MODELING THE SUPERCTITICAL FLUID EXTRACTION OF FIELD HORSETAIL (*EQUISETUM ARVENSE*) OLEORESIN

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The supercritical fluid extraction (SFE) of field horsetail (*Equisetum arvense*) oleoresin was studied using CO_2 as solvent. Field horsetail extracts are indicated as excellent diuretic and adstringent and present activities reducing hemorrhage and healing wounds. The fixed bed was formed with grounded field horsetail (aerial parts) (-20 to +32 mesh) with an apparent density of $350 kg/m^3$. The effect of the extraction conditions was analyzed in a series of experiments developed at 30 and 40ºC and 120, 150 and 200bar. The modeling of the overall extraction curves (OEC) was performed using solubility experimental data that varied from 1.05×10^{-4} to 4.63×10^{-4} g oleoresin/g CO_2. The range for the solvent flow rate (supercritical CO_2) varied from 1.85×10^{-5} to 7.65×10^{-5} kg CO_2/s. The maximum extraction yield (mass of extract/mass of dried feed) was up to 1.10%, obtained at 40ºC, 4.73×10^{-5} kg CO_2/s, 200bar. The experimental data were correlated using the mass transfer model proposed by Sovová, that considered the mass transfer rate in the solvent phase and indicate the importance of the initial oil content in the raw material. The modeled results of the OEC shown good agreement with experimental data.

Keywords: Supercritical fluids, field horsetail , natural products, mass transfer rate.

INTRODUCTION

The use of gas solvents for natural product extractions has became a viable alternative compared to conventional processes. The supercritical fluid extraction (SFE) presents characteristics such as non toxicity, non inflammability and non solvent residue in the extract, among others, which justify the interest from different areas. Also, the SFE allow to obtain products without thermal degradation, an important characteristic for pharmaceutical, food and chemical industries [1, 2].

Field horsetail (*Equisetum arvense*) can be considered one of the most used plants in herbal medicine. It is an excellent diuretic and astringent, reducing hemorrhage and healing wounds. It is also considered for cases of inflammation or benign enlargement of the prostate gland, among other several applications [3].

Also, the use of simple models such as based on differential mass balance, that requires little experimental information can be useful for scale-up purposes. Therefore, the purpose of this work was to investigate the kinetics aspects of the extraction process of the field horsetail oleoresin with supercritical CO_2 and evaluate the effect of the operational conditions (temperature and pressure) on the process yield. For the mass transfer aspects of the process the model described by Sovová (1994) was used in order to investigate the influence of the initial amount of solute mass ratio in the solid phase (X_0) in the extraction curves modeling [4]. The mass transfer model was also used to investigate both the spatial and the time dependence of the fluid phase solute concentration. The experimental data selected for the extraction curve modeling were the ones obtained by Michielin (2002) [1].

I - MATERIALS AND METHODS

Dried field horsetail aerial parts (Chamel Ind. e Com., Campo Largo, PR, Brazil) were grounded immediately before the SFE in a domestic coffee grinder (Melitta, SP, Brazil). The material was classified and the fixed bed formed using particles between mesh 20 and 32. The bed porosity [$e = 1 - (da/dr)$] was obtained considering the real density (dr), experimentally evaluated by helium picnometry and the apparent density (da), for the extractor volume.

The experiments were performed with the plant material forming a fixed bed in an stainless steel column (40 cm length x 2.1 cm intern diameter - Suprilab, SP, Brazil), and with the CO_2 flowing through the bed in a dynamic mode. The overall extraction curves were obtained with the mass of solute *vs.* extraction time, for each operational condition (temperature and pressure). The experiments were carried out at 30 and 40 ºC and at 120, 150 and 200 bar and the results presented elsewhere [1].

II. MASS TRANSFER MODEL

The mass transfer mechanism in SFE of natural products is complex to model due to the elevated number of components in the mixture. Also, it is difficult to establish the interactions between the extract's components, the solvent and the solid phase, present in the extraction system. In this work the was considered the model proposed by Sovová (1994) that assumes pseudo steady state, plug flow and constant temperature, pressure and solvent velocity. The bed is homogeneous with respect to the solute and particle size distributions [4]. Therefore, the mass balance for a bed element is given by

solid phase: $\quad - \rho s(1 - \varepsilon)\dfrac{\partial X}{\partial t} = J(X,Y)$ (1) $\qquad$ fluid phase: $\rho_f .U \dfrac{\partial Y}{\partial h} = J(X,Y)$ (2)

