Mathematical Modeling of the Extraction Process Essential Oils *Schinus terebinthifolius Raddi* Using Supercritical Fluids

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***Schinus terebinthifolius Raddi* is a plant rich in nutrients and is used medicinally and industrially. Supercritical oil extraction from *S. terebinthifolius* can result in higher value-added products. Mathematical models (Sovová and Esquível) are used to describe the behavior of supercritical extractions. This study aims to compare both models in terms of yields in conditions of 223 bar and 50°C. We observed that the model proposed by Sovová provided good reproducibility and representativeness.**
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Brazil has abundant plant species with great economic and medicinal potential. Aroeira (*Schinus terebinthifolius Raddi*) is one example of a nutrient-rich plant, which is used both medicinally and industrially due to the chemical components and carotenoids.

Several extraction methods of essential oils can be used. However, one of the most promising is supercritical extraction because it leaves no trace of the solvent in the product, has excellent quality and also because environmental legislation prohibits waste of solvents in industrial processes. According to Brunner [1], no substance is a supercritical fluid, but it can become one by increasing heat and pressure beyond the critical point.

Thus, a supercritical fluid is a pure fluid above such characteristics. The most used solvent in this type of extraction is CO_2. It's safer and has a lower cost when compared to other fluids that are usually expensive or have low access or leaves waste after extraction.

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Sovová's model [2] considers that the material to be extracted contains intact innercells and the outer cells are ruptured, wrapped in a spherical greenhouse. It also takes into account the solvent-solute balance inside the cell during pressurization, with the concentration unchanged in the intact cell [3].

Esquivel [4] proposed a model in order to expose the extraction curves that are easily modeled using an empirical equation for the experimental curve fit, and this empirical model does not consider solute-matrix interactions [5]. This paper aims to compare oil extraction yields provided by the mathematical models proposed by Sovová and Esquível [2,4] for the oil extraction of *Schinus terebinthifolius Raddi*.

Methods

Data and Tools

The data used herein is related to an extraction process performed at 223 bar and 50°C. The Microsoft Excel Solver® was used to carry out the calculations, and the curves were plotted in a Microsoft Excel spreadsheet.

For modeling the extraction curves of *Schinus terebinthifolius Raddi* oil, two mathematical models were used: Sovová [2] and Esquivel [4].

Both require the proper determination of process variables and parameters, such as solvent density, particle density (ρS), particle diameter, solubility, bed porosity (ε), bed height, and extractor radius obtained for the condition of interest (223 bar and 50°C). Table 1 presents the experimental data.

Table 1. Experimental data used for extraction curve modeling.

Temperature	323.15 K
Pressure	220.08 atm
QCO_2	23.13 mL/s
ε (Porosity)	0.3231
Rs	0.50 g/mL
Dp	0.00168m
rCO_2	0.84 g/mL
Bed height	0.24400 m
Solubility	3.40 Kg solute/ m^3 solvent
Bed diameter	0.01350 m
Solvent flowrate	1.38775 L/min
Sample mass	10.00310 g
%(w)solute	3.9804
%(w) solute inaccessible	30.83
elim	3.98
Cross-sectional area	0.00014 m^2
Solvent molar mass	44 g/gmol
Sample solute mass	0.39817 g
Solute free sample mass	9.60493 g
Solute inaccessible mass	0.12277g

Extraction Curves

A typical extraction curve consists of three regions (Figure 1).

Each region is characterized by the predominance of one or more mass transfer phenomena. The first part of the curve is a straight line that indicates a constant extraction rate, i.e., governed by convective mass transfer between the surface of the solid and the solvent.

The next region is a transitional, where the extraction rate drops rapidly as soon as a change from the convection predominates over diffusion, where the later control mass transfer and the slope of the curve decreases and becomes asymptotic [1].

Sovová's Model [2]

This model considers a pseudo-steady state, in which the temperature, pressure, and solvent velocity are kept constant. There is an axial flow of the solvent with superficial speed through a fixed bed of cylindrical cross-section, and the solute is inside the plant cells. We also assumed that pretreatment of the material, such as grinding, which increases the contact surface between solid and solvent, separates the total amount of available solute into two parts, one of easy access and other of difficult access. Each extraction curve region was determined using the following equations [2]:

$$CER = \left(\frac{X_k \tau}{Z}\right)\left(1 - e^{-Z}\right) \quad \tau < \tau_m \qquad (1)$$

$$FER = \left(\frac{X_k}{Z}\right)\left(\tau - \tau_m e^{(Z_w - Z)}\right) \quad \tau \le r < \tau_n \qquad (2)$$

$$DC = X_0 - \left(\frac{X_k}{KZ}\right)\ln\left(1 + e^{(r_0 KZ)} - 1\right)\frac{e^{(K(\tau_m - \tau))}}{r_0} \quad \tau > \tau_n \qquad (3)$$

For instance, τ is the criterion to define the dominant region in a specific time interval of the extraction process.

