

Extraction of volatile oil from *Croton zehntneri* Pax et Hoff with pressurized CO₂: solubility, composition and kinetics

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Received 20 February 2004; accepted 13 August 2004

Abstract

Croton zehntneri Pax et Hoff is indigenous to the Northeastern of Brazil; is rich in (E)-anethole and is largely used in cooking to impart flavor to a variety of foods; is used in folk medicine to treat indigestion, insomnia, etc. In this work the volatile oil from *C. zehntneri* was extracted using pressurized CO₂. Both kinetic and solubility experiments were performed at pressures of 66.7 and 78.5 bar and temperatures from 10 to 28 °C. The composition of the volatile oil was determined using gas chromatography. The maximum solubility (2.83×10^{-2} kg/kg) was observed at 15 ° and 66.7 bar while the maximum global yield (3.4%, mass) was detected at 20 °C at the same pressure. The volatile oil was formed predominantly by (E)-anethole (73.6%, area), alpha-muurolene (7.51%), methyl chavicol or estragole (2.52%), germacrene D (2.11%) and small amounts of other terpenoidic compounds. The overall extraction curves were fitted by several models from the literature. The models that best described the overall extraction curves were the Goto et al., Martínez et al., and Sovová.

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Keywords: *Croton zehntneri* Pax et Hoff; Modeling; Solubility; Supercritical fluid extraction

1. Introduction

Croton zehntneri Pax et Hoff is indigenous to the Northeastern of Brazil; its popular name is “canela de Cunhã” (cinnamon of Cunhã). Among the Euphorbiaceae family the *Croton* genus is the most widely spread in the Brazilian Northeast. The *C. zehntneri* grows as part of the local vegetation called as caatinga. It is a delicate bush, of fine branches, dark brown color, small and oval leaves, presenting leaves with starry hair, and

strong scent of anisette (Craveiro et al., 1981). The species is rich in anethole (Matos, 1989) and is largely used in cooking to impart flavor to a variety of preparations (Craveiro et al., 1981); in certain foods and beverages, the leaves and branches of *C. zehntneri* are used as sweeteners. The infusion of its leaves is used in folk medicine for the treatment of nervous and gastric disturbs, such as insomnia and indigestion and also as an antispasmodic for the intestinal musculature. Lately, several pharmacological applications have been confirmed in literature. Giorgio, Batatinha, Bernardi, De Souza Spinoza, and Palermoneto (1991) and Bernardi, De Souza-Spinosa, Batatinha, and Giorgio (1991) studied the effects of the aqueous extracts of *C. zehntneri* on the behavior of laboratory rats and mice; they verified

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Nomenclature

b	parameter of Martinez, Monteiro, Rosa, Marques, and Meireles model	OEC	overall extraction curve
CER	constant extraction rate period	P	pressure
DC	diffusion controlled extraction rate period	Q^*	solvent mass flow rate
FER	falling extraction rate period	SQD	sum of the square deviation
FI	parameter of Goto, Sato, and Hirose model related to the mass transfer rate	SFE	supercritical fluid extraction
k	constant of empirical model	T	temperature
k_D	desorption constant in Tan and Liou model	t_{CER}	end of the CER
k_{XA}	mass transfer coefficient in the solid phase	t_{mi}	time of the maximum extraction rate in Martinez et al. model
k_{YA}	mass transfer coefficient in the fluid phase	X_0	maximum amount of extractable solute
K	partition coefficient in Goto et al. model	X_k	fraction of hardly extractable solute
M_{CER}	mass transfer rate in the CER	X_p	fraction of easily extractable solute
		Y^*	solubility

