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MATHEMATICAL MODELING AND SIMULATION OF SUPERCRITICAL CO_2 EXTRACTION OF ZIZIPHORA TENUIOR VOLATILES

Mojtaba Sinaei NOBANDEGANI[1], Tayebeh DARBANDI[2], Bizhan HONARVAR[3], Mohammad Mohsen SARAFRAZ[4]

[1]Department of Chemical Engineering, International Campus, University of Sistan & Baluchestan, Chabahar, Iran
[2]Department of Chemical Engineering, Shahrood Branch, Islamic Azad University, Shahrood, Iran
[3]Department of Chemical Engineering, University of Fars Science and Research, Islamic Azad University, Iran
[4]School of Chemical, Gas and Petroleum Engineering, Semnan University, Semnan, Iran

ABSTRACT

Ziziphora Tenuior is an edible medicinal plant which belongs to Labiatae family. It is often used as a treatment for some diseases such as edema, insomnia, and hypertension in Turkey, Iran and China. The main components of the Ziziphora Tenuior essential oil are p-mentha-3-en-8-ol and pulegone. In this study, the extractions of Ziziphora essential oil has been described by a two-dimensional mathematical model, and the effects of some extraction parameter variations on the extraction yield have been examined. Amongst the said parameters were fluid flow rate, extractor diameter and length and mean particle size.

Keywords: Carbon dioxide, Extraction, Supercritical Fluid, Modeling, Ziziphora Tenuior

1. INTRODUCTION

The Labiatae family is a large family of herbs with some members such as peppermint, spearmint, rosemary and ziziphora. This family has aromatic species, which are used as culinary and therapeutic [1, 2]. Ziziphora is an herbaceous, flocculent, slender, edible, medicinal and erect plant with a height of 5-15 cm [3-5]. It is also a seasonal plant, which flowers in April, May, June and July [6, 7]. Ziziphora Tenuior consists of four species namely: Ziziphora Clinopodioides Lam., Ziziphora Capitata L., Ziziphora Persica BUNGE. and Ziziphora Tenuior [4]. This plant is widespread all over Iran, Turkey, Afghanistan, Iraq and Azerbaijan [6, 8]. The major constituent found in the oil of Ziziphora Tenuior has been reported to be pulegone, p-mentha-3-en-8-ol and p-mentha-3,8-diene [4, 9]. These components cause the antimicrobial and antioxidant activities of its essential oil. Ziziphora essential oil is used traditionally as an appetitive, sedative, carminative, antiseptic and wound-healing material [10, 11]. This essential oil is also used as an additive to yogurt and chees to improve its aroma and flavor [5, 12-13]. Regarding to above-mentioned importance, extraction of its essential oil is a serious problem.

There are different techniques to extract a plant's essential oil such as liquid-liquid extraction, hydrodistillation and supercritical fluid extraction (SFE). Among these techniques, SFE is preferable because it decreases the operating costs, and solvent can be recycled easily. Moreover, Low viscosity and high diffusivity of supercritical fluids cause a better mass transfer as compared to organic solvents. One of the most common solvent in this technique is supercritical CO_2 (SC-CO_2), because it is a non-toxic, non-flammable and environmental-friendly solvent and has a moderate critical temperature and pressure [14-16].

