THE OPTIMAL PACKING OF GROUND PARTICLES IN SUPERCRITICAL FLUID EXTRACTION

Andrey Egorov, Arthur Salamatin*
Mail address: 420008, Russia, Kazan, 35 Kremlyovskaya str., room 503
E-mail: Arthouse131@rambler.ru; Fax: +7 (843) 292-72-79

ABSTRACT

This theoretical study examines different possible ways of packing polidisperse ensemble of ground particles in supercritical fluid extraction (SFE) vessels to achieve maximum extraction rates. The research is based on the shrinking-core (SC) model for the micro-scale mass transfer inside particles.

The so-called packing function χ is introduced to describe the local particle-size distribution in the pack along the extraction vessel and is considered as an optimization (controlling) parameter of the SFE process. In the framework of the SC model, it is proven that for any overall particle-size distribution function F and filtration velocity v, the corresponding locally-monodisperse stratified (LMS) packed bed characterized by the packing function χ_o minimizes the full depletion time t_+ of the packed bed. Quantitative estimates showed that the LMS packed beds can reduce the full depletion time by up to two times.

Further minimization of t_+ with respect to the LMS packing function χ_o (i.e. particle-size distribution function F) and variable-in-time filtration velocity revealed a diverse class of distribution functions for which LMS packed beds provide the global minimum of t_+. For all these optimal distributions the solvent reaches the outlet of the extraction vessel, being saturated with the solute throughout the whole SFE process.

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 plant 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 CO_2 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. The SFE optimization is usually focused on the best tuning of extraction conditions such as constant filtration velocity, 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 filtration rate and spatial inhomogeneity of particle-size distribution in a polydispersed packed bed for given thermodynamic conditions. Practical significance of such

controlling factors together with other technological parameters (grinding rate and extractor dimensions) could be evaluated on the basis of an appropriate SFE model. Herein we employ the shrinking core (SC) model [3] to theoretically describe the extraction process and study the optimization problem.

In the first section, the dimensionless form of the SC model is presented, and the problem of full depletion time minimization 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 the variable filtration velocity v are considered as the optimization parameters.

In the second section, we discuss practical importance of obtained theoretical results in case of constant flow velocity as well as possible practical advantages of using variable filtration rates.

MODEL AND OPTIMIZATION PROBLEM FORMULATION

A generalized shrinking core (SC) model [4, 5] for polydisperse packed bed with variable-in-time filtration rate is employed in our study. The model is formulated below in dimensionless form typical for conditions of oilseeds (rapeseed, sunflower seed etc.) and relatively high filtration rates resulting in a quasi-stationary convective mass transport in the fluid phase.

Let us introduce the normalized time t and spatial coordinate z varying from 0 to 1 along the vessel, from its inlet to outlet. Let $v(t)$ be the dimensionless filtration velocity and $F(a)$ – the overall particle-size distribution function (ODF) of ground plant material with the distribution density $f(a)$. By definition, $dF = fda$ is the volumetric fraction of particles with dimensionless size from a to $a+da$. These functions result from and characterize grinding conditions. The SC model is presented in terms of normalized solute concentration $c(z,t)$ in the fluid phase and fraction of oil $s(z,t,a)$ extracted from particles of size a at the moment t in the cross-section z; $0 \le c, s \le 1$.

The scales for the above characteristics designated by subscript "sc" are

$$c_{\mathrm{sc}} = \theta_*; \quad z_{\mathrm{sc}} = H; \quad v_{\mathrm{sc}} = \frac{m_{\mathrm{oil}}}{\theta_* S t_{\mathrm{sc}}}; \quad a_{\mathrm{sc}}^2 = 2nDt_{\mathrm{sc}} \frac{\theta_* HS(1-e)}{m_{\mathrm{oil}}}.$$

Here, θ_* is the solubility of oil in the solvent, H – the vessel height, m_{oil} – the initial oil mass in the packed bed at given temperature and pressure, S – the vessel cross-section area, D – the apparent coefficient of oil diffusion in ground particles, e – the bed porosity, n – the particle shape factor ($n = 1, 3$ for flat and spherical particles, respectively).

The time scale t_{sc} is hereinafter defined as the time needed to pump the minimum volume $q_{\mathrm{s}} = m_{\mathrm{oil}} / \theta_*$ of the solvent which is capable to dissolve the total mass of the solute m_{oil}. Hence, for any $v(t)$

$$\int_0^1 v dt = 1$$

As a result, at a constant flow rate the dimensionless filtration velocity is $v = 1$.

