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Fixed bed property changes during $scCO_2$ extraction of natural materials – Experiments and modeling

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ABSTRACT

Properties of the fixed bed of plant material during the extraction with $scCO_2$ from rapeseed were investigated for the two types of mechanical pretreatments: flaking and impact milling. Obtained results indicated that particle density, bulk density of the bed and consequently the bed porosity changed during the extraction. In the case of flaked rapeseed, the change of particle diameter was also detected and quantified. On the basis of experimental data linear relationships between the particle density/bed porosity/mean particle diameter and oil content in solid were established. Mathematical model based on the mass balances for the supercritical and solid phase which took into account particle density, bed porosity and particle diameter (for flaked plant material) as variables was derived. The proposed model described experimental data with high accuracy. Possible error due to neglecting the change of the fixed bed properties was presented as well.

1. Introduction

Extraction with supercritical carbon dioxide ($scCO_2$) is a well investigated extraction technique for a broad variety of plant materials. The main benefit of the application of carbon dioxide as a solvent is the unrestricted use in pharmaceutical and foodstuff applications due to its harmlessness and high quality of the obtainable extracts. In addition to experimental studies, models that describe the extraction process were developed. Thorough reviews on mathematical modeling of supercritical fluid extraction (SFE) processes are given in the works of Sovová and Stateva [1], Sovová [2], Reverchon and De Marco [3] and Pereira et al. [4]. Modeling of extraction kinetics of oilseeds – the substrate class that is also investigated in the present study was recently presented by Boutin et al. [5]. In general, the models are based on mass balances of the fluid and the solid phase. The main differences can be divided into the following aspects: description of the intra-particle mass transfer, particle shapes, consideration of hydrodynamic effects such as axial dispersion and description of solute–matrix interaction. While the description of extraction mechanisms varied broadly, all the models took into account the same simplification – properties of the fixed bed of plant material during the extraction were considered to be constant. This assumption might be quite true in the case of plant materials with relatively low quantity of extractables. However, the question is if the fixed bed properties remained the same in the case of extraction from material with high quantities of extractables, like in the case of oilseeds where high yields are expected. In this work, the change of fixed bed properties – porosity, particle density and particle size, in the course of the $scCO_2$ extraction of rapeseed was observed. Consequently, a model which took into account the continuous change of fixed bed properties during the extraction was derived.

2. Materials and methods

2.1. Rapeseed

Rapeseed was purchased from a German Agriculture Trade Association (LHG eGSchmölln). The moisture content was approximately 5%.

2.2. Mechanical pre-treatment

Mechanical pre-treatment was carried out with two different methods: flaking and impact-milling. For flaking rapeseed grains were processed in a roller mill consisting of two rollers (D = 60 mm, gap width: 0.15 mm, stainless steel) counter-rotating at a revolution of 144 min^{-1} without slip velocity. The surface of the one roll is plane and the other is riffled to ensure proper feeding of the material.

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Nomenclature

List of symbols

a	the specific surface of the particle of plant material, 1/m
D_{12}	binary diffusion coefficient, m^2/s
d_{eq}	equivalent diameter of the particle of plant material, m
d_p	diameter of the particle of plant material, m
e_j	experimentally determined yield in point j, kg/kg
$e_{mod,j}$	yield in point j according to mathematical model, kg/kg
G	fraction of cells opened by pretreatment
$J(x,y)$	mass transfer term, kg/m^3s
k_f	mass transfer coefficient in the supercritical phase, m/s
k_s	mass transfer coefficient in the solid phase, m/s
m	number of experimental points
Q_{CO_2}	mass flow rate of the supercritical carbon dioxide, kg/h
t	time, s
u_{CO_2}	superstitial velocity of the supercritical carbon dioxide, m/s
x	concentration of the solute in the solid phase, kg/kg
x_0	the initial concentration of extract in the solid phase, kg/kg
y	concentration of the solute in the supercritical phase, kg/kg
y_r	the solubility of the solute in the supercritical fluid, kg/kg
z	axial coordinate of the extractor vessel, m

Greek symbols

ε	bed porosity
μ	viscosity of the supercritical fluid, Pas
ρ	density of the supercritical fluid, kg/m^3
ρ_s	density of the particle of plant material, kg/m^3
ρ_{bulk}	bulk density of the fixed bed of natural material, kg/m^3
σ	standard deviation

Impact-milling was carried out in an ultracentrifugal mill (Retsch ZM 200) that consisted of a 12-teeth rotor (n = 6000 rpm). The mill was operated without the static sieve as provided by the supplier to avoid extensive shearing of the material.