that the extracts from leaves and branches affected differently the behavior of rats and mice. Batatinha, Bernardi, and De Souza Spinoza (1995) demonstrated the effects of the volatile oil in the behavior of rats and mice. Albuquerque, Sorenson, and Cardoso (1995) demonstrated the effects of the *C. zehntneri* volatile oil in the skeletal muscles of rats. The effects of the volatile oil were different from that of pure anethole and estragole (methyl chavicol): the volatile oil enhanced the twitches evoked by nerve stimulation, estragole partially enhanced while anethole did not significantly induce the twitches. Coelho de Sousa, Barata, Magalhães, Lima, and Leal Cardoso (1997) studied the effects of the volatile oil and the estragole on guinea-pig ileum; the results have shown that the volatile oil has a predominantly antispasmodic effect on the intestinal smooth muscle, which is partially due to the presence of estragole. Coelho de Sousa, Criddle, and Leal Cardoso (1998) studied the effects of the volatile oil on the mechanical activity of various in vitro preparations of guinea-pig smooth muscle; the results gave support to the traditional use of *C. zehntneri* as a gastrointestinal antispasmodic. Lazarini, Uema, Brandão, Guimarães, and Bernardi (2000) demonstrated that the volatile oil of *C. zehntneri* produced central depressor effects in rats without any anxiety alterations. Oliveira, Leal-Cardoso, Santos, Morais, and Coelho de Souza (2001) showed the antinociceptive effects of the essential oil of *C. zehntneri* in mice. Some of these properties are related to the combined action of anethole and methyl chavicol (estragole).

The objectives of this work were (i) to measure the solubility for the system *C. zehntneri* + CO₂; (ii) to determine the composition of the SFE extracts and compare it to the composition of the volatile oil (steam distillation) and oleoresin (ethanol extraction); (iii) to evaluate the kinetics of the process through the modeling of the overall extraction curves.

2. Materials and methods

2.1. Raw material characterization and preparation

The *C. zehntneri* leaves were from the municipality Serra do Ibiapaba (State of Ceará, Brazil) located in the Brazilian Northeastern. The leaves were dried naturally in the shade. The dried raw material was conditioned in plastic bags under vacuum and stored in a domestic freezer (Consul, model 280, São Paulo, Brazil). The humidity of the *C. zehntneri* leaves was determined by the xylol distillation method (Jacobs, 1973), recommended for odoriferous plants. Before each experimental run the material was triturated in a domestic food processor (Arno, model PRO, Brazil) for 15 s. The particle size distribution of the solid was determined using a vibratory agitator (Produtest, model 3614, Brazil) for 15 min (rheostat at position 10) and sieves of the Tyler series meshes 20, 28, 35, and 48.

2.2. Characterization of the particles and fixed bed

The true density of the *C. zehntneri* particles was measured by helium pycnometry at the Analytical Facilities of the Chemistry Institute—IQ/Unicamp. The apparent bed density was calculated using the mass of solid loaded into the fixed bed cell and the cell's volume. The total porosity of the bed plus particles was determined using the true and the apparent densities.

2.3. SFE unit and experimental procedure

The assays were performed using the SFE unit described by Sousa et al. (2002). The apparatus contains a fixed bed extractor of 200 ml (0.0217 m of diameter and 0.60 m of length); extracts sampling was

accomplished using a flash tank and a capture column, both assembled downstream to the fixed bed. For each load about 120 g of triturated *C. zehntneri* were packed into the fixed bed; the particle size distribution was 25% (mass) particles of meshes $-35/+48$, 50% (mass) particles of meshes -20 to $+35$, and 25% (mass) particles of meshes $-28/+35$. The solid particles were placed inside of the extraction cell with the aid of a funnel and compressed with the help of a stem in order to achieve a complete and uniform accommodation of the bed. Once the extraction cell was assembled into the SFE unit the system was allowed to reach the desired temperature and pressure. Then, the downstream valve was opened and the extraction began. Extract samples were collected at pre-selected time intervals, in the collector flask and capture column in order to build the overall extraction curves.

The solubility for the system *C. zehntneri* + CO₂ was measured using the dynamic method (Rodrigues et al., 2002); in order to identify the solvent flow rate at which saturation occurred assays were performed at flow rates of 0.58×10^{-5} to 2.1×10^{-5} kg/s.

