EXTRACTION AND MODELING OF ALGERIAN ROSEMARY ESSENTIAL OIL USING SUPERCRITICAL CARBON DIOXIDE

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ABSTRACT

Experimentally measured data concerning the supercritical CO_2 extraction of essential oil from Algerian rosemary leaves, are presented along with the effects of key parameters such as pressure and temperature on the yield of extraction.Yield values expressed as g of oil / g of dried *Rosemary* and ranging from 0.95 to 3.52%were obtained, with the optimal value at a pressure of 22 MPa and temperature of 40°C. The shrinking-core model was used for the modelingof the experimental results of the extraction, with the effective diffusivity D_e as the only adjustable parameter, and a good fitting was obtained. The GC-MS analyses showed that the major compound detected in the essential oil was camphor, at 48.89 %.

Keywords: Supercritical fluid extraction; Rosemary; Essential oil; Shrinking-core model.

INTRODUCTION

The development of new separation techniques for the chemical and food industries has received a great attention due to the environmental restrictions and the human health regulations as well as the need for minimizing the energy costs [1]. Since the last decade supercritical fluid extraction is regarded as an alternative to the classical liquid-solid extraction techniques such as maceration, percolation, lixiviation, microwave assisted extraction, etc. which are characterised by certain major drawbacks, such as the solvent toxicity, its cost and impact on the environment, contrarily to the supercritical fluid extraction, a clean process which enables to achieve high extraction yields and hence important degrees of purity of the desired compounds. However the performance of the supercritical fluid extraction depends upon the solvent power of the fluid according to the operating pressure and temperature.

In the present work, beside an experimental part which consisted of measuring the extracted amount of essential oil from Algerian rosemary plant leaves by means of the supercritical CO_2 extraction, the modeling of the process by means of the shrinking-core model was also carried ou.The choice of this model was mainly guided by its reliability as reported in the literature [3, 6 and 7].

MATERIALS AND METHODS
Materials
Dried rosemary leaves were ground in a small coffee grinder for a short but sufficient period of timeto get a uniform particle size distribution. The obtained charge was sieved using a Retsch-type vibrating system. The water content in the rosemary leaves was determined as 5.92% by means of drying for 6 h in a vacuum oven at 105 *°C*, whereas the bulk density of

the ground rosemary was 335.4 kg/m^3, determined by means of a helium pycnometer. Gaseous carbon dioxide of 99.95% purity was supplied by Carboxyque Française Company.

Experimental Procedure
The supercritical CO_2 extraction experiments were carried out in a dynamic extraction unit previously conceived and assembled at the Chemical Engineering Sciences Laboratory in Nancy (*LSGC, Nancy, France*). Such an apparatus mainly consists of a CO_2 reservoir, an extractor vessel and three separator vessels in series, accompanied by a thermostatic bath, a metering pump, a cryostat, the necessary instrumentation to control the pressures, temperatures, mass flow rates and valves for the extract collection. As a pretreatment, rosemary leaves were dried and finely ground. A mass of 20g of the resulting powder with a determined mean particle diameter of 1mm was then packed into a sample unit leading to a bed 300mm high with a void fraction of 0.54. When the sample reached the constant extraction temperature in the range of 35–60°C, $CO_2$was charged into the high-pressure pump from the storage cylinder and was further compressed up to the desired pressure of the pump between 10 and 22MPa. Samples were taken every 15*min*, by means of the valves placed at the bottom of the separators, and weighed to obtain the mass of the essential oil. The dynamic extraction was pursued for 3.5 *h*, after which it was noted that the extracted mass was very low. Finally, the glass containing the extracted essential oil was kept in a freezer, ready for chromatographic analysis. The experiments were performed at four different temperature and pressure values of 35,40, 50 and 60°C and 10, 14, 18 and 22 MPa, respectively with a gas flowrate fixed a 7g/min, a constant bed void fraction of 0.54, a particle diameter of 1mm, a solid phase density of 335.4 kg/m^3 and a fluid density calculated accordingly at each temperature and pressure by means of the DIAGSIM software [8] varied between 280.4 and 840.2 kg/m^3.The separation (CO_2/essential oil) was carried out at 10°C in the first separator and at 30°C in the two others. The temperature of the first separator was set at 10 °C in order to enable the recovery of certain secondary components such as waxes, resins, fatty acids etc. present in the solid matrix and, hence, a greater purity of the essential oil feeding the second separator. Since it is important to maintain a constant temperature, the three separators were connected to two other thermostatic baths. Also, the extracted essential oil could be recovered from the separators and CO_2 vented to the atmosphere. The CO_2 mass flow rate was maintained around an optimal mean value of 7 g/min, corresponding to the best extraction yield.

