



Optimization of supercritical fluid extraction: Polydisperse packed beds and variable flow rates



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ABSTRACT

This theoretical study examines variable-in-time flow rates $v(t)$ and different ways of packing polydisperse ensemble of ground particles as controls in supercritical fluid extraction (SFE) to maximize the extraction yield. The so-called packing function χ is introduced to describe the local particle-size distribution in the pack along the extraction vessel. The research is based on the modified shrinking-core (SC) model for the mass transfer inside particles and assumes the pseudo-steady solvent flow in the SFE vessel. It is rigorously proven that for any variable flow rate $v(t)$ and overall particle-size distribution F , the corresponding locally-monodisperse stratified (LMS) packing χ_0 maximizes the current amount of extracted solute, while the appropriate filtration policy extends the domain of efficient particle-size distributions. Sufficient conditions that guarantee a certain extraction degree at a fixed time are deduced and formulated in terms of F -distribution. Being of obvious practical significance for finely ground substrates, optimization is shown to be rather limited for relatively big particles (commonly used in laboratory experiments), and only longer extraction times, higher oil solubility and diffusion rates allow noticeable increase in the extraction yield in this case.

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1. Introduction

Industrial technologies which use supercritical fluids become more and more popular in production of new materials, natural products, pharmaceuticals and others. One of the most attractive applications of supercritical fluids is extraction of natural products from packed beds of ground plants or other granular material – the supercritical fluid extraction (SFE) [1]. This technique gradually substitutes for traditional extraction methods all over the world, being environmentally friendly and providing selective extraction. Supercritical CO₂ is conventionally used in SFE as a solvent because it is non-toxic, non-flammable and readily available. It also has low critical temperature (~31 °C) which is crucial for extraction of thermally labile compounds (such as essential oils).

As a consequence, significant attention is drawn to understanding and optimization of the SFE process. SFE practice is usually focused on experimental tuning of extraction conditions such as solvent flow rates, temperature, and pressure in the framework of “experimental design approach” or “response surface method” to achieve the highest mass of extract at a fixed extraction time [2].

However, these research lines require a large number of experiments and do not consider more sophisticated controls which account for temporal variation of solvent flow rates and spatial inhomogeneity of particle-size distribution in a polydisperse packed bed for given thermodynamic conditions. Practical significance of such controlling factors together with other technological parameters (grinding rate and extractor dimensions) could be theoretically evaluated on the basis of an appropriate SFE model [3].

Various mass-transfer models [4–7] have been presently employed for SFE predictions and data interpretations [4–11]. Among them, the two, shrinking core (SC) [5] and broken-and-intact cell (BIC) [4], models cover a wide range of possible approaches and have shown [4,8,9,12,13] to match the overall extraction curves (OECs) with high accuracy. Based on the general description of oil diffusion in ground material, one could deduce that, in principle, the BIC model is valid in the limit of relatively small particles, when the inner part of a particle can be described in terms of spatially averaged characteristics. On the other hand, the SC model becomes more preferable in the case of relatively big particles with high oil content, when the diffusive front thickness in particles is much less than their typical size [5].

Herein we employ the modified SC modeling approach discussed [12–16] previously in detail and verified (validated) [12,13] on various available data sets.

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Nomenclature

Symbol

a	particle size (half-thickness and radius for flat and spherical particles, respectively)
A	optimal domain area
c	normalized solute concentration in the fluid phase
D	effective coefficient of oil diffusion in ground particles ($\text{m}^2 \text{s}^{-1}$)
e	bed porosity
H	vessel height (m)
f	density of overall distribution function F
F	overall particle-size distribution of original ground plant material
m_{oil}	extractable mass of the solute in the packed bed (kg)
n	particle shape factor
q	current consumption ratio
Q	total volume of solvent (m^3)
Q_{min}	minimum volume of the solvent needed to dissolve all extractable mass m_{oil} (m^3)
s	fraction of oil extracted from particles
s_1	fraction of oil extracted from particles at the end of SFE process defined by Eq. (12)
S	vessel cross-section area (m^2)
t	normalized extraction time
v	normalized variable-in-time flow rate
y	zonal oil fraction extracted from the packed bed interval $[0, z]$
Y	overall extraction curve, $Y=y(1,t)$
z	normalized spatial coordinate
UD	uniformly distributed pack
LMS	locally-monodisperse stratified pack
ILMS	inverse LMS pack

Greek symbols

α	total extraction degree, $\alpha = Y(1)$
γ	solvent consumption ratio, $\gamma = Q/Q_{\text{min}}$
δ	Dirac “delta”-function
η	solvent consumption efficiency, $\eta = \alpha\gamma^{-1}$
θ	initial density of extractable oil in ground plant material (kg m^{-3})
θ_*	equilibrium concentration of oil in the solvent (kg m^{-3})
λ	cumulative diffusion coefficient in Eq. (2)
χ	packing function, represents the local density of particle-size distribution for any given cross-section of the packed bed along the extraction vessel
ω	flow rate policy $\omega(t) = v(t)/\gamma$
ω_a	analytical approximation of optimal flow rate policy

Subscripts

0	optimal value
sc	typical scale
max	maximum value
c	the “most coarse” grinding

The paper consists of two parts. First, in Section 2, the dimensionless form of the earlier developed model is presented, and the SFE optimization problem is formulated. As mentioned above, the principal point is that original polydisperse ground plant material can be distributed along the vessel in different ways. Mathematical description of particles' packing is given in terms of the packing function χ which, by definition, represents the local density of particle-size distribution for any given cross-section of the

packed bed along the extraction vessel. Three functions: the overall particle-size distribution F of original ground plant material (or its density f), packing function χ and variable-in-time superficial velocity v (or its normalized representation – the so-called flow rate policy ω) are considered as the optimization parameters.