Esquível's Model [4]

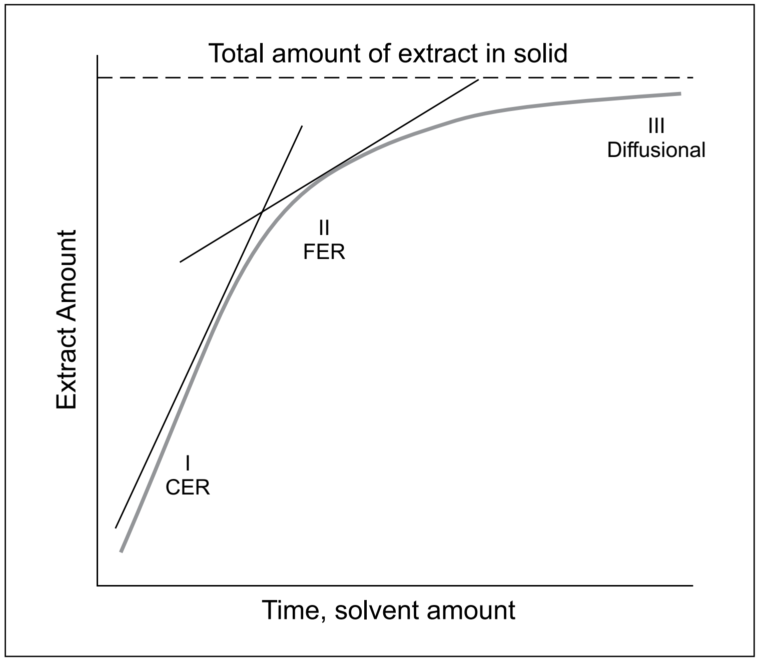
Monod model uses the microbial growth kinetic equation proposed to represent the microbial extraction yield as a function of extraction time [5]. This model describes the extraction curves, however, it does not consider the solute and solid matrix interactions. It is simpler than Sovova's model [2], with only two parameters to be determined [6]. The following equation describes it:

e=e_lim (t/(b+t)) (4)

The character "e" is the ratio of the mass of oil recovered in time t(s) and e_limis the e value for infinite extraction time.

We did a a regression with the experimental data, and the parameters that gave the maximum yield and minimum error were determined.

Figure 1. Extraction curve with two straight lines adjusted.



CER: Constant Extraction Rate Stage - transfer predominance mass due to fluid phase convection. FER: Falling Extraction RateStage - convective effects on stage fluid, and solid-phase diffusions determine the speed of the process. DC: Almost Zero Extraction Rate Stage - the predominance of diffusional effect.

Results and Discussion

The great extraction' yield was obtained at 50°C 223 bar (Sovová model) (Figure 2), diferently from Esquível model [4] (Figures 3, 4). At the same condition, the curve presents precisely the behavior described by Sovová in the CER region, passing through a transition range until it stabilizes at a particular value (elim).

The beginning part of the curve represents a line that indicates a constant oil extraction rate. At this time, a surface oil layer surrounds the solid matrix particles. At this point, the extraction is characterized by convective mass transfer between the surface of solid and solvent. The constant extraction rate region follows a transition stage, during which the extraction rate drops rapidly. Therefore, the diffusional process begins to control the mass transfer, as the solvent finds free space for the penetration in the matrix, product solubilization, and subsequent diffusion of the oil-solvent mixture to the particle surface.

Almost no extraction performed in the last region. At this level, the slope of the curve decreases, and the plot approaches the value that represents the theoretical content of the extractable oil of *Schinus terebinthifolius Raddi* [2].

In addition, the parameters kf (fluid-phase mass transfer coefficient), Z (fast extraction period parameter), W (slow extraction period parameter), Yr (solubility) and ks (solid-phase mass transfer coefficient) were generated for the model Sovová [1] and estimated for the previous conditions using regression analysis to minimize the square of the difference between the experimental values and calculated by the model. Mass transfer coefficients of the solid and fluid phases were calculated from these parameters. For instance, the parameter Xk

Figure 2. %Yield (Experimental and model based on Sovová [2,3]).