Mathematical Model
Extraction of a solute from the solid matrix occurs in three stages: diffusion of fluid to particle pores, dissolution of extractable matter in the fluid, and transfer to the bulk fluid. In this work, the shrinking-core model was applied. It is also known as quasi-steady-state model because of the assumption of no axial dispersion in the fixed bed [9]. Moreover, the following assumptions are also made during model solution: (1) the extraction is an irreversible desorption process, (2) the matrix is a porous material where lavender oil is uniformly distributed throughout the particle, (3) the system is isothermal, (4) the fluid physical properties, are constantduring the extraction. Based on these assumptions, the material balance in the extractor is described as [9]:

$$\frac{\partial C}{\partial t} + \upsilon \frac{\partial C}{\partial z} = -\frac{1-\varepsilon}{\varepsilon}\frac{3K_f}{R}\left[C - C_i(R)\right] \tag{1}$$

Average solid-phase oil concentration (q) variation with time is equated to the rate of mass transfer of the solute within the external film surrounding the particle:

$$\frac{\partial \overline{q}}{\partial t} = \frac{3K_f}{R}\left[C - C_i(R)\right] \tag{2}$$

The diffusion to the outer region in the particle is expressed by:

$$\frac{D_e}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_i}{\partial r}\right) = 0 \tag{3}$$

The average solid-phase oil concentration is described as a function of the particle diameter:

$$\frac{\overline{q}}{q_0} = \left(\frac{r_c}{R}\right)^3 \tag{4}$$

The boundary conditions are given as follow:

The liquid phase concentration is equal to its saturation value (C_{sat}=0.075kmol/m^3) [10]:

$$(r = r_c): \quad C_i = C_{sat} \tag{5}$$

The diffusion flux at the external particle surface is equal to the mass transfer across the external film and hence:

$$\left(D_e\frac{\partial C_i}{\partial r}\right)_{r=R} = K_f\left[C - C_i(R)\right] \tag{6}$$

- The Danckwert boundary conditions [3] in the bed exit are given as follow:

$$z = 0 \Rightarrow C = 0 \tag{7}$$

$$z = L \Rightarrow \frac{\partial C}{\partial z} = 0 \tag{8}$$

The initial conditions are given as follow:

$$t = 0 \Rightarrow r_c = R \tag{9}$$

$$t = 0 \Rightarrow C = 0 \tag{10}$$

The mass balance equations and the boundary and initial conditions can be written in terms of the following dimensionless variables:

$$x = \frac{C}{C_{sat}}, \quad x = \frac{C_i}{C_{sat}}, \quad y = \frac{r}{R}, \quad Z = \frac{z}{L}, \quad a = \frac{\upsilon R^2}{D_e L}, \quad \theta = \left(\frac{D_e}{R^2}\right)t, \quad \overline{y} = \frac{\overline{q}}{q_0}, \quad b = \frac{C_{sat}}{q_0}, \quad Bi = \frac{K_f R}{D_e}$$

Substitution of these variables into equations (1)-(3) gives:

$$\frac{\partial x}{\partial \theta} + a\frac{\partial x}{\partial Z} = -\frac{1-\varepsilon}{\varepsilon}3Bi\left[x - x_i(1)\right], \frac{\partial \overline{y}}{\partial \theta} = 3Bib\left[x - x_i(1)\right]$$

$$\frac{1}{y^2}\frac{\partial}{\partial y}\left(y^2\frac{\partial x_i}{\partial y}\right) = 0$$

$$x_i = 1 \Rightarrow y = y_c$$

$$\left(\frac{\partial x_i}{\partial y}\right)_{y=1} = Bi\left[x - x_i(1)\right]$$

