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Supercritical extraction of essential oil from Mentha and mathematical modelling– the influence of plant particle size

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Abstract

Supercritical CO₂ extraction was studied using dried leaves of Mentha, originated from the northern part of Libya. Leaves were milled and sieved to obtain different average particles ($d_p = 0.25 - 0.80$ mm). They were treated with supercritical CO₂ at 313 K and 10 MPa in order to isolate essential oil. The new approach of supercritical extraction modelling on the basis of proposed “pseudo kinetic model” (PKM) was investigated and compared to most applied in literature Sovova’s model. The main focus of these investigation was to determine the influence of particle size on extractions yield and to determine optimal methodology for determination parameters of PKM. Achieved results showed good agreement between both models and experimental results and good prospects for further usage of PKM.

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Keywords: Supercritical CO₂ extraction; pseudo kinetic model; particle size

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1. Introduction

Mathematical modelling of supercritical extraction of essential oils from plant materials always has been challenge for scientists and researchers. The model of extraction process is mostly presented by corresponding relation between yield of extract and time. In this study supercritical CO₂ was used for extraction of essential oil from Libyan Mentha. The new approach for modeling supercritical extraction was based on so called “pseudo kinetic” model (PKM). One of tasks was also to compare the PKM and Sovova’s models. The main focus of investigation in this study was to determine the influence of particle size on extraction yield and parameters of PKM at specified working conditions (pressure, temperature and supercritical fluid flow rate).

There are various models employed to describe the supercritical fluid extraction of oils or other compounds from plant material. Del Valle and de la Fuente [1] and Oliveira [2] reported reviews of different models used for describing supercritical extraction process. All of them consider that the particles are packed inside an extractor column as a batch while supercritical fluids (mainly supercritical carbon dioxide (scCO₂) or some lighter hydrocarbon) are flowing through the packed bed in continuous mode. Several mostly employed assumptions for defining mathematical model are: isothermal operation of extraction, negligible pressure drop across the extractor, constant bed porosity and constant solid material density along packed bed of plant material. It is usually assumed that solubility of solute in the supercritical fluid is low and, therefore, supercritical fluid density and velocity through the packed bed remain approximately constant or that axial dispersion of supercritical fluids might be neglected. These assumptions reduce the number of equations necessary to describe the extraction process to equation of a. mass balances; b. equilibrium relations, and c. kinetics laws [2].

The most comprehensive classification of mathematical models of supercritical extraction of plant material is presented by Reverchon [3]. Models were classified into three categories: a. empirical models; b. models based on heat transfer analogy, and c. models based on differential mass balance. The first category of models is little more than an interpolation of the experimental results and can be useful when information on the mass transfer mechanism and on the equilibrium relationship is missing. Models based on heat transfer analogy apply the second Fick’s law and Fourier transforms and treat each single particle as a hot ball cooling in a uniform medium. The third and the most abundant type of models, because of flexible mathematical tool, define the mass balances for:

a. differential volume of extractor to describe the behavior of fixed beds during extraction [4]:

$$\frac{dc_f}{dt} + u \frac{dc_f}{dz} - D_L \frac{d^2 c_f}{dz^2} = \frac{3}{R} \frac{1-\varepsilon}{\varepsilon} J \quad (1)$$

b. in pores of solid (plant) particle, which is usually considered as sphere [4]:

$$\frac{dc_p}{dt} + \frac{1}{\varepsilon_p} \frac{dc_s}{dt} = - \frac{D_e}{r^2} \frac{d}{dr} \left(r^2 \frac{dc_p}{dr} \right) \quad (2)$$

All other model classifications and differences between them are result of some simplification and additional assumptions, which are in almost all cases related to equation (2) like: i. Shrinking Core model (SC model); ii. Desorption – Dissolution – Diffusion model (DDD model); iii. models which neglect axial dispersion of solute; iv. models with differential layer; v. External Mass Transfer Control model (EMTC model); vi. Linear Driving Force model (LDF model); vii. Single Sphere Model (SSM model); viii. Sovova’s model (Extended Lack’s model); ix. Reverchon’s model; x. Broken and Intact Cells model (BIC model), etc.

