking core (SC) model, and the Fiori et al. (2009) bridge model (combined BIC-SC model) can be classified.

Substantial efforts have been made in the literature to compare the relative performances of the various models. For example, Bernardo-gil et al. (1999) applied empirical, HBD model, and BIC models to the SCO_2 extraction of olive husk oil. Campos et al. (2005) applied desorption, logistic, single plate, HBD, and BIC models to the SCO_2 extraction of marigold (*Calendula officinalis*) oleoresin. Machmudah et al. (2006) applied BIC and SC models to the SCO_2 extraction of nutmeg oil. Domingues et al. (2012) applied desorption, logistic, single plate and HBD models to the SCO_2 extraction of *Eucalyptus globulus* bark.

There is no holistic agreement in the research community regarding the model which performs the best under all the experimental conditions. The fact that the models are applied to different solid substrates with different initial extractable substances under various operating conditions hinders the comparisons across the literatures. During the derivation of kinetic models, the type of simplifying assumptions made and the governing principles on which the mechanism of extraction is based on make one type of model to best fit to a specific extraction situation than the others. However, it must be stressed that the best fitting alone should not be considered the only objective of the extraction kinetics models, which should not be only merely capable to provide a simple input output mapping. The models should describe the underlining physical phenomena occurring during extraction and, in addition, they should be reasonably simple.

In this work we only focus on the Sovovà (1994) BIC model, the Goto et al. (1996) SC model and the Fiori et al. (2009) bridge (combined BIC-SC) model. These models have been selected considering that they attempt to describe the extraction kinetics mechanism accounting for the morphological structure of the substrates, the vegetable seeds.

The models have been compared in terms of effectiveness in predicting experimental data and in terms of the calculated (through optimization) parameters: internal and external mass transfer coefficients, percentage of easily extractable oil. To this regards, the common selected parameter was the effective diffusivity (D_{eff}) which governs the extraction from the inside of the seed particles. The experimental data for this study were taken from a previous work (Fiori, 2007).

2.1 The Broken and Intact Cell (BIC) model

The Sovovà (1994) BIC model assumes that as a result of mechanical milling pretreatment some cells in the solid matrix are broken and the remaining cells in the particle core are intact. The oil in the broken cells (referred as “free oil”) is exposed to the particle surface, i.e. to the SCO_2, and can be easily extracted. Under this condition the rate of extraction depends in particular on the oil solubility in the supercritical fluid, while the oil in the intact cells (referred as “tied oil”) is much more difficult to extract as a result of high mass transfer resistances. Under steady state plug flow conditions with homogenous particle size distribution, the analytical solution for the extraction yield is given by Šťastová et al. (1996) as:

$$\frac{E}{Nx_0} = \begin{cases} \psi\left[1-e^{-Z}\right] & for \quad \psi \le \frac{G}{Z} \\ \psi - \frac{G}{Z}e^{[Z(h_k-1)]} & for \quad \frac{G}{Z} \le \psi \le \psi_k \\ 1-\frac{1}{Y}\ln\left\{1+\left[e^{Y}-1\right]e^{\left[Y\left(\frac{G}{Z}-\psi\right)\right]}(1-G)\right\} & for \quad \psi \ge \psi_k \end{cases} \tag{1}$$

Where $\psi = \frac{tQy_s}{Nx_o}$, $Y = \frac{Nk_s a_p x_o}{Q(1-\varepsilon)y_s}$, $Z = \frac{Nk_f a_p \rho_f}{Q(1-\varepsilon)\rho_s}$, $\psi_k = \frac{G}{Z} + \frac{1}{Y} ln\{1 - G[1 - e^Y]\}$,

$$h_k = \frac{1}{Y}\ln\left[1 + \frac{\left\{e^{\left[Y\left(\psi-\frac{G}{Z}\right)\right]}-1\right\}}{G}\right]$$

Where E is amount of solute extracted, N is the mass of the solid, x_o is the initial solute concentration in the solid, t is extraction time, Q is solvent mass flow rate, ε is bed porosity, a_p is interfacial area, ρ_f is solvent

density, ρ_s is solid density, k_f is external mass transfer coefficient, k_s is internal mass transfer coefficient, y_s is solute solubility and G is grinding efficiency.