$$\overline{y} = y_c^3, \quad \theta = 0 \Rightarrow y_c = 1, \quad \theta = 0 \Rightarrow x = 0, \quad Z = 0 \Rightarrow x = 0, \quad Z = 1 \Rightarrow \frac{\partial x}{\partial Z} = 0$$

$$\frac{\partial x}{\partial \theta} + a\frac{\partial x}{\partial Z} = -\frac{1-\varepsilon}{\varepsilon}\frac{3Bi(x-1)}{1 - Bi\left(1-\dfrac{1}{y_c}\right)} \tag{11}$$

$$\frac{\partial y_c}{\partial \theta} = \frac{bBi(x-1)}{y_c^2\left[1 - Bi\left(1-\dfrac{1}{y_c}\right)\right]} \tag{12}$$

The above obtained equations are solved by means of the finite difference method and the yield or the cumulated extract quantity for a time θ is calculated according to the followingrelationship:

$$yield = \frac{\varepsilon ab}{1-\varepsilon} \int_0^\theta x d\theta$$

(13)

This provides a model for the extraction process, in terms of time for different pressures and temperatures, and which contains just one adjustable parameter: the effective diffusivity (D_e) [11]. The best value of this latter was used for the correlation of the experimental data. A computer code based on *Mathcad* was developed for this purpose.

RESULTS AND DISCUSSION

The obtained experimental results are given in Table 1 where it can be noted that at the four considered different temperatures, the essential oil extraction yield, increases as the pressure increase from 10 to 22 MPa. However this increase is attenuated between 18 to 22 MPa comparatively to the range of 10 to 18 MPa.

Table1: Influence of the temperature and the pressure on the yield of the extraction

Temperature[°C]	Pressure [MPa]			
	10 MPa	14MPa	18 MPa	22 MPa
35°C	R= 1.59 %	R= 2.45 %	R= 2.87 %	R= 2.99 %
40°C	R= 1.35 %	R= 2.02 %	R= 3.04 %	R=3.52 %
50°C	R= 1.18 %	R= 1.38 %	R= 2.81 %	R= 2.94 %
60°C	R= 0.95 %	R= 1.29 %	R= 2.57 %	R= 2.69 %
	$Y_S = 0.546$	$Y_S = 1.116$	$Y_S = 1.323$	$Y_S = 1.470$

The plots of the extraction yield of the essential oil versus the extraction time are shown in Figure 1a, b for two temperature conditions, 35 and 40°C, respectively. For the lower pressures of 10 and 14MPa, the 40°C isotherms were characterized by slightly lower extraction velocities in comparison to the 35 °C isotherms, and this can be explained by the decrease in the CO_2 density as the temperature increases and, hence, a lower diffusivity particularly for the heavier compounds which are more difficult to carry away. However, for pressures equal to 18 or 22MPa, the percent extraction yields are higher than those at $35°C$. The effect of temperature on the extraction yield of oil from rosemary plants is complex since, at 10 and 14MPa, the yield of extraction increased with the temperature while, at 18 and 22MPa, the reverse effect was observed. This is surely a compromise between two opposite effects: Increasing the temperature decreases the density of the supercritical fluid and thus its solvatation capacity; on the other hand, it increases the vapor pressure of the solutes and therefore increases their solubility in the supercritical solvent. Each curve of Figures1a& b has two distinct parts, suggesting two possible mechanisms. For both temperatures, during the first 15min (first part), the essential oil is readily available at the solid surface and hence is easily extracted by the supercritical fluid at a fast and constant rate. For this step, the extraction process is controlled by the external mass transfer resistance. During the second part the extraction yield of the essential oil increases in a much slower manner, tending to a practically constant value, due to the fact that the oil is rather extracted from deeper sections

