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Kinetics model for supercritical fluid extraction with variable mass transport

Yi Song [a,b,c], Liancun Zheng [a,*], Xinxin Zhang [c]

[a] School of Mathematics and Physics, University of Science and Technology Beijing, Beijing 100083, China
[b] College of Mathematics and Systems Science, Shandong University of Science and Technology, Qingdao 266590, China
[c] School of Energy and Environmental Engineering, University of Science and Technology Beijing, Beijing 100083, China

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ABSTRACT

This paper studies supercritical fluid extraction in which we take the effects of solute concentration variation on mass transport into account. A kinetics model with variable mass transfer coefficients proposed to describe supercritical fluid extraction of grape and almond seed oil. Three distinct stages are found for extraction process, i.e., fast-extraction, slow-extraction, transition period, with a very short overflow oil in first stage. The overflow oil period is so short and the concentration variation is so slight that we think this period belongs to the fast-extraction stage. Theoretical predictions for yield distributions of supercritical fluid extraction are highly in agreement with the experimental data in literatures, which implies that the proposed model can be used to predict more mechanism for the extraction process. Moreover, the effects of involved parameters on mass transport and supercritical extraction process are shown graphically and analyzed.

1. Introduction

For decades, the applications of supercritical fluid technology have attracted a considerable attention both in science research and engineering applications, such as extraction separation, environmental protection, and chemical reaction engineering. Among those applications, the supercritical fluid extraction is commonly used in industry today. Different from most traditional extraction separation processes which caused serious environmental pollution, supercritical fluid extraction is nontoxic and green. Various supercritical fluids can be used for extraction, but supercritical CO_2 have been the most widely used because it is inexpensive, healthy and safe [1–4].

It is essential to model the extraction process for optimizing the variables and estimating the extraction. Sovová [5] proposed a broken and intact cells model for vegetable oil extraction process, in which the effects of milling of grape seeds, solvent flow rate and flow direction on the course of extraction were investigated. Meanwhile mass transfer coefficients in the supercritical and solid phases were evaluated from extraction curves using a plug-flow model. Sovová et al. [5,6] regarded the solid phase as divided between broken and intact cells containing the vegetable oil.

Based on Sovová's work, Reverchon and Marrone [7] modeled and simulated supercritical CO_2 extraction for vegetable oils under various operating conditions. Reinoso [8] studied the supercritical CO_2 extraction of antioxidant compounds from vegetal materials, with particular attention to those of a phenolic nature. Silva and Martínez [9] evaluated the mass transfer in supercritical fluid extraction from red pepper (Capsicum frutescens) using CO_2. Fiori et al. [10] investigated sensitivity analysis and operative conditions of a supercritical fluid extractor. They demonstrated that the particle size and internal mass transfer coefficient were important in the extraction modeling.

The shrinking core model was used to describe extraction process by several researchers. The particle was modeled as an inner zone, the core, and an outer zone; the core shrinked with the process of the extraction. The supercritical CO_2 extraction of nutmeg oil was studied by Machmudah [11], in which the broken and intact cells model and shrinking core model were applied to explain the extraction. Döker et al. [12] used shrinking core model to analyze supercritical extraction of β-carotene and the influence of parameters. Goto [13] applied the same model to characterize extraction process, and the axial dispersion was calculated numerically. The shrinking core model and the porous sphere model were used by Tezel et al. [14] to predict the selective extraction and possibilities for selective extraction of the mixture constituents. Ayas and Yilmaz [15] utilized the shrinking core and empirical kinetics models to simulate supercritical extraction from safflower seed.

* Corresponding author.
E-mail address: liancunzheng@ustb.edu.cn (L. Zheng).

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Nomenclature

a	specific surface of the solid, 1/m
C	solute concentration in the solvent, kg/kg
C_0	solute concentration in the solvent at saturation, kg/kg
C_s	initial oil concentration per unit volume of the granule, kg/kg
D_{ax}	axial dispersion coefficient, m^2/s
ID	internal diameter of the extractor, m
k	overall mass transfer coefficient, m/s
L	extractor length, m
m_0	mass of seed charged, kg
m_s	cumulative mass of solvent used, kg
Q	solvent flow rate, kg/s
R_p	particle radius, m
t	time, s
u	interstitial velocity of the solvent, m/s
x	exhaustion degree of the particle
z	axial coordinate, m
Greek letters	
ε	voidage of the extraction bed
ρ_s	density of the seeds, kg/m^3
ρ_f	density of the solvent, kg/m^3
ω_{oil}	weight fraction of oil in the seeds