*Corresponding Author: m_sinai@pgs.usb.ac.ir

The SFE of vegetables oils has been studied since 1980s [17], consequently there is a suitable literature about this technique. In one of the oldest studies, the extraction of lipophilic fractions from cocoa has been studied using supercritical fluid by Vitzthum et al. [18]. The studies about this technique have been continued till now. The SFE studies have also been increasing in recent years. Bensebia et al., in 2009, investigated the effects of process parameters on supercritical CO_2 extraction of rosemary oil and also used a mathematical model to describe this process [19]. In another study in this year, Melreles et al. represented a mathematical modeling study for SFE of vetiver root oil and solved the model numerically [20]. They also investigated effects of some extraction parameters on extraction yield. One year later, Vargas et al. extracted the essential oil of Abajeru from its dried leaves using SFE. They also did the extraction process by hydrodistillation and soxhelt and compared the results [17]. Grosso et al. provided a numerical study on SFE of volatile oils from six aromatic plants. The modeling was performed by five mathematical models which were obtained from differential mass balances [21]. Ghasemi et al. extracted the Myrtus Communis L. essential oil by SFE and hydrodistillation technique. They identified the chemical compositions of the essential oil by GC-FID and also optimized pressure, temperature, modifier volume and extraction time by response surface methodology and central composite design. They reported that the SFE is more selective than hydrodistillation under the proper conditions [22]. The SFE of Chamomile was studied experimentally and numerically by Rahimi et al. Their model was represented for both particle and fluid phase and had reliable results. They also optimized the pressure and temperature [23]. Ansari and Goodarznia studied the SFE of spearmint essential oil and optimized this process using Taguchi method in 2012. They used L16 array in Taguchi optimization [24]. In another study in this year, Ahmed et al. extracted Algerian Rosemary essential oil using supercritical CO_2. They studied the effects of temperature and pressure on the extraction yield. They also modeled the process using the shrinking-core model [25]. Hu et al. studied the SFE of Cuminum Cyminum essential oil and optimized this process. They used Taguchi method with L16 array and four factors namely: pressure, temperature, CO_2 flux and mean particle size. The antifungal activity of this essential oil has studies, too [26]. The SFE of Nigella sativa seeds oil has studied by Salea et al. They optimized the process using Taguchi method and full factorial design. They also extract the oil using high pressure soxhelt with CO_2, n-hexane soxhelt and percolation with ethanol and reported the extraction yield for each extraction techniques [27]. Optimization of SFE of phenolic compounds from Mango Ginger Rhizome has been done by Murthy and Manohar. They used response surface methodology with three-level Box-Behnken factorial design. Moreover, the phenolic compounds were identified and quantified for optimum conditions by the HPLC analysis [28].

Although there are many studies have been done on supercritical fluid extraction of Ziziphora Tenuior essential oil [1, 3, 7, 9], no report has yet appeared on the SFE of this plant, except the one which has done by Darbandi et al. [4]. In the present work, the mathematical modeling and simulation of this process is represented. Moreover, a parametric study is done on the process and model.

2. MATERIAL AND METHODS

2.1. Plant Material

Ziziphora Tenuior was collected from the northern part of Shiraz, Iran, in October 2013. Then it was dried in a dark place and at the room temperature (around 25°C). The sample was ground in a Panasonic blender (Model MX-J225G) to produce powder.

2.2. Reagent

Carbon dioxide with the purity of 99.95% was obtained from Abu-Qaddareh Company (Shiraz). Dichloromethane with the purity of 99.99%, purchased from Merk KgaA, was used as a solute recovery.

2.3. Experiments

The experiments apparatus and procedure was the same as described by Darbandi et al. and is shown in Figure 1 [4].

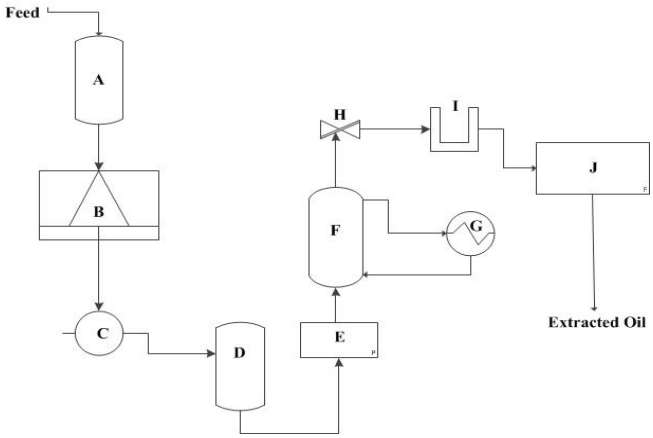

Figure 1. The experimental apparatus for the extraction of Z. Tenuior: A- Cylinder of CO_2, B- Refrigerator, C- Handle Reciprocating Pump, D- A Tank for CO_2 Loading, E- Barometer, F- Extraction Tank, G- Heater for Heating Water, H- Joule-Thomson Valve, I- Dichloromethane in U-Shape Tube at 0°C , J- Flow meter [4]

Amongst the reported operating conditions [4], the best ones were selected for the current study. Five experiments were done with 5 different extraction times. The operation conditions are indicated in Table 1. Then, the extraction yield was measured for each run. Finally, the experimental data were compared to model results.