2.2 The Shrinking Core (SC) model

The SC model accounts for an irreversible desorption of oil from the solid followed by diffusion in the porous solid through the pores as proposed by Goto et al. (1996). It is assumed that there is a moving boundary between the extracted and non-extracted parts. The core of inner region shrinks inward with the progress of the extraction leaving behind an irreversibly exhausted solid matrix. Solute in the core diffuses to the surface of the particle through a network of pore without refilling the space already exhausted. The internal mass transfer from inner core to the pore is much greater than the convective transport through the pores.
The general mass balance equations in dimensionless form are given by Eqs(2) and (3) which can be solved numerically under proper initial and boundary conditions (Goto et al. 1996):

$$\frac{\partial \chi}{\partial \theta}+\alpha\frac{\partial \chi}{\partial z}=\frac{\alpha}{p_e}\frac{\partial^2 \chi}{\partial z^2}-\frac{(1-\varepsilon)}{\varepsilon}\frac{3B_i(\chi-1)}{1-B_i(1-1/\xi_c)} \tag{2}$$

$$\frac{\partial \xi_c}{\partial \theta}=\frac{bB_i(\chi-1)}{[1-B_i(1-1/\xi_c)]\xi_c^2} \tag{3}$$

The dimensionless groups are defined as $\chi=\frac{y}{y_s}$, $\alpha=\frac{uR^2}{LD_{eff}}$, $B_i=\frac{k_f R}{D_{eff}}$, $\theta=\frac{tD_{eff}}{R^2}$, $P_e=\frac{uL}{D_{ax}}$, $b=\frac{y_s}{x_o}$, $\xi_c=\frac{r_c}{R}$
Where y is the solute concentration in the bulk fluid phase, u is solvent flow rate, R is radius of the particle, L is length of extractor, D_{eff} is effective diffusivity, D_{ax} is axial dispersion, r_c is the un-extracted core radius, z is axial coordinate and the others variables are as defined in Section 2.1. In this work, the so called quasi-steady state solution was applied (Goto et al. 1996).

$$E=\frac{\alpha b\varepsilon}{1-\varepsilon}\int_0^{\theta}\chi d\theta \tag{4}$$

2.3 The combined BIC-SC model

The BIC-SC model was proposed by Fiori et al. (2009) and is a model somehow between the broken and intact cell and the shrinking core models. In this model it was assumed that the milled seed particles contain M concentric shells of oil bearing cells of diameter d_c. The cells on the surface of the particles are broken as a result of the mechanical pretreatment like in the BIC model. The oil in the broken cells is exposed to the surface and can be easily extracted while the oil in the inner concentric shells is irreversibly depleted starting from the external layer towards the internal core resembling the SC model. The general mass balance over the extractor is given by:

$$\frac{\partial y}{\partial t}+u\frac{\partial y}{\partial z}-D_{ax}\frac{\partial^2 y}{\partial z^2}=\frac{1}{\varepsilon}Ka_p(y_s-y) \tag{5}$$

Where K is overall mass transfer coefficient.
In order to model the internal mass transfer resistance, three cases were proposed, namely, discrete, semi continuous and continuous. In the case of discrete model, it was assumed that the mass transfer resistance of the jth shell is equal to the sum of the external mass transfer resistance plus the resistance of each shell up to the jth concentric shell, i.e.

$$\frac{1}{k_j}=\frac{1}{k_f}+\frac{1}{k_c}\sum_{n=1}^{j-1}\left[\frac{M}{M-n}\right]^2 \quad \text{for} \quad j=1...M \tag{6}$$

Where k_j is overall mass transfer coefficient up to j^{th} shell, k_c is the single layer inner shell mass transfer coefficient (equal for each concentric layer), and M is the number of entire spherical shells. The exhaustion degree of the particle ϕ is given by:

$$\phi_j = 1 - \left[\frac{M-j}{M}\right]^3 \tag{7}$$

$$K = K_j \text{ for } \phi_{j-1} \le \phi \le \phi_j \tag{9}$$

2.4 Model adjustable parameters

The adjustable parameters of each models are as follows:
For BIC model, the grinding efficiency (G), the external ($k_f a_p$) and internal mass transfer coefficient ($k_s a_p$).
For SC model, the effective diffusivity (D_{eff}) and the external mass transfer coefficient (k_f).
For BIC-SC model the inner shell mass transfer coefficient (k_c).
Thus, BIC, SC and BIC-SC models have, respectively, three, two and one adjustable parameters.
All the three models were compared by taking the effective diffusivity as common parameter. For BIC and BIC-SC models the effective diffusivity was calculated, respectively, as follows:

