

EXTRACTION OF *Coriandrum sativum* ESSENTIAL OIL WITH PRESSURIZED CARBON DIOXIDE

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Abstract. In this work, two different models presented in the literature, proposed by Esquível et al. [1] and Martínez et al. [2], were used to describe the overall extraction curves for the supercritical extraction of *Coriandrum sativum* oil using CO₂ as solvent. The experimental data used for modeling purposes were obtained at 20, 30 and 40 °C and 120, 150 and 200 bar, indicating a variation of solvent density between 719.10 and 937.60 kg/m³. The maximum extraction yield was 0.91% (w/w), obtained at the highest solvent density, i. e., at 200 bar and 20 °C. The models investigated in this study satisfactorily represented the experimental data and the lowest quadratic mean errors (magnitude of 10⁻⁴) were achieved when using the logistic model by Martínez et al. In order to perform the essential oil fractionation, the extract samples obtained at 200 bar and 20 °C were adsorbed in silica-gel and desorbed using CO₂ with a loading ratio of 1:4 (oil:silica-gel) at temperatures of 20 and 40 °C and pressures of 120 and 200 bar. The kinetics of the desorption curves showed that the effects of increasing vapor pressure with increasing temperature were responsible for shorter desorption times. The chemical analysis of the obtained samples is a subject under investigation and will be presented in the near future.

Keywords : *Coriandrum sativum*, kinetics, modeling, supercritical fluid extraction.

1. Introduction

The supercritical fluid extraction process (SFE) is a well known technique used to extract and fractionate natural substances from plant materials like seeds, flowers, roots, leaves and other solid substrates. Among several supercritical fluids used for extraction, supercritical CO₂ (SCCO₂) is the most widely used because it is nontoxic, non-flammable, non-corrosive and easy to handle, allowing supercritical operation at near room temperature. In addition, it is relatively cheap and readily available in bulk quantities with a high degree of purity. Thus, SCCO₂ extraction is a very attractive technique when products of high quality are desired [3, 4].

Extraction processes in general must be optimized in order to obtain the desired products and minimize the amount of solvents used at relatively short time operations. Thus, the knowledge of SFE parameters such as solubility and mass transfer coefficients, as well as the solvent density dependence, are required for an appropriate mathematical representation of SFE processes. These parameters are directly related to the thermodynamic and kinetic aspects of the process. The thermodynamic aspects are referred to the solute concentration in the supercritical phase (solubility) as a function of oil composition and solvent density. On the other hand, kinetic aspects are related to the rate of solute (oil) transferred from the solid particles to the supercritical solvent phase through dissolution or desorption. The solute/solvent mixture diffuses to the solid surface and finally moves along the stagnant film around the particle to the bulk fluid phase [4].

There are several mathematical models available in the literature to correlate overall extraction curves (OECs) for the SFE of natural materials, especially oils and essences. Among the available models in the literature, many of them are based on differential mass balance integration, such as the Sovová model [5], the logistic model (LM), presented by Martínez et al. [2] and the desorption model proposed by Tan and Liou [6]. Esquível et al. [1] proposed one empirical model, where an analogy to the Monod kinetics equation for

microbial growth was used to describe the OECs. Several mathematical models have been intensively used in the SFE of different natural products [7-11].

In this work, two mathematical models discussed above [1, 2] were considered for correlating SFE experimental data of *Coriandrum sativum* oil. The main goal was to evaluate if the models used in this study were able to fit the experimental extraction data by comparing the deviations obtained at different extraction conditions, i.e., at 20, 30 and 40 °C and at 120, 150 and 200 bar. Additionally, ad-/desorption experiments were performed at 20 and 40 °C and pressures of 120 and 200 bar.

2. Materials and Methods

2.1 Experimental

The raw material (*C. sativum* seeds) was obtained directly from local producers. The material was first milled and the fraction between 20-32 mesh was kept sealed under vacuum prior to the realization of the experiments. CO₂ (99.5% purity) was purchased from Linde Industrial Gases.