Table 1. The operation condition

Parameter	Value
Pressure (bar)	175
Temperature (° C)	45
Mean Particle Size (m)	212e-6

2.4. Mathematical Model

Figure 2 indicates a simple schematic of the extraction tube. The model was written considering some assumptions:

1) Axial dispersion is neglected;
2) Radial gradients are neglected in the fluid phase;
3) The solid particles are assumed as a lumped system;
4) The system is an isotherm and isobar system;
5) Bed and particle porosity are constant during the process;
6) A local equilibrium exists at the fluid and solid phase interface.

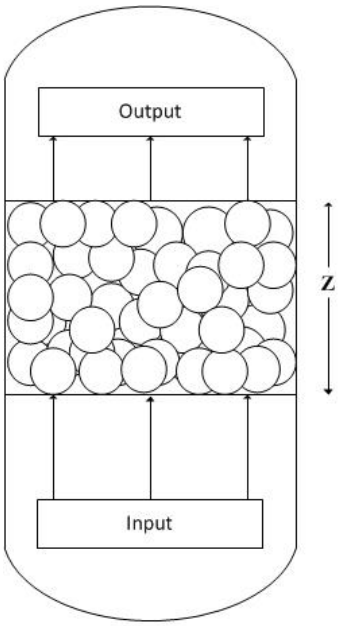

Figure 2. The extractor tube schematic

The final form of the model equation, for the tube illustrated in Figure 2, could be written as follow:

Solute concentration in fluid phase:

$$\frac{\partial C}{\partial \tau} + \frac{\partial C}{\partial Z} + \frac{1-\varepsilon}{\varepsilon}\frac{3L}{R_p}\frac{Bi}{Pe_p}(C - C_S) = 0 \qquad \begin{matrix} \text{at} \quad t=0: \quad C=0 \\ \text{at} \quad z=1: \quad \frac{\partial C}{\partial Z} = 0 \end{matrix} \qquad (1)$$

Solute concentration in solid phase:

$$\frac{dq}{d\tau} = 3\frac{k_f}{R_P}\frac{L}{v}(C - C_S) \qquad \text{at} \quad \tau=0 : q=q_0 \qquad (2)$$

According to thermodynamic, a linear relation could be written at the equilibrium point:

$$q = KC_s \qquad (3)$$

In which K is the proportionality constant and is called equilibrium constant. This constant is the adjustable parameter. It is calculated so that minimizes the following objective function:

$$O.F. = \sum\left(F_{exp.} - F_{cal.}\right)^2 \qquad (4)$$

The algorithm, indicated in Figure 3, was represented by Melreles et al. to calculate the equilibrium constant [20]:

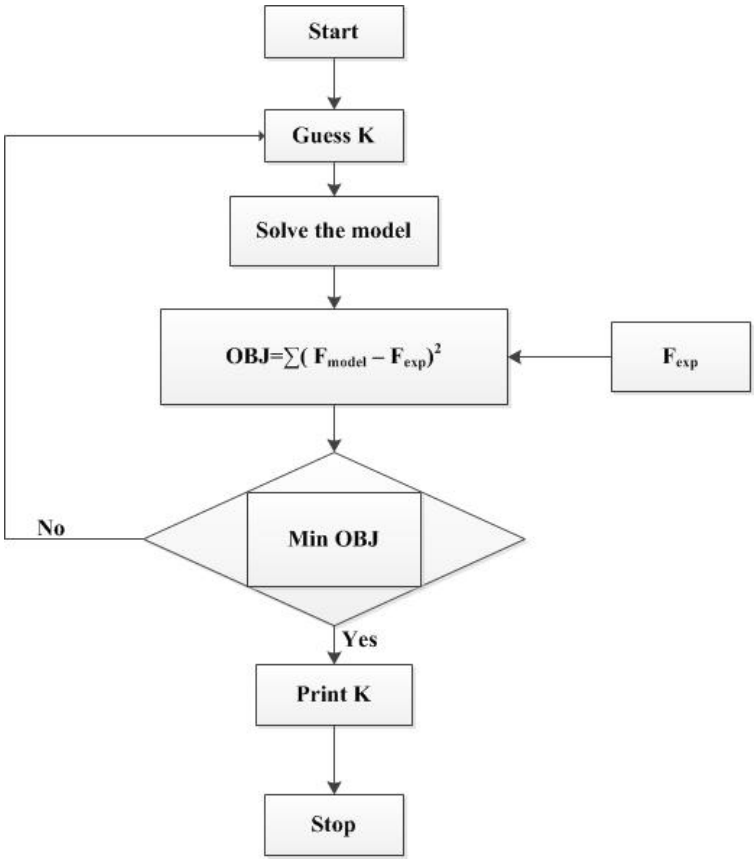

Figure 3. Procedure of equilibrium constant calculation [20]