2.3. Soxhlet extraction

Soxhlet extractions of pre-treated rapeseed were carried out by an accredited laboratory (Labor Iben GmbH, Bremerhaven) according to the method L13.05-3 of the German Food and Feed Code (§35 LMBG) with the solvent petrol ether. The reproducibility (R) of the method is given to be 0.7 g/100 g.

2.4. Supercritical CO_2 extraction

High pressure extractions with $scCO_2$ were performed in a CO_2 extraction plant with solvent recycle as previously described [6]. The extractor volume was 1.3 L. The diameter of the extraction cartridge was 4.9 cm. The extraction conditions were p = 30 MPa and T = 60 °C at CO_2 flow rates between 9 kg/h and 14 kg/h. The conditions of the separator stage were p = 6–7 MPa and T = 40–50 °C.

2.5. Fixed bed properties

2.5.1. Particle density

The particle density of pre-treated rapeseed and extraction residue from CO_2 extractions were determined on a helium pycnometer (Micromeritics, Model 1305). Each sample was measured five times.

2.5.2. Bulk density

About 100 g of pre-treated rapeseed were filled into a graduated cylinder and gently tapped in order to obtain a filling height with a straight edge. Then, the mass and volume of the fixed bed were measured. This procedure was carried out in triplicate.

2.5.3. Particle size distribution

The particle size distributions of the mechanically pre-treated rapeseed and extraction residue from $scCO_2$ extractions were determined with a set of sieves with mesh widths of 0.5, 0.71, 1.0, 1.25 and 1.4 mm. The measurements were carried out with the entire extraction charge on the basis of the DIN 66165 method for determining particle size distributions.

2.5.4. Fixed bed swelling under CO_2 atmosphere

The swelling behavior of a fixed bed of untreated and mechanically pre-treated rapeseed was determined in a high pressure view cell (Sitec, p_{max} = 50 MPa, T_{max} = 120 °C). The experimental set-up shown in Fig. 1 is similar to that used in a former study [7].

2.6. Mathematical modeling

Mathematical representation of the SFE process in this work is based on differential mass balance for the extractor vessel. Taking into account the fixed bed porosity and the particle density as variables, the mass balances for the supercritical and the solid phase could be written as follows:

- supercritical phase:

$$\rho\frac{\partial(\varepsilon y)}{\partial t} + \rho u\frac{\partial y}{\partial z} = J(x, y) \tag{1a}$$

- solid phase:

$$\frac{\partial((1-\varepsilon)\rho_s x)}{\partial t} = -J(x, y) \tag{1b}$$

where y and x are the concentrations of the solute in the supercritical and solid phase respectively, ρ and ρ_s are the densities of the supercritical fluid and particle of plant material, respectively, ε is the bed porosity, t is the time, z is the axial coordinate of the extractor vessel and $J(x,y)$ is the mass transfer term.

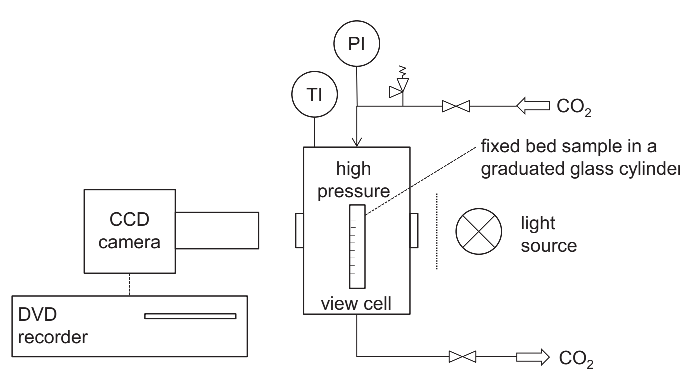

Fig. 1. Experimental set-up for the determination of swelling of a fixed bed of natural material.