$$D_{eff} = \frac{3 d_p k_s}{2} \tag{9}$$

$$D_{eff} = k_c d_c \tag{10}$$

Furthermore, the external mass transfer coefficient $k_f a_p$ between the BIC and SC models were compared. For obtaining $k_f a_p$ for the SC model, the SC model output k_f was multiplied by a_p which was calculated according to:

$$a_p = (1-\varepsilon)\frac{6}{d_p} \tag{11}$$

Finally, the fraction of free oil was compared for BIC and BIC-SC models. In BIC model the grinding efficiency G is one adjustable parameter through which the fraction of free oil can be calculated: Gxo. For BIC-SC model the fraction of free oil was calculated according to the Eqn. (12) which was originally proposed by Reverchon and Marrone (2001) and later modified by Fiori and Costa (2010):

$$\varphi_f = 3\omega \frac{d_c}{d_p} \tag{12}$$

Where, φ_f is the fraction of the particle volume filled by the free oil, d_p is diameter of the particle and ω is a free oil parameter (0< ω <1) which was optimized to be 0.472 for grape seed according to what was called the double shell hypothesis (Fiori and Costa, 2010). In Table 1, the parameter G and $f = \varphi_f / xo$ were compared. The deviation between the model's predictions and experimental data was quantified using mean square error (MSE).

3. Materials and Methods

The oil extraction kinetics data for grape seeds were previously obtained (Fiori, 2007). In particular, data obtained with different seed particle diameters were utilized here. The experimental data were fit to the models by minimizing mean squares error using MATLAB^R 7.10 with nonlinear optimization lsqcurvefit function for BIC model, and ode45 followed by fminsearch optimization algorithm for SC model. Previously, the BIC-SC model was simulated in FORTRAN environment (Fiori et al., 2009).

4. Results and Discussion

Grape seeds contains 8-16 % of oil (Fiori et al., 2014). Actually, the oil content varies according to cultivar and other environmental factors. In this paper 12 % was chosen to represent the initial oil content in the seeds, i.e. the maximum value obtained from the experiment.
Figure 1 shows the kinetics of extraction modeled by BIC and SC models.
The models adjustable parameters and the MSE between experimental data and model output are presented in Table 1 for the different seed particle size. The effective diffusivity (D_{eff}), the parameter which is made deliberately common among the models, is in close agreement for all the three models.

