EXTRACTION OF THE VOLATILE OIL FROM *Croton zehntneri* PAX ET HOFF WITH PRESSURIZED CARBON DIOXIDE: MODELING OF THE OVERALL EXTRACTION CURVES

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ABSTRACT. *Croton zehntneri* Pax et Hoff is a native plant from northeastern Brazil, popularly known as "canela-de-cunhã". It is often used in folk medicine as an infusion for the treatment of nervous and gastric disturbs, and also as an antispasmodic for the intestinal musculature. In food and beverages, the leaves and branches of *Croton zehntneri* Pax et Hoff are used as flavoring agents. In this work, the overall extraction curves for the system *Croton zehntneri* Pax et Hoff plus pressurized carbon dioxide, obtained at a pressure of 66.7 and temperature of 15°C were modeled. The models used were: empirical, Goto et al, Tan and Liou, Martinez et al and Sovová. The models that best described the overall extraction curves were the Goto et al, Martinez et al and Sovová.

Keywords: SFE; *Croton zehntneri*; mass transfer modeling

INTRODUCTION

Supercritical extraction from solid has being extensively studied and several results were reported in literature. In general, the experimental data were reported as overall extraction curves (OEC: mass of extract or percentage of extraction against CO_2 mass or CO_2 mass divided by the mass of solid matrix). This knowledge is required in order to effectively design SFE processes. Several models are available in literature to describe the OEC; nonetheless, none is yet accepted as a general model for any system. The reason is that the OECs are a strong function of the solid substratum, thus, a model that is indicated for one system maybe is not satisfactory to describe the mass transfer phenomena for another system. Thus, the objective of this work was to compare the adequateness of the following literature models to describe the system: *Croton zehntneri* Pax et Hoff plus CO_2.

MATHEMATICAL MODELS: A BRIEF DESCRIPTION

The selection of the models to describe the OECs of the system *C. zehntneri* + CO_2 was based on: (i) the physical meaning of the parameters of a specific model (Sovová's model); (ii) the simplicity of the model (empirical and Tan and Liou models); (iii) the fact that the model was used for a similar system (Goto et al model, which was applied SFE from mint leaves); and (iv) the capability of the model to describe various shape of the OECs (Martinez et al). Follows a brief description of each model used in this work.

The model of Sovová

The oils 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 [1] proposed a model in which the solute is divided in two fractions: the easily accessible solute (Xp) and the hardly accessible solute (Xk). During SFE process Sovová [1] 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 [1] 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.

The model of Goto et al

Goto et al. [2] define the solid particle as a plain plate with defined thickness and much lower than its other dimensions. So, mass transfer occurs only between the two greatest particle surfaces, which can be treated as a porous mean. Hence, Goto et al. [2] differentiate the solute concentration inside the particle from the concentration in the pores, and define 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 desorption.

The model of Martínez et al

The elaboration of the model of Martínez et al. [3] 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 [4] 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. The model of Martínez et al. [3] proposed the logistic growth equation to describe the same function. After solving the mass balance equations for the system, Martínez et al. [3] obtained an equation for the extraction curve. The model of Martínez et al. [3] 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.

The empirical model

The empirical model is based on Langmuir´s equation for kinetics for microbial growing. This equation was uses by Esquível et al. [5] to describe OECs. The modeling is quite simple, with only one adjustable parameter.

The model of Tan and Liou

Tan and Liou [6] 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 of the temperature. Tan and Liou [6] neglected the axial dispersion and the intra-particle diffusion, so they could reach an analytical solution for the mass balance inside the extraction bed.

MATERIALS AND METHODS

The overall extraction curves of *C. zehntneri* volatile oil obtained in the kinetic experiments were adjusted with the models of Sovová [1], Goto et al. [2], Martínez et al. [3], Tan and Liou [6] and the empirical model, The model of Martínez et al. [3] 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, there were obtained parameters that helped to describe the kinetics of the process, according to each model.

RESULTS AND DISCUSSION

Table 1 shows the parameters used to model the OECs. The parameters fitted to the various models are in Table 2, 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}.

Figures 1 and 2 show the comparison between the experimental and modeled OECs: As can be observed, the models of Sovová [1], Goto et al. [2] and Martínez et al. [3] provided the best fits to experimental data, which is confirmed by the SQDs in Table 2.

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 [1], 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 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 [1] 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. [2] and Martínez et al. [3] 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 2, the values of t_{mi} for the model of Martínez et al. **[3]** are negative. This means that the rate of the extraction is always decreasing, having its maximum value at the initial instant.