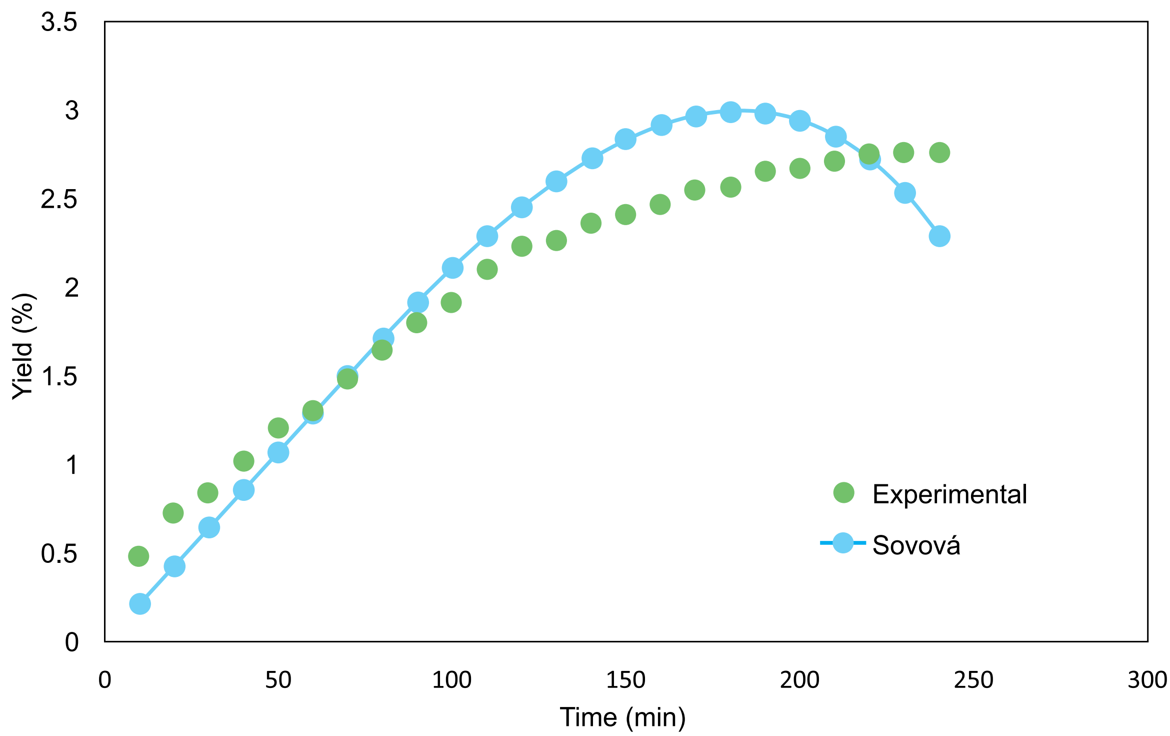


Table 2. Estimated parameters and mass transfer coefficients.

Xk	Z	W	yr	kf (m/s)	ks (m/s)
0.013	1.296	0.059	0.0088	0.0004	0.0009

Table 3 presents the algorithm parameters determined by the regression according to the Esquivel model [4].

Table 3. Parameters from the linear regression of the experimental curve.

b (calc)	59.11
e_{lim} (calc)	3.04
Equation	e= 3.039 (t/(59.1134 + t)

New parameters needed to be estimated due to the existence of residuals in the calculation of the model (Table 4).

Table 4. New parameters.

b (calc)	104.13
e_{lim} (calc)	3.98
Equation	e= 3.9804(t/(104.1301 + t)

Figure 3. Experimental *vs*. simulated data using Esquivel model [4].