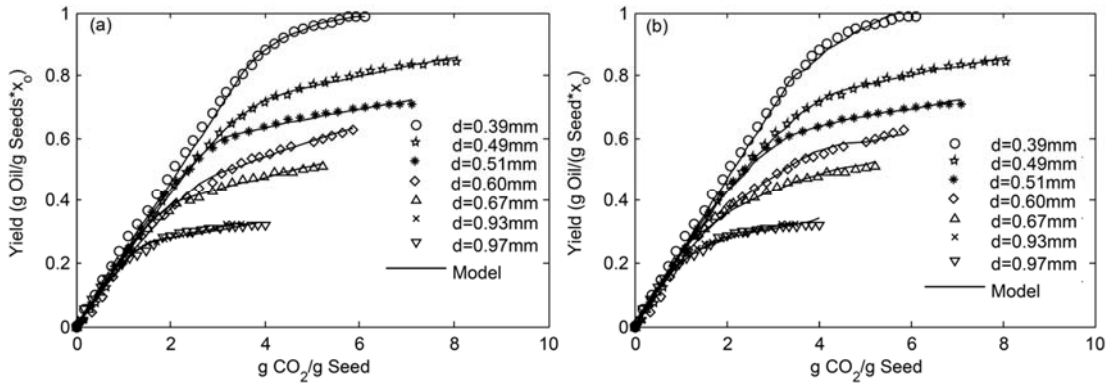

Figure 1: Extraction kinetics: (a) BIC model; (b) SC model

The average values of D_{eff} of 4.13 10^{-12}, 2.69 10^{-12} and 1.09 10^{-12} m^2/s were obtained respectively for BIC, SC and BIC-SC models. Theoretically, D_{eff} should not depend on the milled particle size, but the output reported in Table 1 seems to contradict this. The SC model seems to predict higher D_{eff} values when the particle size is large, while the BIC-SC model shows an opposite trend; the BIC model does not show any particular trend though it predicted relatively higher values of D_{eff} at small particles sizes like the BIC-SC model. The maximum deviations from average values are observed at small particle size for BIC and BIC-SC models and at the two extremes for SC model. To find an explanation to the model output obtained at the extreme values of the particle diameter, it is worth considering that, when the ground seed particle size is very large, substantial amount of the outer surface of the particle is covered by the hard woody structure of the outer surface of the seed: this can influence the extraction kinetics. Conversely, when the particles are very small, the model output are influenced to a large extent by the value assumed for the oil content (12 % in the present case). Moreover, at low particle size, the bed is more prone to compaction, so the void fraction may change during the course of the extraction (Meyer et al. 2012) which creates delay in extracted solute flow and/or even channeling. Furthermore, if there is any correlation between particle size and D_{eff}, particle size distribution should be accounted for (Fiori et al., 2008). Finally, the possibility of solute-solid interactions (not taken into account in any of these models) can influence the extraction kinetics.

As far as the free oil fraction is concerned, the values of G (BIC model) and f (BIC-SC model) are quite similar for the various particle diameters. Unsurprisingly, the smaller was the particle, the larger the free oil.

Consistent values of $k_f a_p$ were obtained for BIC and SC models.

A minimum deviation in terms of mean square error was observed for the BIC model followed by the SC model. In general, for all the models a remarkable good agreement between experimental data and model predictions was achieved.

Table 1: Adjustable parameters for grape seed oil SCO_2 extraction and deviations from experimental data

Models	P (bar) / T (°C)	550 / 40							
	d (mm)	0.39	0.49	0.51	0.60	0.67	0.93	0.97	Average
BIC	k_f a·10^2 (min^{-1})	34.9	3.38	4.88	2.52	3.68	2.98	2.53	2.20
	k_s a·10^3(min^{-1})	13.5	2.46	1.40	1.72	0.93	0.44	0.59	2.20
	G	0.45	0.66	0.56	0.42	0.36	0.25	0.26	0.42
	D_{eff} (m^2/s)· 10^{12}	14.8	4.31	2.62	4.40	2.90	2.49	4.06	4.13
	MSE·10^2	1.00	0.20	0.13	0.25	0.14	0.043	0.28	0.35
SC	k_f a·10^2 (min^{-1})	2.68	4.00	3.73	3.42	1.21	3.08	3.10	3.34
	D_{eff} (m^2/s)· 10^{12}	0.63	1.29	1.41	2.44	1.59	7.66	8.77	2.69
	MSE·10^2	1.93	0.43	0.59	0.37	0.91	0.17	0.33	0.81
BIC-SC	k_c(m/s) ·10^8	12.7	6.98	4.75	4.87	3.13	3.09	2.56	5.44
	D_{eff} (m^2/s)· 10^{12}	2.54	1.40	0.95	0.97	0.63	0.62	0.51	1.09
	MSE·10^2	0.80	1.56	1.66	0.74	0.60	0.34	0.80	0.98
	F	0.61	0.48	0.46	0.39	0.35	0.25	0.24	0.40

5. Conclusions

Supercritical CO_2 extraction of seed oil was modeled by using different models: BIC, SC, and BIC-SC. The deviation between model predictions and experimental data was quantified using mean square error MSE. Remarkable good agreement between all the three models and experimental data was achieved. The values of model adjustable parameters were consistent among the various models. The BIC model allowed for the minimum MSE followed by SC and BIC-SC model. These results reflect the number of adjustable parameters of the different models: 3, 2 and 1 for BIC, SC and BIC-SC respectively. All the three models, which account for the morphological structure of the seeds, represent significant tools for addressing process scale-up.

Acknowledgements

Supported by Progetto Ager, grant n° 2010-2222

References

Bernardo-gil M.G., King M. B., Esquı M.M., 1999, Mathematical models for supercritical extraction of olive husk oil, J. Supercrit. Fluids, 16, 43–58.