The SFE experiments with high-pressurized CO₂ were conducted using a dynamic extraction unit already described in the literature [7] (Figure 1) and a mass of approximately 30 g of milled seeds was used to form the fixed bed of particles. The experimental runs were divided in two groups: (1) OEC runs, where the experiments were performed with oil samples collected at pre-established time intervals and operational conditions to represent the extraction kinetics, and (2) ad-/desorption runs, where silica-gel (Vetec, Brazil) was loaded with the obtained oil samples and pressurized CO₂ was used in order to achieve desorption of the oil components.

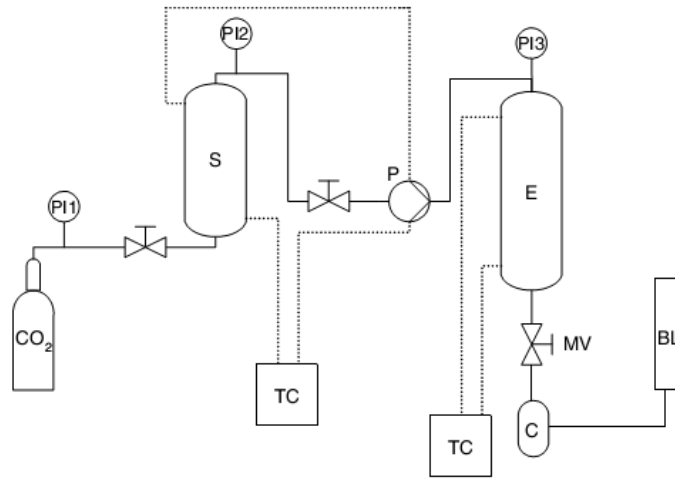


Figure 1. SFE unit: CO₂ reservoir; S (surge tank); P (pump); E (extractor); TC (thermostatic baths); MV (decompression valve); C (sample flask); BL (rotameter), PI1, PI2 and PI3 (pressure gauges)

2.2 Mathematical modeling

The experimental data obtained were fitted to the Esquível et al. [1] and LM [2] models using MATLAB 7.0 (The MathWorks Inc., Natick, MA, USA).

The model presented by Esquível et al. [1] can be represented by Eq. 1:

$$m_{ext}(h = H, t) = X_0 F \left[\frac{t}{b_e + t} \right] \quad (1)$$

where m_{ext} is the mass of oil extracted (kg); F represents the mass of solid material (kg); H is the bed height (m); t corresponds to the extraction time (s); X_0 is the initial solute mass ratio in the solid phase (kg/kg) and b_e is an adjustable parameter (s).

The logistic model proposed by Martínez et al. [2] is based on the mass balance of the extraction bed and neglects the accumulation and dispersion in the fluid phase because these phenomena present no significant influence on the process when compared to the effect of convection. The LM model can be applied to the solute transfer to the fluid phase and assumes the solute represented by a single group of compounds. The OECs can be represented by Eq. 2 [2]:

$$m_{ext}(h=H, t) = \frac{m_t}{\exp(bt_m)} \left\{ \frac{1 + \exp(bt_m)}{1 + \exp[b(t_m - t)]} - 1 \right\} \quad (2)$$

where m_{ext} is the mass of oleoresin extracted (kg); m_t is the total initial mass of solid in the extraction bed (kg); t is the extraction time; b and t_m are the adjustable parameters expressed in (s^{-1}) and (s), respectively.

3. Results and Discussion

The SFE experiments were performed at different temperature and pressure levels, which are presented in Table 1. For comparison purposes, the CO₂ flow rate was stipulated as 2.00 g/min. Table 1 also presents the extraction yields obtained at different operational conditions.

Table 1. Operational conditions investigated and extraction yields obtained in the SFE experiments.

| T (°C) | P (bar) | CO ₂ density ^a (kg/m ³) | Extraction yields (%, w/w) |
|--------|---------|--|-------------------------------|
| 20 | 120 | 878.60 | 0.43 |
| | 150 | 904.42 | 0.60 |
| | 200 | 937.56 | 0.91 |
| 30 | 120 | 809.73 | 0.38 |
| | 150 | 849.79 | 0.53 |
| | 200 | 890.87 | 0.82 |
| 40 | 120 | 719.10 | 0.33 |
| | 150 | 781.27 | 0.37 |
| | 200 | 841.47 | 0.76 |

^a - according to Angus et al. [12].