of the solid substrate. At this point, diffusional and internal mass transfer resistances dominate the extraction process.
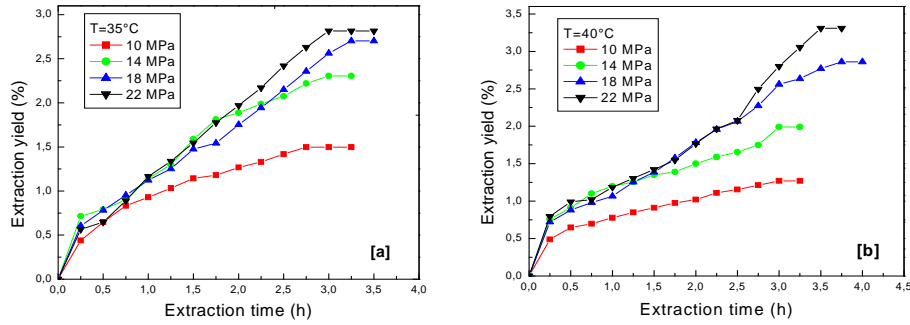

Figure1: Curves of oil extraction yield from *Rosemary*
(a) T = 35°C, P = 10, 14, 18 and 22MPa; (b) T = 40°C, P = 10, 14, 18 and 22MPa; dp = 1mm; Q= 7 g /min.

For the temperature effect and at a fixed pressure, the same temperature values are considered by the model, for its assessment. The results are shown in figure2 (a, b, c and d).
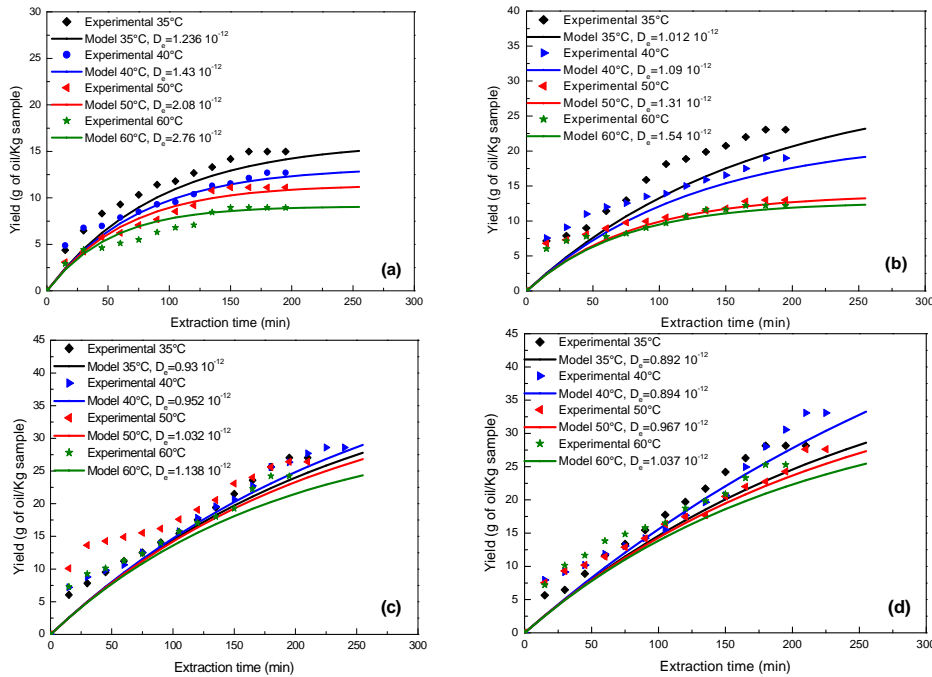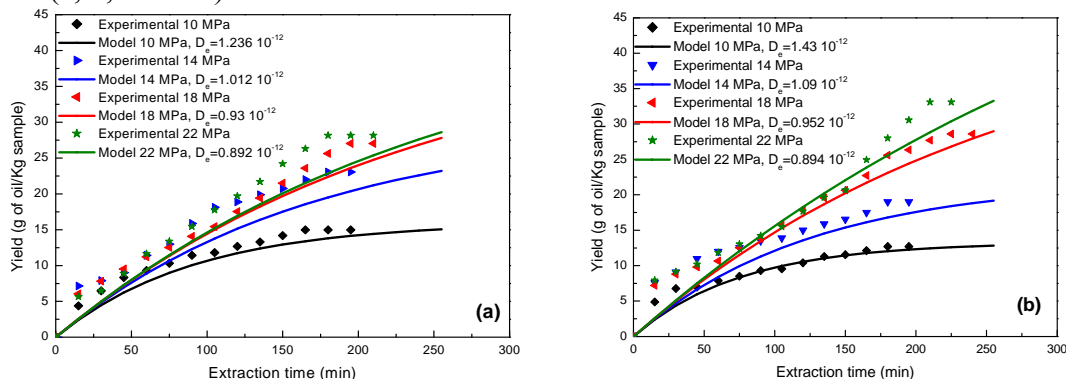