Campos L.M.A.S., Michielin E.M.Z., Danielski L., Ferreira S.R.S., 2005, Experimental data and modeling the supercritical fluid extraction of marigold (Calendula officinalis) oleoresin, J. Supercrit. Fluids, 34, 163–170.

Crank J., 1975, The Mathematics of Diffusion, Clarendon Press, Oxford, UK.

Domingues R.M.A., de Melo M.M.R., Neto C.P., Silvestre A.J.D., Silva, C.M., 2012, Measurement and modeling of supercritical fluid extraction curves of Eucalyptus globulus bark: Influence of the operating conditions upon yields and extract composition, J. Supercrit. Fluids, 72, 176–185.

Dos W.J., Silva E.A., Taranto O.P., 2013, Supercritical Fluid Extraction from Mango (Mangifera indica L.) Leaves : Experiments and Modeling, Chemical Engineering Transactions, 32, 2005–2010.

Fiori L., 2007, Grape seed oil supercritical extraction kinetic and solubility data: Critical approach and modeling, J. Supercrit. Fluids, 43, 43–54.

Fiori L., Basso D., Costa P., 2008, Seed oil supercritical extraction: Particle size distribution of the milled seeds and modeling, J. Supercrit. Fluids, 47, 174–181.

Fiori L., Basso D., Costa P., 2009, Supercritical extraction kinetics of seed oil: A new model bridging the “broken and intact cells” and the “shrinking-core” models, J. Supercrit. Fluids, 48, 131–138.

Fiori L., Costa P., 2010, Supercritical Extraction of seed oil: Analysis and comparison of up-to-date models. In M. Belinsky R (Ed.), Supercritical Fluids (pp. 707–724). New York: Nova Science Publishers,Inc.

Fiori L., Lavelli V., Duba K.S., Sri Harsha P.S.C., Mohamed H.B., Guella G., 2014, Supercritical CO_2 extraction of oil from seeds of six grape cultivars: Modeling of mass transfer kinetics and evaluation of lipid profiles and tocol contents, J. Supercrit. Fluids, 94, 71–80.

Goto M., Roy B.C., Hirose T., 1996, Shrinking-core leaching model for supercritical-fluid extraction, J. Supercrit. Fluids, 9, 128–133.

Machmudah S., Sulaswatty A., Sasaki M., Goto M., Hirose T., 2006, Supercritical CO_2 extraction of nutmeg oil: Experiments and modeling, J. Supercrit. Fluids, 39, 30–39.

Martınez J., Monteiro A.R., Rosa P.T.V., Marques M.O.M., Meireles M.A.A., 2003, Multicomponent model to describe extraction of ginger oleoresin with supercritical carbon dioxide, Ind. Eng. Chem. Res., 42, 1057–1063.

Meyer F., Stamenic M., Zizovic I., Eggers R., 2012, Fixed bed property changes during $scCO_2$ extraction of natural materials – Experiments and modeling, J. Supercrit. Fluids, 72, 140–149. Naik S.N., Lentz H., Maheshwari R.C., 1989, Extraction of perfumes and flavours from plant materials with liquid carbon dioxide under liquid-vapor equilibrium conditions, Fluid Phase Equilibria, 49, 115–126.

Oliveira E.L.G., Silvestre A.J.D., Silva C.M., 2011, Review of kinetic models for supercritical fluid extraction, Chem. Eng. Res. Des., 89, 1104-1117.

Reverchon E., Marrone C., 1997, Supercritical extraction of clove bud essential oil: isolation and mathematical modeling, Chem. Eng. Science, 52, 3421–3428.

Reverchon E., Marrone C., 2001, Modeling and simulation of the supercritical CO_2 extraction of vegetable oils, J. Supercrit. Fluids, 19, 161–175.

Sovová H., 1994, Rate of the vegetable oil extraction with supercritical CO_2-I Modeling of extraction curves, Chem. Eng. Science, 49, 409–414.

Šťastová J., Jež J., Bártlov, M., Sovová, H., 1996, Rate of the vegetable oil extraction with supercritical CO_2-III, Extraction from sea buckthorn, Chem. Eng. Science, 51, 4347–4352.

Tan C.S., Liou D.C., 1989, Modeling of desorption at supercritical conditions, AIChE Journal, 35, 1029–1031.