

# MODELLING AND SIMULATION OF EXTRACTION OF MARJORAM ESSENTIAL OIL USING SUPERCRITICAL CO<sub>2</sub>

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This work develops a model that can be used to explore the recovery of Marjoram essential oil from marjoram leaves. The model can be used for semi-continuous isothermal and isobaric supercritical extraction processes. Concentration profiles in both phases are shown and can be observed at any section of the extractor and at any time of the process. The model should be useful for examining extractor configurations and developing extraction profile alternatives.

## INTRODUCTION

Essential oils are complex mixtures of a great number of different components that can be divided in three main groups: terpenic hydrocarbonates, oxygenated hydrocarbonates and sesquiterpenoids. Marjoram is one of the most popular flavoring material used in food, pharmaceutical and perfumes. The major component of marjoram essential oil is *cis*-sabinene [1]. Conventional extraction methods for obtaining these essential oils involve chemical solvents that can contaminate end products. Essential oil extractions of rosemary, basil and marjoram leaves using supercritical carbon dioxide were reported by Reverchon et al. [1-3]. Reverchon et al. [2] and Reverchon [4] model the extraction from herbaceous matrices with supercritical CO<sub>2</sub> that consider internal and film resistances, focusing the particle geometry as an important factor for fitting experimental data. Roy et al. [5] in the extraction of ginger root with supercritical CO<sub>2</sub> used the shrinking core model with the effective diffusivity and solubility parameters as fitting parameters. Goodarznia and Eikani [6] presented a two-phase model, base of our work, and reported specific data for the extraction of basil essential oil using supercritical CO<sub>2</sub>. However, much remains to be understood on the time-dependent extraction behavior and the mass transfer mechanism of essential oils extraction. In this paper, a mathematical model is developed and concentration profiles for the solid and supercritical phase are analyzed. Further, concentration profiles of the extractor are calculated.

## Mathematical model

Extraction processes from vegetable matrices such as leaves involves the release of solute from the porous or cellular matrix into a solvent. The solutes fixed or trapped in a matrix by physical or chemical forces must be released and transferred to the supercritical fluid by dissolving. Then, the dissolved solute diffuses through the matrix to the surface of the particle. Finally, they move across a film around the particle to the bulk fluid-phase. The dissolution kinetics involved in the model may depend on the ratio of the solute content to the saturation concentration in the fluid phase, the bound state of the solute on a matrix and the association with coexisting materials [7]. The mechanism in which the essential oil is transferred from a condensed state into the gaseous state (supercritical solvent) was discussed by Saldaña et al. [8].

A two-dimensional, unsteady state mathematical model was used for a fixed bed extractor (**Figure 1**). Essential oil content of the leaves was assumed to change with time and distance along the axis of the extractor. Flow rate, temperature, pressure and bed properties were regarded as constant. For this case, the material balances for an element of bed are given by:

**Solid phase:** ( $C_s$ : Solid phase oil concentration)

$$\frac{\partial C_s}{\partial t} = \frac{2}{Pe_p} \frac{L}{R} \left[ \frac{1}{x^2} \frac{\partial}{\partial x} \left( x^2 \frac{\partial C_s}{\partial x} \right) \right]$$

(1)

$Pe$ : Peclet number,  $R$ : seed radius,  $x$ : dimensionless radius

Initial conditions:

$$\tau = 0 \quad 0 \leq \xi \leq 1 \quad C_s = C_{s0}$$

(2)

Boundary conditions:

$$\tau > 0 \quad \xi = 0 \quad \frac{\partial C_s}{\partial x} = 0$$

(3)

$$\tau > 0 \quad \xi = 1 \quad -\frac{\partial C_s}{\partial x} = Bi(C_{fs} - C_f)$$

(4)

$C_{fs}$ : Oil concentration at particle surface

**Supercritical phase:** ( $C_f$ : CO<sub>2</sub> phase oil concentration)

$$\frac{\partial C_f}{\partial t} = \frac{1}{Pe_b} \frac{\partial^2 C_f}{\partial Z^2} - \frac{\partial C_f}{\partial Z} + \frac{6(1-e)L}{eR} \frac{Bi}{Pe_p} (C_{fs} - C_f)$$

