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Extraction and Modeling of Algerian Rosemary essential oil using supercritical CO_2: Effect of pressure and temperature

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Abstract

In this work essential oil was extracted from Algerian Rosemary leaves by the supercritical CO_2 extraction. The effects of the key parameters such as pressure and temperature on the yield of extraction were examined. The obtained yield were in the range of 0.95-3.52 g of dry oil / g of rosemary, and the best value was obtained at a pressure of 22 *MPa* and temperature of 40°C. The model of shrinking-core was used to analyse the experimental results of the extraction, this model contains one adjustable parameter, effective diffusivity *De*, the experimental results were successfully fitted.

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

1. Introduction

The development of new separation techniques for the chemical and food industries has received a lot of attention due to the environmental restrictions, the need for minimizing the energy costs, and human health regulations. [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 a number of inconvenients, particularly 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 principle of the supercritical fluid extraction depends upon the solvent power of the fluid according to the operating pressure and temperature.

The great majority of research works on supercritical fluid extraction is of an experimental nature. However mathematical modeling has provided an important tool for the development and the optimisation of the extraction process, testing numerically different materials and exploring large ranges of operating conditions. As an illustration, one can cite the work of Reverchon and Poletto [2] who developed a model for the extraction from flowers based on differential mass balance. Goto et al [3] adapted the shrinking-core model to the, modeling of supercritical fluid extraction of natural materials by adjusting just the mass transfer coefficient. Roy et al [4] obtained interesting results concerning the modeling of the extraction of gingember essential oil applying still the shrinking-core model. Sovova [5] proposed a model with the solute was divided into two fractions where the first one is easily accessible to the fluid contrarily to the second one. The mass transfer coefficients in the fluid and the solid phases were used as adjustable parameters.

In the present work, it is proposed to apply the shrinking-core model for the extraction of essential oil from Algerian rosemary, using supercritical fluid extraction. The choice of this model was mainly guided by its fiability as reported in the literature [3, 6, 7].

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Nomenclature					
C	Concentration in the fluide	[kmol/m^3]	R	Yield (g of oil/kg sample)	[-]
C_i(R)	Concentration of oil in the couche limite	[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	Particle diameter	[m]	Y_S	Solubility (g of oil/kg of SC CO_2)	[-]
K_f	Coefficient of external mass transfert	[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]

2. Materials and Experimental Procedure

2.1 Materials

The used rosemary was sampled from the October 2008 local production (in Constantine, north east of Algeria). As a first step, dried rosemary leaves were ground in a small coffee grinder for a short but sufficient period of time (15 *s*) to 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.

