SUPERCRITICAL EXTRACTION OF *CARQUEJA* ESSENTIAL OIL: EXPERIMENTS AND MODELING

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Abstract - *Baccharis trimera* is a native Brazilian plant which has medicinal properties. In this work a method of supercritical extraction was studied to obtain the popularly essential oil from *Baccharis trimera*, known as carqueja. The aim was to obtain experimental data and to compare two mathematical models used in the simulation of carqueja (*Baccharis trimera*) oil extraction by supercritical CO_2. The two mathematical models are based on mass transfer. One of the models, proposed by Reverchon, is solved numerically and requires two adjustable parameters from the experimental data. The other model chosen is the one proposed by Sovová. This model is solved analytically and requires four adjustable parameters. Numerical results are presented and discussed for the adjusted parameters. The experimental results are obtained in a temperature range of 313.15 K to 343.15 K at 90 bar. The extraction yield of carqueja essential oil using supercritical carbon dioxide ranged between 1.72 % (w/w) at 323.15 K and 2.34 % (w/w) at 343.15 K, 90 bar with a CO_2 flow rate of $3.34.10^{-8}$ m^3/s for a 0.0015 kg sample of *Baccharis trimera*.
Keywords: Carqueja; Essential oil; Supercritical extraction; Mass transfer modelling.

INTRODUCTION

The essential oil from *Baccharis trimera* has strong anti-inflammatory and analgesic properties (Gené et al., 1996). Moreover, carqueja is taken as an anti-inflammatory for hepatic and renal troubles and for stomach pain. It is also antihelminthic (Di Stasi et al., 2002). This plant is found easily in the Brazilian South (Simões et al., 1986), and the design and scale-up of the process of CO_2 supercritical extraction is related to the future commercialization of carqueja essential oil.

Traditional extraction processes, such as steam distillation, result in the hydrocracking of heavy hydrocarbons, and this phenomenon modifies the medicinal properties of the essential oil, thus justifying use of the high-pressure technology. Generally, the authors reported in the literature the use of processes of CO_2 supercritical extraction to obtain natural essential oils as an alternative to processes using high temperatures or liquid solvents (Reverchon, 1997; Cassel and Vargas, 2002; Gaspar et al., 2003).

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supercritical fluid extraction requires knowledge of the thermodynamic constraints (solubility) as well as the mass transfer parameters. Because the flow pattern in a fixed bed is complex, it has been found useful to develop semi-empirical correlations to describe the mass transfer between the solute dissolved in the solid phase and that in the solvent phase (Ferreira and Meireles, 2002; Ferreira et al., 1997). The SFE modeling was developed by means of different approaches: empirical models, models based on a heat transfer analogy, and models based on differential mass balance. Empirical kinetics models have been proposed by several authors (Nguyen et al., 1989; Kandiah and Spiro, 1990). Others have used the analogy between heat and mass transfer (Bartle et al., 1990; Reverchon et al., 1993; Gaspar et al., 2003). The SFE process has also been successfully modeled by integrating the differential mass balances written on a section of a fixed bed composed of vegetable particles (Bulley et al., 1984). This approach has been extensively studied, with the simulation of different mass transfer mechanisms (Goto et al., 1993), and it is possible to switch from one mechanism to an other (Sovová, 1994). Furthermore, different particle shapes spelled differently in References can be considered (Reverchon et al., 1995; Reverchon, 1996; Poletto and Reverchon, 1996; Reis-Vasco et al., 2000).

In this work, the purpose was to evaluate the mass transfer aspects of carqueja essential oil extraction with supercritical carbon dioxide, using the models proposed by Sovová (1994) and Reverchon (1996). Both mathematical models require adjustment of the parameters. These parameters were estimated for each experimental condition using Matlab R12.

EXPERIMENTS

The essential oils were extracted using leaves and twigs of plants picked in the Experimental Farm of the Institute of Biotechnology at the University of Caxias do Sul in the state of Rio Grande do Sul in southern Brazil. The experiments were conducted using the aerial part of dried and milled plants.