In Section 3, we investigate the formulated optimization problem and discuss practical importance of obtained theoretical results in case of constant flow rates as well as possible practical advantages of using variable flow rate policies.

2. SFE model and optimization problem

2.1. SFE model formulation

A generalized SFE model [12–16] based on SC approximation for the micro-scale mass-transfer phenomena inside individual particles and extended to polydisperse packed beds is employed below in our study. The convective solute-mass transport/exchange process on macro-scale level (fluid phase) is described under conventional assumption of the homogeneous flow pattern (plug flow regime [8,9]) in the bed of uniformly packed particles with constant porosity. The model has been formulated in one-dimensional presentation, in terms of the cross-sectional mean characteristics of the SFE process, in the limit of pseudo-steady (quasi-stationary) convective mass transfer [9,17] in the vessel and negligibly small axial dispersion [5,8,9,17]. Due to high diffusivity of oils in supercritical CO_2 , resistance to external oil-mass exchange between particles' surface and fluid (solvent) phase has been also neglected [16]. Model validity and practical applicability under SFE conditions typical for oilseeds (e.g. rapeseed, sunflower seed etc.) with relatively high oil content have been earlier discussed and illustrated in [12,13,15,16,18].

Aimed at mathematical investigations, we reformulate the model in dimensionless form. Hereinafter t is the normalized time, $0 \leq t \leq 1$; z – the spatial coordinate varying from 0 to 1 along the vessel, from its inlet to outlet; $v(t)$ – the dimensionless variable-in-time superficial solvent velocity and $F(a)$ – the overall particle-size distribution function (ODF) of ground plant material with the distribution density $f(a)$. By definition, $dF = f da$ is the volumetric fraction of particles with the normalized size from a to $a + da$. The particle-size distribution (functions F and f) results from grinding conditions. Let us also introduce the normalized solute concentration $c(z,t)$ in the fluid phase and the oil fraction $s(z,t,a)$ extracted from particles of size a at the moment t in the cross-section z ; $0 \leq c, s \leq 1$. It should also be noted that oil fraction s is directly linked to the shrinking core radius in spherical or flat particles [12,14,18].

The scales of the above characteristics, deduced on the basis of scale analysis and designated by subscript “sc”, are [12,18]

$$c_{\text{sc}} = \theta_*; \quad z_{\text{sc}} = H; \quad v_{\text{sc}} = \frac{Q_{\text{min}}}{St_{\text{sc}}}; \quad a_{\text{sc}}^2 = 2nDt_{\text{sc}} \frac{\theta_*}{\theta}, \quad (1)$$

where θ_* is the equilibrium concentration of oil in the solvent, θ – the initial density of extractable oil in ground plant material, H – the vessel height, S – the vessel cross-section area, $Q_{\text{min}} = m_{\text{oil}}/\theta_*$ – the minimum volume of the solvent needed to dissolve all available (extractable) mass $m_{\text{oil}} = \theta HS(1 - e)$ of the solute (oil) in the packed bed with porosity e at given temperature and pressure, D – the apparent (effective) coefficient of oil diffusion in ground particles, n – the particle shape factor ($n = 1, 3$ for flat particles of thickness $2a$ and spherical particles of radius a , respectively). The time scale t_{sc} is the duration (fixed value) of the SFE process.

Physically, the characteristic particle size a_{sc} is the boundary value which divides the ground particle ensemble in two parts of smaller ($a < 1$) and bigger ($a > 1$) particles, separating the smaller ones that can be fully extracted (at least in the limiting conditions of pure solvent, at $c \rightarrow 0$) from those that remain only partly

extracted after the given extraction time t_{sc} . Accordingly, the superficial velocity scale v_{sc} is the flow rate at which Q_{min} -volume of solvent passes through the vessel during the t_{sc} -time interval.

Eventually, the convective mass transport equation in the fluid phase and the diffusive mass transfer equation in particles can be transformed to and written in the following dimensionless form [12,14,18]:

$$v(t) \frac{\partial c}{\partial z} = \int_0^{+\infty} \frac{\partial s}{\partial t} \chi(a, z) da \quad (2)$$

$$\frac{\partial s}{\partial t} = \frac{\lambda(s)}{a^2} (1 - c) \quad (3)$$

with the respective initial and boundary conditions

$$s(z, 0, a) = 0, \quad c(0, t) = 0. \quad (4)$$

Here the cumulative diffusion coefficient $\lambda(s)$ depends on the particle shape factor n , and for spherical and flat particles is

$$\lambda|_{n=3} = \frac{0.5(1-s)^{1/3}}{1-(1-s)^{1/3}}, \quad \lambda|_{n=1} = \frac{1}{2s}.$$

The packing function $\chi(a, z)$, introduced in Eq. (2), represents the local density of particle-size distribution in a cross-section z of the vessel [14]. Usually [3–13,15–21], it is assumed that ground (polydisperse) particles are uniformly distributed in the vessel, and $\chi(a, z) = f(a)$.

Furthermore, it is convenient to rewrite Eq. (2) in terms of the zonal oil fraction $y(z, t)$ extracted from the packed bed interval $[0, z]$,

$$y(z, t) = \int_0^z v(\tau) c(z, \tau) d\tau \leq z$$

normalized by $y_{sc} = m_{oil}$. Obviously, $Y(t) = y(1, t)$ is the OEC measured in experiments.