2.4. Conventional process: steam distillation and ethanol extraction

Sixty grams of *C. zehntneri* were used in a steam distillation apparatus to obtain the volatile (essential) oil. The ethanol extraction was performed as described by Povh, Garcia, Marques, and Meireles (2001): 30 g of *C. zehntneri* and 180 ml of ethanol (Vetec, 99.5%, Brazil) were placed in an Erlenmeyer (250 ml) and kept under agitation (Tecnal, model TE 412, Piracicaba, Brazil) at 180 rpm for 8 h. Afterwards, the mixture was vacuum filtered. The oleoresin quantification was made gravimetrically: 20 ml of the filtered micelle (oleoresin + solvent) was weighted in Petri plates and allowed to rest for 48 h in a room with the temperature set at 18 °C. The amount of solvent evaporated was, then, gravimetrically determined. In order to quantify the amount of volatile oil in the oleoresin the Petri plates containing the oleoresin were taken to an oven with air circulation (Marconi, model MA035, Piracicaba, Brazil) with the temperature set at 165 °C for 6 h. Afterwards, the plates were allowed to cool in a desiccator (30 min) and weighted. The Petri plates returned to the oven for additional periods of 3 h up to constant mass.

2.5. Characterization of the extract: chemical composition and physical properties

The chemical compositions of the *C. zehntneri* extracts were determined using a gas chromatographer with FID detector (Varian, model Star 3400 CX, Palo Alto, USA) equipped with a capillary column DB-5

(30 mm \times 0.25 mm \times 0.25 μ m, J & W Scientific, Folsom, USA). The carrier gas was nitrogen (99.99% purity, White Martins Gases Industriais, 1.0 ml/min). The injector and detector temperatures were 220 °C and 240 °C, respectively. The column temperature was programmed from 60 °C to 240 °C, at 3 °C/min. The sample injected consisted of 1 μ L of extract diluted in hexane (0.005 g of extract diluted in 1 ml of hexane, chromatographic grade, Brazil) and the split ratio was 1/10. Quantification of the chemical substances of the *C. zehntneri* extracts was based on their GC-FID peak areas; the identification of the substances was based on the retention index of SFE *C. zehntneri*.

The density of the *C. zehntneri* extracts was measured using a digital densimeter (Anton Paar, model DMA 602, Graz, Austria) at atmospheric pressure and temperatures of 10, 15, 20, 25 and 30 °C. The refraction index was determined using a refractometer (Atago, model 1T, Tokyo, Japan) at 25 °C. The optical rotation was measured using a polarimeter (ausJENA, model, $\pm 0.05^\circ$, Switzerland) at 25 °C. The viscosity was measured using a rheometer (RheoStress Haake, model RS 150, thermostat DC 50, sensor DG41 Ti, factor A: 3701 Pa/Nm, factor M: 72.670 s^{-1} (rad/s), gap 5.1 mm, elements definition: tab, 9–30 °C, CR, 10 s^{-1} , # 6, Woburn, USA).

2.6. Calculations: solubility and modeling the extraction curves

In order to calculate the solubility the overall saturation curves were fitted to a spline using two straight lines. The first line was identified with the constant extraction rate period (CER). The rate of mass transfer for the CER period (M_{CER}) as well as the time corresponding to the interception of the two lines (t_{CER}) was computed from the spline. The spline was fitted using multiple-regression analysis (STATISTICA 5.0). MS Excel 97 was used to determine the interception of the two lines. The solubility was obtained dividing M_{CER}^* by the mean solvent flow rate for the CER period. The overall extraction curves of *C. zehntneri* volatile oil were adjusted with the models of Sovová (1994), Goto, Sato, and Hirose (1993), Martínez, Monteiro, Rosa, Marques, and Meireles (2003), Tan and Liou (1989) and the empirical model (Esquivel, Bernardo-Gil, & King, 1999). The model of Martínez et al. (2003) was applied considering the solute as a single pseudo-compound. The curve fits were done with the help of the software Tecanalysis, developed in LASEFI-DEA/FEA-UNICAMP. This software uses the maximum likelihood method to minimize the sum of the squares of the residues. Hence, parameters that helped to describe the kinetics of the process, according to each model, were obtained.