The average particle diameter was 5.10^{-4} m and the material was milled with a cutting mill (Tecnal, Willye TE650, Brazil). A 0.0015 kg amount of sample was used for extraction. The oils were extracted in a Hewlett Packard 7680T module, fully automated and equipped with a stainless steel thimble, 7.10^{-6} m^3; an analysis trap type, OD5; a temperature trap, 268.15 K for extracts; and an automatic system to collect the samples and then elute them with 10^{-6} m^3 of n-hexane (Merck, Germany), collected in vials.

The bed height (m), diameter (m), and volume (m^3) are respectively 0.045, 0.011, and $4.173.10^{-6}$. Liquid CO_2, 99.9% purity (White Martins, Brazil) was used for extractions and the flow rate of the solvent was $3.34.10^{-8}$ m^3/s. The experimental data on plant density, bed porosity, and maximum oil concentration are respectively 1087.2 kg/m^3, 0.669, and 27.0 kg/m^3. The experimental yield of the carqueja essential oil is shown in Table 1.

The oils were analyzed by GC and GC-MS. The GC/MS analysis of the oil was performed in a Hewlett-Packard 6890 equipped with a Wiley library. A 30 m x 0.25 mm HP Innowax Polyethylene Glycol Capillary column with a 0.25 μm film thickness (Hewlett-Packard, USA) was used. Identification of the volatile compounds was based on a comparison with the spectral data (MacLafferty et al., 1997) and their retention times (Figure 1).

Table 1: Experimental yield of carqueja essential oil (% w/w) at P = 90 bar

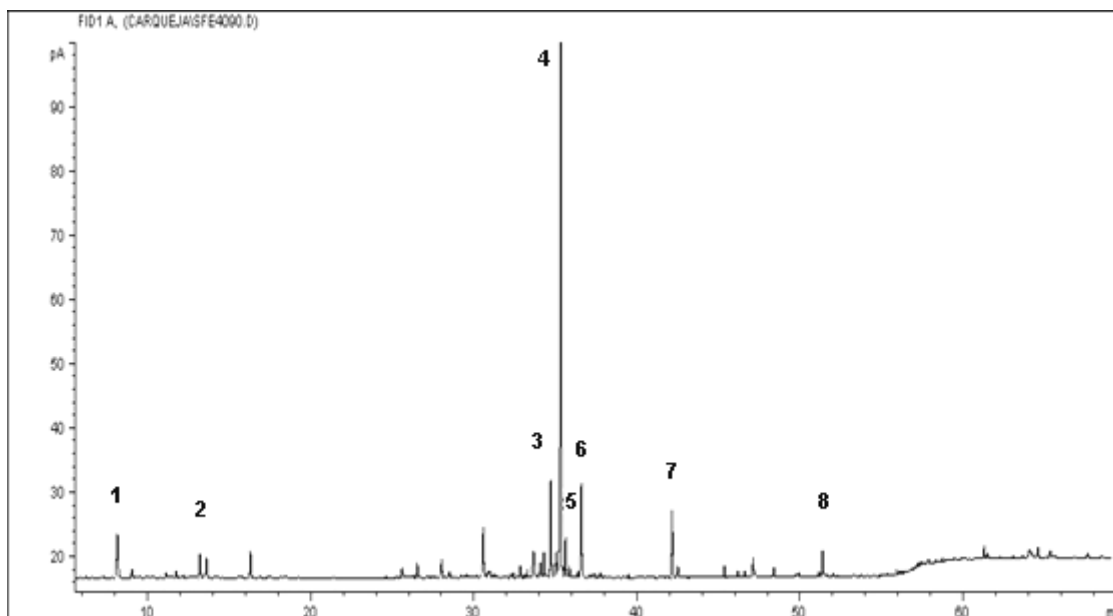| t (min)	T (K)			
	313.15	323.15	333.15	343.15
3	1.81	0.72	1.00	0.45
6	1.95	1.08	1.53	1.45
9	1.96	1.34	1.79	1.72
12	1.99	1.96	1.94	1.98
15	1.99	1.69	2.02	2.10
20	1.99	1.69	2.07	2.20
30	1.99	1.71	2.11	2.26
40	2.00	1.72	2.12	2.31
60	2.00	1.72	2.12	2.34

Figure 1: GC/MS for carqueja essential oil obtained by SFE at 90 bar and 323.15 K:
1 - d-limonene; 2 - trans-β-ocimene; 3 - germacrene ; 4 - carquejil acetate;
5 - beta-elemene; 6 - δ-cadinene; 7 - palustrol; 8 - β-eudesmol.