The data presented in Table 1 showed that, for all cases evaluated, the highest extraction rates and higher extraction yields were obtained at higher solvent density conditions (lower temperatures at constant pressure). The highest extraction yield (0.91 %) was obtained at 20 °C and 200 bar (highest solvent density). The literature shows extraction yields of approximately 1.00 % (w/w) [13].

The results presented in Table 1 can be visualized in Figure 2, where the presented isotherms did not reach the crossover region (inversion of isotherms). This is an indication that, for the conditions evaluated, the solvent density presented a higher effect in the solute solubilization than its vapor pressure.

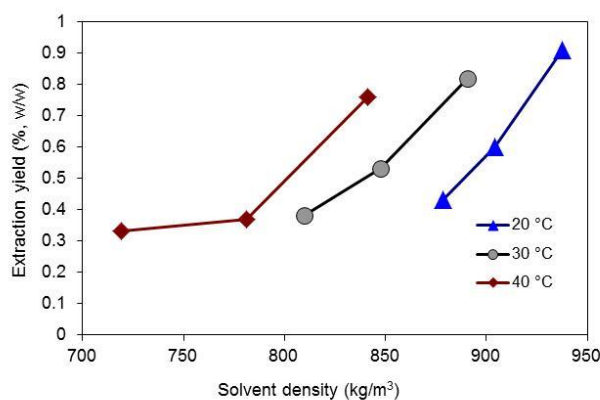


Figure 2. Extraction yields obtained at different solvent densities and temperatures.

The mathematical modeling of the system *C. sativum* oil + SCCO₂ was carried out using the models proposed by Esquivel et al. [1] and Martínez et al. (LM) [2], as previously presented. Figure 3 show the modeling results obtained at 20 and 40 °C and at 120 and 200 bar, where black lines represent the data generated by the LM model [2] and blue lines represent data generated by the model of Esquivel et al. [1].

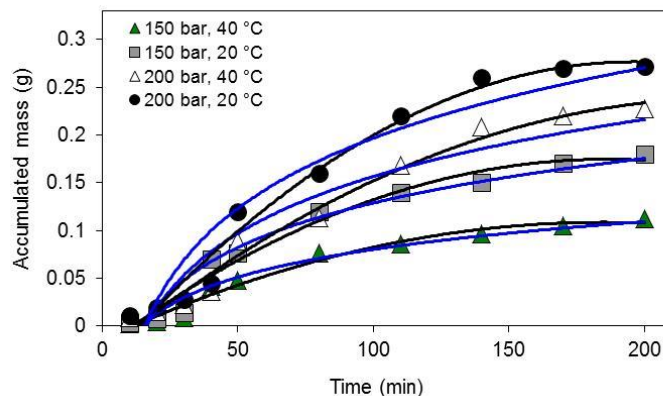


Figure 3. Modeled OECs obtained at different operational conditions: blue lines represent data generated by the model of Esquivel et al. [1] and black lines represent data generated by the LM model [2].

Table 2 presents the values for the adjustable parameters obtained for the LM (b , t_m) and Esquivel et al. (b_e) models. In addition, Table 3 presents the analysis of the mean quadratic errors (MQEs) between the experimental data and the modeled results highlighted in Figure 3. In general, larger errors were obtained when the pressures of the extraction solvent and densities were higher. The LM model [2] presented the smaller MQE values under the conditions investigated.

Table 2. Adjustable parameters obtained for the investigated mathematical models

| P (bar) | T (°C) | $b \times 10^3$ (min^{-1}) | t_m (min) | b_e (-) |
|------------|-----------|--|----------------|--------------|
| 150 | 20 | 5.67 | 222.52 | 1825 |
| | 40 | 5.73 | 231.40 | 2803 |
| 200 | 20 | 7.35 | 210.23 | 3230 |
| | 40 | 5.92 | 229.20 | 2934 |

Table 3. MQEs obtained in modeling the SFE of *C. sativum* oil ($\times 10^4$)

| P (bar) | T (°C) | Esquivel et al. [1] (-) | Martínez et al. [2] (-) |
|------------|-----------|----------------------------|----------------------------|
| 150 | 20 | 0.82 | 0.21 |
| | 40 | 0.71 | 0.15 |
| 200 | 20 | 1.04 | 0.28 |
| | 40 | 1.03 | 0.22 |