To solve the model, the PDEs equations (1-3) should solve simultaneously. The finite difference method was employed for this purpose. In this way, the obtained ODEs should be solved instead of the above PDEs. In order to solve the ODEs, MATLAB software was used.

2.5. Model Parameters

The external mass transfer coefficient is calculated according to the following relation [29]:

$$k_f = \frac{Sh.D_m}{D_p} \tag{5}$$

Where the Sherwood number is calculated using the Zahedi et al. correlation [20].

$$Sh = 0.038\, Re^{0.83} Sc^{0.33} \tag{6}$$

In eq. (6) Re and Sc are calculated as below:

$$Re = \frac{2R_p v \rho_f}{\mu_f} \tag{7}$$

$$Sc = \frac{\mu_f}{\rho_f D_m} \tag{8}$$

The fluid density and viscosity estimated using the NIST database [30]. To calculate the axil dispersion coefficient, the following correlation was represented by Funazukuri et al. [31]:

$$\frac{\varepsilon D_1}{D_m} = 1.317(\varepsilon.Re.Sc)^{1.392} \tag{9}$$

In which the molecular diffusion coefficient is calculated as below [32]:

$$D_m = A \times 10^{-11} (V_f^k - B) \frac{T}{\sqrt{M_s}} \quad (10)$$

for $\rho_r \geq 1.2$: k=1

for $\rho_r < 1.2$: $k = 1 + \frac{(\rho_r - 1.2)}{\sqrt{M_f}}$

$$A = 0.29263 + 1.6737 \exp\left(-0.75832 \frac{\sqrt{M_f V_{cf}}}{P_{cf}}\right) \quad (11)$$

$$B = 0.077\, T_{cf} \quad (12)$$

The Bi and Pe_p are calculated by following equations:

$$Pe_p = \frac{R_p v}{D_e} \quad (13)$$

$$Bi = \frac{k_f R_p}{D_e} \quad (14)$$

Where the D_e is the effective intra particle diffusion coefficient and calculated as below [20]:

$$D_e = D_m \varepsilon_p^2 \quad (15)$$

The experimental parameters are indicated in Table 2:

Table 2. The experimental parameters value

Parameter	Value	Parameter	Value
Extractor Length (m)	0.3000	Particle Porosity	0.9020
Fluid Velocity (m/s)	0.0772	Void Fraction of Packed Bed	0.7020

3. Results and Discussion

3.1. Model Validation

To evaluate the model validation, the predicted model data are compared with the experimental data. The results are demonstrated in Figure 4 and Table 3.

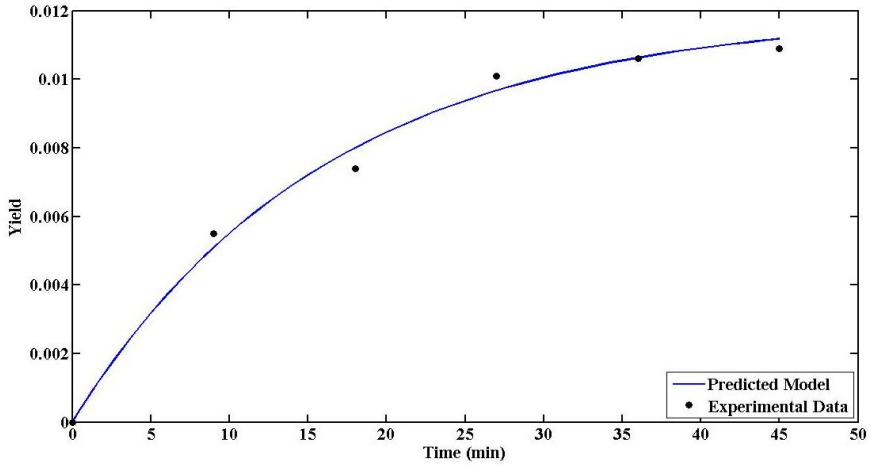

Figure 4. Model prediction and experimental data for extraction yield

Table 3. The experimental parameters value

Time (min)	Experimental Yield (%)	Predicted Yield (%)	AAD (%)
0	0	0	0
9	0. 55	0.51	7.27
18	0. 74	0.81	9.46
27	1.01	0.97	3.96
36	1.06	1.07	0.94
45	1.09	1.12	2.75