Quantitative analyses were carried out in a Hewlett-Packard 6890 GC equipped with a flame ionization detector (FID) and a 30 m x 0.32 mm i.d. HP-Innowax fused silica capillary column with a 0.25 μm film thickness. The compounds were quantified using a suitable internal standard added to the extracts obtained: 3-octanol, 97% purity (Aldrich, USA), and hexadecane, 98% purity (Fluka Chemika, Switzerland). Extractions and analysis were performed in triplicate.

MATHEMATICAL MODELING

Two mathematical models of the extractive process were analyzed in this work. The first model used to represent the supercritical extraction of carqueja essential oils with CO_2 was proposed by Reverchon (1996), here referred to as MR. In this model, the solvent density and CO_2 flow rate are constant throughout the bed. The oil extracted is assumed to be one component due to the lack of experimental phase equilibrium data. Thus, the mass balance over an element of the extraction vessel of height *dh* can be written as

$$uV\frac{\partial c}{\partial h} + \varepsilon V\frac{\partial c}{\partial t} + (1-\varepsilon)V\frac{\partial q}{\partial t} = 0 \qquad (1)$$

for the fluid phase and

$$(1-\varepsilon)V\frac{\partial q}{\partial t} = -A_p K(q - q^*) \qquad (2)$$

for the solid material.

The initial conditions are t=0, c(h,0)=0 , and q(h,0)=q_0, and the boundary condition is h=0, c(0,t)=0. ε is the bed porosity; V is the extractor volume; c is the extract concentration in the fluid phase; q is the extract concentration in the solid phase; u is the superficial solvent velocity; A_p is the total surface of particles; q* is the concentration at the solid-fluid interface, which according to the internal resistance model is supposed to be at equilibrium with the fluid phase; h is the spatial coordinate along the bed; t is the extraction time; q_0 is the initial concentration in the solid phase; and K is the internal mass-transfer coefficient.

Mass balances can be solved if the solid-liquid phase relationship q*(q) is known. As a rule, a linear relationship is used due to the lack of experimental phase equilibrium data

$$c = k_p q^*, \qquad (3)$$

where k_p is the volumetric partition coefficient of the extract between the solid and the fluid phase at equilibrium.

Taking

$$t_i = \frac{(1-\varepsilon)V}{A_p K}, \qquad (4)$$

where t_i is the internal diffusion time, Equation 2 can be rewritten as

$$\frac{\partial q}{\partial t} = -\frac{1}{t_i}(q - q^*). \qquad (5)$$

In this work, the hypothesis of Villermaux (1987) is assumed valid. The author relates the internal diffusion time as follows in Equation 6:

$$t_i = \mu \frac{l^2}{D_i} \qquad (6)$$

where μ is a coefficient that depends on particle shape and l is a characteristic dimension. In this work the particle is assumed to be in the shape of a slab; thus μ is equal to 1/3 and l is the thickness of the leaf. D_i is an internal diffusion coefficient.

The other model used, here referred to as MS, was proposed by Sovová (1994). This model describes a situation when solvent flows axially with superficial velocity U through a bed of milled plant material in a cylindrical extractor. The solvent is solute-free at the entrance of the extractor. Pressure and temperature are assumed to be constant throughout the bed. The solid bed is homogeneous with respect to both particle size and initial distribution of solute. The solute is deposited in plant cells and protected by cell walls. However, some of the walls has been broken open by milling, so that some of the solute is directly exposed to the solvent. The mass of oil contained initially in the solid phase, O, consists of the mass of easily accessible solute, P, and of the mass of inaccessible solute inside the solid-phase particles, K. The mass of the solute-free solid phase, N, remains constant during extraction. Amounts of solute are related to this quantity so the initial concentrations are (Sovová, 1994)