Accordingly, after integration of Eqs. (2) and (3) with respect to time with initial condition (4) we finally arrive at

$$\frac{\partial y}{\partial z} = \int_0^{+\infty} s \chi da, \quad y(0, t) = 0 \quad (5)$$

$$a^2 \varphi(s) = \min \left\{ a^2; t - \int_0^t c(z, \tau) d\tau \right\}, \quad 0 \leq \varphi = \int_0^s \frac{d\xi}{\lambda(\xi)} \leq 1. \quad (6)$$

By definition, $\lambda(s)$ is positive, and $\varphi(s)$ is a monotonic function of s for $0 \leq s \leq 1$. Consequently, relationship (6) determines s implicitly as the inverse function φ^{-1} of the complex variable ξ :

$$s(\xi) = \varphi^{-1}(\min\{1; \xi\}), \quad \xi(z, t, a) = \frac{1}{a^2} \left(t - \int_0^t c(z, \tau) d\tau \right) \geq 0.$$

It should be noted that the typical particle size a_{sc} has been introduced so as to normalize the diffusive resistance of particles, and $\varphi(1) = 1$.

2.2. Optimization problem formulation and analysis

To specify the principal controls of the SFE model, let us also introduce the total available volume of solvent Q , confining

possible variations of superficial velocities to the solvent mass balance condition

$$\int_0^1 v dt = \frac{Q}{Q_{min}} \equiv \gamma \quad (7)$$

with γ defined as the solvent consumption ratio. Thus, the flow rate policy is reduced to the normalized control $\omega(t) = v(t)/\gamma$.

As explained in introduction, the packing function $\chi(a, z)$ describes the particle distribution along the vessel and is linked to the overall particle-size distribution density $f(a)$ by the particle number conservation condition for each size a

$$f(a) = \int_0^1 \chi(a, z) dz. \quad (8)$$

The most important overall characteristics of the SFE process are the total extraction degree $\alpha = Y(1)$ and the solvent consumption efficiency $\eta = \alpha \gamma^{-1}$ – the ratio of the minimum solvent volume αQ_{min} needed to dissolve the extracted fraction α of solute to the actually used solvent volume Q .

Consequently, for given thermodynamic conditions, the SFE optimization problem can be rigorously formulated as maximization of the goal function

$$\alpha [F, \chi, \omega] \rightarrow \max \quad (9)$$

determined on solutions of SFE model (5) and (6) at constraints (7) and (8) with particle-size distribution function F (or its density f), packing function χ , and flow rate policy ω as controls (optimization parameters). Obviously, for a fixed parameter γ , problem (9) is equivalent to maximization of solvent consumption efficiency η .

It is useful to explicitly evaluate some of the upper bounds of the goal function (9). For example, extraction degree α becomes independent of filtration policy $\omega(t)$ and packing distribution $\chi(a, z)$, when $c \rightarrow 0$ at $\gamma \rightarrow \infty$, and, as follows from Eqs. (5), (6), and (8), at $t = 1$, for any ODF its maximum value is

$$\alpha_{max} [F] = \int_0^{+\infty} s (a^{-2}) f(a) da. \quad (10)$$

Physically, $\alpha_{max} \leq 1$, and unity is the global maximum of α . Relationship (10) shows that if a finite fraction of the bigger particles (of size $a > 1$) exists in the packed bed then, in accordance with s -function properties, $\alpha_{max} < 1$, and it is not possible to reach the global maximum of α for any γ only by varying ω . This limitation should be taken into account when an extractor and/or an extraction procedure are designed.

Furthermore, since $\alpha \leq \gamma$, the global maximum of η is also unity and can be achieved only if the outlet solute concentration equals its maximum (equilibrium) value for the whole extraction period. Additionally, at a given ODF, there is no reason to consider $\gamma < \alpha_{max}$, because the α_{max} -level of extraction would be unattainable ($\alpha \leq \gamma$), and hereinafter it is assumed that $\gamma \geq \alpha_{max}$.

The major part of the following section is focused on evaluating different ways of packing polydisperse particle ensembles along the SFE vessel and on the effect of flow rate policy ω on the set of optimal ODFs. The obtained results are compared with other related studies [3].

3. Results and discussion

3.1. Different types of packing functions

In principle, three different limiting cases of particles' packing can be distinguished. First assumes that ground particles are

uniformly distributed in the vessel, independently of their size, and $\chi^{\text{UD}}(a, z) = f(a)$ represents the uniformly distributed (UD) pack commonly used in SFE practice and simulations [3–13, 15–21].

Another way of packing, the so-called locally-monodisperse stratified (LMS) packed bed [14], is the bed composed of original ground plant material sorted and packed along the extraction vessel in the order of particle size decrease. The LMS particle size $\hat{a}(z)$ at a certain location z inside the extractor is uniquely determined via the overall particle-size distribution function $F(a)$ by equation

$$F(\hat{a}) = 1 - z, \quad (11)$$

or, using the inverse relationship F^{-1} , we write

$$\hat{a} = F^{-1}(1 - z),$$

and the corresponding packing function is expressed by the Dirac “delta”-function δ

$$\chi^{\text{LMS}}(a, z) = \delta(a - F^{-1}(1 - z)).$$

The third case is the inverse LMS (ILMS) packing [14] with corresponding particle fractional size $a^\vee(z)$ monotonically increasing with z and related to $F(a)$ by

$$F(a^\vee) = z, \quad a^\vee = F^{-1}(z), \quad \chi^{\text{ILMS}}(a, z) = \delta(a - F^{-1}(z)).$$

In the framework of the SFE model (5) and (6) with constraint (8) at a constant flow rate, $v = \gamma$, it was theoretically proven [14] that, for any size-distribution function $F(a)$, the LMS pack is the searched optimal packing function χ_0 , which delivers the maximum current yield of the solute. Reversely, the ILMS packed bed results in the minimum current yield. These conclusions hold both for spherical and flat particles. It can be also shown (to be published elsewhere) that the above formulated statements remain true for any pair $(F; \nu)$ with variable-in-time filtration rates.