2.2 Experimental Procedure

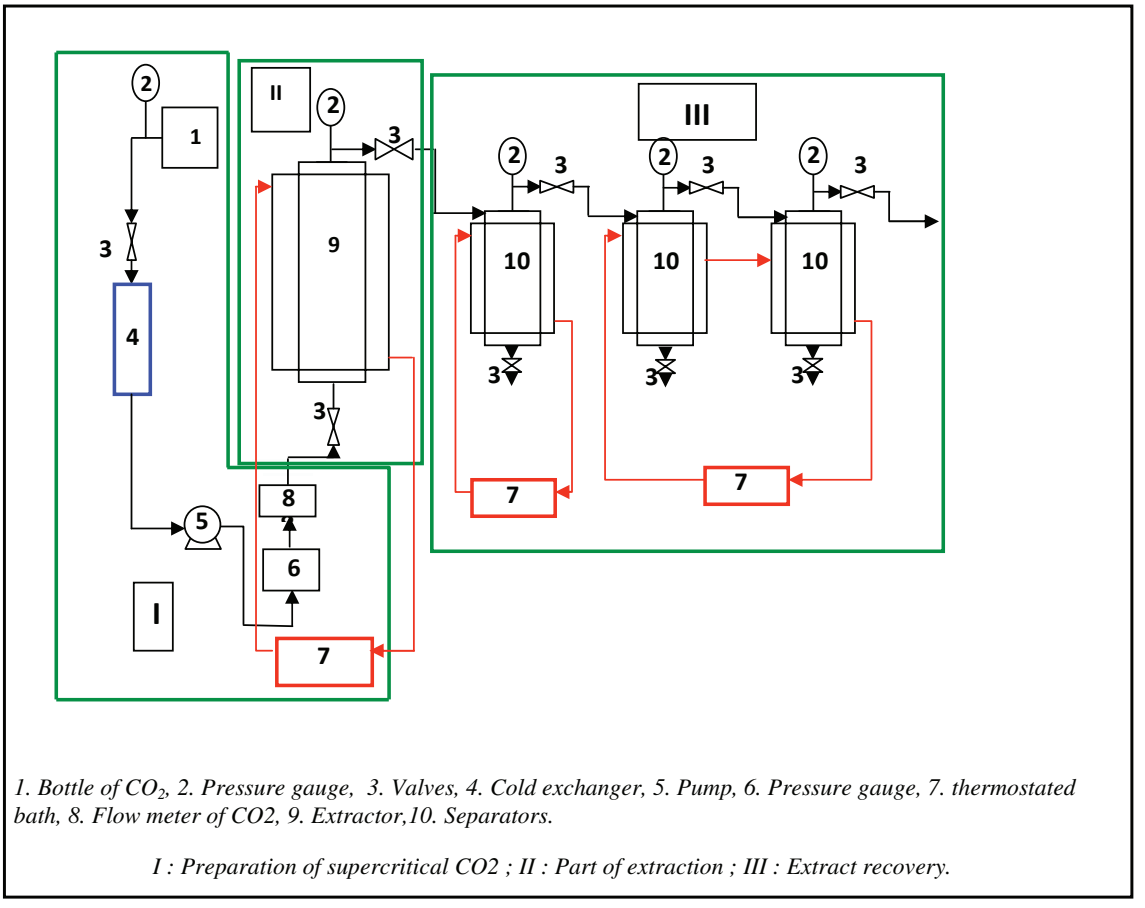
The experiments were carried out in the dynamic extraction unit shown in *Fig. 1*, which mainly consists of three parts: (I) a CO_2 reservoir, (II) an extractor vessel, and (III) three separator vessels in series, accompanied by a thermostatic bath, a metering pump, a cryostat, the necessary instrumentation to control the pressures, temperatures, mass flow rates and valves for the extract collection. It has been previously conceived and assembled at the Laboratoire des Sciences du Génie Chimique de Nancy (*LSGC*, Nancy, France). The operating temperature and pressure can reach up to 80°C and 25*MPa*, respectively, with a maximum gas mass flow rate of 3.2 *kg/h*. As a pretreatment, rosemary leaves were dried and finely ground. A mass of 20 g was weighed in a precise Scaltec instrument balance (precision of ±0.1*mg*) and the mean particle diameter of the resulting powder was determined at around 1mm. This mass was then packed into a sample unit, with glass wool placed at its top and bottom in order to prevent the entrainment of the rosemary during the extraction process, to homogenize the gas flux in the extractor and to fill any dead volume. The glass wool mass used was of the order of 2 *g*. The void fraction of the particle bed was 0.54 and its height was measured before the introduction of the sample unit in the extractor (volume of 125 *cm^3*, 23mm inside diameter, and 300*mm* height). This operation was carried out with care in order to avoid any rosemary mass loss. The sample was then allowed to reach the constant extraction temperature before charging CO_2 into the high-pressure pump from the storage cylinder. The CO_2 gas was further compressed to the desired pressure of the pump. After 1 *h*, a time corresponding to the static extraction, the extractor valve was opened and the intermediate valves between the separators were continuously adjusted in order to regulate the pressure and, hence, to keep a constant flow rate. 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 operating conditions such as pressure, temperature, density of solid and fluid, particle diameter and supercritical fluid flow rate were fixed as shown in Table. 1, In the present work, the extractions were performed at temperatures in the range of 35–60*°C* and at pressures between 10 and 22*MPa*. These ranges are the most frequently adopted for similar system types where the CO_2 is at its supercritical state. Therefore, the temperature was controlled thermostatically and the pressure was regulated by means of a membrane pump (Dosapro Milton Roy – MilRoyal *D*), which enabled to reach the extraction pressure. The maximum mass flow rate was 3.2 kg/h through the pump, which was also connected to a cryostat in order to liquefy the CO_2. The flow rate of the latter was measured by means of a Coriolis force flow meter (Micro Motion) and, hence, indicated the amount of CO_2 used during the extraction. 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.