Finally, the convective mass transport equation in the fluid phase and the diffusive mass transfer equation in particles take the following dimensionless form:

$$v(t)\frac{\partial c}{\partial z} = \int_0^{+\infty} \frac{\partial s}{\partial t}\chi(a,z)da \tag{1}$$

$$\frac{\partial s}{\partial t} = \frac{d(s)}{a^2}(1-c) \tag{2}$$

with initial and boundary conditions

$$s(z,0,a) = 0, \quad c(0,t) = 0. \tag{3}$$

Here the cumulative diffusion coefficient $d(s)$ depends on the particle shape factor n and is respectively given for spherical particles of radius a and flat particles of thickness $2a$ as

$$d\big|_{n=3} = \frac{1}{2}\cdot\frac{(1-s)^{1/3}}{1-(1-s)^{1/3}}; \qquad d\big|_{n=1} = \frac{1}{2s}.$$

It is convenient to reformulate equations (1)-(3) in terms of oil fraction $y(z,t)$ extracted from the packed bed interval $[0;z]$

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

normalized by $y_{sc} = m_{oil}$.

Accordingly, the overall extraction curve (OEC) measured in the experiments is $Y(t) = y(1,t)$.

After integration of equations (1)-(2) with respect to time we have

$$\frac{\partial y}{\partial z} = \int_0^{+\infty} s\chi da, \quad y(0,t) = 0; \tag{4}$$

$$a^2\varphi(s) = \min\left\{a^2; t - \int_0^t c(z,\tau)d\tau\right\}, \quad 0 \le \varphi = \int_0^s \frac{d\xi}{d(\xi)} \le 1. \tag{5}$$

It should be mentioned that the typical particle size a_{sc} defined above has been chosen so as to normalize the diffusive resistance of particles, i.e. $\varphi(1)=1$. Equations (4)-(5) must be also coupled with the obvious constraint imposed on the packing function χ

$$f(a)=\int_0^1 \chi(a,z)dz \tag{6}$$

which is the particle number conservation for each size a.

The full depletion time t_+ of the packed bed determined by $Y(t_+)=1$ is now introduced as the goal function to be minimized,

$$t_+ \to \min, \tag{7}$$

in the SFE optimization problem (4)-(7) with the three controls: particle-size distribution function F (or its density f), packing function χ, and time-dependent filtration rate v, considered as the optimization parameters at fixed thermodynamic conditions.

RESULTS AND DISCUSSIONS

Hereinafter we distinguish three different types of particles' packing χ. First assumes that particles are uniformly distributed in the vessel, $\chi(a,z)=f(a)$, and is the Uniformly Distributed Pack (UDP). It is commonly used in practice and SFE simulations.

The second type of packing, the so-called Locally Monodisperse Stratified (LMS) packed bed [6], is composed of original ground plant material sorted and packed along the extraction vessel in the order of particle fractional size decrease. The LMS particle size $a^{\wedge}(z)$ at a certain location z inside the extractor is uniquely determined by overall particle-size distribution function $F(a)$ as

$$F(a^{\wedge})=1-z.$$

The third type is the Inverse LMS (ILMS) packing with corresponding particle fractional size $a^{\vee}(z)$ monotonously increasing with z and related to $F(a)$ by

$$F(a^{\vee})=z.$$

In the framework of the SC model, for any constant flow rate it was theoretically proven [6] that for a given size-distribution function $F(a)$ the LMS packed bed is the searched optimal packing function χ_o, which delivers the minimum to the full depletion time t_+ on the set of all possible packing functions χ. This statement remains also true for any fixed pair $\{F,v\}$ with variable-in-time filtration rate. Another important property of the LMS packed bed is that, apart from being optimal, it simultaneously provides the maximum current yield of the solute at any moment t for any fixed pair $\{F,v\}$. Reversely, the ILMS packed

bed results in the minimum current yield [6]. All the above formulated conclusions hold both for spherical and flat particles [6].

Next, it is shown that the form of χ-distribution may significantly affect extraction rates. Practical advantages of LMS packed beds especially in combination with variable filtration velocities are also demonstrated.

Constant flow rate. In this case $v=1$, and zone fraction of extracted oil $y=\int_0^t c(z,\tau)d\tau$ is uniquely expressed via solute concentration c in equations (4)-(5). This allows to explicitly determine the full depletion times for LMS (t_+^{LMS}) and ILMS (t_+^{ILMS}) packed beds. The latter one is equal to the extraction time t_+^{UDP} of the uniformly distributed pack [5, 6],

$$t_+^{\mathrm{LMS}}=\max_a\left(1-F(a)+a^2\right)\geq 1; \qquad t_+^{\mathrm{UDP}}=t_+^{\mathrm{ILMS}}=1+a_{\max}^2 .$$

These formulas present the global minimum and maximum of t_+ at a constant flow rate and show that the LMS packed beds reduce the full depletion time by up to two times as compared with ILMS or UDP packs.