Figure2: Effect of the temperature on the yield of the extraction
(a)   P = 10 MPa ;(b) P= 14 MPa ;(c) P= 18 MPa ; (d) P= 22 MPa, Q=7 g/min, d_p=1 10^{-3}m.

The mean deviation between the calculated model results and the experimental values is about 5.68%. The results concerning the effect of the pressure on the extraction yield are shown in Figure 3 (a, b, c and d):
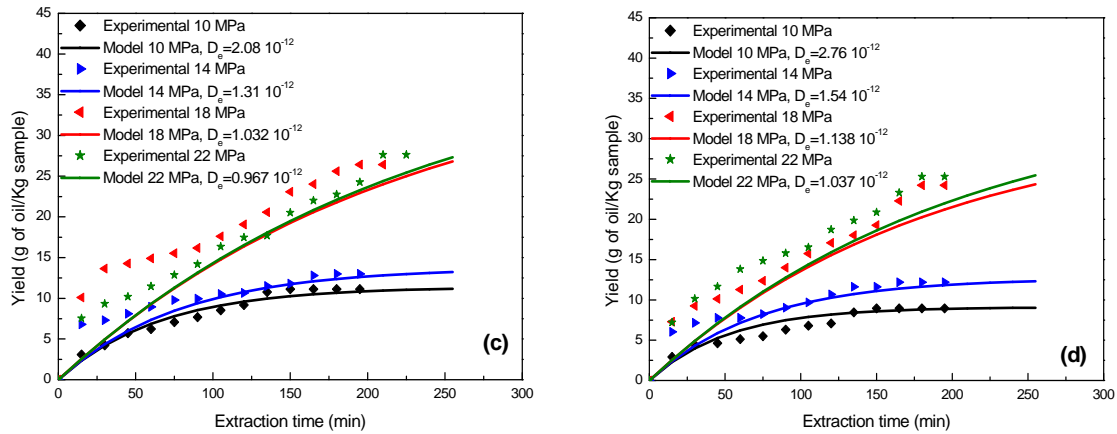

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Figure3: Effect of the pressure on the yield extraction
(a) T= 35°C ; (b) T= 40°C ; (c) T= 50°C ; (d) T= 60°C ; Q=7 g/min; d_p=1 10^{-3}m.

Similarly to the temperature effect, the shrinking core model gave coherent results qualitatively where the extraction yields are for high pressure values of 18 and 22MPa. This is also in agreement with the experimental part where the pressure increases lead to more solvencies. Quantitatively, the mean deviation between the calculated model results and the experimental values is about 4.23%, which is less than the deviation for the temperature case.

Determination of the Physical Parameters and Properties

A priori parameters like the fluid mass transfer coefficient (K_f), the diffusion coefficient of the solid phase (D_e), and physical properties of the fluid like the viscosity and the density, have to be determined. The mass transfer coefficient in an extractor under supercritical conditions can be calculated by means of the empirical correlation proposed by Tan et al. [12]. The supercritical CO_2 viscosity (μ) can be estimated using the empirical correlation of *Jossi*et al. [13] whereas its density is calculated at each temperature and pressure by means of the *Diagsim* software based on *Soave, Redlich* and *Kwong* equation of state [8]. The effective diffusivity coefficient, D_e, is found by fitting model results to experimental results, and it is different for different kinds of plant material[14]. *Reverchon* et al. [15] explained that these differences could be related to the different mass-transfer resistances because of different types of cell structure and mechanisms of solute extraction. *Roy* et al. [4] pointed out that this could also be related to the different diffusion resistances due to the different solute nature such as molecular size, hydrophilic property, etc. In this work, the best fit was obtained as (D_e =1.43 10^{-12} m^2/s) for the Algerian *Rosemary*. Table2 shows all the properties of the supercritical CO_2 as well as those of the considered Algerian *Rosemary* solid sample at the experimental operating conditions.