Physically it means that within the concept of shrinking core it is favorable to locate the bigger particles near the inlet to be ‘washed’ all the time by the solvent at the lowest content of dissolved oil, whereas the smaller particles can ‘wait’ near the vessel outlet until the bigger particles (upstream the flow) become depleted and the solvent with low oil concentration reaches the outlet vicinities to quickly complete the extraction of oil from the smallest particles of high specific surface area.

Further, we concentrate mainly on the LMS packs, reducing the list of controls in goal function (9) to F and ω .

3.2. Optimal ODF domains of LMS packs

The unique quality of LMS packs suggests further analysis of particle-size distribution functions F to sort out the ground particle ensembles for which LMS beds provide the guaranteed extraction degrees $\alpha \geq \alpha_0$ at $0 \leq \alpha_0 \leq 1$. For a given γ , this set of the so-called α_0 -optimal LMS distributions depends on the flow rate policy $\omega(t)$ and α_0 .

Let us note that the finer particle grinding is the higher extraction rates are, and, consequently, the higher α -values can be achieved. This fact is expected in practice and is theoretically predicted in the framework of the SC model concept, particularly, for LMS packs (see Appendix A). Consequently, one can conclude that for two distribution functions $F_1(a) \geq F_2(a)$ the corresponding extraction degrees satisfy the same inequality $\alpha_1 = \alpha[F_1, \omega] \geq \alpha_2 = \alpha[F_2, \omega]$. Thus, for any limiting ODF $F_c(a)$ of the “most coarse” grinding which provides the extraction degree α_0 , all distributions $F \geq F_c$ will be α_0 -optimal, and $F = F_c(a)$ will represent a lower boundary of the α_0 -optimal ODF domain on the (a, F) -plain. Equally, the corresponding LMS distribution of particle size along

the extractor – decreasing function $a = a_c(z) = F_c^{-1}(1 - z)$ – will be an upper boundary of the α_0 -optimal LMS packing domain on the (z, a) -plain.

By definition, $a_c(z)$ must satisfy the following mass balance condition

$$\alpha_0 = \int_0^1 s_1(z) dz, \quad \frac{\partial a_c}{\partial z} \leq 0, \quad (12)$$

where $s_1(z) = s(z, 1, a_c)$ is the oil fraction extracted from cross-section z as predicted by the SFE model (5) and (6).

Furthermore, if all fully extracted particles in LMS pack $a_c(z)$ have been depleted simultaneously at the end of the extraction period, $t = 1$, then from Eq. (6) we get

$$1 - \int_0^1 c(t, z) dt = a_c^2(z) \varphi(s_1). \quad (13)$$

Physically, as illustrated by the computational algorithm described below, it could be well understood that, in the framework of model (5) and (6), for any triplet $(\omega; \gamma; \alpha_0)$, each $s_1(z)$ -dependence is uniquely, one-to-one, related with the LMS pack $a_c(z)$ by Eq. (13), and there exists a representative subset of limiting ODFs $\{F_c(a)\}$, i.e. the set of LMS distributions $\{a_c(z)\}$, given by Eqs. (12) and (13). One of the simplest options corresponds to $s_1(z) = \alpha_0$. The general question of complete description of the full set $\{F_c(a)\}$ still remains open.

To calculate a particular LMS distribution $a_c(z)$ for a given function $s_1(z)$, which satisfies conditions (12), one has to solve Eq. (13). Since at any z -level the SFE process depends only on the extraction prehistory in the up-flow (inlet) side of the vessel, the searched values of the grid approximation $a_c^j = a_c(z_j)$ in the z_j -nodes, $0 = z_0 < z_1 < \dots < z_N = 1$, can be computed sequentially step by step. The boundary value a_c^0 at $z = 0$ is explicitly determined by Eq. (13) for the fixed solute concentration $c = 0$ as prescribed by Eq. (4). Further on, once the grid values $a_c^0, a_c^1, \dots, a_c^j$ have been found, the next one a_c^{j+1} at the z_{j+1} -node is calculated iteratively from Eq. (13), starting from initial approximation $a_c^{j+1} \approx a_c^j$, until the set accuracy is attained. Numerous computational experiments confirmed the convergence of this algorithm for a wide variety of superficial velocities $v(t)$ and functions $s_1(z)$.

The α_0 -optimal ODF domains are studied numerically below in Section 3.4.

3.3. LMS packs of complete extraction

Optimal ODFs of complete extraction for $\alpha_0 = 1$ are of special practical interest. In this case conditions (12) permit only one possibility: $s_1(z) \equiv 1$, and Eq. (13) uniquely determines the optimal domain boundary, $a = a_c(z) = F_c^{-1}(1 - z)$. As discussed above, in Section 3.2, there might exist, at least in principle, other limiting optimal ODFs not constrained by condition (13). However, numerical optimization tests showed that such solutions, even if they do exist, would not noticeably expand the ODF domain of complete extraction. Hence, the general optimization problem (9) can now be reformulated solely in terms of the flow rate policy $\omega(t)$ as the only control to maximize the optimal domain area $A[\omega]$ at a given solvent consumption ratio $\gamma \geq 1$,

$$A[\omega] = a_{\max} - \int_0^{a_{\max}} F da = \int_0^{a_{\max}} a f da \rightarrow \max, \quad (14)$$

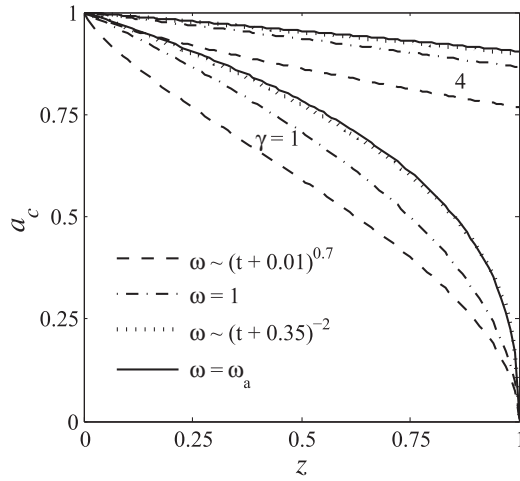


Fig. 1. Domains of complete extraction (boundary functions $a_c(z)$) for different flow rate policies $\omega(t)$ in case of spherical particles.

where (in case of complete extraction) the maximum particle size $a_{\max} = 1$. Obviously, problem (14) is equivalent to the mean-particle-size maximization, i.e. to searching the ODF of the most coarse grinding.