In order to calculate the absolute average deviation (AAD (%)) in Table 3, the following relation has been employed:

$$AAD(\%) = \frac{1}{NP}\sum_{i=1}^{NP}\left(\frac{\left|Experimental - Calculated\right|_{Value}}{Experimental_{value}}\right)_i \times 100 \tag{16}$$

In which the NP is the number of data points. As it is illustrated in Table 3, the average error of model in about 4.88% which indicates the presented model is a reliable one.

By ensuring about the model validation, the process simulation can be done, and its results will be reliable.

3.2. Simulation Results

In this section, the effects of some process parameters on the extraction yield are investigated. Amongst the said parameters are: mean particle size, fluid flow rate and extractor length and diameter.

3.2.1. The effects of mean particle size

To study the mean particle size, variation of the extraction yield with the mean particle size in constant pressure and temperature has been indicated in Figure 5. As it is shown, the extraction yield rose with the particle size of raw materials decrease. This is due to increase in interfacial area, releasing oil from the cells and decrease in the intraparticle resistance to mass transfer which are occurred by milling the particles.

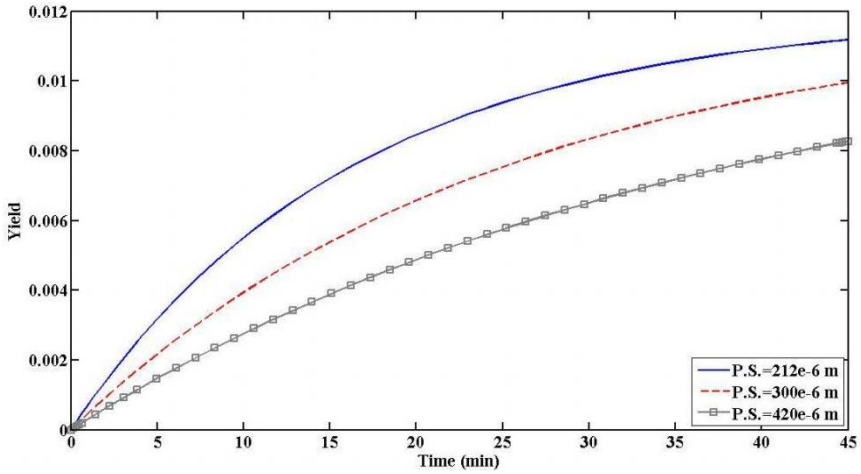

Figure 5. The effects of mean particle size on the extraction yield

3.2.2. The effect of fluid flow rate

Fluid flow rate is the next parameter which is investigated in process simulation. As it was expected, there is a reduction in the amount of extraction yield when the fluid flow rate is increased. In the current extraction condition, the intraparticle diffusion controls the process. As a result, the higher fluid flow rate decreases the contact time between the solvent and the particle surface, and the extraction yield will reduce. This effect is implied in Figure 6.