(5)

$Z$ : Dimensionless axial coordinates,  $Bi$ : Biot number,  $e$ : void fraction

Initial conditions:

$$\tau = 0 \quad 0 \leq Z \leq 1 \quad C_f = 0$$

(6)

Boundary conditions:

$$\tau > 0 \quad Z = 0 \quad C_f - \frac{1}{Pe_b} \frac{\partial C_f}{\partial Z} = 0$$

(7)

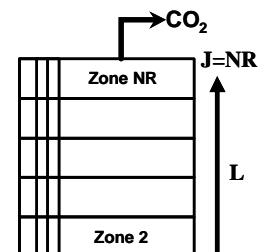
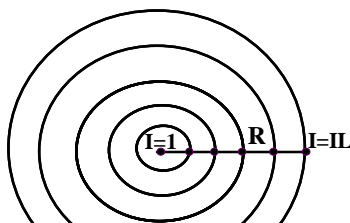
$$\tau > 0 \quad Z = 1 \quad \frac{\partial C_f}{\partial Z} = 0$$

(8)

**Partitioning of oil between Solid and Supercritical Phase**

$$C_{fs} = k_p C_s^+ \quad (9)$$

The differential equations in the solid and supercritical phases were solved using the method of finite differences by Crank Nicolson. The extractor (J) and particle (I) were divided into several grids of NR=10 and IL=6, respectively. These grids were selected considering the boundary conditions.



a)

b)

**Figure 1.** Schematic of the extraction process: a) diffusion of the oil in the solid phase, b) dissolution of the oil in the bulk phase throughout the extractor.

### Essential oil properties and extraction parameters

The properties adopted for marjoram leaves are shown in **Table 1**. An extraction temperature and pressure of 313.15 K and 10 MPa were chosen for the extraction conditions since these values are typical for EO extractions used by many researchers.

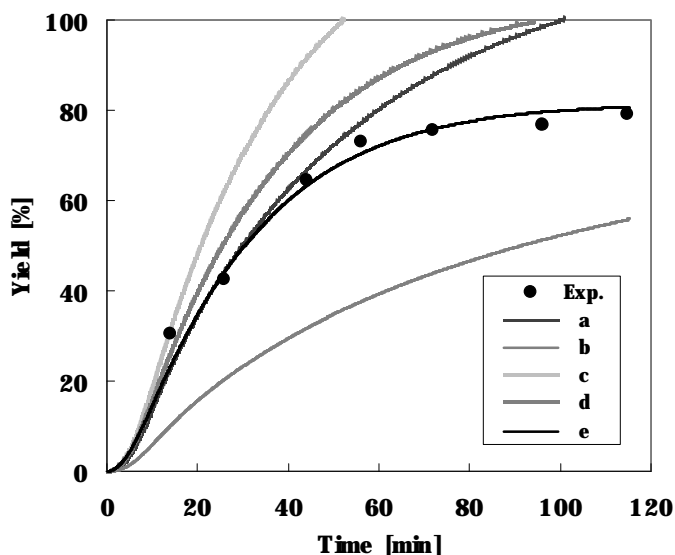
**Table 1.** Parameters of marjoram leaves used

Essential oil	PM (g/mol)	$m_0$ (kg)	$C_0$ (kg/m <sup>3</sup> )	$d_p$ (mm)	Source
Marjoram	151	0.23	8.0	0.15	Reverchon (1992)

Extraction parameters were as follows: extractor volume, length, and diameter were 0.0004 m<sup>3</sup>, 0.188 m, and 0.052 m, respectively. The flow rate of the solvent used was 20 g CO<sub>2</sub>/min and the porosity value was 0.514. A mean value of  $k_p$  of 0.45 for the leaves at 10 MPa and 313.15 K was reported by Reverchon [4] and Sovová et al. [9-10] which was adopted in this work.