This optimization problem has been analyzed theoretically and solved numerically. First of all, an analytical approximation of the most efficient flow rate policy

$$\omega_a = \kappa \sqrt{\lambda (\varphi^{-1}(t))}, \quad \kappa^{-1} \approx 0.8329$$

has been intuitively derived under assumption that the optimal flow rate variations $\omega_a(t)$ must result in the minimum inlet slope of the boundary LMS-packing $a = a_c(z)$ at $z=0$. The $\omega_a(t)$ policy remains same at any γ , α_0 and $s_1(z)$. It is a decreasing function of time, abruptly tending to zero at $t \rightarrow 1$.

Numerical optimization in case of spherical particles for different γ confirms that the analytical flow rate policy ω_a closely reproduces the principal features of the computed optimal control and delivers practically same ODF-domain area and shape. Sensitivity tests show that the goal function $A[\omega]$ and the boundary LMS-distribution are not affected much if the flow rate control $\omega(t)$, reasonably deviated from the optimal solution, remains a decreasing function of time. Hence, the dependence $\omega_a(t)$ can be considered as a reliable uniform analytical approximation of the optimal flow rate, at least for the complete extraction limit of SFE procedure.

Fig. 1 illustrates the general importance of the flow rate policy $\omega(t)$ as the control of the LMS-packs domain of complete extraction at different γ . For comparison, the frequently used constant flow rates $\nu = \gamma$ ($\omega = 1$) result in domains with the dash-dotted boundaries described by inequalities

$$F(a) \geq F_c(a) = 1 + \gamma (a^2 - 1),$$

$$a(z) \leq a_c(z) = \sqrt{1 - z/\gamma}.$$

Clearly, the close-to-optimal flow rate policy ω_a noticeably expands the region of LMS packs (solid lines) that allow complete extraction. Nevertheless, even simpler and less variable flow rate policy

$$\omega \sim (t + 0.35)^{-2}, \quad (15)$$

decreasing in time, permits practically same domains of complete extraction as shown by dots in Fig. 1.

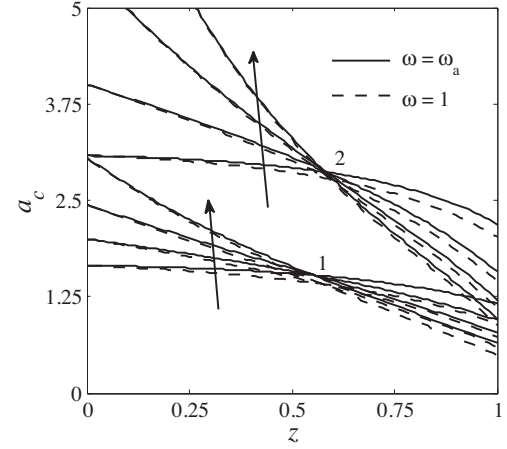


Fig. 2. α_0 -optimal domains (boundary functions $a_c(z)$) for different flow rate policies $\omega(t)$, and $s_1 = p(z - 0.5) + \alpha_0$, $-0.2 \leq p \leq 0.4$; $1 - \alpha_0 = 0.7$, $\gamma = 0.85$, $2 - \alpha_0 = 0.4$, $\gamma = 0.45$. Arrows indicate direction of p increase at step 0.2.

On the contrary, increasing flow rates lead to much stronger limitations on the optimal LMS packs than, even, those imposed by the constant flow rate policy. An example (dashed lines) shown in Fig. 1 corresponds to

$$\omega \sim (t + 0.01)^{0.7}. \quad (16)$$

As could be expected, the domains of LMS-packs of complete extraction expand with increase in solvent consumption ratio γ , and the optimization effect becomes less prominent as $\gamma \rightarrow \infty$ and the domain boundary tends to $a_c = 1$.

It should be emphasized that each ODF domain of complete extraction determined for the given flow rate policy $\omega(t)$ and solvent consumption ratio $\gamma \geq 1$ outlines the set of all possible LMS packed beds of dimensionless particle size $a \leq 1$ which allow full depletion for the fixed (finite) period of time. The domain of complete extraction could be essentially expanded if optimal or, at least, monotonically decreasing flow rate policies $\omega(t)$ are employed. However, at minimum solvent consumption, $\gamma = 1$, the complete extraction cannot be achieved for finite time if the size of the finest particle fraction does not tend to zero.

3.4. LMS packs of incomplete extraction

In many practical cases, with relatively big particles in the ground material, full extraction can not be attained for reasonable times, and, in accordance with Section 3.2, general optimization problem (9) must be considered on the set of ODFs (LMS packs) characterized by $\alpha_{\max} < 1$ in Eq. (10) at different consumption ratios γ .

In other words, we have to study the α_0 -optimal ODF domains at $\alpha_0 < 1$. A series of computational experiments have been performed to calculate the limiting LMS distributions $a_c(z)$ for various extraction degrees α_0 and functions $s_1(z)$ at given pairs $(\omega; \gamma)$.

Some results of simulations which demonstrate the effect of α_0 , ω and s_1 are gathered in Fig. 2. Values of γ are intentionally set only slightly higher than α_0 because for lower α_0 and bigger particles solute concentration c decreases, and the effect of the flow rate policy ω on the optimal domain diminishes with γ as demonstrated in Fig. 1.