The evaluation of the SFE process in the extraction of *C. sativum* oil followed with the analysis of ad-/desorption using silica gel as adsorbent and SCCO₂ as solvent. Crude oil samples obtained at 20 °C and 200 bar (experiments performed in triplicate) were stored in a single amber glass flask for the following experiments. The samples obtained under these conditions were used because under these conditions the highest extraction yield was obtained (Table 1). 20 g of silica gel were previously mixed in a beaker with a 25% loading, i. e., 5 g of crude oil. The curves presented in Figure 4 show the results of the desorption curves obtained at two different pressure levels at 20 and 40 °C.

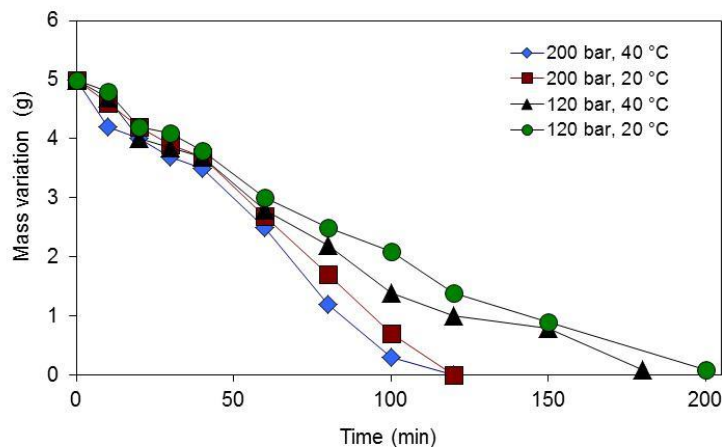


Figure 4. Desorption curves obtained under the conditions of 120 and 200 bar at 20 and 40 °C.

Through the analysis of Figure 4, it was possible to observe that the experiments conducted at 200 bar reached approximately 99.5% oil recovery (desorption) after 120 minutes. At 120 bar, the desorption time was higher, reaching 200 minutes of process at 20 °C (and considering a constant CO₂ flow of 3.00 g/min). The desorption was more efficient at higher pressure and temperature levels (200 bar, 40 °C), which led to the conclusion that the vapor pressure of the oil presented a considerable relevance in the evaluation of the process.

During the SFE of *C. sativum* oil, it was observed that the vapor pressure presented no effect on the predominant increased density of the solvent (Table 1 and Figure 2). However, during the desorption process the opposite was observed: the effect of increasing vapor pressure of the solute with increasing temperature at constant pressure was responsible for shorter desorption experiments under the conditions evaluated. This is likely due to the different interactions existing between the crude oil and the structures of solids involved, i.e., the vegetable matrix in the case of SFE and silica gel in the desorption step.

Thus, the desorption process could be evaluated quantitatively for the SFE of *C. sativum* essential oil. However, experiments of ad-/desorption can only be justified when the chemical analysis of each sample obtained is carried out, intending to achieve the selective fractionation of a particular compound or class of compounds that may present some property/activity of interest. The chemical analysis of the desorpted samples and the remaining residues in the solid phase (adsorbent) are expected to take place in a near future.

4. Conclusions

This work investigated the SFE of *C. sativum* oil with CO₂ as solvent at 20, 30 and 40 °C and 120, 150 and 200 bar, where the maximum extraction yield obtained could be corroborated with literature data. Additionally, the applicability of two different mathematical models was tested, and the mean quadratic errors (MQEs) obtained could be compared with the MQEs presented in the literature. The LM model [2] presents two adjustable parameters and generated lower MQE values. Thus, it was considered the most suitable to describe the extraction kinetics of the SFE of *C. sativum* oil with SCCO₂. The ad-/desorption process using silica gel as adsorbent and CO₂ as solvent was also investigated. However, a desorption process may be considered viable only after a complete characterization of the samples obtained.

Acknowledgements

The authors would like to thank CNPq and FACEPE (Brazil) for the financial support.

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