where X and Y are the solute mass ratio in the solid and fluid phases respectively, t is time, U is the supercritical velocity, h is the axial direction, e is the bed porosity, r_s and r_f are the solid and fluid phases densities respectively and $J(X,Y)$ the interfacial mass transfer rate. Usually, for SFE the fluid phase can be treated as a diluted solution therefore the solvent density (r_{CO2}) can replace the fluid phase density. The solution to Eq.(1) and (3) given by Sovová (1994), can be written as:

for CER period: $t < t_{CER}$ $\qquad\qquad\qquad$ for FER period: $t_{CER} \le t < t_{FER}$

$$m_{extr} = Y^*[1 - \exp(-Z)]Q_{CO_2}.t \quad (3) \qquad m_{extr} = Y^*\left[t - t_{CER}.\exp(z_W - Z)\right]Q_{CO_2} \quad (4)$$

for the diffusion controlled period: $t \ge t_{FER}$

$$m_{extr} = N\left\{ X_O - \frac{Y^*}{W}\ln\left[1 + \left[\exp\left(\frac{WX_O}{Y^*}\right) - 1\right]\exp\left(\frac{W.Q_{CO_2}}{N}(t_{CER} - t)\right)\frac{X_k}{X_O}\right]\right\} \quad (5)$$

with the following restrictions:

$$Z = \frac{N.k_{Ya}.\rho_{CO_2}}{Q_{CO_2}.(1 - \varepsilon)\rho_s} \quad (6) \qquad Y_{CER} = \frac{M_{CER}}{Q_{CO2}} \quad (7) \qquad z = \frac{k_{Ya}}{U}h \quad (8)$$

$$\tau = \frac{k_{Ya}.\rho_{CO2}.Y^*}{(1 - \varepsilon).\rho_{CO2}.X_k} \quad (9) \qquad t_{CER} = \frac{X_O - X_k}{Y^*.Z}\frac{N}{Q_{CO_2}} \quad (10) \qquad X_p = X_0 - X_k \quad (11)$$

$$\frac{z_W}{Z} = \frac{Y^*}{WX_O} \ln\left\{ \frac{X_O \cdot \exp\left[(W \cdot Q_{CO_2}/N)(t - t_{CER})\right] - X_k}{X_O - X_k} \right\}$$ (12)

$$W = \frac{N \cdot k_{Xa}}{Q_{CO_2} \cdot (1 - e)} = k \frac{ZY^*}{X_k}$$ (13) $\quad t_{FER} = t_{CER} + \frac{N}{Q_{CO_2} \cdot W} \ln\left[\frac{X_k + (X_O - X_k) \cdot \exp(WX_O/Y^*)}{X_O} \right]$ (14)

where m_{ext} is the mass of extract (kg), N is the mass of inert solid (kg), Y^* is the solubility of the extract in the solvent (kg/kg), k_{Ya} is the fluid phase mass transfer coefficient (s^{-1}), k_{Xa} is the solid-phase mass transfer coefficient (s^{-1}), X_0 is the initial and solute mass ratio for the unruptured cells in the solid phase, and X_p is the solute mass ratio for the easily accessible solute also in the solid phase.

The field horsetail oleoresin solubility was obtained for low flow rate experiments and using the program SAS- version 6.11 (SAS Institute Inc., Cary, NC, USA), that performed a simultaneous adjustment of three straight lines to the overall extraction curve. The slope of the line in the first portion of the curve corresponds to M_{CER}, which leads to Y_{CER} (Eq. 7) and to t_{CER} experimental value. The initial solute mass ratio (X_0) was obtained through the highest yield extraction; X_p was obtained from Eq. 11 and considering the t_{CER} value. The fluid phase mass transfer coefficient (k_{Ya}) and the solid phase mass transfer coefficient (k_{Xa}) were calculated from Eq. 15 and 16, respectively [5].

$$k_{Ya} = \frac{M_{CER}}{\rho_{CO_2} \cdot S.H. \cdot \overline{\Delta Y}}$$ (15) $\qquad k_{Xa} = \frac{k_{Ya} \cdot \rho_{CO_2} \cdot \Delta Y}{\rho_S \cdot \Delta X}$ (16)

Where:

$$\overline{\Delta Y} = \frac{Y_{CER}}{\ln[Y^*/(Y^* - Y_{CER})]}$$ (17) $\quad \Delta Y = \frac{M_{CER}}{\rho_{CO_2} \cdot S.H. \cdot K_{Ya}}$ (18) $\quad \Delta X = \frac{(X_p + X_K)}{2}$ (19)

III. RESULTS AND DISCUSSION

The results for mean particle diameter are presented in **Table 1**, that also shows the apparent and real density and bed porosity for samples from mesh 20 to 32, used in this work.