### RESULTS AND DISCUSSION

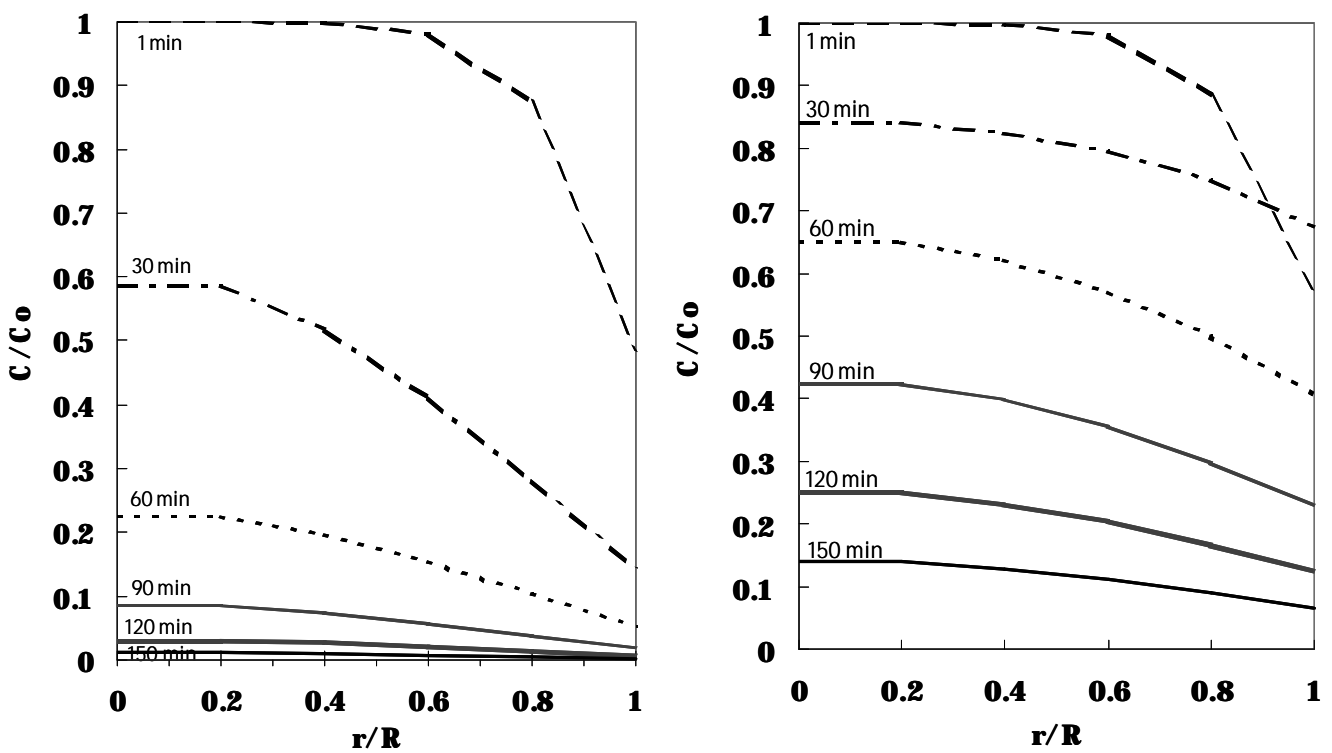
**Figures 2 - 6** show some results obtained using this model for the marjoram essential oil extraction with supercritical carbon dioxide at 313.2 K and 10 MPa. The best fit of the experimental data has been obtained using a non-linear fitting method with two adjusted parameters ( $k_f$  and  $D_m$ ). As can be seen from **Figure 2**, the two-parameter model can predict the trend of the extraction yield. In this Figure lower values of  $k_f$  and  $D_m$  lead to lower extraction yields while higher values of these parameters lead to a higher extraction yield in less time. The mass transfer coefficient  $k_f$  and  $D_m$  values obtained in this work were  $1.52 \times 10^{-7}$  m/s and  $9.70 \times 10^{-13}$  m<sup>2</sup>/s, respectively. The  $D_m$  value obtained in this work is in the same order of magnitude and in good agreement with the one reported earlier by other researchers [2-3,6].