Table 1: 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 pf 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 2: Parameters fitted to and sums of squares of the residues

		Experiment 1		Experiment 2	
Model		Parameter	SQD$\times10^6$	Parameter	SQD$\times10^6$
Empirical	k (s)	3612	1.391	2406	3.447
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.	ϕ (-)	6.96	0.153	14.29	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

The empirical model is able to describe OECs with a hyperbolic shape, which is not the case in 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 **[6]**. It can be clearly observed in the OEC for experiment 2, in Figure 2, that the extraction yield becomes higher than 100% for the model of Tan and Liou **[6]**. 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 is problems like the one observed for the OEC for experiment 2.

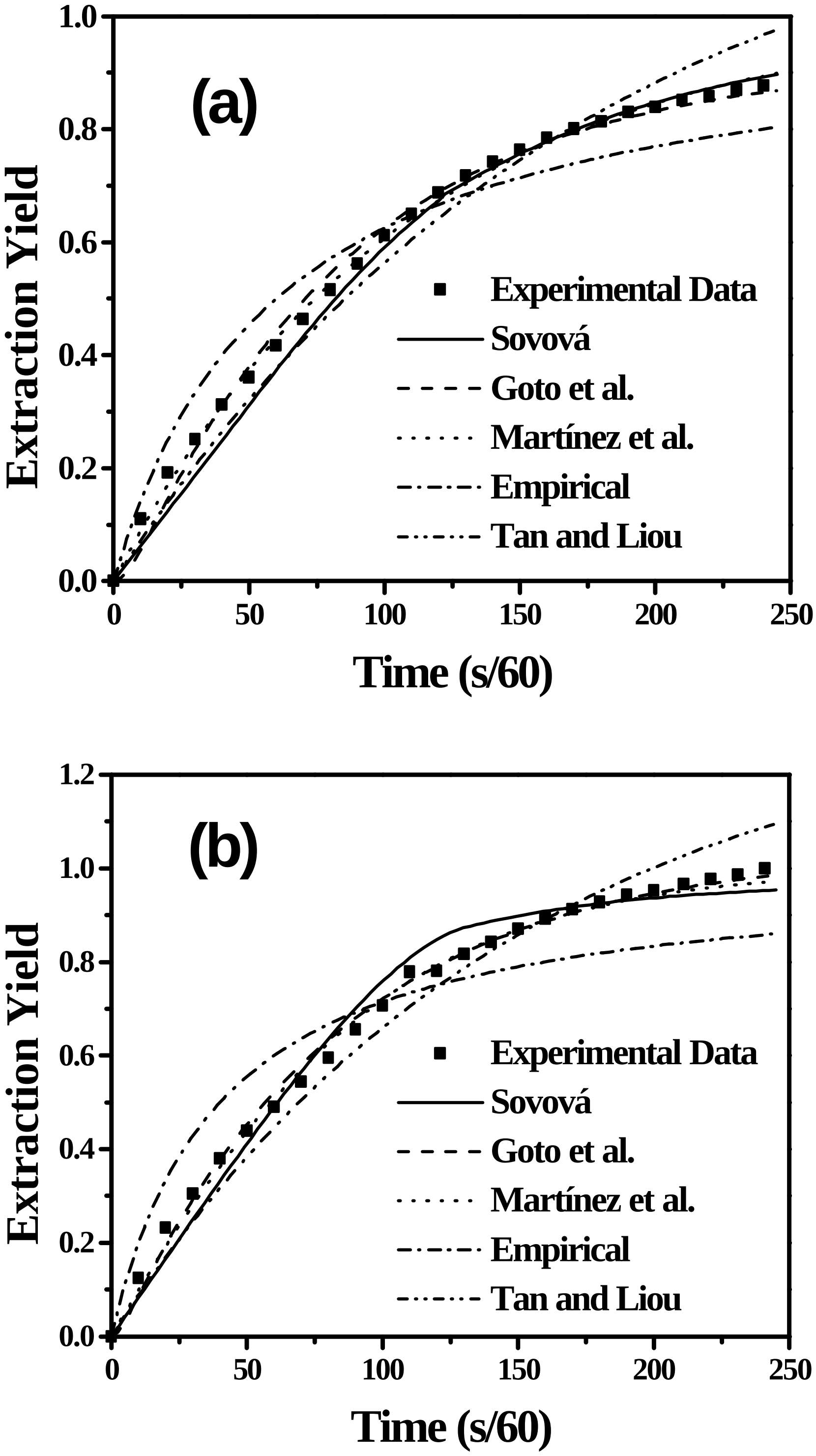

Figure 1. OECs for SFE of *Croton zehntneri* Pax et Hoff oil: (a) Experiment 1; (b) Experiment 2

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