Table 1. Particle and bed characteristics

Mesh	Mean diameter x10^3 (m)	da(kg/m^3)	dr(kg/m^3)	e
-20 +32	0.92	350	1410	0.75

Figures 1 and **2** show overall extraction curves (OEC) in accumulated mass of solute against extraction time for the SFE of field horsetail oleoresin. The influence of the solvent pressure shown in **Figure 1** indicate an increase in the extraction rate with solvent pressure, due to the increase in the solvent density, which enhance the solvating power of the CO_2.

The temperature influence presented in **Figure 2**, on the other hand, is more complex. At 200 bar an increase in temperature increases the extraction rate, although the solvent density decreases. It may be explained for the solute vapor pressure, that increases with temperature. Also, at 120 bar an increase in temperature practically did not affect the

extraction rate. This behavior indicates that the level of temperature and pressure studied in this work show the path to indicate the cross over region.
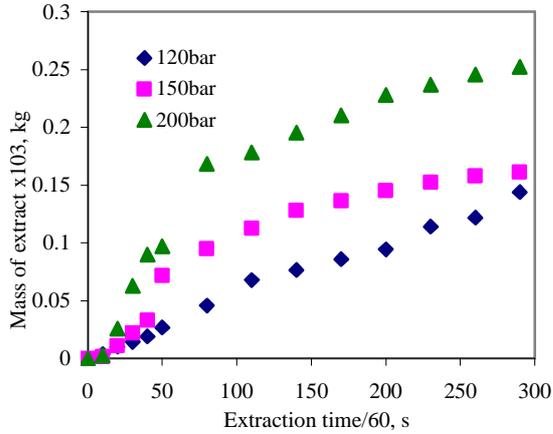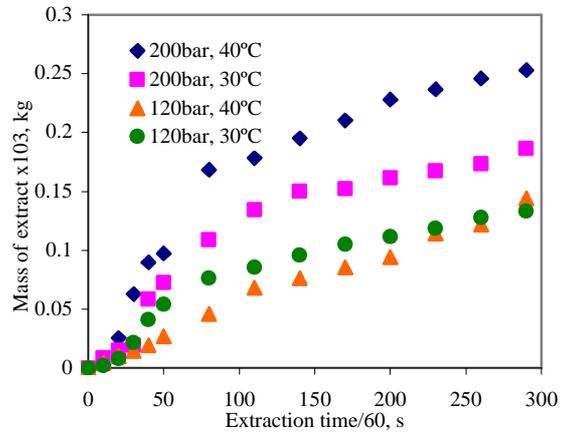

Figure 1. Pressure effect.

Figure 2. Temperature effect.

Mathematical model

Table 2 presents the operational conditions of the extraction curves modeled in this work and the solubility experimental values obtained by Danielski (2002) [6]. **Table 3** shows the kinetic parameters used in the mass transfer model and obtained from the experimental data and the equations listed in section II.

Table 2. Experimental conditions of the field horsetail extraction.

Exp.	T (k)	P (bar)	$QCO_2(x10^5)$ (kgCO$_2$/s)	ρ CO_2 (kg/m^3)	$Y^*(x10^4)$ (kg/kg)
1	313.15	200	4.73	841.47	4.63
2	303.15	150	6.50	847.79	3.31
3	313.15	150	6.18	781.27	2.79

Table 3. Kinetic parameters for Sovová's model.

Exp.	$t_{CER}/60$ (s)	$t_{FER}/60$ (s)	$M_{CER}(x10^8)$ (kg/s)	$Y_{CER}(x10^4)$ (kg/kg)	$X_k(x10^3)$ (kg/kg)	Z	$K_{Ya}(x10^4)$ (s^{-1})	$K_{Xa}(x10^4)$ (s^{-1})
1	268.58	574.32	1.703	3.601	1.608	1.079	5.1024	1.3970
2	88.02	172.73	1.348	2.079	1.829	0.796	5.4520	3.3480
3	89.38	100.80	1.159	1.875	1.205	0.091	6.3689	3.5050

Figures 3, **4** and **5** show a comparison between experimental and the modeled OEC, as a result of the Sovová´s mass transfer model [4]. The X_0 value was obtained from experiment 1 where the extracted solute (3.936x10^{-4} kg de oleoresin) was defined as 90 % of the total amount of oleoresin present in the solid phase, due to the fact that the OEC almost reach the null extraction rate. Therefore, for the amount of solid used in the extraction, 0.035 kg, the value for X_0 was 0.01247 kg oleoresin/kg solid.