Lucas et al. [16] analyzed the mass transfer by a two-parameter mathematical model in which the analytical solution was given by using modified Bessel functions. Cocero and García [17] studied supercritical CO_2 extraction of sunflower seed oil by desorption model, the numerical solution and semi-analytical solution were obtained by Laplace Transformation. Ciftci et al. [18] investigated supercritical CO_2 extraction of corn distiller's dried grains with soluble both in experiments and mathematical modeling. Their study revealed that distiller's dried grains with solubles (DDGS) is a good inexpensive source of lipids and valuable minor lipid components and that SC-CO_2 extraction can be used as a "green" process to add value to corn DDGS by recovering such high-value lipids. A list of the key references in the vast literature concerning this field is given in Refs. [19–25].

Grape seeds were used to feed animals before. Recently, it is found that grape seed oil is beneficial to human health due to it is abundant in unsaturated fatty acids and antioxidant-rich compounds [26]. About 70% of grape seeds were used effectively in Italy and France, but in China most grape seeds were thrown away which created unnecessary waste and pollution. So it is worth to study how to take full advantage of those seeds. There are several methods to utilize the seeds, in which extraction of grape seed oil is a nice way. Extraction of grape oil was investigated and a model with parallel plug flows was published in [6]. The supercritical CO_2 extraction from grape seed was studied experimentally and theoretically [27].

In most classical models for supercritical extraction, the overall mass transport coefficient is generally considered to be related to particle diameter. Fiori et al. [28] proposed three different models: the discrete, the semi-continuous and the continuous model. Fiori confirmed that the discrete and the semi-continuous models were superior to the continuous one, but there were still deviations in comparison with experimental data.

It is known that extraction process is depended on the solute concentration, i.e., the overall mass transfer coefficient k should be a continuous function of solute concentration. In this paper, we study supercritical fluid extraction of seed oil, in which the effect of solute concentration variation on mass transport is taken into account. The governing equations are formulated and solved numerically and the effects of various parameters on supercritical extraction process will be graphically shown and analyzed.

2. Mathematical formulation

Consider supercritical CO_2 extraction of grape seed oil. The facility consists in typical supercritical extraction equipment. The cylinder on the top uniformly distributes the solvent, the other one on the bottom is a basis for the material to be extracted [27]. Grape seeds are processed first as following: de-alcoholized, pressed and dried. The seeds are milled in the following steps. The milling is conducted by loading about 60 g of seeds into the miller, then flaking for 15 s, shaking the contents and starting again with the milling [27]. The milled grape seed granules are in a column extractor with supercritical CO_2 passing through at 550 bar and 40 °C. The extraction process starts as follows: with the equipment at a certain temperature, the system is pressurized until the desired set point. Then, it is maintained in static conditions for 20 min before fluxing. The seed oil is collected and weighed every 10 min [27].

The whole extraction process is assumed to be isothermal and isobaric, physical properties of supercritical fluid and bed void fraction donot change during this course. The experimental materials, extractor and procedure were described detailed in literature [27,28]. Fiori [27] conducted a set of experimental tests to analysis the extraction process with different conditions. A mathematical model based on broken and intact cells and shrinking-core models was given in [28] as:

$$\frac{\partial C}{\partial t} + u\frac{\partial C}{\partial z} - D_{ax}\frac{\partial^2 C}{\partial z^2} = \frac{1}{\varepsilon}ka(C_0 - C) \quad (1)$$

$$\frac{dx}{dt} = 3\frac{k}{R_p}\frac{C_0 - C}{C_s}\rho_f \quad (2)$$

where C is solute concentration in the solvent, x is exhaustion degree of the particle, u is interstitial velocity of the solvent, D_{ax} is axial dispersion coefficient, ε is voidage of extraction bed, k is overall masstransfer coefficient, C_0 is solute concentration in solvent at saturation, R_p is particle radius, C_s is initial oil concentration per unit volume of the granule ($C_s = \rho_s\omega_{oil}$), ρ_s is density of the seeds, ω_{oil} is the weight fraction of oil in the seeds, ρ_f is the density of the solvent. The initial and boundary conditions are

$$C|_{0\leqslant z\leqslant L, t=0} = C_0 \quad (3)$$

$$C|_{z=0, t>0} = 0 \quad (4)$$

$$\left.\frac{\partial C}{\partial z}\right|_{z=L, t>0} = 0 \quad (5)$$

$$x|_{t=0} = 0 \quad (6)$$

The Eq. (1) governs the extraction process, and Eq. (2) expresses the particle exhaustion over time. These two equations are coupled and have to be solved synchronously. The above mentioned model