$$x(t=0) = x_0 = O/N = x_p + x_k = P/N + K/N. \qquad (7)$$

The material balance for an element of the bed are given by

$$-\rho_s(1-\varepsilon)\frac{\partial x}{\partial t} = J(x,y) \text{ and} \qquad (8)$$

$$\rho\varepsilon\frac{\partial y}{\partial t} + \rho U\frac{\partial y}{\partial h} = J(x,y), \qquad (9)$$

where ε is the void fraction of the bed of particles, ρ_s is the density of the solid phase, ρ is the density of the solvent, h is the axial direction, J is the interfacial mass transfer rate, x is the solid-phase concentration of the solute-free solvent and y is the solvent-phase concentration of the solute-free solvent. Sovová solves the set of equations neglecting the first term in the fluid-phase balance, assuming the initial and boundary conditions to be $x(h, t=0) = x_0$ and $y(h=0, t) = 0$ and assuming $J(x,y)$ to be a function of the difference in concentration using a local mass transfer coefficient for both phases. Due to the assumption of accessible and inaccessible solute in the plants, the solution attained is related for three distinct periods (Sovová, 1994; Ferreira and Meireles, 2002):

$$e = qy_r \left[1 - \exp(-Z)\right] \qquad (10)$$

$$e = y_r \left[q - q_m \exp(z_w - Z)\right] \qquad (11)$$

$$e = x_0 - \frac{y_r}{W}\ln\{1 + [\exp(Wx_0/y_r) - 1]$$
$$\exp\left[W(q_m - q)\right]x_k/x_0\} \qquad (12)$$

with

$$Z = \frac{k_f a_0 \rho}{(1-\varepsilon)\dot{q}\rho_s} = \frac{F}{\dot{q}} \qquad (13)$$

$$W = \frac{k_s a_0}{\dot{q}(1-\varepsilon)} = \frac{S}{\dot{q}}, \qquad (14)$$

where e is the mass of extract in relation to N, q ($=Q/N$) is the specific amount of solvent and is obtained by multiplying time by the mass flow rate of solvent in relation to N ($\dot{q}$), Q is the mass of solvent, N is the mass of the solute-free solid phase, Z and F are the parameters of the fast extraction period, z_w is the dimensionless coordinate of the boundary between fast and slow extraction, y_r is the solubility, x_0 is the overall initial concentration in

relation to the solute-free solid phase, and W and S are the parameters of slow-extraction period. The subscript m refers to the start of the extraction from inside the particles and the subscript n refers to the end of the extraction of easily accessible solute. Equation 10 is valid for $q < q_m$; during this period the easily accessible solute is extracted at the solvent entrance. Equation 11 is valid for $q_m \leq q < q_n$; during this period the accessible and inaccessible solute are extracted in different regions of the bed. Equation 12 is valid for $q \geq q_n$, which refers to the last period when only inaccessible solute is extracted in the extractor.

RESULTS AND DISCUSSION

The mathematical model, reported in Equations 1 to 5, was resolved using the fourth-order Runge-Kutta method for the set of discretized equations for 10 stages. The parameters, k_p, and t_i, were adjusted using the experimental data on the supercritical fluid process and it is possible to

observe in Table 1 that pressure and temperature were near the CO_2 critical point. In Figure 1, the experimental and modeling yield results of the process of carqueja essential oil extraction for a range of temperatures at the same pressure are shown. These parameters were estimated by minimization of the sum of squares of errors between the experimental data and the prediction using the model. To find the minimum, the Nelder-Mead simplex method (1965) was used with the software Matlab version 6. The estimated parameters for MR can be seen in Table 2 and the accuracy of this estimation can be seen in Figures 1 and 2, in agreement with the theory. It is possible to infer by the observation of the yield curves that progressive extraction is imposed on the solid phase with time. The concentration of the fluid phase is smaller than that of the solid phase. Furthermore, different solvent conditions result in different oil yields at the outlet of the extractor, but the mass transfer behavior is the same. Thus, the mass transfer mechanism depends on the external resistance as much as the internal resistance, but the internal resistance controls the process (Reverchon, 1996).