Which model will be chosen depends on many effects. Sovova [5] recently reported that in addition to the usually applied working conditions and particle size distribution must be also considered: a. effect of flow pattern; b. the solute–matrix interactions, and c. the microstructure of particles which are variable from case to case. The method how to analyze either the effects of changes in operation conditions and/or pre-treatment of extracted plant on the equilibrium and mass transfer model parameters was proposed [5]. That method consists of simplified equations, including equilibrium expressions, which depend on possible solute-matrix interactions and characteristic times of mass transfers and residence time, which depend on flow patterns (plug flow or completely mixed flow). It was concluded that the model for supercritical extraction should be selected rather after the preliminary experimental data evaluation than in advance [5].

One of the goal in this work was directed to investigate the influence of plant particle size. Thus, some of above mentioned models would be analyzed with more details because they are of special concern related to this study.

Melreles et al [6] used DDD model to describe supercritical extraction of vetiver root. This model include the axial dispersion and neglect the radial concentration gradient in supercritical fluid phase. System is lumped and there is local equilibrium at interface of fluid and solid phase. Other assumptions are that the void fraction of packed bed as well as the porosity of particle are constant during extraction. It was shown that in the case of small particle diameter per bed diameter ratio the side effect along the packed bed might be neglected when the void fraction is only a function of particle arrangement and independent of particle diameter. It is also shown that particle porosity is independent of particle diameter [6]. Using the same model for supercritical CO₂ extraction of chamomile, Rahimi et al. concluded that extraction yield is week function of particle diameter, although agreement of model and experimental data was acceptable [7].

Sovova [8] developed model when supercritical solvent flows axially through a packed bed of milled plant material in a cylindrical extractor. The supercritical solvent is solute-free at the entrance of the extractor, and the temperature and pressure inside extractor are constant. The packed bed is assumed as homogeneous with respect to both the particle size and the initial distribution of solute inside particles. The solute is deposited in plant cells and protected by cell walls. However, some cells wall has been broken open by milling, so that a part of the solute is directly exposed to the solvent [8]. This model was used by Nagy and Simandi [9] to describe supercritical fluid extraction of paprika for different particle sizes. They reported that decrease of particle size increases the extraction efficiency, and that oil was most rapidly removed from small particles of paprika [9].

Sovova's model [8] is limited to situation when solute-matrix interaction does not exist and for plug flow of supercritical fluids in extractor. Further improvement of model proposed by same author [10] was done with more fitting parameters (flexible relationships both for phase equilibrium and flow pattern). Four types of extraction curves are defined with respect to the initial composition of solid and fluid phases. The main practical advantage of improved model is its ability to simulate different types of extraction curves and characterize them with mutually comparable parameters as mass transfer coefficients and equilibrium constants [10].

BIC model is based on few assumptions, of which the main are: a. the solute is assumed to be homogeneously distributed in untreated particles which are arranged as packed bed in the extractor; b. the particles contain broken cells near the surface and intact cells in the core; c. the solute from broken cells is transferred directly to the fluid phase, d. the solute from intact cells diffuses first from these cells and then to the fluid phase; e. equilibrium between the fluid phase and the solid phase with broken cells is established before the extraction starts, and f. the concentration in the intact cells is equal to the original concentration in the untreated material.

SC model consider extraction as irreversible desorption, take into account effect of axial dispersion but neglect the radial dispersion of supercritical fluids in extractor. When the mass transfer rate of the solute in the non-extracted inner part is much slower than that in outer part, or if solute concentration is much

higher than the solubility in the solvent, a shape boundary may exist between outer and inner region. A core of inner region shrinks with the progress of the extraction.

Machmudah et al. [11] and Doker et al. [12] compared BIC and SC models in the case of supercritical CO₂ extraction of nutmeg oil and sesame seed oil, respectively. It was shown that SC model could describe the experimental data well for all extraction conditions, while BIC model only for predicting lower extraction yield which is obtained using larger particles.

In this study supercritical CO₂ was used for extraction of essential oil from Libyan Mentha. The new approach for modeling supercritical extraction was based on so called “pseudo kinetic” model (PKM). One of tasks was also to compare the PKM and Sovova’s models [5, 8, 11]. The main focus of investigation in this study was to determine the influence of particle size on extraction yield and parameters of PKM at specified working conditions (pressure, temperature and supercritical fluid flow rate).

2. Materials and methods

Dried leaves of Mentha, originated from the northern part of Libya, were milled and sieved to obtain different average particles ($d_p = 0.25 - 0.80$ mm). They were treated with supercritical CO₂ at 313 K and 10 MPa in order to isolate essential oil. Collected mass of essential oil was measured at different used amount of supercritical CO₂. The flow rate of solvent of 0.65-0.70 kg/h and initial mass of prepared Mentha about 30g were used in all the experiments of this study.

