J. of Supercritical Fluids 55 (2010) 176–183

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu

Effects of differential permeability on packed bed supercritical extractors: A theoretical insight

Luca Fiori[a,*], Paolo Costa[b]

[a] DICA, Trento University, Via Mesiano 77, 38123 Trento (TN), Italy
[b] DICAT, Genova University, Via Opera Pia 15, 16145 Genova (GE), Italy

ARTICLE INFO

Article history:
Received 18 February 2010
Received in revised form 11 June 2010
Accepted 16 June 2010

To the memory of Prof. Paolo Costa.

Keywords:
Bed permeability
Extraction kinetics
Supercritical extraction
Column models
Seed oil
Axial dispersion coefficient

ABSTRACT

This paper analyses the effects on the extraction kinetics of a solvent flow which is non-uniform in the extraction column bed cross-section. When modeling the extraction kinetics of a solute from a solid matter (for instance of oil from seeds), the solvent motion is normally assumed as consisting in plug flow, eventually corrected by the axial dispersion coefficient. Some experimental evidence put into question this simplified description. We have shown to which extent the effects of a non-uniform extraction bed permeability reflect on the extraction kinetics: in particular conditions, these effects could be even more significant than the effects due to the mass transport resistances governing the extraction of the solute out from the matrix.

1. Introduction

Several models have been developed to describe the supercritical extraction process occurring in packed bed extractors. Typical examples are represented by the models predicting the extraction of oil from vegetable seeds [1–8]. These models represent the flow pattern of the solvent as being uniform inside the extractor: the solvent motion is described in terms of plug flow and in some cases the bed axial dispersion is considered [4,6–8], in other cases it is not [1–3,5]. Anyhow, the presence of the bed axial dispersion term does not significantly affect the modeling predictions, given that the bed Peclet number for supercritical extractors is, in general, much higher than the typical reference value for plug flow behavior [9]. These models stress the mass transfer mechanism between substrate and solvent and, some of them [5,6,8], also the structure of the vegetable substrate. A common feature among some of them [2,5–8] is, on one hand, the subdivision of the extractable matter in fractions with different availability and, on the other, the utilization of one or more transport coefficients governing the oil transfer from the substrate to the solvent. Typical examples of this approach allowed defining a 'free oil' fraction occurring at the surface of the milled seed particles, and identifying an internal mass transfer coefficient linked to the vegetable structure of the seeds.

On the other hand, some experimental findings seem to reveal the possible presence and relevance of solvent flow patterns which are different from a simple plug flow. In particular, some differences in the extraction kinetics have been encountered when changing the flow direction [10,11]. This behavior has been explained in terms of natural convection [11]. In some circumstances, the formation of preferential flow channels for the solvent (due to the presence of natural convection or caused by the packing of the substrate in the bed) cannot be neglected.

When in the modeling we consider only the average flow rate of the solvent in the extractor bed cross-section we do not take into account the occurrence of these channeling phenomena. In order to consider them, a possibility is referring to an extractor bed having zones with permeability which is different from the average bed permeability, or, equivalently, referring to a solvent flow rate distribution inside the extractor cross-section. An accurate description of these phenomena would imply the utilization of complex percolation models. They could take into account, on a statistical basis, the complex interconnections among the subsequent tracts at different velocity of the solvent route. Moreover, they could also take into account the interaction among adjoining routes.

Considering the above, we decided to take a first step forward considering the extraction column as consisting of several extraction columns in parallel, each one characterized by its own solvent

---

[*] Corresponding author. Tel.: +39 0461 282692; fax: +39 0461 282672.
E-mail address: luca.fiori@ing.unitn.it (L. Fiori).

0896-8446/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.supflu.2010.06.007

mean velocity. A similar approach has been already followed by Sovovà et al. [11], who proposed a model where the flow pattern was represented by several parallel solvent flows of different velocities in different parts of the extraction bed cross-section.

We considered a velocity distribution in the extraction bed cross-section, which can be easily linked to a column residence time distribution. Some experimental residence time distributions in supercritical extraction columns have been recently measured [12], testifying the weakness of the plug flow hypothesis. These experimental findings suggest the necessity of a more in depth approach to the subject.

The analysis presented here allows us to underline some (to our opinion) important aspects:

(1) In this section and, more in details, in Section 7, the discussion focuses on the models available in the literature, on their assumptions regarding the solvent motion inside the extractor bed, on the consistency of the same assumptions in the light of experimentally measured distribution of permanence times.