Composition of the Extracted Essential Oil

Analysis of the composition of the essential oil was carried out by means of a gas chromatograph (*Shimadzu GC-2010*) coupled to a mass spectrophotometer (*Shimadzu GCMS QP-2010*) equipped with an AOC-20i series auto injector, and using an AT-5ms column (30 m, 0.25 mm, 0.25 lm). The identification of the essential oil components was performed by comparison of the obtained spectra shown in Figure4with those stored in the National Institute of Standards andTechnology (*NIST*) general library (*Standard Reference Data Program, Gaithersburg, MD, USA*). To ensure the reproducibilityof the results, the analysis was repeated twice, and theobtained values were very close.

Table2: Physical proprieties at the experimental conditions

Pressure (MPa)	Temperature (°C)	$Q \times 10^4$ (kg/s)	$U \times 10^4$ (m/s)	$v \times 10^4$ (m/s)	ρ_f (Kg/m³)	$d_p \times 10^{-3}$ (m)	$\mu \times 10^4$ (kg.m/s)	$K_f \times 10^5$ (m/s)
10	35	1.166	6.021	11,15	616.8	1	4.654	7.925
10	40	1.166	6.920	12,81	536.4	1	3.938	8.854
10	50	1.166	10.330	19,13	359.4	1	2.809	12.480
10	60	1.166	13.244	24,53	280.4	1	2.474	15.650
14	35	1.166	5.088	9,42	729.9	1	6.018	6.996
14	40	1.166	5.400	10,00	687.3	1	5.475	7.307
14	50	1.166	6.250	11,57	594.1	1	4.499	8.179
14	60	1.166	7.467	13,83	497.3	1	3.725	9.463
18	35	1.166	4.678	8,66	793.8	1	7.012	6.602
18	40	1.166	4.880	9,04	760.8	1	6.499	6.798
18	50	1.166	5.370	9,94	691.7	1	5.577	7.289
18	60	1.166	5.988	11,09	620.1	1	4.805	7.925
22	35	1.166	4.419	8,18	840.2	1	7.862	6.358
22	40	1.166	4.570	8,46	812.2	1	7.358	6.503
22	50	1.166	4.922	9,11	754.5	1	6.449	6.848
22	60	1.166	5.340	9,89	695.4	1	5.671	7.269

A chromatogram reading indicated that most of the main oil primary components are present in good proportions with Camphor as the major constituent with 48.89%, followed by Camphene (7.63%), 1-8 Cineol (9.95%) and α- Pinene (6.96%).
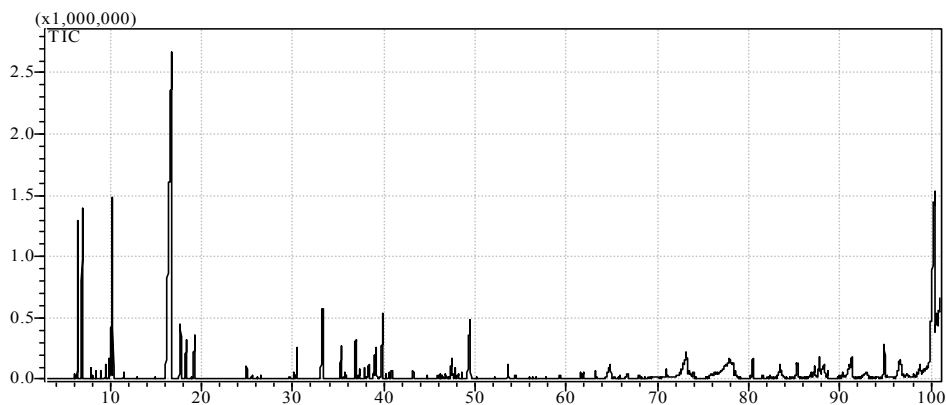

Figure 4: Chromatogram of Rosemary oil by *GCMS*.

