Experimental and modelling of supercritical oil extraction from rapeseeds and sunflower seeds

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ABSTRACT

The supercritical oil extraction from oleaginous seeds (sunflower and rapeseeds) is presented here through experimental and modelling results. The experimental setup allows an accurate following of the mass of the oil extracted and to derive the experimental influences of pressure, temperature and supercritical CO_2 flowrate on the extraction curves. These parameters are very sensitive and highlight the necessity of precise optimisation of experimental conditions. In order to complete the behaviour of supercritical fluids extraction, an improved modelling is proposed. The modelling basic equations are based on others modelling published previously. In this work, the determination of several parameters comes from correlations and the other constants are fitted with all the experimental results. Thus the modelling is more representative and predictive as other ones. The modelling results present a good agreement with the experimental results, and hence it can be used for the dimensioning of some extraction autoclaves.

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1. Introduction

1.1. Generalities

For vegetable oil production from seeds, the traditional process is a mechanical pressing extraction and/or extraction with organic solvents. In the latter case, the solid matrix is in contact with an organic liquid phase. The different compounds are extracted from the matrix and diffuse in the fluid. These methods need long residence time and large quantity of organic solvent (hexane, acetone, ether, etc.), which are usually non selective. Moreover, residual traces of organic solvents are always found in the oil, especially when hexane is used, leading to a final step of purification. Following the REACH requirements, the lower limit decreases year by year. For these reasons, alternative extraction processes are always under development for reducing environmental impact by decreasing the toxic residues and effluents and by increasing the use of the by-products. One possibility is the use of supercritical fluids instead of organic solvent. In particular, supercritical carbon dioxide (SCO_2) has been used for extraction processes for many years and it has been developed for more and more applications.

In this work, the extraction of oil from two seeds, sunflower and rapeseeds, is studied. The objective is to obtain extraction kinetic and to develop a generalised model in particular for further development of the process. New experimental results and modelling is hence presented. Many parameters are well known for influencing extraction yields with SCO_2:

- Humidity rate (Dakovic et al., 1999; Dunford and Temelli, 1997).
- Pre-treatment before extraction in order to improve mass transfer by increasing exchange surface and seed destructuring (del Vallé et al., 2005; Temelli, 1992; Fattori et al., 1988; Eggers and Sievers, 1989).
- Even if the retro solubility phenomenon has been observed for oleaginous seeds, previous results indicate that temperature, in supercritical conditions, has not a determining influence on extraction yield (Goodrum and Eiteman, 1996;

Nomenclature

a_s	specific area between intact and broken cells (m^{-1})
a_p	specific area between broken cells and SCO_2 fluid (m^{-1})
C_1, C_2	constant used for the modelling of the mass transfer
c_u	solid content in the untreated solid (kg solute/kg solid)
e	extraction yield (kg oil extracted/kg insoluble solid)
E	mass of oil extracted (kg)
j_f, J_f	flux between the broken cells and SCO_2, and its adimensional form ($j_f\, t_r/(\rho_f \varepsilon y_0)$)
j_s, J_s	flux between the broken cells and the intact cells, and its adimensional form ($j_s t_r/(\rho_s(1-\varepsilon)x_{1,0})$)
K	partition coefficient
k_f	mass transfer coefficient in fluid phase ($m\,s^{-1}$)
k_s	mass transfer coefficient in solid ($m\,s^{-1}$)
P	pressure (MPa)
Q	SCO_2 mass flowrate ($kg\,s^{-1}$)
q	relative amount of solvent (kg solvent/kg insoluble solid)
q_C	SCO_2 flowrate at the transition point ($kg\,s^{-1}$)
r	fraction of broken cells
T	temperature (K)
t	extraction time (s)
t_r	residence time of SCO_2 (s)
v	interstitial speed ($m\,s^{-1}$)
x	oil concentration in the solid (kg solute/kg insoluble solid)
x_0	solute concentration in the untreated solid (kg solute/kg insoluble solid)
x_f	solute concentration in the fluid phase (kg solute/kg insoluble solid)
x_t	solute concentration at the transition point (kg solute/kg insoluble solid)
x_1	solute concentration in broken cells (kg solute/kg insoluble solid)
X_1	dimensionless solute concentration in broken cells ($x_1/x_{1,0}$)
x_{10}	initial solute concentration in broken cells (kg solute/kg insoluble solid)
x_2	solute concentration in intact cells (kg solute/kg insoluble solid)
X_2	dimensionless solute concentration in intact cells ($x_2/x_{1,0}$)
x_{20}	initial solute concentration in intact cells (kg solute/kg insoluble solid)
y_0	solute solubility (kg solute/kg solvent)
y^*, Y^*	equilibrium concentration in the fluid phase and dimensionless form (kg solute/kg solvent)
Y	dimensionless form of solute concentration in the fluid
z	axis coordinate for the extractor height (m)
ε	bed porosity
ρ_f	fluid density ($kg\,m^{-3}$)
p_s	solid density ($kg\,m^{-3}$)
τ	dimensionless extraction time t/t_r
Γ	dimensionless initial distribution of solute between the solvent and the broken cells
Θ_e	dimensionless mass transfer external resistance
Θ_i	dimensionless mass transfer internal resistance
ϕ	dimensionless extraction yield $= E/(Nc_u)$

Klein and Schulz, 1989; Salgin et al., 2001; Boutin and Badens, 2009).

- Concerning pressure, oil extraction from sunflower seeds is not interesting for pressures lower than 20 MPa (Salgin et al., 2001; Boutin and Badens, 2009). Many studies indicate that extraction yield increases with pressure (from 3.63 to 18.63 g CO_2 kg^{-1} from 20 to 60 MPa, Salgin et al., 2001) due to the solubility increase of the different compounds (mainly triglycerides) with pressure.

1.2. *First modelling*

The main modellings representing the extraction using supercritical fluids are derived from classical models of mass transfer and extraction kinetics. The different modellings found in literature have some common points. They consider that, even if oil is a complex mixture of many compounds, it is well represented by one compound called solute, which solubility is an average of the solubility of the different molecules, obtained through experimental runs. The solid matrix of the seeds is porous, homogeneous, and with constant physical properties during extraction. The physical properties of the fluid are constant as well. Usually, pressure and temperature gradients that appear in the fixed bed are not taken into consideration.

The first modelling considered one solid phase and one fluid phase, as for instance in the work of Perrut et al. (1997). For these modellings, the mechanism controlling the process is external mass transfer (no limitation of internal mass transfer and hence no concentration gradient in the seed). Moreover, no axial dispersion is taken into account inside the autoclave. The seed is represented with an external envelope containing many pores filled with oil. The oil concentration y^* at the solid – SCO_2 interface depends on an equilibrium relation, function of pressure and temperature (Eq. (1)).

$$y^* = f(x, P, T) \tag{1}$$

A mass balance is written in the fluid phase (Eq. (2)) and in the solid phase (Eq. (3)).

$$\rho_f \varepsilon \cdot \left(\frac{\partial x_f}{\partial t} + v \cdot \frac{\partial x_f}{\partial z} \right) = j_f \tag{2}$$

with $v = \dfrac{Q/\rho_f}{\text{extractor section}} \cdot \dfrac{1}{\varepsilon}$

$$\rho_s \cdot (1 - \varepsilon) \cdot \left(\frac{\partial x}{\partial t} \right) = -j_f \tag{3}$$