



Method development in inverse modeling applied to supercritical fluid extraction of lipids



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ARTICLE INFO

Article history:

Received 25 August 2015

Received in revised form 6 January 2016

Accepted 7 January 2016

Available online 8 January 2016

Keywords:

SFE

Inverse modeling

Kinetics

Partition isotherm

ABSTRACT

Modeling of the supercritical fluid extraction of solid materials is an important aspect in order to understand and predict the process. A comparison of two empirical models, two semi-empirical models and two mechanistic models is performed using calibration of single experiments. It is concluded that the best fit is obtained using a simple empirical expression. Furthermore, single calibrations did not generate reliable parameters with physical meaning and a methodology is proposed for inverse modeling with complete calibration using several experiments. The experimental dataset contained 29 extractions of lipids from crushed linseeds with varying temperatures, pressures and flow rates. A general rate model and a proposed extension of the hot ball model were evaluated for this purpose. The methodology includes data acquisition, model structure estimation, model calibration and a cross-validation. In general, it was found that the solubility model of Sovová outperformed the other evaluated correlations, and for the general rate model the Toth partition isotherm was also found in the top model structures. However, no generalization could be made regarding the correlations describing the Nernst diffusion layer and diffusivity.

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1. Introduction

Supercritical fluid extraction (SFE) has been widely accepted as an alternative to conventional extraction techniques. The process is almost exclusively carried out using supercritical carbon dioxide (scCO₂) due to the fact that it is non-toxic, non-flammable, easy to handle, inexpensive and readily available and it has a low critical pressure and temperature. Additionally, the operator has the ability to alter solubility of various compounds by adjusting temperature, pressure or by adding co-solvent and thereby influencing the composition of the extract. The above-mentioned properties along with efficient mass transfer due to low viscosity and high diffusivities makes SFE a powerful extraction technique [1].

Abbreviations: BPR, back-pressure regulator; CV, cross-validation; DLT, diffusion-layer theory; DOE, design of experiments; EHBM, extended hot ball model; ELSD, evaporative light scattering detector; GA, genetic algorithm; GRM, general rate model; HBM, hot ball model; LHS, Latin hypercube sampling; ODE, ordinary differential equation; PSO, particle swarm optimization; RMSE, root mean square error; RMSEC, root mean square error of calibration; RMSECV, root mean square error of cross-validation; scCO₂, supercritical carbon dioxide; SFE, supercritical fluid extraction.

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The applications of SFE span over a great field and has been extensively reviewed over the years [2–4], however much attention has been given to extraction from plant matrices [5]. It is worth emphasizing that the scales of SFE range from small scale within e.g. analytical chemistry in order to obtain compounds of interest for further analysis, to large scale in industrial applications for the removal of unwanted compounds or recovery of valuable compounds. The extraction is carried out batch-wise in either static, dynamic mode or a combination of both. In either case the material is contained in an extraction vessel with frits on either side to ensure that the material is kept in place [1].

Naturally it is of great interest to fundamentally understand and to be able to describe the extraction process in order to optimize the method or to scale-up the process. Mathematical modeling of SFE provides an opportunity to address both issues and many examples exist in the literature trying to either explain or to predict observed phenomena of SFE applied to solid materials. Extensive reviews of mathematical models which have been proposed and in many cases also been applied, are found in the literature [5–8].

In general, the mathematical models used range from purely empirical to almost solely fundamental equations based on thermodynamics and mass transfer phenomena. Rather simply put, the rate of the SFE process is governed by solubility, mass transfer in the bulk fluid part of the packed bed, within particle mass transfer,