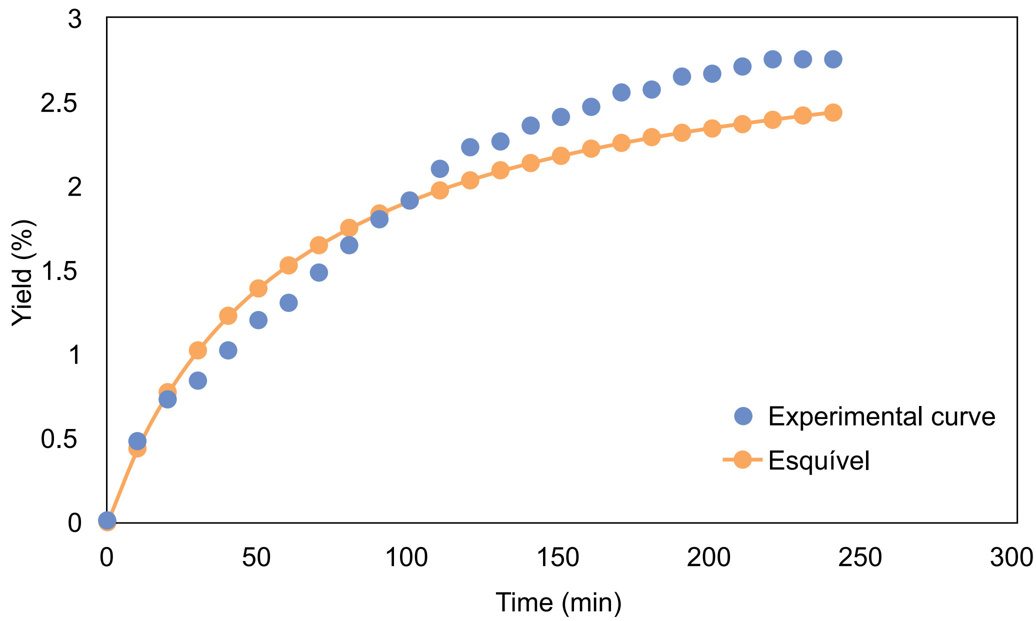
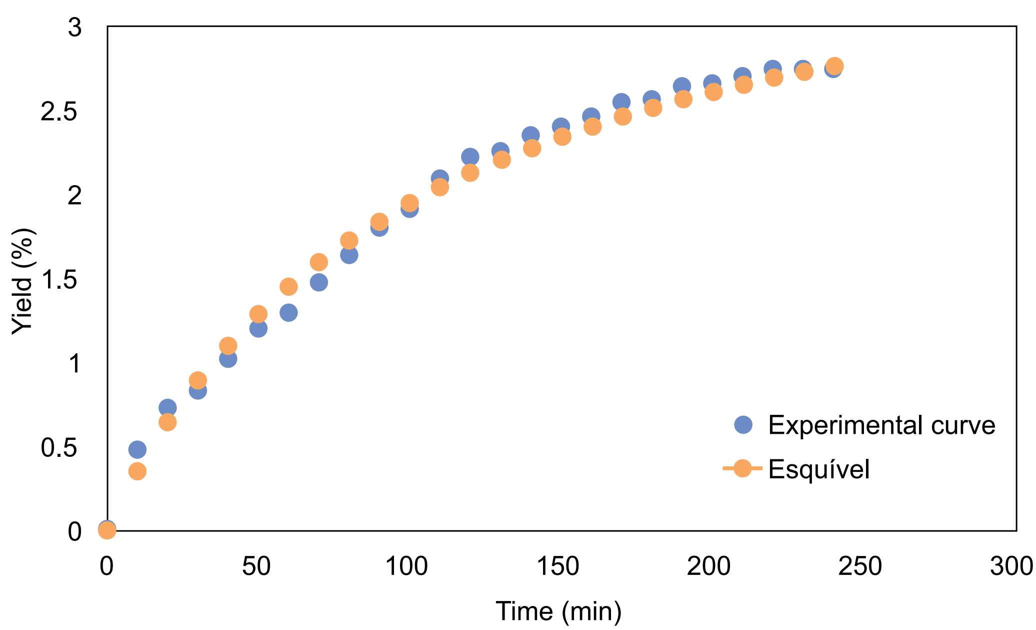


Figure 4. Experimental *vs*. simulated data through corrected Esquivel [4].



(inaccessible solute mass within the solid phase particles) presented the lowest values. So, most of the solute has been extracted by the previous two phases. Table 2 shows the mass transfer coefficients for the pressure of 223 bar and 50°C.

Conclusions

The present study allowed an analysis of the extraction curves of *Schinus terebinthifolius Raddi* (Aroeira) oil using two mathematical models [2,4]. Subsequently, the figures observations concluded that Sovová's model has a higher yield than the experimental one. After 150 minutes, Sovová curve surpasses the experimental curve, due to the constant oil extraction rate. However, the values are not discrepant, having a small margin of error. Esquivel's mathematical model is less accurate since it is a simplified model using only two parameters, neglecting the axial and radial dispersions.

Therefore, the most accurate *Schinus terebinthifolius Raddi* oil extraction curve under conditions of 223 bar and 50°C, is that presented by the Sovová model.

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