Table 1. Operating conditions

T (°C)	P (MPa)	ρ_s (kg/m^3)	ρ_f (kg/m^3)	E	d_p (mm)	Q (g/min)
35	10	335.4	616.8	0.54	1.00	7.00
35	14	335.4	729.9	0.54	1.00	7.00
35	18	335.4	793.8	0.54	1.00	7.00
35	22	335.4	840.2	0.54	1.00	7.00
40	10	335.4	536.4	0.54	1.00	7.00
40	14	335.4	687.3	0.54	1.00	7.00
40	18	335.4	760.8	0.54	1.00	7.00
40	22	335.4	812.2	0.54	1.00	7.00
50	10	335.4	359.4	0.54	1.00	7.00
50	14	335.4	594.1	0.54	1.00	7.00
50	18	335.4	691.7	0.54	1.00	7.00
50	22	335.4	754.5	0.54	1.00	7.00
60	10	335.4	280.4	0.54	1.00	7.00
60	14	335.4	497.3	0.54	1.00	7.00
60	18	335.4	620.1	0.54	1.00	7.00
60	22	335.4	695.4	0.54	1.00	7.00

ρ_f : is the density of *SC* CO_2 expressed in *g/cm*^{3} and calculated by the software Diagsim [8] for each temperature and pressure.



1. Bottle of CO_2, 2. Pressure gauge, 3. Valves, 4. Cold exchanger, 5. Pump, 6. Pressure gauge, 7. thermostated bath, 8. Flow meter of CO2, 9. Extractor,10. Separators.

I : Preparation of supercritical CO2 ; II : Part of extraction ; III : Extract recovery.

Fig 1. Schema of dynamic extraction unit

3. Mathematical Model

Extraction of a solute from the solid matrix occurs in three stages of diffusion of fluid to particle pores, dissolution of extractable matter in the fluid, and transfer to the bulk fluid. Therefore, several models have been developed based on empirical kinetic models or differential mass balances for the fixed bed. In this work, the shrinking-core model was applied to the extraction of lavender flowers. Actually, this model is called 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 physical properties of the fluid are constant during the extraction. Based on these assumptions, the material balance in the extractor is described as [9].

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

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:

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

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

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

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

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

The boundary conditions are given as follow:

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

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

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

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

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

$$z = 0 \quad \Rightarrow \quad C = 0 \quad (7)$$

$$z = L \quad \Rightarrow \quad \frac{\partial C}{\partial z} = 0 \quad (8)$$

The initial conditions are given as follow:

$$t = 0 \quad \Rightarrow \quad r_c = R \quad (9)$$

$$t = 0 \quad \Rightarrow \quad C = 0 \quad (10)$$

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

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

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

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

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

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

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

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

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

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

The above obtained equations are solved by means of the finite difference method.

The yield or the cumulated extract quantity for a time θ is calculated according to the following relationship:

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

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* (*MATHCAD 2001*) was developed for this purpose.

4. Results and Discussion

4.1 Experimental Results

The obtained experimental results are given in Table 2 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 et 22 MPa comparatively to the range of 10 to 18 MPa.

Table 2. Influence of the temperature and the pressure on the yield of the extraction

Temperature[°C]	Pressure [MPa]			
	100 MPa	140 MPa	180 MPa	220 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 %

The plots of the extraction yield of the essential oil versus the extraction time are shown in Fig.2a, 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 22*MPa*, 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 14*MPa*, the yield of extraction increased with the temperature while, at 18 and 22*MPa*, 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 solvation capacity; on the other hand, it increases the vapor pressure of the solutes and therefore increases their solubility in the supercritical solvent. It is clear from Fig. 2a, b that there are two distinct parts in each extraction curve, suggesting that two possible mechanisms are acting on the *SFE* process from the rosemary plant. For the first 15min, which constitutes the first part of the curve, 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, and this at both considered temperatures. For this step, the extraction process is controlled by the external mass transfer resistance. Subsequently, the extraction yield of the essential oil increases in a much slower manner, tending to a practically constant value at the end of the extraction process. This second part of the curve can be explained by the fact that the superficial oil gets exhausted and then oil is extracted from deeper sections of the solid substrate by the solvent. At this point, diffusional and internal mass transfer resistances dominate the extraction process.