Table 2: Parameter values for the MR model

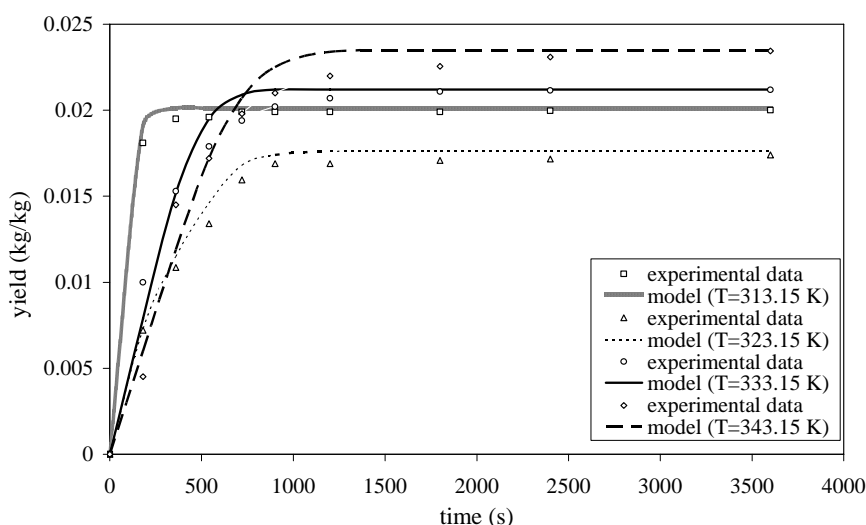| T (K)	k_p	$D_i (m^2/s)$
313.15	0.8133	3.03E-11
323.15	0.6944	3.66E-11
333.15	0.1041	1.97E-10
343.15	0.0667	2.73E-10

Figure 2: Yield curve for the supercritical extraction of carqueja essential oil: MR model and experimental data

It is possible to observe that the diffusivity of the carqueja essential oil in supercritical CO_2 increases with temperature. These results are in agreement with the theory in respect to temperature. The values of effective diffusivity of the essential oil in the solid matrix are of the same order of magnitude as that reported in the literature (Peker et al., 1992; Reverchon, 1993). In this work these values had been determined with Equation 6, which is valid for the process of mass transfer in a solid matrix with single porosity, in processes of simultaneous diffusion and adsorption. In our study, neither transient concentration gradients in the pores of the leaves nor internal porosity were considered. The volumetric partition coefficient, k_p, is different, decreasing as temperature increases up to 343.15 K, and then increasing after that. It is possible to observe that the maximum volumetric partition coefficient is found near the solvent critical temperature, the point of the maximum solubility of the solvent.

In the MS it was necessary to adjust four parameters with experimental data: S – the parameter associated with the solid mass transfer coefficient, F – the parameter associated with the fluid mass transfer coefficient, x_k – inaccessible oil concentration inside the solid phase particles, and y_r – solubility. An efficient milling operation diminishes the difficult access initial oil concentration, and increases the solid mass transfer coefficient and the fluid mass transfer coefficient (Sovová, 1994), justifying the choice of leaf size in this study. The curves for MS model implementation are shown in Figure 3. The ordinate represents the "e" parameter, the dimensionless extract quantity, and the abscissa represents the "q" parameter. As in the MR model it was possible to observe agreement between the MS model calculated and the experimental data. The MS parameters are presented in Table 3. There are high values for the solubility parameter near the critical point, similar to results found in the literature (Mukhopadhyay, 2000). The value of this parameter decreases as temperature increases up to 323.15 K and increases above that temperature. The F and S transfer coefficients have similar values at different temperatures and the S transfer coefficient has a lower value than the F transfer coefficient. The little variations can be the result of the numerical method applied to adjust the parameters (Nelder and Mead, 1965).
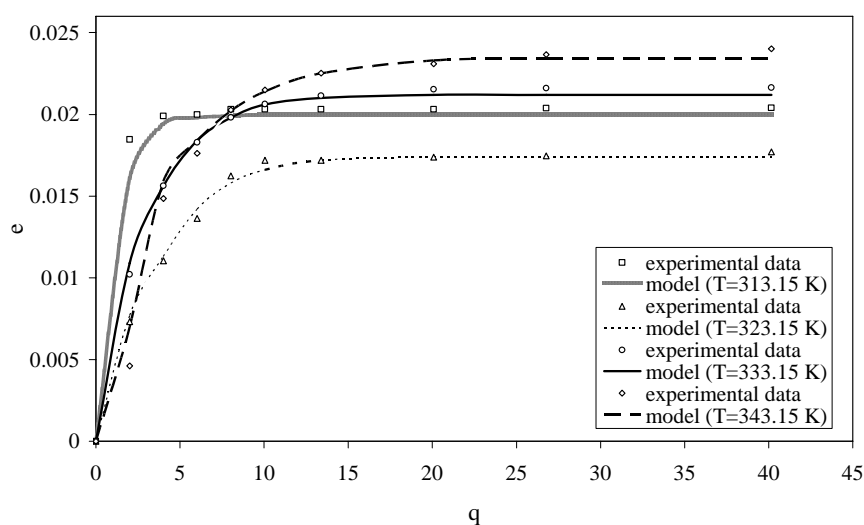