CONCLUSION

The experimental results show that the extraction rate of essential oil from rosemary leaves increases with increasing temperature because of increasing vapor pressure of the components. The extraction rate increases with increasing pressure because of the solubility increase of essential oil components. The shrinking core model modeled reasonably well the extraction process and enabled the determination of the just one adjustable parameter which is the effective diffusivity D_e coefficient. Most of the main oil primary components are present in good proportions and the GC-MS analyses showed that the major compound detected in the essential oilof the Algerian *Rosemary* was camphor, at 48.89 %.

NOMENCLATURE

C	Concentration in the fluid	$[kmol/m^3]$	R	Yield (g of oil/kg sample)[-]
$C_i(R)$	Concentration of oil in the boundary layer	$[kmol/m^3]$	R	Radial coordinate in particle[m]
D_e	effective diffusivity	$[m^2/s]$	r_c	Radius of the core[m]
D_l	Diffusion Coefficient	$[m^2/s]$	U	Superficial velocity[m/s]
d_p	Particlediameter	$[m]$	Y_s	Solubility (g of oil/kg of SC CO_2)[-]
K_f	Coefficient of external mass transfer	$[m/s]$	E	Bed void fraction[-]
q_0	Initial concentration of oil in the solid	$[kmol/m^3]$	N	Interstitial velocity of the fluid[m/s]

REFERENCES

[1] L.A.F. Coelho, J.V. Oliveira, S.G. d'Avila, Braz. J. Chem. Eng. 13 (1996) 51.

[2] E. Reverchon, M. Poletto, Mathematical modelling of supercritical CO2 fractionation of flower concretes, Chem. Eng. Sci. 51 (1996) 3741.

[3] Goto, M.; Roy, B. C.; Hirose, T. Shrinking-Core Leaching Model for Supercritical Fluid Extraction. J. Supercrit. Fluids 1996, 9, 128.

[4] Roy B. C., Goto M., Hirose T. Extraction of Ginger Oil with Supercritical Carbon Dioxide: Experiments and Modelling. Ind. Eng. Chem. Res. 1996, 35, 607.

[5] H. Sovov´a, Rate of the vegetable oil extraction with supercritical CO2. I. Modeling of extraction curves, Chem. Eng. Sci. 49 (1994) 409.

[6] Association of Official Analytical Chemists (AOAC), in: P. Cuniff (Ed.), Official Methods of Analysis of AOAC International. 16th ed., third revision, AOAC International, Gaithersburg, Maryland, 1997.

[7] M Akgun, Nalan A. Akgun, S. Dincer. Extraction and Modeling of Lavender Flower Essential Oil Using Supercritical Carbon Dioxide.Ind. Eng. Chem. Res. 2000, 39, 473-477.

[8] J.N. Jaubert. Logiciel DIAGSIM. Laboratoire de thermodynamique des séparations, ENSIC-INPL, Nancy, 1997.

[9] Goto, M.; Roy, B. C.; Hirose, T. Shrinking-Core Leaching Model for Supercritical Fluid Extraction. J. Supercrit. Fluids 1996, 9, 128.

[10] Fernandez-lopez J. et al. Antioxidant and antibacterial activities of natural extracts: application in beef meatballs. Meat Science, Alicante/Newton Abbot, v. 69, n. 3, p. 371-380, 2005.

[11] I. Goodarznia, M.H. Eikani. Supercritical carbon dioxide extraction of essential oils: modelling and simulation, Chem. Eng. Sci. 53. 1998. 1387-1395.

[12] Tan C. S., Liang S. K., Liou D. C. Fluid-solid mass transfer in a supercritical Fluid extractor. Chem. Engng J. 38. 1988, 17-22.

[13] Reid R. C., Prausnitz J. M., Poling B. E. The Properties of Gases and Liquids, 4th ed.; McGraw-Hill: New York, 1987.

[14] Catchpole, O. J.; Grey, J. B.; Smallfield, B. M. Near-Critical Extraction of Sage, Celery and Coriander Seed. J. Supercrit. Fluids 1996, 9, 273.

[15] Reverchon, E.; Donsi, G.; Osseo, L. S. Modelling of Supercritical Fluid Extraction from Herbaceous Matrices. Ind. Eng. Chem. Res. 1993, 32, 2721.