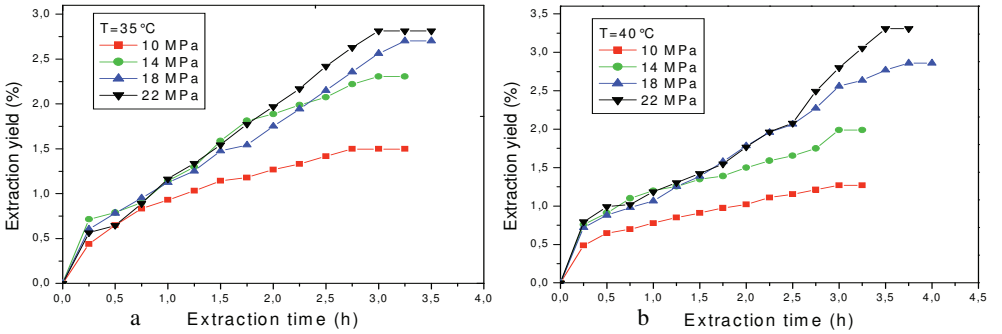
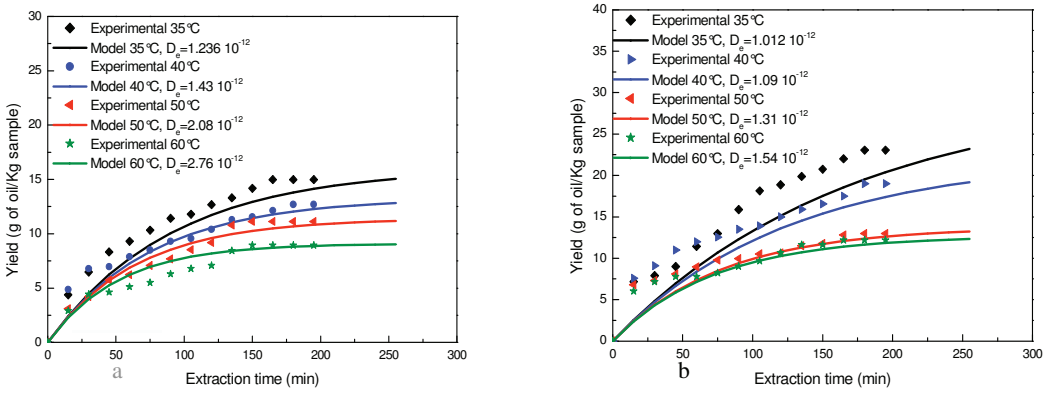


Fig. 2. Curves of oil extraction yield from rosemary at (a) T = 35 °C, P = 10, 14, 18 and 22MPa; (b) T = 40 °C, P = 10, 14, 18 and 22MPa; dp = 1mm; Q= 7 g /min.

The temperature effect on the extraction yield of the essential oil from the Algerian rosemary was investigated experimentally at four different temperatures 35, 40, 50 and 60°*C*. At a fixed pressure, the same temperature values are considered by the model, for its assessment. The results are shown by the following figures:



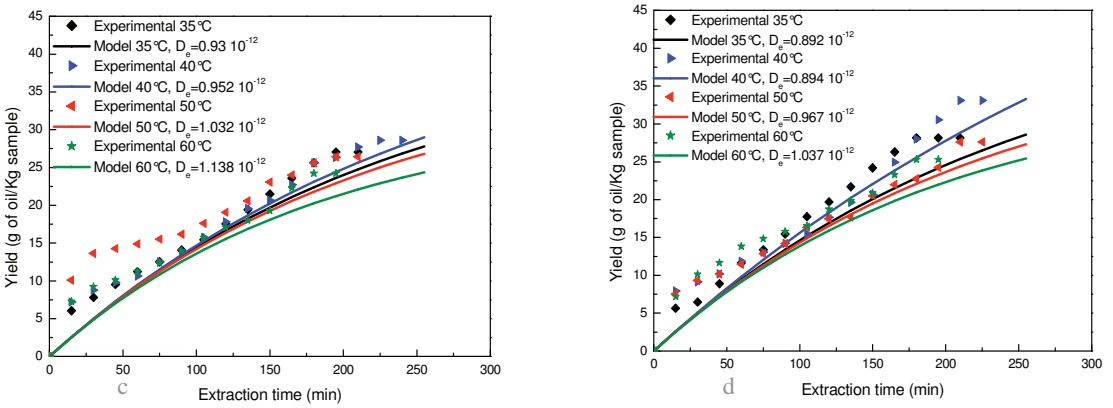


Fig 3. Effect of the temperature on the yield of the extraction: a) P = 10 MPa ; b) P= 14 MPa ; c) P= 18 MPa ; d) P= 22 MPa, Q=7 g/min, d_p=1 10^{-3}m).