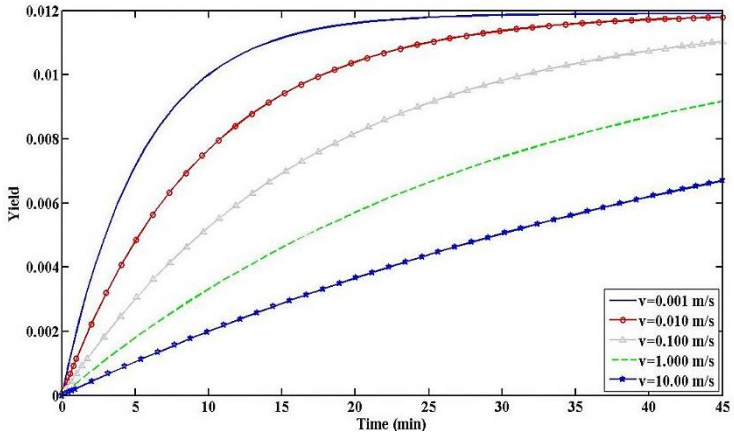

Figure 6. The effects of fluid flow rate on the extraction yield

3.2.3. The effects of extractor length and diameter

To evaluate this parameter, the ratio of the extractor diameter on the extractor length was changed in the range of 0.001 to 0.16, and the effect of this variation on the extraction yield is shown in Figure 7. As it is seen, the higher the (D/L) is, the higher the extraction yield becomes.

The higher D/L means the decrease in extractor length or the increase in its diameter, in which the flow behaves more likely to plug flow, and the mass transfer increases. Consequently, it is expectable that the reduction occurred in the extraction yield while the D/L is increased.

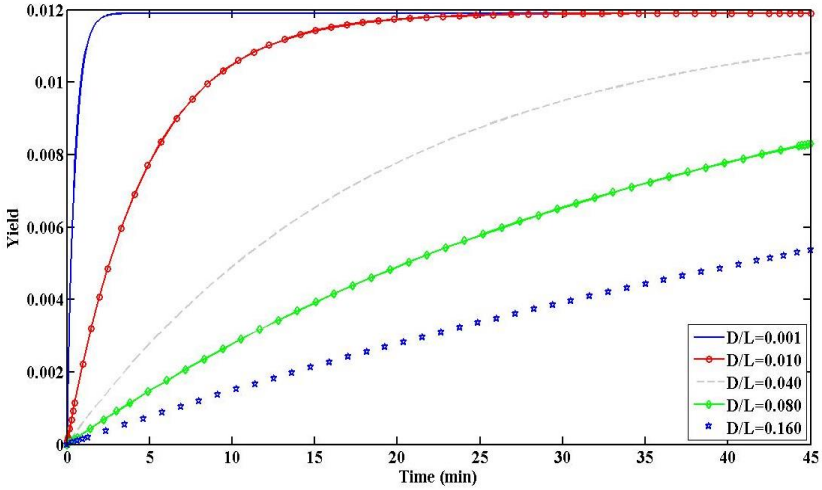

Figure 7. The effects of extractor length and diameter on the extraction yield

4. CONCLUSION

In this study, the supercritical extraction of Ziziphora Tenuior was mathematically modeled. The model validation has evaluated by comparison the model results with the experimental ones. Then the effects of some operation parameters on the extraction yield were studied. It was concluded that the particle size reduction causes the extraction yield increase. Decrease in the fluid flow rate has the same effect on the extraction yield. Furthermore, when the extractor diameter decreases or its length increases, the extraction yield will increase.

Nomenclature

Symbols

C	[kmol/m^3]	Oil Concentration in the Supercritical Phase
d_p	[m]	Particle Diameter
D_1	[m^2/s]	Axial Dispersion Coefficient
D_e	[m^2/s]	Effective Intra Particle Diffusion Coefficient
D_m	[m^2/s]	Molecular Diffusion Coefficient
F		Extraction Yield
K		Equilibrium Constant between Solid and Fluid Phase
k_f	[m/s]	External Mass Transfer Coefficient
L	[m]	Extractor Length
M	[kg/kmol]	Molecular Weight
P	[bar]	Extraction Pressure
Pe_p		Peclet Number for Particle
Q	[m^3/s]	Supercritical Fluid Flow Rate
Q	[kmol/m^3]	Oil Concentration in the Solid Phase
R_p	[m]	Particle Radius
Re		Reynolds Number
Sc		Schmidt Number
Sh		Sherwood Number
T	[k]	Extraction Temperature
T	[s]	Extraction Time
V	[m^3/kmol]	Molar Volume
V	[m/s]	Fluid Velocity
Z		Dimensionless Axial Coordinate Along the Bed

Greek letters

M	[kg/m/s]	Viscosity
P	[kg/m^3]	Density
E		Bed Void Fraction
ε_p		Particle Porosity
T		Dimensionless Time

Subscripts

C	Critical
cal.	Calculated
exp.	Experimental
F	Fluid
P	Particle
R	Reduced
S	Solid

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