Figure 3: Yield curve for the supercritical extraction of carqueja
essential oil: MS model and experimental data

Table 3: Parameter values for the MS model

T (K)	x_k	$F(s^{-1})$	$S(s^{-1})$	y_r
313.15	0.0008	0.0082	0.0069	0.0191
323.15	0.0058	0.0155	0.0045	0.0067
333.15	0.0064	0.0182	0.0047	0.0066
343.15	0.0085	0.0231	0.0028	0.0083

CONCLUSIONS

In the two chosen models, the experimental data for carqueja essential oil yields correlate very well. In the MR model, due to the lack of solubility experimental data it was necessary to adjust parameter k_p. Determination of the values for the adjusted parameters agreed with data in the available literature in terms of order of magnitude. In the MS model, four parameters are adjusted, but this model has an analytical solution that facilitates the mathematical simulation. The values attained for these parameters are supported by the theory, as discussed in the body of this work. It was observed that good results obtained for the extraction curves for both models, depended heavily on the initial evaluation parameters used to start the numerical technique. Finally, the evaluation of model parameters in this work could be useful during the scale-up of the extraction process and/or during pilot or industrial operation to evaluate the extraction time required to obtain a given yield at a different temperature.

NOMENCLATURE

A_p	total surface of particles	(m^2)
c	concentration of extract in the fluid phase	(kg/m^3)
D_i	internal diffusion coefficient	(m^2/s)
e	mass of extract relative to N	(-)
F	parameter of fast extraction period	(s^{-1})
h	spatial coordinate in the bed	(m)
h	axial direction	(m)
J	interfacial mass transfer rate	(kg/s m^3)
K	internal mass transfer coefficient	(m/s)
K	mass of inaccessible solute inside the solid-phase particles	(kg)
k_p	volumetric partition coefficient of the extract between the solid and the fluid phase at equilibrium	(-)
l	characteristic dimension	(m)
m	refers to the start of extraction from inside the particles	(-)
N	mass of the solute-free solid phase	(kg)
n	refers to the end of extraction of easily accessible solute	(-)
O	mass of the solute contained initially in the solid phase	(kg)

P	mass of easily acessible solute	(kg)
Q	mass of solvent	(kg)
q	concentration of extract in the solid phase	(kg/m^3)
q*	concentration at the solid-fluid interface	(kg/m^3)
S	parameter of slow-extraction period	(s^{-1})
t	extraction time	(s)
t_i	internal diffusion time	(s)
V	extractor volume	(m^3)
u	superficial solvent velocity	(m/s)
U	superficial velocity	(m/s)
W	parameter of slow-extraction period	(-)
x	solid-phase concentration related to solute-free solvent	(-)
x_k	inaccessible oil concentration inside the solid phase particles	(-)
x_0	overall initial concentration related to solute-free solid phase	(-)
y	solvent-phase concentration related to solute-free solvent	(-)
y_r	solubility	(-)
Z	parameter of fast extraction period	(-)
z_w	dimensionless coordinate of the boundary between fast and slow extraction	(-)

Greek Letters

ε	bed porosity	(-)
μ	coefficient dependent upon particle shape	(-)
ρ_s	density of solid phase	(kg/m^3)
ρ	density of solvent	(kg/m^3)

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