3. Results and discussion

The humidity of the *C. zehntneri* leaves was $13.2 \pm 0.1\%$; the apparent bed density was 542.8 kg/m^3 and the true density $1313 \pm 1 \text{ kg/m}^3$ resulting in a porosity of 0.59. The overall extraction curves had the typical shape with the three distinctive regions: (i) Constant extraction rate period (CER), (ii) falling extraction rate period (FER), and (iii) diffusion controlled extraction rate period (DC). The saturation solvent flow rate varied from 1.0 to $1.32 \times 10^{-5} \text{ kg/s}$. Table 1 shows the solubility for the system *C. zehntneri* + CO₂ for the isobar of 66.7 bar; the solubility was also measured at 78.5 bar and 15°C. The solubility varied from $16.4 \times 10^{-3} \text{ kg/kg}$ at 10°C to $28.3 \times 10^{-3} \text{ kg/kg}$ at 15°C. Comparison of data of Table 1 with solubility data for the system clove + CO₂ (Rodrigues et al., 2002) shows that the solubility of the two systems vary by an order of magnitude; the solubility for the system clove + CO₂ being higher. Rodrigues et al. (2002) also reported solubility data for the systems ginger + CO₂ and eucalyptus + CO₂ for these systems the solubility is smaller than for the system *C. zehntneri* + CO₂. Nonetheless, the solubility of the system *C. zehntneri* + CO₂ (Table 1) are of the same order of magnitude of the solubility for the

system *L. sidoides* + CO₂ reported by Sousa et al. (2002), but, at the same pressure (66.7 bar) the maximum solubility was observed at 20°C instead.

The yield for the SFE process expressed as mass of extract divided by mass of dry feed is show in the last column of Table 1 (X_0). It is interesting to observe that the maximum in solubility occurred at 15°C while the maximum yield occurred at 20°C, instead. This indicates that a region of retrograde behavior should be observed near 66.7 bar at either the 15 or the 20°C isotherms. The yields for the steam distillation and ethanol extraction processes were 3.06% and 2.68%, respectively.

For design purposes one requires to have a knowledge of the volatile oil (which is a multicomponent mixture of terpenoidic compounds) composition as well as other properties such as density, viscosity, and the like, which characterize the product. Tables 2–5 shows the properties of the *C. zehntneri* SFE extracts. Table 2 shows the composition of the *C. zehntneri* SFE extract obtained at 66.7 bar and 15°C as a function of extraction time intervals, the composition of the volatile oil (steam distillation) and oleoresin (ethanol extraction) are also shown for comparison. The major component of the extracts *C. zehntneri* was (E)-anethole reaching the content of 86.8% for the volatile oil. The content of methyl chavicol (estragole) that has been reported (Albuquerque et al., 1995; Coelho de Sousa et al., 1997) as the major component of *C. zehntneri* is well below the content of (E)-anethole and alpha-murolene.

Approximately 5.5% of the extract was retained in the capture column; the content of (E)-anethole was 82.0% a value that is roughly 11% higher than the content in the samples retained in the collector flask. The contents of (Z)-anethole and methyl chavicol were 1.1% and 2.3%, which are similar to the content of the

Table 1
Solubility for the system *C. zehntneri* + CO₂

<i>T</i> (°C)	<i>P</i> (bar)	$Q^* \times 10^5$ (kg/s)	$Y^* \times 10^3$ (kg/kg)	X_0 (%)
10	66.7	1.30	16.4	3.31
15	66.7	1.03	28.3	3.71
20	66.7	1.18	26.0	3.80
25	66.7	1.32	24.1	3.43
28	66.7	1.32	20.9	2.09
15	78.5	1.28	23.1	3.69

Table 2
Effect of the extraction time interval in the content of the major components of the SFE extracts obtained at 66.7 bar, 15°C, $1.03 \times 10^{-5} \text{ kg/s}$ (saturation flow rate)