For $\alpha_0 < 1$, optimization problem (14) has also been investigated numerically for a representative set of α_0 , γ and selected functions $s_1(z)$. As in conditions of the complete extraction, the computed optimal flow rate policies do not significantly expand

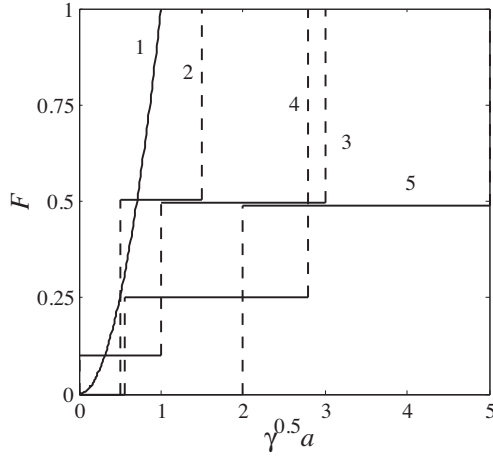


Fig. 3. ODFs of polydisperse ground plant material used for OEC simulations in Fig. 4. 1 – $F_c(a) = a^2$ resulting in maximum extraction rates at $\nu = 1$.

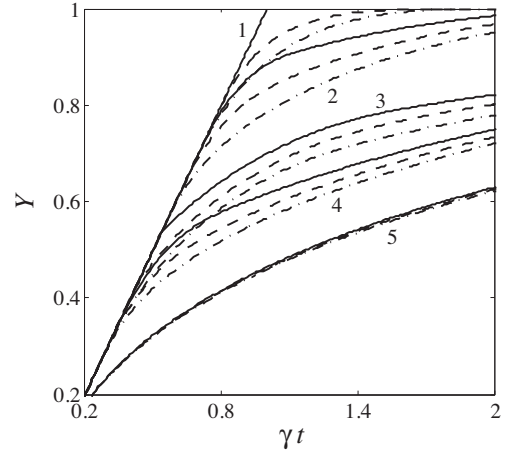


Fig. 4. OECs for different ODFs as shown and numbered in Fig. 3. Solid, dashed, and dash-dotted curves correspond to LMS, UD, ILMS packing, respectively.

the α_0 -optimal domains of LMS packs in comparison with the case of ω_a .

Hence, we repeat after Section 3.3 that flow rate policies of ω_a -type result in close-to-optimal SFE process with LMS distribution of ground material along the extractor for any ODF. However, constant flow rates, being not the worst option (see Fig. 1), may be preferred in some cases and deserve more attention.

3.5. Extraction at constant flow rates

The zonal fraction of extracted oil at $\nu = \gamma$ is

$$y = \gamma \int_0^t c(z, \tau) d\tau.$$

For any overall distribution function $F(a)$ and particle packing function $\chi(a, z)$ with solute concentration $c(z, t)$ given by model (5) and (6), the latter relationship at $y(1, 1) = 1$ determines the minimum solvent consumption ratio γ required for extracting all available solute for the given dimensional time t_{sc} with the highest efficiency $\eta = \gamma^{-1}$.

For UD and ILMS packs these values are identical [14] and depend only on the largest particle size a_{max} in the batch,

$$\gamma^{UD} = \gamma^{ILMS} = (1 - a_{max}^2)^{-1}. \quad (17)$$

As follows from Eq. (17), a_{max} must be less than unity to achieve full extraction with a finite volume of solvent for a finite time.

A more complicated expression holds for LMS packs [14]

$$\gamma^{LMS} = \max_a \left(\frac{1 - F(a)}{1 - a^2} \right). \quad (18)$$

Again, only for $a_{max} \leq 1$ the complete extraction ($\alpha = 1$) can be achieved. Nevertheless, comparison of Eqs. (17) and (18) shows [14] that LMS packs even at constant flow rate ($\omega = 1$) allow essential reduction of solvent consumption by up to two times.

Overall extraction curves calculated for five types of particle-size distributions shown in Fig. 3 and different ways of particles' packing in the extractor are compared in Fig. 4. Obviously, the packing function $\chi(a, z)$ appears to be an important factor in SFE process and must be controlled, at least to avoid the ILMS or similar unfavourable packs considerably reducing the extraction rates. Importantly, in case of big, coarsely ground, particles, extraction

rates (see curves 5 in Fig. 3) practically do not depend on the way of particles' packing.

3.6. Optimization problem in the limit of big particles

In accordance with the scaling procedure (1), the big particles of dimensionless size $a > 1$ can not be fully extracted (for the given extraction time t_{sc}). The relation between a_{sc} and t_{sc} ,

$$\frac{a_{sc}^2}{t_{sc}} = 2nD \frac{\theta_*}{\theta},$$

shows that for typically low effective diffusion coefficients [12,13,15] (e.g. $D < 10^{-12} \text{ m}^2 \text{ s}^{-1}$) and reasonable extraction time t_{sc} [9,11,17,19–21], threshold particle size a_{sc} remains relatively small and most of the batches of ground plant materials, used in experiments, correspond to the big particle fraction of $a \gg 1$. The specific surface area (SSA) in the ensembles of big particles is also relatively small as well as the amount of solute totally extracted from a single particle. As a result, particle geometry does not significantly affect the extraction rates [12], and, as demonstrated in previous Section 3.5, solute concentration in the solvent flow $c \rightarrow 0$, reducing to minimum the effect of particles packing. Consequently, a monosize approximation can be assumed in the limit of big particles with the mean particle size of equivalent SSA. Thus, only flow rate policy $\omega(t)$ controls the goal function (9), and the optimization problem is studied here for different solvent consumption ratios γ at a given mean particle size a in the batch.