**Figure 2.** Effect of the mass transfer and diffusion coefficients in the extraction of Marjoram essential oil at 313.2 K and 10 MPa ( $d_p$ : 0.15 mm).

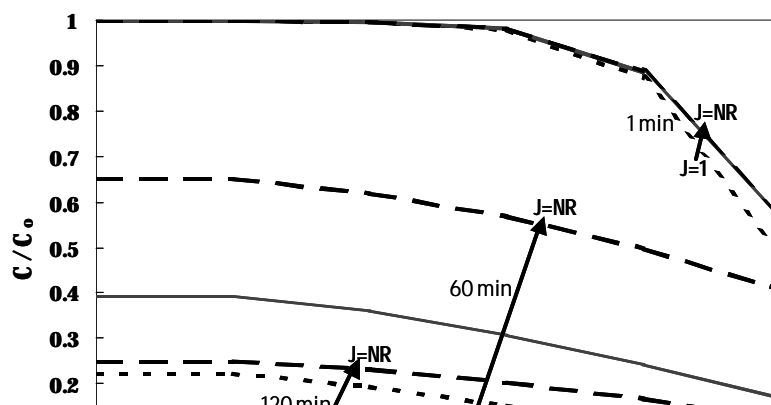
a)  $k_{f1}$ : $2.00 \times 10^{-7}$  m/s &  $D_{m1}$ : $2.50 \times 10^{-13}$  m<sup>2</sup>/s, b)  $k_{f2}$ : $1.44 \times 10^{-7}$  m/s &  $D_{m2}$ : $1.10 \times 10^{-13}$  m<sup>2</sup>/s, c)  $k_{f3}$ : $2.09 \times 10^{-7}$  m/s &  $D_{m3}$ : $6.55 \times 10^{-13}$  m<sup>2</sup>/s, d)  $k_{f4}$ : $1.87 \times 10^{-7}$  m/s &  $D_{m4}$ : $5.49 \times 10^{-13}$  m<sup>2</sup>/s, e)  $k_{f5}$ : $1.52 \times 10^{-7}$  m/s &  $D_{m5}$ : $9.70 \times 10^{-13}$  m<sup>2</sup>/s

**Figure 3** shows concentration profiles of essential oil extraction in the solid phase in two positions inside the extractor (down and upper side) and different extraction times at a constant temperature and pressure of 313.2 K and 10 MPa, respectively. In **Figure 3**, the dimensionless concentration decreased when the essential oil was diffusing from the center of the particle to the surface (along the radius of the particle of  $d_p$ : 0.15 mm). Further, the concentration profiles in the solid phase should decrease if the extraction time is increased since the initial quantity of essential oil is decreasing. When comparing the concentration profiles obtained for the bottom part of the extractor (NR=1) with the upper side of the extractor (NR=7) at a constant time, the amount of solute extracted decreased at the upper side of the extractor. The extraction rate of oil from the particle at the upper side of the extractor was lower, which may be attributed to the saturation of the solvent with the solute in the bottom part of the extractor.



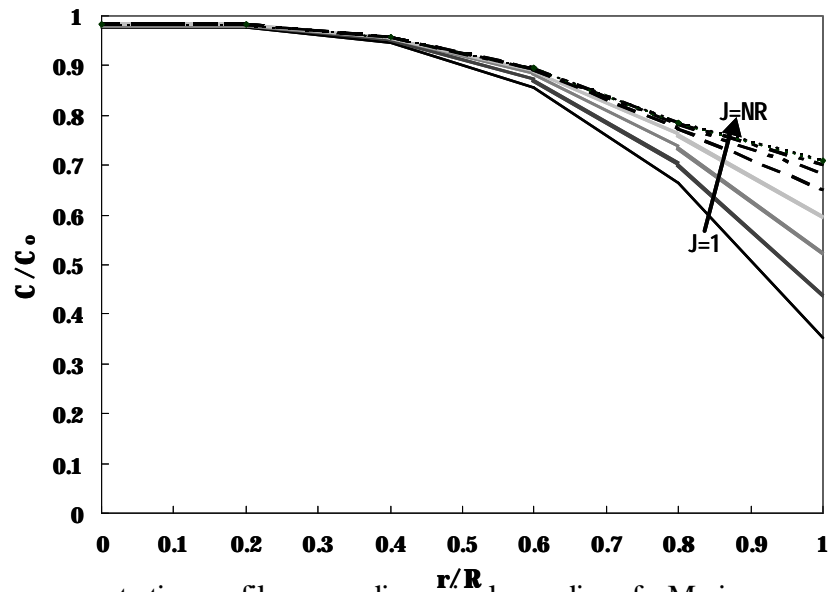
**Figure 3.** Dimensionless concentration profile in the solid phase at the: a) bottom and b) upper side of the extractor, for marjoram essential oil extraction along the particle radius ( $d_p$ :0.15mm) at 313.2 K and 10 MPa.