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 on the following figures:

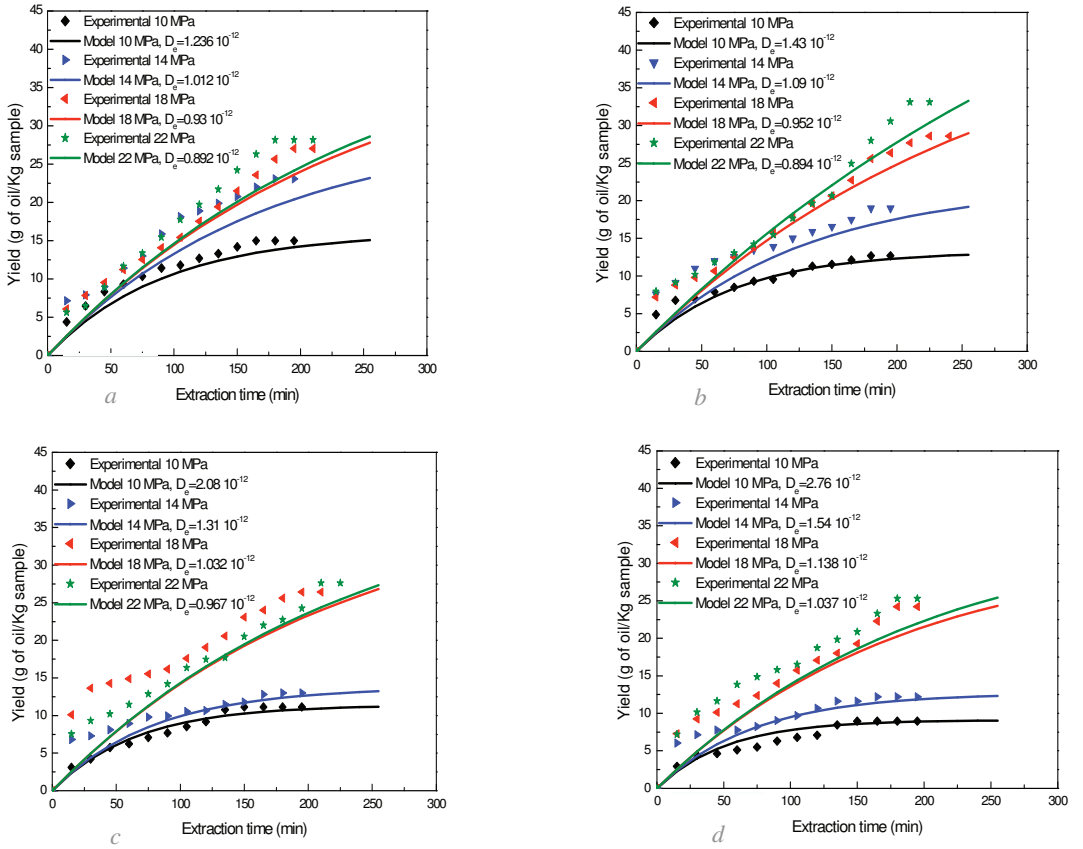


Fig.4. Effect of the pressure on the yield extraction at: a) T= 35°C ; b) T= 40°C ; c) T= 50°C ; d) T= 60°C ; Q=7 g/min; d_p=1 10^{-3}m)

Similarly to the temperature effect, the shrinking core model gives coherent results qualitatively where the extraction yields are for high pressure values of 18 et 22 MPa. 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.

4.2 Determination of the Physical Parameters and Properties

A priori, before any calculation, parameters like the fluid mass transfer coefficient (K_f) and 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 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. For example, D_e is 2.5 10^{-10} m^2/s for ginger oil [4]. and 5.1 10^{-12}, 3.1 10^{-12}, 1.4 10^{-12} and 1.2 10^{-11} m^2/s for coriander, sage, celery, and lavender flower respectively. [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. Table 3 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:

Table 3 Physical proprieties at the experimental conditions

Pressure (MPa)	Temperature (°C)	$Q\times10^4$ (kg/s)	$U\times10^4$ (m/s)	$\nu\times10^4$ (m/s)	ρ_f (Kg/m^3)	$d_p\times10^{-3}$ (m)	$\mu\times10^4$ (kg.m/s)	$K_f\times10^5$ (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

5. Conclusion

The essential oil of the Algerian rosemary used was extracted using supercritical carbon dioxide to measure the effects of temperature, and pressure on the extraction rate. The experimental results show that the extraction rate 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. Moreover, the extraction process was modeled using the shrinking core model with one adjustable parameter, the effective diffusivity D_e coefficient. The model using the best fit of D_e correlates the data satisfactorily.

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