Component	Composition (Area%)					Steam distillation	Ethanol extraction
	Extraction time interval (minutes) for the SFE process						
	0–50	50–100	100–150	150–260	260–300		
Sabinene	–	0.1	–	0.14	–	0.21	–
Myrcene	0.66	0.53	0.56	0.42	0.4	1.60	–
1,8-cineole	0.63	0.6	0.47	0.61	0.62	0.81	–
(E)-beta-ocimene	0.21	0.17	–	0.14	0.25	0.51	–
Alpha-terpineol	–	0.12	–	0.13	0.1	0.11	–
Methyl chavicol	2.1	2.09	2.32	1.85	0.64	2.59	–
(Z)-anethole	0.73	1.02	1.06	0.91	1.23	1.10	0.83
(E)-anethole	88.8	85.0	88.5	89.7	86.2	86.8	86.1
Delta-elemene	–	0.18	–	0.1	0.1	0.07	–
Beta-elemene	–	0.24	–	0.2	0.2	0.02	–
Trans-caryophyllene	1.2	0.9	1.1	0.9	1.0	0.62	1.3
Germacrene D	0.3	1.6	1.2	0.8	1.8	0.13	–
Alpha-murolene	0.46	1.41	0.97	0.37	–	0.49	1.7
Beta-bisabolene	–	0.2	0.1	0.3	0.2	–	–
Non-identified	4.9	5.8	3.7	3.5	7.1	4.9	10.1

Table 3
Effect of solvent flow rate on the composition of the SFE extracts obtained at 66.7 bar and 15°C during the CER period

Substance	Composition (Area%)				
	5.83×10^{-5} (kg/s)	1.03×10^{-5} (kg/s)	1.57×10^{-5} (kg/s)	2.05×10^{-5} (kg/s)	2.13×10^{-5} (kg/s)
Sabinene	0.08	–	0.06	0.06	0.04
Myrcene	0.92	0.56	0.56	0.91	0.9
1,8-cineole	0.86	0.47	0.99	0.78	0.84
(E)-beta-ocimene	0.22	–	0.16	0.17	0.28
Alpha-terpineol	0.17	–	0.17	0.18	0.43
Methyl chavicol	2.4	2.3	2.6	2.2	2.4
(Z)-anethole	1.2	1.1	1.1	1.4	2.1
(E)-anethole	82.1	88.5	83.5	80.7	82.5
Delta-elemene	0.15	–	0.18	0.17	0.08
Beta-elemene	0.26	–	0.36	0.26	0.23
Trans-caryophyllene	1.31	1.1	1.4	1.3	1.2
Germacrene D	2.2	1.2	2.27	2.30	2.11
Alpha-murolene	1.4	0.96	1.4	1.6	1.3
Beta-bisabolene	0.39	–	0.41	0.20	0.19
Non-identified	6.4	3.7	4.8	7.8	5.4

Table 4
Effect of temperature on the composition of the SFE extracts obtained at 66.7 bar and at the saturation flow rate

Substance	Composition (Area%)				
	10°C 1.3×10^{-5} kg/s	15°C 1.03×10^{-5} kg/s	20°C 1.18×10^{-5} kg/s	25°C 1.32×10^{-5} kg/s	28°C 1.32×10^{-5} kg/s
Sabinene	–	–	0.05	0.07	0.06
Myrcene	0.68	0.56	0.72	0.82	0.75
1,8-cineole	0.86	0.47	0.69	0.78	0.84
(E)-beta-ocimene	0.12	–	0.25	0.2	0.2
Alpha-terpineol	0.15	–	0.23	0.10	0.42
Methyl chavicol	2.0	2.3	2.05	1.1	2.3
(Z)-anethole	1.1	1.1	0.92	1.2	1.5
(E)-anethole	87.1	88.5	87.7	87.2	82.5
Delta-elemene	0.14	–	0.11	–	0.10
Beta-elemene	0.08	–	0.25	0.1	0.21
Trans-caryophyllene	0.99	1.1	1.05	1.1	1.3
Germacrene D	1.90	1.2	2.1	1.1	2.3
Alpha-murolene	0.15	0.96	0.97	0.74	1.3
Beta-bisabolene	–	0.1	0.2	–	0.22
Non-identified	4.7	3.7	2.7	5.5	5.9

collector's flask sample. This indicates that the collector flask or the flash tank has behaved as an additional equilibrium stage, thus, resulting in further fractionating of the SFE extract.

Table 3 shows that the composition of the SFE extract was approximately constant during the CER period for the saturation flow rate, which is a condition required in order to use the dynamic method to measure solubility (Rodrigues et al., 2002). Table 4 shows that the solvent flow rate marginally affected the composition of the SFE extracts. The effects of temperature on the composition of the SFE extract for the CER period are in Table 5, again, the effect was negligible and a similar behavior was observed for the pressure.