The model could determine the concentration profiles in the particles at any time along (through) the extractor. **Figure 4** shows that if the supercritical carbon dioxide is flowing from the bottom to the top of the extractor, the concentration of essential oil should increase due to the dissolution of the essential oil in the fluid and the effect of the mass transfer coefficient ( $k_f$ ).

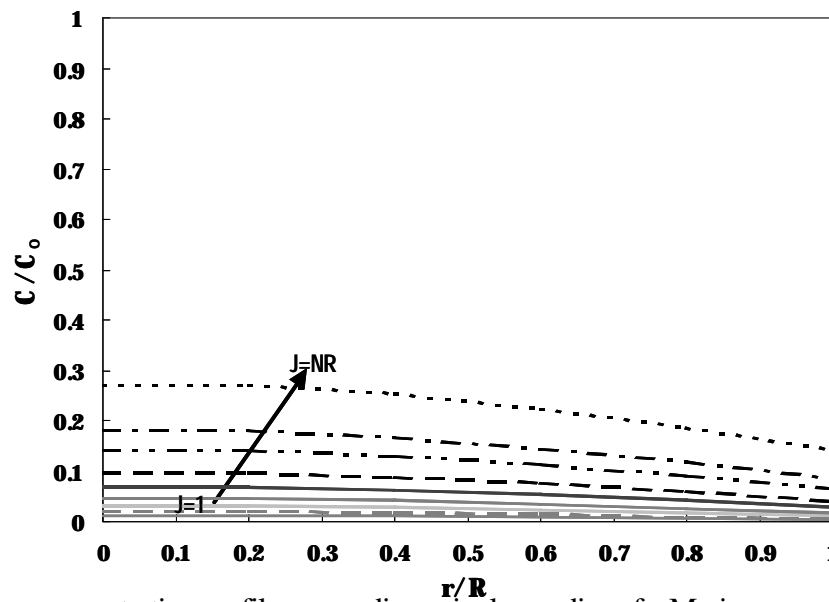


**Figure 4.** Dimensionless conc. profile versus radius of a marjoram particle at 313.2 K and 10 MPa.

**Figure 5** shows concentration profiles of essential oil extraction with supercritical carbon dioxide at the beginning (8 min) and at the end (150 min) of the extraction process, respectively. While in **Figure 5a** can be observed that the oil concentration is the highest, there is very little quantity of oil that can still be extracted in **Figure 5b**.