First of all, it is easy to derive, as a particular case of Eq. (10), an analytical expression for the maximum extraction degree $\alpha_{max}(a)$ which at $\gamma \rightarrow \infty$ depends solely on particle size a

$$\alpha_{max}(a) = s(a^{-2}).$$

For flat and spherical particles we have

$$n = 1: \quad \alpha_{max} = \min \left\{ 1; \frac{1}{a} \right\},$$

$$n = 3: \quad \alpha_{max} = \sqrt{3}a^{-1} - 2a^{-2}/3 + O(a^{-3}), \quad a \rightarrow +\infty. \quad (19)$$

Extraction degrees attainable at constant flow rates are plotted in Fig. 5 versus particle size ($5 < a < 20$) for different γ . For flow rate policy $\omega = \omega_a$ and those defined by Eqs. (15) and (16) same α -values are obtained. In this particle-size range, the limiting dependence $\alpha_{max}(a)$ practically coincides with asymptotic expansion (19) and

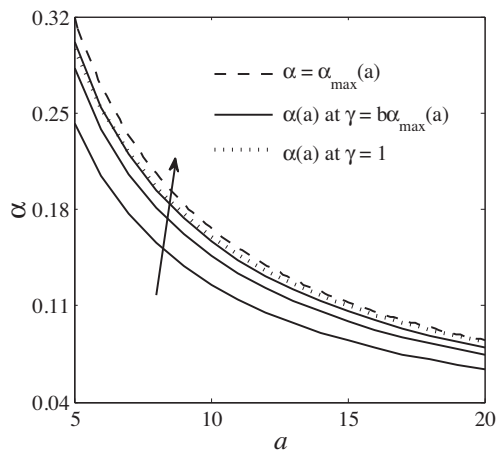


Fig. 5. Extraction degree α for $\omega = 1$. Solid lines are plotted for $b = 1, 2, 4$. Arrow indicates direction of b increase.

is shown in Fig. 5 by the dashed curve. The dots correspond to $\gamma = 1$ and are very close to the α_{\max} -limit. Hence, further increase in consumption ratios for $\gamma > 1$ and/or any variations of the flow rate in the course of SFE process would not result in noticeable growth of extraction degrees at, possibly, significant loss of the solvent consumption efficiency $\eta = \alpha\gamma^{-1}$.

The principal conclusion is that coarse grinding and absence of small particles in the ground plant material reduces to minimum the usefulness of particle packing and flow rate policy as controls in the SFE optimization. Only polydisperse batches of ground plant material with fine (small) particle fractions allow various options of SFE process improvement. Thus, in case of relatively big particles (coarse grinding) it might be more reasonable to consider a general economical problem of minimization of total oil-production costs, which, among other items of expenses, would account for (de)pressurization of solvent ($\sim \eta^{-1}$) and raw material cultivation ($\sim \alpha^{-1}$).

3.7. Overall extraction curves. Comparison with other studies

The final extraction degree (yield) $\alpha = Y(1)$ at the end of SFE process and its maximization have been the principal target of the above considerations. Nevertheless, the extraction development in time – overall extraction curve $Y = Y(t)$ – could be also very important for deeper understanding of the role of different controls: flow rate policy ω , solvent consumption ratio γ , and mean particle size a , even in monodisperse approximation. Typical OECs simulated in case of spherical particles for two (constant and variable) flow rate policies are presented in Figs. 6 and 7 versus time t and versus current consumption ratio $0 < q(t) < \gamma$

$$q = \int_0^t v dt.$$

As might be expected from previous Section 3.6, for big particles ($a > 1$) the total amount of extracted solute depends only on the particle size a and consumption ratio γ . In spite of this, the decreasing-in-time flow rates $\omega_a(t)$ provide higher yields during the extraction progress. However, as illustrated by Fig. 7, the reverse conclusion is true with respect to solvent consumption: equal amounts of solvent q result in smaller extraction yields for changing flow rate policy $\omega_a(t)$ in comparison with the constant flow rate $\omega = 1$, although at $q = \gamma$ (i.e. at $t = 1$) the extraction degrees for different policies converge to the same total yield. Hence, the

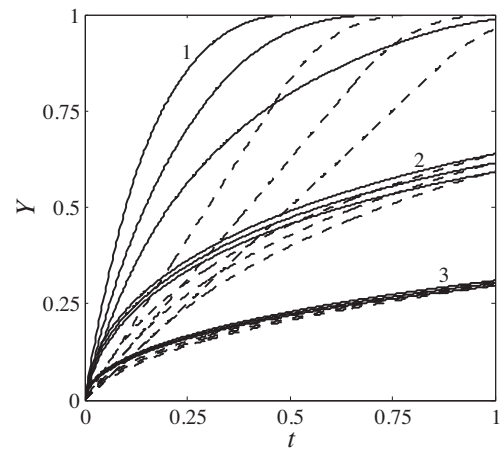


Fig. 6. OECs for monodisperse packed beds with different particle sizes and $\gamma = 1, 1.25, 1.67$. Solid and dashed lines correspond to $\omega = \omega_a$ and 1, respectively; 1 – $a = 0.5$, 2 – $a = 2$, 3 – $a = 5$.

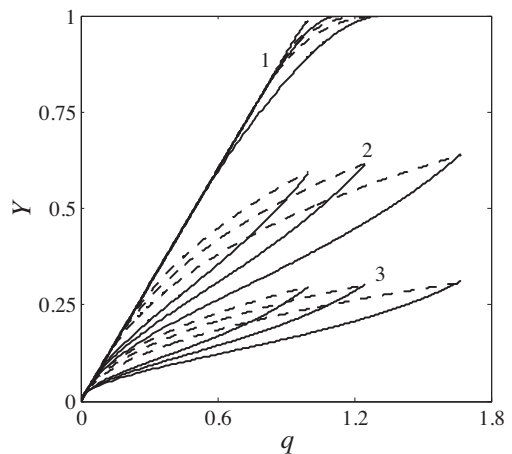


Fig. 7. OECs for monodisperse packed beds with different particle sizes and $\gamma = 1, 1.25, 1.67$ plotted versus consumption. Solid and dashed lines correspond to $\omega = \omega_a$ and 1, respectively; 1 – $a = 0.5$, 2 – $a = 2$, 3 – $a = 5$.

constant flow rate policy may be more preferable to minimize solvent losses in case of possible unpredictable interruption of SFE process.