Extraction with supercritical carbon dioxide was carried out in the Autoclave Engineers Screening System presented in Fig. 1.

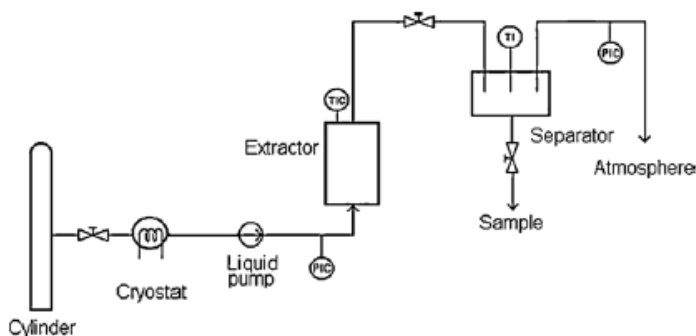


Fig. 1. Schematic presentation of the Autoclave Engineers SFE Screening System

Simulation of supercritical extraction of Libyan Mentha was done by using Polymath Educational, Matlab and Origin Pro Software to obtain dependence of total extraction yield on percentage time and comparison of results with results of Sovova’s model applied for the same purpose.

3. Models description

3.1. Pseudo kinetic model

Model, developed in this work, is based on assumption that supercritical extraction can be considered as chemical reaction, although it is a physical phenomenon. The fact is that supercritical extraction consists of two main steps: the first, so call fast period, in which essential oil from disrupted cells by milling of plant material is separated and the second, slow period, in which essential oil form intact cells is extracted after diffusion of supercritical CO₂ within the particles. The rate of extraction from disrupted cells of plant material depends on resistance to the external mass transfer which is governed mainly by hydrodynamic conditions inside extractor and particle size, while the rate of extraction from intact cells depends mainly on resistance to diffusion through the cells membrane and it is time dependent process. This situation can be shown using three kinetic equations:



where Y_1 is percentage quantity of easy accessible essential oil, Y_2 is percentage quantity of essential oil placed in intact cells, E_1 and E_2 are extraction yields in first and second periods of extraction respectively, which are related to appropriate quantities of Y_1 and Y_2 . A total yield of essential oil is determined as: $E = E_1 + E_2$. The whole process is considered as "conversion" of essential oil from free state to supercritical solution without change of its chemical composition and presented in the form of three first order chemical reactions. The rate of the first extraction period is actually governed by external mass transfer rate and defined by external mass transfer coefficient (k_1), and it is related to quantity of extract obtained from disrupted cells. Slow step of extraction is described by apparent mass transfer coefficient in solid phase, k_2 , at the beginning of this phase, and by time dependent internal mass transfer coefficient, k_3 , because diffusion of supercritical CO₂ and extract within the particles is time dependent process.

Y_1 and Y_2 values are assessed from experimental curve (yield versus time) for all experiments of this study. External mass transfer coefficient, k_1 , could be estimated as a slope of relation $[-\ln(Y_1)]$ and time. The apparent internal mass transfer coefficient, k_2 , which is related to the second reaction, it was assumed that its value is two order of magnitude lower than for k_1 . Internal mass transfer coefficient for third reaction, or reaction rate constant k_3 , which describes disruption of cells, is time dependent and it can be presented as function $k_3 = at^2$, where a is coefficient, which is 20-50 times lower than the values of k_2 . This concept was applied for all experiments analysis in this study.

This approach suggests that PK model is empirical, but it relies on assumptions that are also characteristic for models based on differential mass balance.

3.2. Sovova's model (Extended Lack's model)

This model defines three extraction periods. In the initial period (Δt_1), extraction takes place at a constant rate which is determined by resistance of the film of supercritical fluid. At the end of this period the particles at the site of entrance of fluid in extractor (position of the fastest extraction during the piston flow) will lose the free solute. However, the solute, which is located deeper in interior of the particles will still remain present in these particles and the next, the transition period, will begin its extraction. During the transition period (Δt_2), free solute is removed from the surface of other particles and other particles become partially exhausted. Zone, in which particles are exempted of solute moves in the direction of fluid flow and proceeds as front of exhaustion, which is located in front of the free solute particles. At the

beginning of the third extraction period, in all the particles only bound solute or solute which is located deeper inside the particles is present. Quantity of extract e which is removed during the first, second and third period of extraction, is shown as a function of specific consumption of solvent q [13]:

$$e = \begin{cases} y_r [1 - \exp(-Z)] & q < q_m \\ y_r [q - q_m \exp(z_w - Z)] & q_m \leq q < q_n \\ x_0 - \frac{y_r}{W} \ln \{ 1 + [\exp(Wx_0 / y_r) - 1] \exp[W(q_m - q)] x_k / x_0 \} & q \geq q_n \end{cases} \quad (6)$$