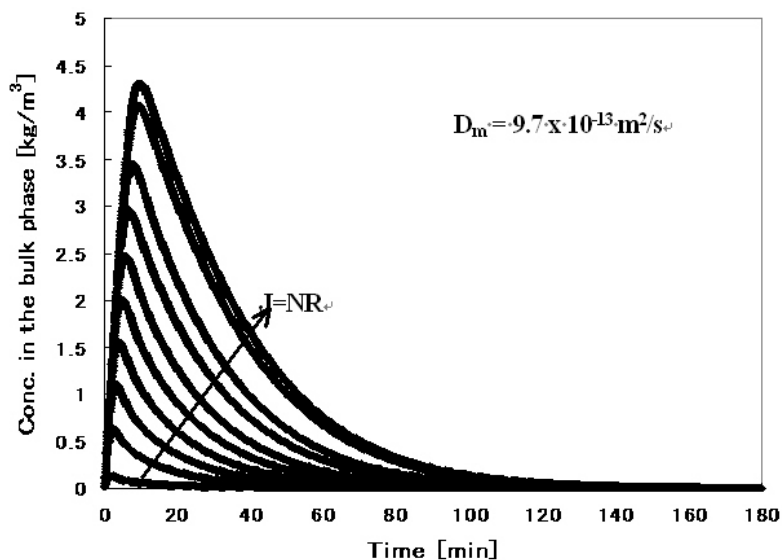


**Figure 5a.** Dimensionless concentration profile versus dimensionless radius of a Marjoram particle at 313.2 K and 10 MPa through the extractor height  $L$  ( $J=1$  to  $J=NR$ ).



**Figure 5b.** Dimensionless concentration profile versus dimensionless radius of a Marjoram particle at 313.2 K and 10 MPa in 150 min through the extractor height ( $J=1$  to  $J=NR$ ).

**Figure 6** shows concentration profiles in the supercritical phase for the extraction of marjoram essential oil using supercritical carbon dioxide at 10 MPa, 313.2 K and particle diameter of 0.15 mm. Through this Figure can be observed that the maximum concentration will be a function of the extractor height and extraction time. In this case, the highest concentration will be reached in less than 20 min. By this Figure can be observed that the concentration will increase when supercritical carbon dioxide is flowing from the bottom to the top of the extractor. Besides, higher extraction rates are obtained in the first stages of the extraction process that will decrease as time increases. After 120 min, the extraction rate is very low and inconvenient for an industrial process. Diffusivity and mass transfer values obtained with this model were  $9.7 \times 10^{-13} \text{ m}^2/\text{s}$  and  $1.52 \times 10^{-7} \text{ m/s}$ , respectively.



**Figure 6.** Concentration profile in the supercritical phase for Marjoram essential oil extraction at 313.2 K and 10 MPa ( $d_p$ : 0.15 mm).

## CONCLUSIONS

Marjoram essential oil extraction with  $\text{SCCO}_2$  was estimated using a two-dimensional model. The model predictions are satisfactory and have reliable trends compared to experimental data. Concentration profiles in the solid and supercritical phase can be observed at any section of the extractor and at any time of the process. Two mass transfer coefficients ( $D_m$  &  $k_f$ ) influence extraction yields in the process. The maximum concentration will depend on  $D_m$  and  $k_f$ , which can be estimated with this model. Through modelling, the extraction time can be optimized for an optimum essential yield for industrial processes.

## ACKNOWLEDGMENTS

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## REFERENCES

- [1] REVERCHON, E., *Journal of Supercritical Fluids*, 5(4), **1992**, p. 256.
- [2] REVERCHON, E., DONSI, G. AND SESTI OSSEO, L., *Ind. Eng. Chem. Res.*, 32(11), **1993**, p. 2721.
- [3] REVERCHON, E. AND SESTI OSSEO, L., *Journal of Supercritical Fluids*, 7, **1994**, p. 185.
- [4] REVERCHON, E., *AIChE Journal*, 42, **1996**, p. 1765.
- [5] ROY, B.C., GOTO, M. AND HIROSE, T., *Ind. Eng. Chem. Res.*, 35, **1996**, p. 607.
- [6] GOODARZANIA, I. AND EIKANI, M.H., *Chem. Eng. Science*, 53(7), **1998**, p. 1387.
- [7] SALDAÑA, M.D.A., PhD Thesis, Unicamp, **2002**, pp. 400.

- [8] SALDAÑA, M.D.A., SMITH, R.L.JR. AND INOMATA, H., Proc. Autumn Meeting of the Soc. Chem. Eng. Japan, **2002**, Japan.
- [9] SOVOVÁ, H., Chem. Eng. Science, 49(3), **1994**, p. 409.
- [10] SOVOVÁ, H., KUCERA, J. AND JEZ, J., Chem. Eng. Science, 49(3), **1994**, p. 415.