In the light of the above similarity analysis, OECs for packed beds of different particle sizes at fixed γ must reveal the effect of extraction time t_{sc} on the SFE kinetics. This question as well as influence of flow rate policies (related to the outlet oil concentration) on the cumulative extracted mass was also numerically studied in the case of monodisperse packs by Fiori et al. [3] on the basis of Marrone's et al. modeling approach [6]. The principal goal was to maintain the outlet concentration greater than a certain fixed value by adjusting (reducing) flow rate. It was shown [3] that, for particular flow rate policies, increase in t_{sc} from ~ 400 to 700 min could be counterbalanced by the simultaneous decrease in γ from ~ 2.1 to ~ 1.1 at the same total extraction degree $\alpha \approx 0.73$. In our dimensionless denotations, these simulations correspond to relatively big particle size $a \approx 1.8$ and 1.3 for the shorter (~ 400 min) and longer (700 min) extraction periods, respectively. Our computational experiments based on model (5) and (6) are in close (within $\sim 10\%$) agreement with this conclusion. With the assumed normalization scales (1), in accordance with Section 3.6, this result could be expected in the limit of big particles and appears to be common

for different models. Additional simulations in the framework of SC model also demonstrated that in all cases considered in [3] the total extraction degree α would not noticeably depend on the flow rate policy and could be equally achieved at constant flow rates with the same consumption ratios γ .

4. Conclusions

A model based on shrinking core (SC) approach is proposed to study SFE process in polydisperse packed beds with variable-in-time flow (filtration) rates. With the use of scale analysis, the model is presented in dimensionless form in the limit of pseudo-steady (quasi-stationary) approximation of convective solute-mass transport in the extractor at conditions typical for vegetable oil extraction from ground oilseed material.

Based on the SC model, the SFE optimization problem is formulated as maximization of the total extraction degree (yield) α at the end of the SFE process with overall particle-size distribution function $F(a)$, packing function $\chi(a, z)$ of particle distribution along the vessel, and variable-in-time flow rate policy $\omega(t)$ as the controls (optimization parameters). At a given solvent consumption ratio γ , the optimization problem is equivalent to maximization of solvent consumption efficiency η .

Three different limiting cases of particles' packing are considered: uniformly distributed (UD), locally monodisperse stratified (LMS), and inverse LMS (ILMS) packed beds. For any overall size-distribution function $F(a)$ and any flow rate policy, the LMS packing of particle size $a = F^{-1}(1 - z)$ monotonically decreasing with distance z along the extractor is proven to be the optimal packing function, which delivers the maximum current yield of the solute. Reversely, the ILMS packed bed results in the minimum current yield. These conclusions hold both for spherical and flat particles.

Optimal domains of LMS packs that provide the guaranteed extraction degrees $\alpha \geq \alpha_0$ are introduced; their area and shape are studied theoretically and numerically in the cases of complete and incomplete extraction processes to determine the largest, most extended, domains of LMS packs and corresponding optimal flow rate policies $\omega(t)$. In accordance with scale analysis, efficiency of optimization strongly depends on the dimensionless size a of particles in the ground material and reduces to minimum in the limit of big particles with $a \gg 1$.

By definition, for LMS packs of small particles ($a \leq 1$), complete extraction for a fixed (finite) period of time becomes possible even at minimum solvent consumption, $\gamma = 1$, if the size of the finest particles tends to zero. It is shown that the domain of LMS packs can be essentially expanded both in case of complete or incomplete extraction if optimal or, at least, not increasing flow rate policies $\omega(t)$ are employed. An analytical approximation $\omega_a(t)$ of the optimal flow rate policy has been derived under assumption that the most efficient flow rate variations must result in the minimum inlet slope of the boundary LMS-packing at $z = 0$.

Appendix A. Finer grinding increases extraction degree in LMS packed beds

According to definition of the zonal oil fraction $y(z, t)$, in the framework of SC model (5) and (6), the integral of c with respect to time linearly depends on y ,

$$I[y] \equiv \int_0^t c dt = \int_0^t \frac{\dot{y}}{v} dt = \frac{y}{v} + \int_0^t y \frac{\dot{v}}{v^2} dt,$$

and s is the monotonic function of the combined argument

$$s = s\left(\frac{t - I[y]}{a^2}\right).$$

Consequently, for LMS packs we arrive at the following Cauchy problem with respect to y as a function of z with parameter t :

$$\frac{\partial y}{\partial z} = s\left(\frac{t - I[y]}{a^2(z)}\right), \quad y(0, t) = 0, \quad (\text{A1})$$

where $a(z)$ is determined by Eq. (11).

To compare extraction degrees of two different batches of ground particles with corresponding ODFs $F_1(a) \geq F_2(a)$ and respective LMS distributions of particle size along the vessel $a_1(z) \leq a_2(z)$, let us note that for monotonic function $s = s(\xi)$

$$s\left(\frac{t - I[y]}{a_1^2(z)}\right) \geq s\left(\frac{t - I[y]}{a_2^2(z)}\right).$$

As follows from Chaplygin theorem [22], the latter inequality together with identical initial conditions in problem (A1) leads to the required relation

$$\alpha_1 = y_1(1, 1) \geq y_2(1, 1) = \alpha_2.$$

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