The initial concentration of easily accessible oil in the cells opened by milling is $x_0 - x_k$, the initial concentration of oil inside the seed particles is x_k . The amounts of solvent q_m , q_n , which define the transition region between the fast- and slow-extraction periods, and the dimensionless axial coordinate z_w , indicating the plane in the bed where the oil concentration is equal to x_k , are calculated as [10]

$$q_m = (x_0 - x_k) / y_r Z \quad (7)$$

$$q_n = q_m + \frac{1}{W} \ln \frac{x_k + (x_0 - x_k) \exp(Wx_0 / y_r)}{x_0} \quad (8)$$

$$\frac{z_w}{Z} = \frac{y_r}{Wx_0} \ln \frac{x_0 \exp[W(q - q_m)] - x_k}{x_0 - x_k} \quad (9)$$

Parameters Z and W are directly proportional to the fluid phase and to the solid-phase mass transfer coefficients, respectively, and are given below [10]

$$Z = \frac{k_f a_0 \rho}{\dot{q}(1 - \varepsilon) \rho_s} \quad (10)$$

$$W = \frac{k_s a_0}{\dot{q}(1 - \varepsilon)} \quad (11)$$

4. Results and discussion

4.1. Effect of particle size

These experiments were performed using two particle fraction ranges at 313 K, 10 MPa and 0.65-0.70 kg/h CO₂ and results are shown in Fig.2.

The oil yield increased with a decrease in particle size due to the fact that the grinding process not only increased the interfacial area but also released oil from the broken cells [14]. The particle size controls the mass transfer kinetics and the access of CO₂ to the soluble components. Higher extraction efficiencies can be achieved applying smaller particle sizes, which resulted in an increase in mass transfer surface, and in quantity of soluble fraction on this surface. The reduction in extraction yield with increasing particle size indicates that oil was not transported through the unbroken cell walls, and only surface oil was removed. By the way, in most cases the effect of particle size was examined in the literature by fractionation of the crushed raw material followed by extraction of the fractions of different size ranges separately [9].

4.2. Results of models and discussion

In this study Sovova’s model was compared with ‘‘pseudo kinetic’’ model (PKM) defined in this study. The modelling results are shown in Fig.2.

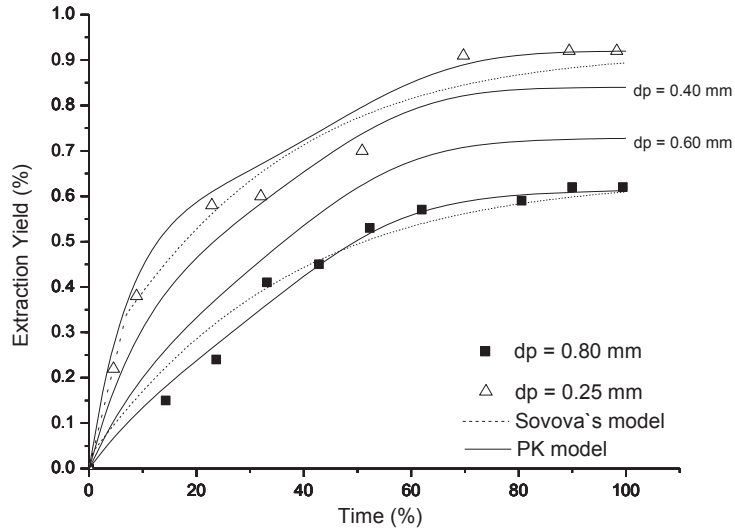


Fig. 2. PKM and Sovova’s model ($d_p=0.25$ mm and $d_p=0.80$ mm) and extraction curves (PKM) for $d_p=0.40$ mm and $d_p=0.60$ mm

Some parameters for Sovova’s model had to be optimized and their values are given in Table 1. All parameters for PKM were also optimized and their values are given in Table 1.