In **Figure 3,** related to experiment 1, we observe good adjustment to experimental data, especially in the first part of the extraction curve, i. e., in the period of constant extraction rate (CER), where the solubility data are obtained. The X_o value used to model the extraction curves and represented as continuous line in **Figures 3**, **4** and **5** was the one obtained through experiment 1. After the CER period, the modeled curves presented high

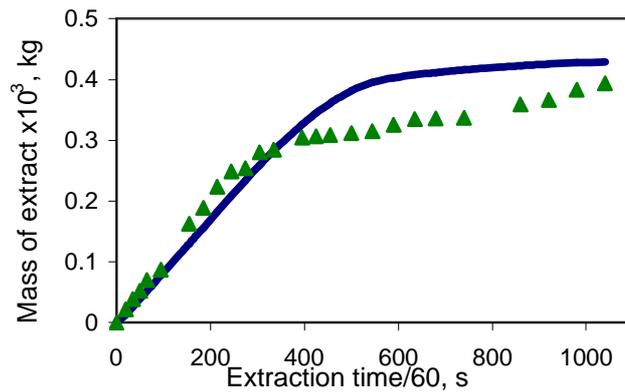**Figure 3:** Comparison between experimental and modeled OEC for exp. 1.
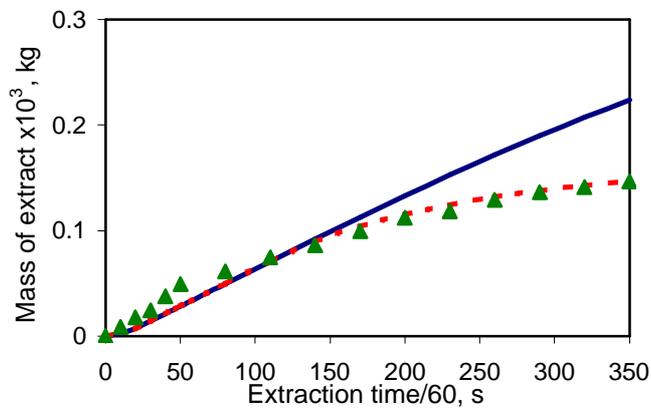? Experimental data ¾ Sovová's model

Figure 4: Comparison between experimental and modeled OEC for exp. 2
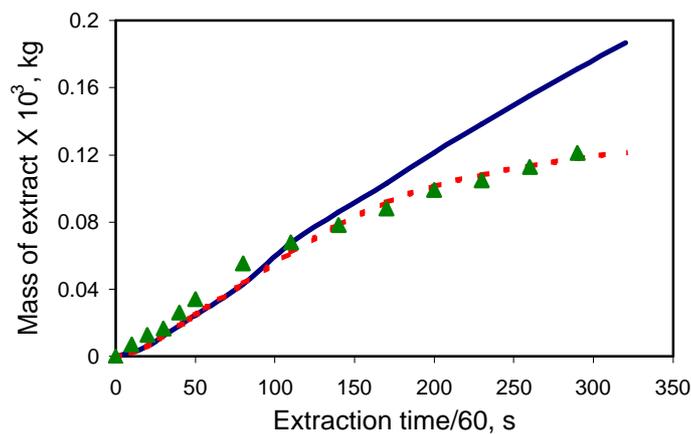? Exp. Data; ¾ Xo=0.01247kg/kg; ----- Xo=0.00412kg/kg.

Figure 5: Comparison between experimental modeled OEC for exp. 3
? Exp.; ¾ Xo=0.01247kg/kg; ----- Xo=0.003384kg/kg.

deviation from experimental values in extractions 2 and 3 (**Figures 4** and **5**). This behavior may indicate that the X_o value (based on exp. 1) is not adequate for all range of temperature and pressure because it represents the amount of extractable oleoresin, a function of solvent density. Because the exp. 1 represents a solvent with high solvating power, the amount of

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extractable oleoresin is high, super estimating the extraction with low CO_2 density (experiments 2 and 3).

Therefore, the X_0 value obtained based on high density solvent may not be adequate for low density extractions. Then to evaluate the X_0 influence on OEC model, **Figures 4** and **5** also present modeled curves (dashed lines) using X_0 values obtained specifically according to the experiment density. The dashed lines show a much better agreement to the experimental curves. Lower X_0 values indicate a reduction of the CER period, increasing the influence of the difusional period.

CONCLUSION

The experimental results for the SFE of field horsetail oleoresin with supercritical CO_2 shown an increase in the extraction yield with operating pressure from 120 to 200 bar. The effect of temperature indicate an increase in the extraction rate with temperature at 200bar, showing the importance of the solute vapor pressure in the solubilization process. The Sovová's model [4], used for the description of the OEC, represented the curves adequately, mainly in the CER period. For the description of the decreasing extraction rate, where the diffusion mechanism is important, the model indicate the importance of the adequate definition of the X_0 value, related to the solvent density, in order to allow a good adjustment to the experimental data.

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