The optical rotation of the extract was $(-)$ $0^{\circ}45'0''$ and the index of refraction 1.5460 both measured at

25°C; the influence of temperature on the extracts' density and viscosity are in Fig. 1. The density decreases linearly with the increase in temperature ($R^2 = 0.9977$); the viscosity decrease with temperature can be described by a second order polynomial ($R^2 = 0.9806$).

3.1. Modeling of the overall extraction curves: a brief description of the mathematical models

The selection of the models to describe the OECs of the system *C. zehntneri* + CO₂ was based on: (i) the physical meaning of the parameters of a specific model (Sovová (1994) model); (ii) the simplicity of the model (empirical (Esquivel et al., 1999) and Tan & Liou (1989) models); (iii) the fact that the model was used for a similar system (Goto et al. (1993) model, which was applied for SFE from mint leaves); and (iv) the

Table 5
Effect of pressure on the composition of SFE extracts obtained at 15°C and at the saturation flow rate

Substance	Composition (Area%)	
	66.7 bar (1.03×10^{-5} kg/s)	78.5 bar (1.28×10^{-5} kg/s)
Sabiene	–	0.1
Myrcene	0.56	0.82
1,8-cineole	0.47	0.61
(E)-beta-Ocimene	–	0.20
Alpha-terpineol	–	0.19
Methyl chavicol	2.3	2.2
(Z)-anethole	1.1	1.3
(E)-anethole	88.5	85.9
Delta-elemene	–	0.16
Beta-elemene	–	0.05
Trans-caryophyllene	1.1	1.2
Germacrene D	1.2	1.3
Alpha-murolene	0.96	1.3
Beta-bisabolene	0.1	0.20
Non-identified	3.7	4.5

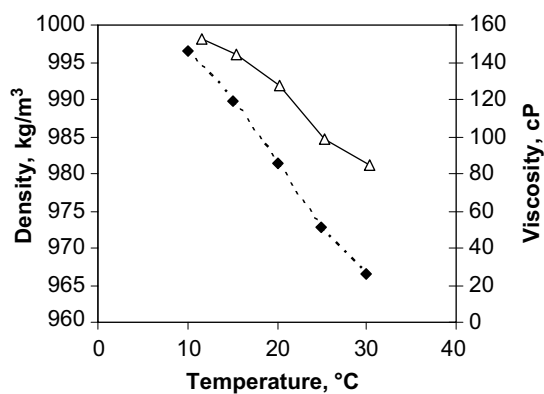


Fig. 1. Density and viscosity of the SFE extracts obtained at 15°C, bar and 1.03×10^{-5} kg/s.

capability of the model to describe various shape of the OECs (Martínez et al., 2003). Follows a brief description of each model used in this work.

3.2. The model of Sovová

The extracts from vegetable raw materials are often inside cells that are protected by a cellulosic wall. The cell wall works as a barrier for the contact of the solvent with the desirable compounds. The pre-treatment of raw material, which includes milling, makes the contact between solute and solvent easier. After milling, a great fraction of the solute becomes free for the contact with the solvent, but some of the cell walls may remain intact, with solute inside the cells. Based in the broken and intact cell walls idea, Sovová (1994) proposed a model in which the solute is divided into two fractions: the easily accessible solute (X_p) and the hardly accessible solute

(X_k). During SFE process Sovová (1994) considers that, for each particle, all the easily accessible solute is extracted before the hardly accessible solute begins to be removed. So, the SFE process can be divided in three steps: in the first step there is easily accessible solute in every particle of the extraction bed; in the second step, the easily accessible solute is gradually depleted from the inlet to the outlet of the bed; and in the third step there is only hardly accessible solute. From the mass balance inside the extraction bed for each step, Sovová (1994) obtained analytically the equations for the overall extraction curve, which can be determined through the adjustment of the mass transfer coefficients for both fluid and solid phases.

3.3. The model of Goto, Sato, and Hirose

Goto et al. (1993) defined the solid particle as a plain plate with defined thickness that is much lower than its other dimensions. So, mass transfer occurs only between the two greatest particle surfaces, which can be treated as a porous media. Hence, Goto et al. (1993) differentiate the solute concentration inside the particle from the concentration in the pores, and defined a desorption process from the particle to its pores. Then, the mass balance inside the particle can be solved analytically, resulting in an equation for the overall extraction curve, which can be obtained through the adjustment of two parameters: one related to convection in the fluid phase and the other to the desorption.