Table 1. Sovova’s and PK model parameters with standard deviation values

Model parameters	Sovova’s model		PKM model			
	$d_p = 0.25$ mm	$d_p = 0.80$ mm	$d_p = 0.25$ mm	$d_p = 0.40$ mm	$d_p = 0.60$ mm	$d_p = 0.80$ mm
$x_0 \times 10^3$ (kg kg ⁻¹ CO ₂)	9.2	6.4	-	-	-	-
$x_k \times 10^3$ (kg kg ⁻¹ CO ₂)	6.5	6.1	-	-	-	-
$y_r \times 10^3$ (kg kg ⁻¹ CO ₂)	1.4	1.4	-	-	-	-
$k_s \times 10^8$ (m s ⁻¹)	2.5	0.7	-	-	-	-
$k_1 \times 10^2$	-	-	12.5	7.9*	5.3*	4.0
$k_2 \times 10^4$	-	-	5.0	4.2*	3.4*	3.1
$a \times 10^3$	-	-	2.0	2.5*	2.8*	3.0
Y_1 (%)	-	-	0.60	0.49*	0.37*	0.24
Y_2 (%)	-	-	0.32	0.34*	0.36*	0.38
$\sigma \times 10^4$	4.30	4.02	8.99	-	-	2.33

* - predicted

Parameters for Sovova’s model had to be calculated using appropriate correlation: Tan’s correlation was used for calculation of external mass transfer coefficient [15]; Jossi’s correlation to calculate

dynamic viscosity of supercritical CO₂ [16], and the binary diffusion coefficient for essential oil/supercritical CO₂ system in supercritical film around the particle was calculated from the equation given by Catchpole and King [17].

For determination of diffusion coefficient, it was necessary to define which compound could be used as pseudo- or key-component. Results of chemical analysis of Mentha essential oil show that carvone could be chosen for that purpose. Determination of supercritical extract composition is shown in Table 2. Carvone is present at levels 38% (d=0.25 mm) and 43% (d=0.8 mm) and about 51% in spearmint oil obtained by Clevenger distillation. It is well known that carvone is main component for *Mentha spicata*.

Table 2. Chemical analysis of the essential oil (Clevenger apparatus) and the supercritical extract of spearmint, respectively

Compound	Mas % (Supercritical extract of spearmint)	
	$d_p = 0.25 \text{ mm}$	$d_p = 0.80 \text{ mm}$
Terpinene<gamma->	0.716	0.648
Borneol	0.792	0.575
Dihydro carvone<trans->	1.781	1.347
Carveol<cis->	0.892	1.146
Carvone	37.577	43.180
Carvyl acetate<cis->	-	0.636
Bourbonene<beta->	1.495	0.959
Elemene<beta->	1.198	0.874
Caryophyllene(E-)	3.033	2.091
Humulene<alpha->	0.807	-
Muurolene<gamma->	4.969	2.719
Cadinene<alpha->	-	0.556
Carvacrol	3.053	4.541
Cadina-1(6),4-diene<cis->	1.728	1.100
Calamenene<trans->	2.099	1.813
Spathulenol	2.009	1.370
Carophyllene oxide	0.816	0.568
Cubenol<1-epi->	1.393	1.187
Cadinol<epi-alpha-> (=tau-cadinol)	-	0.666
Muurolool<alpha-> (=Torreyol)	1.735	1.546
Bisabolol<alpha->	0.920	0.973
cis,cis,cis-7,10,13-Hexadecatrienal(ti)	0.961	0.598
3,7,11,15-Tetramethyl-2-hexadecen-1-ol (ti)	13.556	18.111
(+)-Epi-bicyclosesquiphellandrene	1.061	1.375
Heptacosane	3.454	3.647
Acetylenedicarboxylic acid, di(-)-menthyl- (ti)	0.990	1.049

According to Fig.2., both applied models described satisfactorily the experimental data for given conditions. For smaller particles, there is highly expressed sag on experimental curve, which represents a transitional period of extraction and ``pseudo kinetic`` model (PKM) follows that sag better than Sovova's model.

Validity of fitting was determined by evaluation of standard deviation (σ) for both models and for all particle diameters. Values of standard deviations are also given in Table 1. Standard deviation was calculated by following expression:

$$\sigma = \sqrt{\frac{\sum_{j=1}^m (e_j - e_{j,\text{mod}})^2}{m}} \quad (12)$$

where is: e_j – experimental values of extraction yield, $e_{j,\text{mod}}$ – modeling results of extraction yield and m – number of experimental values.