Nomenclature

A	particle surface area (m^2)
c_b	solute concentration in the bulk fluid (g/m^3)
c_{init}	initial solute concentration (g/m^3)
c_p	solute concentration in the particle (g/m^3)
c_s	solute concentration at the particle surface (g/m^3)
c_{sat}	solute concentration at saturation (g/m^3)
D_{12}	binary diffusion coefficient (m^2/s)
$D_{12,\text{ext}}$	external binary diffusion coefficient in the bulk fluid (m^2/s)
D_e	effective diffusion coefficient (m^2/s)
D_p	particle diameter (m)
h	diffusion layer thickness (m)
H	Henry's constants
k	kinetic constant (1/s)
K_D	partition ratio
k_f	film mass transfer (m/s)
K_{lin}	linear isotherm constant
K_F	Freudlich isotherm constant
K_L	Langmuir isotherm constant
K_{RP}	Redlich–Peterson isotherm constant
K_T	Toth isotherm constant (g/m^3)
K_S	Sips isotherm model constant
L	Length of the extraction vessel (m)
m	Extracted mass (g)
m_0	Extractable mass (g)
Ma1–Ma9	simple correlations for estimating the diffusivity given by Magalhães et al. [44]
n_F	adsorption intensity
n_{RP}	Redlich–Peterson isotherm exponent
n_T	Toth isotherm exponent
n_S	Sips isotherm exponent
P	pressure (MPa)
Q	volumetric flow rate (m^3/s)
q	solute concentration in the solid matrix (g/m^3)
Re	dimensionless Reynolds number
r_p	radial distance in particle (m)
r_s	solute radius (m)
R_p	particle radius (m)
Sc	dimensionless Schmidt number
Sh	dimensionless Sherwood number
t	extraction time (s)
T	temperature (K)
u_{lin}	superficial linear velocity (m/s)
V	void volume in extraction vessel (m^3)
y	measured yield (g)
\hat{y}	predicted yield (g)
z	axial position along the packed bed (m)
$\beta_{\text{Chr},i}$	estimated constants of the Chrastil relationship
β_{DLT}	estimated mass transfer constant of the DLT model (m^3/s)
$\beta_{\text{DT},i}$	estimated constants of the D/T -viscosity correlation
$\beta_{\text{DVA},i}$	estimated constants of the del Valle and Aguilera relationship
$\beta_{\text{Ma},i,j}$	estimated constants of Eqs. (33)–(41)
$\beta_{\text{mSE},i}$	estimated constants of Eqs. (30)–(31)
β_{SE}	estimated combined constant of the Stokes–Einstein equation ($\text{m kg}/\text{s}^2 \text{K}$)
$\beta_{\text{Sh},i}$	estimated constants for estimating the Sherwood number
ε_c	void fraction of the column
ε_p	porosity of the particle
η	viscosity of the scCO_2 (Pa s)
ρ	density of the CO_2 (kg/m^3)

mass transfer resistance in the interface between the intra and inter particulate space, partitioning of compounds between the fluid and the solid matrix and also possibly by adsorption to the solid matrix. Each of the before-mentioned phenomena and properties have been extensively studied in ideal systems and an abundance of correlations and models have been developed.

The numerous equations and expressions describing critical parts of the SFE process can be divided into model classes, where each class describes the phenomena mentioned above. The various model classes have been comprehensively reviewed. Modeling of diffusivity in supercritical fluids has been reviewed by *e.g.* Funazukuri et al. [9] and Medina [10]. Empirical models describing solubility in supercritical fluids have been reviewed by *e.g.* Škerget et al. [11]. Adsorption isotherms are widely used in many research fields and the most commonly used ones have been reviewed by *e.g.* Foo and Hameed [12]. Adsorption isotherms, usually linear, have only sparsely been considered in the modeling of SFE [13–18]. The expressions of adsorption isotherms may be used as partition isotherms [19], which may be more correct in cases where partition is occurring rather than adsorption.

The number of parameters that need to be determined or estimated increase with the complexity of the models. Unknown parameters such as diffusivity, solubility or the parameters of the partition isotherm can be determined by external experiments by independently studying *e.g.* the solubility in an ideal system. Another approach is to apply inverse modeling, also known as the inverse method, by studying *e.g.* extraction yield over time and then estimating the unknown parameters so that the simulated extraction curve matches the experimental equivalent. This is also known as model calibration of the model structure, which contains a set of equations, in order to estimate the unknown parameters and thereby gaining a well-defined process model [20]. A common trend in the literature is that the calibration is usually performed by minimizing a fitness function of residuals using a gradient based numerical solver, however, limiting the number of unknown parameters to between one and three.

The parameters are usually estimated by calibrating a model structure to each individual experiment, thus generating a unique set of parameters and a unique process model for each extraction curve. A few exceptions are available in the literature, for example one study kept a constant density and temperature but altered the flow rate between experiments and estimated the coefficients correlating the dimensionless numbers of Sherwood, Reynold and Schmidt [21].

The inverse method is commonly used in various areas of engineering to indirectly study underlying phenomena, for example in mechanistic modeling of chromatography to partially or fully determine parameters with comparably good success [22]. However, for the purpose of estimating parameters of SFE model structures it has been argued that an individual extraction curve contains relatively little information on its own to calibrate multiple parameters through the inverse method with a good confidence. Depending on the model structure used it can be difficult to discriminate between various effects, *e.g.* between internal mass transfer and solubility [14].

Perhaps the most important and difficult issue is how to choose a model structure consisting of several model classes and thus forming many candidate model structures. In many cases the researcher has an idea of which phenomena might be crucial, motivated by chemical and engineering knowledge and experience. The situation becomes slightly more peculiar in more complex mass balance models where plenty of relationships and models describing the various phenomena are suggested in the literature. As an example of this abundance, there are over 20 reported relationships which in an empirical fashion describes the solubility of solids in scCO_2 [11].

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