3.4. The model of Martínez, Monteiro, Rosa, Marques, and Meireles

The elaboration of the model of Martínez et al. (2003) was motivated by the need to treat the oil as a mixture of compounds, and not as a pseudo-compound, like is done in the previous models. França and Meireles (2000) had proposed a model in which the interfacial mass transfer flux is a function of the concentration of some group of compounds of the extract in fluid phase. In this model the logistic growth equation was proposed to describe the same function. After solving the mass balance equations for the system, an equation for the extraction curve was obtained. This model has two adjustable parameters for each group of compounds: t_{mi} , which is the instant in which the extraction rate reaches its maximum value, and b_i , whose physical meaning is not already well defined. This model can also be applied to SFE curves considering the solute as a single pseudo-compound.

3.5. The empirical model

The empirical model is based on Monod's equation for microbial growing kinetics.

This equation was used by Esquivel et al. (1999) to describe OECs. The modeling is quite simple, with only one adjustable parameter.

3.6. The model of Tan and Liou

Tan and Liou (1989) had modeled the supercritical fluid extraction process representing the interfacial mass transfer flux with a first order kinetic model. The only adjustable parameter in this model is a desorption coefficient, which depends on the temperature. Tan and Liou (1989) neglected the axial dispersion and the intra-particle diffusion, so they could reach an analytical solution for the mass balance inside the extraction bed.

Table 6 shows the parameters used to model the OECs. The parameters fitted to the various models are in Table 7, which also shows the sum of the squares of the residues. For the Sovová’s model, the fluid-phase and solid-phase mass transfer coefficients (k_{YA} and k_{XA} , respectively) were calculated using the fitted t_{CER} .

Fig. 2(a) and (b) shows the comparison between the experimental and modeled OECs. In these figures the extraction yields represent the ratio between the extract mass and the maximum amount of extractable material (X_0 multiplied by the feed mass). As can be observed, the models of Sovová (1994), Goto et al. (1993), and Martí-

nez et al. (2003) provided the best fits to experimental data, which is confirmed by the SQDs in Table 7.

The models with two adjustable parameters were able to obtain the best fits to experimental data, but the reasons for these results should not be limited only to the number of parameters. The shape of the curve that each model provides is of great importance for its efficiency.

The model of Sovová (1994) for example, works quite well when the experimental OECs have a well-defined constant extraction rate period at their beginning. The main vantage of this model is its description of the

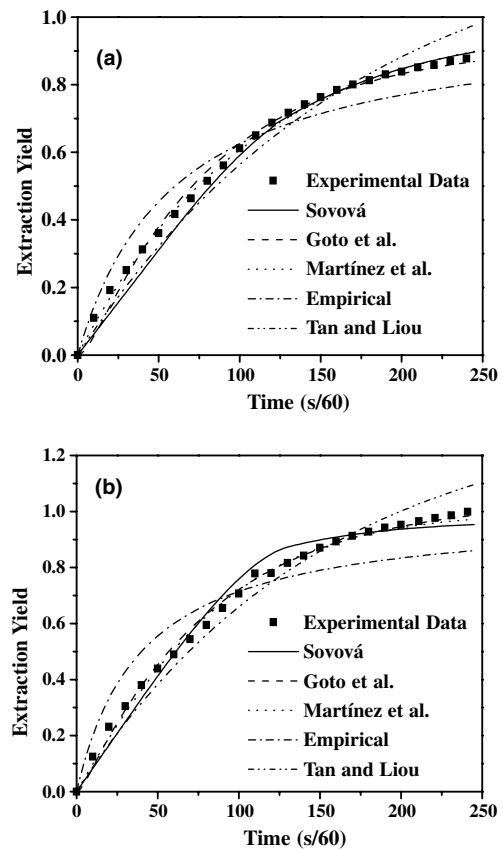


Fig. 2. OECs for SFE of *Croton zehntneri* Pax et Hoff oil: (a) Experiment 1; (b) Experiment 2.