(2) As a consequence of the above, the authors discuss one possible explanation of the experimental findings: the non-uniformity of the extraction bed permeability. The approach starts with the definition of a velocity distribution of the solvent inside the extractor bed cross-section (Section 2). It moves to the expression of the saturation degree of the solvent through the extractor and the extraction yield (Section 3). It accounts for the coupling of velocity distributions with ideal instantaneous extraction kinetics (Section 4). It introduces different velocity distributions (Sections 5 and 6), and non-instantaneous (but simplified) extraction kinetics (Section 8 and Appendix B).

This is a paper that, moving from experimental findings that question one consolidated modeling hypothesis – solvent motion: uniform into the extractor bed cross-section – analyses, on a theoretical basis, to which extent the non-uniformity of the extraction bed permeability would affect the extraction kinetics. The phenomenology, with its simplifications, is reported in the frame of a rigorous physical–mathematical model that could represent a solid theoretical base utilizable in the future by researchers which would enrich this approach with new experimental results.

The precise definition of the velocity distribution is the subject of the following section. Appendix A reports the relations between velocity distributions and column residence time distributions.

2. The velocity distribution

A relatively simple representation of the flow pattern inside an extraction column consists in a velocity distribution of the solvent in the extraction bed cross-section.

We define the velocity distribution function $f(v)$ so that $f(v)dv$ represents the fraction of the bed cross-section traversed by the solvent with a mean velocity, in the entire length of the extractor bed, ranging between v and $v+dv$. The function $f(v)$ is defined in an interval whose extremes are the minimum velocity $v_{\min}$, eventually zero, and the maximum velocity $v_{\max}$. The function $f(v)$ has to fulfill the normalization conditions expressed by Eqs. (1)–(3):

$$\int_{v_{\min}}^{v_{\max}} f(v)dv = 1 \tag{1}$$

$$\int_{v_{\min}}^{v_{\max}} vf(v)dv = u \tag{2}$$

$$\int_{v_{\min}}^{v_{\max}} v^2 f(v)dv = u^2 + \mathrm{var}\, v \tag{3}$$

Nomenclature

a	parameter of the velocity distribution – specific surface of the solid in Appendix B [m^{-1}]
b	parameter of the velocity distribution
c	parameter of the velocity distribution
C	solute concentration in the solvent [kg/m^3]
C_{sat}	solute concentration in the solvent at saturation [kg/m^3]
ΔC_i	variation in the concentration at the extractor inlet
ΔC_u	variation in the concentration at the extractor outlet
$f(v)$	velocity distribution [s/m]
$f(\phi)$	dimensionless velocity distribution
$f_{v,q}(v)$	velocity distribution in respect to the flow rate [s/m]
$f_{v,S}(v)$	velocity distribution in respect to the extractor cross-section [s/m]
f_0	dead zones in the extractor
$f_t(t)$	differential distribution of the residence times [s^{-1}]
$F_t(t)$	integral distribution of the residence times
$G(\phi)$	integral function defined in the text
h	extractor length [m]
h_c	thickness of the column layer necessary for saturating the solvent [m]
Y	extraction yield
k_c	overall mass transfer coefficient [m/s]
m	equilibrium parameter
q	extracted matter per unit volume [kg/m^3] – flow rate in Appendix A [m^3/s]
q_0	extractable matter [kg/m^3]
S	surface or cross-section [m^2]
t	residence time [s]
t_a	time [s]
u	mean velocity [m/s]
var	variance
v	velocity [m/s]
$v_{\max}$	maximum velocity [m/s]
$v_{\min}$	minimum velocity [m/s]
v_e	velocity of the ‘extraction-wave’ [m/s]
x	saturation degree of the solvent – local value
x_1	saturation degree of the solvent at the exit of the elementary column
X	saturation degree of the solvent – average value for the extractor cross-section
X_1	saturation degree of the solvent at the exit of the extractor
z	axial coordinate in the extractor [m]

Greek letters

α	ratio between solute in the substrate before extraction and solute concentration in the solvent at saturation
ϕ	dimensionless velocity
$\phi_{\max}$	dimensionless maximum velocity
$\phi_{\min}$	dimensionless minimum velocity
ξ	dimensionless axial coordinate in the extractor
θ	dimensionless time
θ_c	time necessary for saturating the solvent
θ'_c	time defined by Eq. (B10)
θ_e	dimensionless exhaustion time for the elementary column
θ^*	reduced time
γ	parameter linking the variation in mass transfer with the variation in velocity of the solvent
τ	mean residence time [s]