Although pseudo kinetic model has higher standard deviation for smaller particles than Sovova's model (Table 1) as one can see the shape of curves for 0.25 mm as well as for 0.8 mm is better predicted on the basis of pseudo kinetic model (PKM). The existence of sag on the experimental data curve largely depends on plant microstructure, which mainly consists of glandular trichomes.

Prediction of PKM extraction curves for other particle diameters (0.4 mm and 0.6 mm) was determined bringing model parameters into appropriate relation:

$$\frac{k_1(0.25)}{k_1(0.80)} \approx \frac{0.80}{0.25} \quad \text{and} \quad \frac{k_2(0.25)}{k_2(0.80)} \approx \left(\frac{0.80}{0.25}\right)^{0.5} \quad (13)$$

According to equations (13) and by interpolation, it is possible to predict PKM parameters for various particle diameters and for 0.40mm and 0.60mm these parameters are shown in Table 1. Corresponding extraction curves on the basis of predicted data for constants k_1 , k_2 and k_3 are also shown in Fig 2.

PK model showed good qualifications for describing supercritical extraction of essential oils plants with specific microstructure and future experiments have to prove it.

Conclusion

Essential oil from Libyan Mentha was extracted by using supercritical CO₂ as a solvent to observe the effects of two particle sizes on the extraction yield and to compare developed "pseudo kinetic" with Sovova's model. Higher extraction yield was obtained with smaller particles due to increased quantity of solute initially released by milling pretreatment of Mentha. Experimental data were compared with PKM and Sovova's model and showed that both models agree well with experimental data, but transition period of supercritical extraction is better described using PKM. This advantage of PK model should be tested in future by supercritical extraction of essential oils from plants with developed specific cell microstructure.

Nomenclature

a	coefficient related to k_3 value, s ⁻¹
c_f	concentration of solute in supercritical fluid, kg m ⁻³
c_p	concentration of solute in supercritical fluid inside solid material pores, kg m ⁻³
c_s	concentration of solute in solid phase, kg m ⁻³
d_p	particle diameter, mm
D_e	effective diffusivity coefficient of solute in solid material, m ² s ⁻¹
D_L	axial dispersion coefficient of solute in supercritical fluid, m ² s ⁻¹
e	mass of extract relative to mass of solute-free solid phase (total extraction yield, %)
E	total extraction yield, %

E_1	extraction yield after the first period, %
E_2	extraction yield after the second period, %
J	overall extraction velocity, $\text{mol m}^{-2} \text{s}^{-1}$
k_1	external mass transfer coefficient, s^{-1}
k_2	apparent internal mass transfer coefficient, s^{-1}
k_3	time dependent internal mass transfer coefficient, s^{-1}
$k_f a_0$	fluid-phase mass transfer coefficient, s^{-1}
$k_s a_0$	solid-phase mass transfer coefficient, s^{-1}
q	specific amount of solvent, kg kg^{-1}
\dot{q}	mass flow rate of solvent related to the mass of the solute-free solid phase, s^{-1}
q_m	value of q for which the extraction of solute inside the cells starts, end of the rapid extraction period, kg kg^{-1}
q_n	value of q for which the transition period ends and the slow extraction period begins, kg kg^{-1}
r	radial distance within the particles, m
R	particle diameter, m
t	time, s or %
W	dimensionless parameter in the model that Sovova proposed, which is proportional to internal mass transfer coefficient
x_0	initial concentration of solute in solid material, $\text{kg kg}^{-1} \text{CO}_2$
x_k	initial concentration of solute inside the intact particles of solid material, $\text{kg kg}^{-1} \text{CO}_2$
y_r	solubility of oil in supercritical fluid, $\text{kg kg}^{-1} \text{CO}_2$
Y_1	percentage quantity of easy accessible essential oil, %
Y_2	percentage quantity of essential oil placed in intact cells, %
z	axial distance within the layer, m
z_w	dimensionless coordinates of the border zone between slow and fast extraction
Z	dimensionless parameter in the model that Sovova proposed, which is proportional to external mass transfer coefficient

Greek letters

ε	solid material bed porosity in extractor
ε_p	particle porosity
ρ	density of solvent, kg m^{-3}
ρ_s	density of solid phase, kg m^{-3}

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