Table 6
Experimental conditions and parameters

Parameters	Experiment 1	Experiment 2
Bed porosity (-)	0.591	0.591
Density of CO ₂ (kg/m ³)	847	847
Density of the solid phase (kg/m ³)	1327	1327
Diameter of the bed (m)	0.0216	0.0216
Flow rate of CO ₂ (kg/s)	2.13 × 10 ⁻⁵	2.05 × 10 ⁻⁵
Height of the bed (m)	0.605	0.605
Mass of feed (kg)	0.12	0.12
M _{CER} (kg/s)	4.0 × 10 ⁻⁷	5.3 × 10 ⁻⁷
Porosity of the particles (-)	0.54	0.54
Pressure (bar)	67	67
Solubility of the solute in CO ₂ (kg/kg)	0.0283	0.0283
Temperature (°C)	15	15
X ₀ (kg solute/kg feed)	0.033	0.033

Table 7
Parameters fitted to and sums of squares of the residues

Model		Experiment 1		Experiment 2	
		Parameter	SQD × 10 ⁶	Parameter	SQD × 10 ⁶
Empirical	k (s)	3612	1.391	2406	3.477
Tan and Liou	k_d (S ⁻¹)	9.5.10 ⁻⁵	0.756	1.01 × 10 ⁻⁴	0.904
Sovová	t_{CER} (s)	3474	0.351	2076	0.543
Sovová	k_{YA} (S ⁻¹)	1.28 × 10 ⁻⁴	0.351	2.99 × 10 ⁻⁴	0.543
Sovová	k_{XA} (S ⁻¹)	8.3 × 10 ⁻⁵	0.351	1.11 × 10 ⁻⁴	0.543
Goto et al.	FI (-)	6.96	0.153	0.42	0.138
Goto et al.	K (-)	0.50	0.153	0.42	0.138
Martínez et al.	b (S ⁻¹)	1.55 × 10 ⁻⁴	0.049	2.75 × 10 ⁻⁴	0.126
Martínez et al.	t_m (S)	-62556	0.049	-1536	0.126

phenomena that occur during the SFE process that gives a clear physical meaning to the adjustable parameters. By the other side, the use of the model of Sovová (1994) is limited to SFE systems in which the solubility of the solute in the solvent is known at the temperature and pressure of the process.

Both models of Goto et al. (1993) and Martínez et al. (2003) are useful to describe OECs where the extraction rate has a slow increase at its beginning, before reaching a constant value. In this work, as can be observed in Table 7, the values of t_{mi} for the model of Martínez et al. (2003) are negative. This means that the rate of the extraction is always decreasing, having its maximum value at the initial instant.

The empirical model is able to describe OECs with a hyperbolic shape, which was not the case of this work. In systems where the solute has an easy contact with the solvent the OECs tend to have a hyperbolic shape, once the solute can be quickly extracted.

The maximum amount of extractable solute in a system is an experimental data of great importance for the mathematical modeling of SFE processes. In some cases it works as a boundary condition to the solution of mass balance equations, so when time tends to infinite, the extraction yield becomes closer to 100%. This happens in all the models presented in this work, with one exception: the model of Tan and Liou (1989). It can be clearly observed in the OEC for Experiment 2, in Fig. 2, that the extraction yield becomes higher than 100% for the model of Tan and Liou (1989). The value of X_0 , that represents the maximum amount of extractable solute relative to feed, is not taken into account in this model, which results in problems like the one observed for the OEC for Experiment 2.

4. Conclusions

The overall extraction curves for the system *C. zehntneri* + CO₂ have the typical shape consistent of the CER, FER and DC periods. At 66.7 bar the solubility has a maximum at 15°C; for the global yield the maximum was detected at 20°C. The major compounds present in the SFE extracts were (E)-anethole and alpha-muurolene (menthol); estragole (methyl chavicol) was also detected but in smaller quantities. The models of Sovová (1994), Goto et al. (1993), and Martínez et al. (2003) provided the best fits to the experimental data.

Acknowledgement

This work is part of an international exchange program financed by CNPq (Brazil) and DLR (Germany) called SuperNat; the authors thank CNPq, FAPESP (1999/01962-1), and CAPES (046/02-7).

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