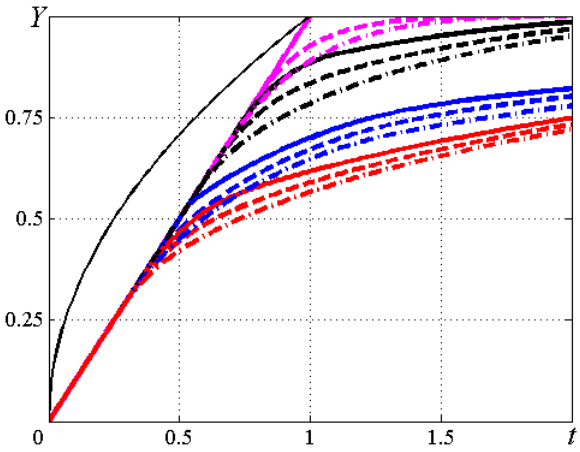

Figure 1: OECs for different ODFs (see Figure 2). Solid, dashed, and dash-dotted curves correspond to LMS, UDP, ILMS packing, respectively.

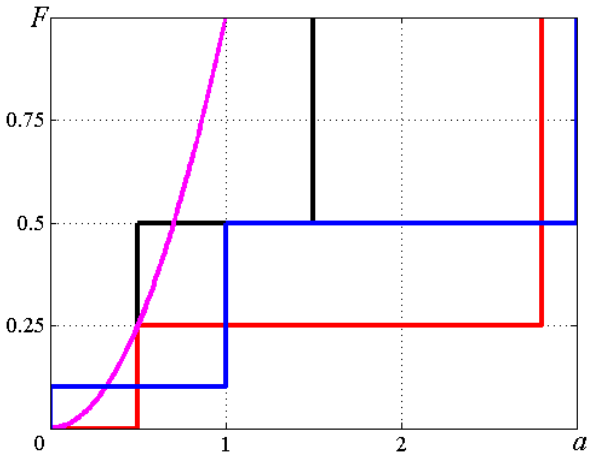

Figure 2: ODFs of polydisperse ground plant material used for simulating OECs (see Figure 1). Magenta curve is the parabolic ODF: $F(a)=a^2$ resulting in the fastest extraction.

The above relation for t_+^{LMS} also shows that for any ODF such as

$$F(a)\geq a^2, \quad a\in[0;1], \tag{8}$$

the LMS packed bed is depleted for the minimum possible extraction time, $t_+=1$ (i.e. after t_{sc} defined as the time scale). Inequality (8) determines the so-called optimal domain of ODFs. Once an $F(a)$-distribution curve lies in this domain, the corresponding LMS packing of the ground plant material guarantees that only the initial, solubility-controlled, extraction stage

persists through the whole SFE process of minimum duration t_{sc} ($t_+ = 1$). This is also the most efficient SFE regime of solvent consumption. The existence of such optimal domains is another important feature of LMS packs. In case of LMS packing there is no need to grind all plant material as fine as possible.

General discrepancy of different packs for a constant flow rate is illustrated by Figure 1. The OECs are modelled for the three different types of packed beds and the corresponding ODFs are shown on Figure 2. Figure 1 demonstrates that the parameter χ should be at least controlled when the extraction is prepared because there is a high probability of that the polidisperse ensemble of ground particles could be packed according to the ILMS pack or similar packs which provide very low extraction rates may occur in the vessel.

Variable flow rate. Here we consider only LMS packed beds with variable filtration velocities. Obviously, the optimal domain of ODFs may be affected by $v(t)$-dependence, and the primary goal is to further extend its boundary beyond the parabolic curve $\left(F(a) = a^2\right)$ found at constant flow rates.

Explicit analytical solutions deduced for flat particles in a particular case of power-type filtration velocities

$$v \sim t^p, \qquad p \geq -0.5$$

reveal that the optimal domain does depend on index p and can be enlarged as compared with that for $v = const$. The optimal domain boundaries are shown in Figure 3 by black solid lines. The red curve is parabola $F(a) = a^2$. The solid lines below the parabolic curve correspond to monotonously decreasing filtration rates $\left(-0.5 \leq p < 0\right)$, while the other (upper) lines – to the monotonously increasing filtration rates $\left(p > 0\right)$. The optimal domain at $p = -0.5$ is the same as for constant flow rates.

Numerical simulations for spherical particles demonstrated analogous tendencies. The optimal domain boundary computed in case of

$$v \sim \sqrt{d\left(\varphi^{-1}\left(t\right)\right)}, \quad n = 3, \tag{9}$$

is depicted in Figure 3 by black dashed line. The assumed time dependency of the filtration velocity is presented in Figure 4, and it is thought to be the optimal one for spherical particles.

Consequently, there exist certain types of monotonously decreasing flow rates which essentially enlarge the optimal domain of ODFs in comparison with constant rates. This is a challenge to formulate the general optimization problem and find the optimal filtration law.

Another advantage of introducing variable filtration rates [7] is to reduce solvent consumption even if ODF does not belong to the optimal domain. However for non-optimal packs this slows down the extraction process. Nevertheless, if only partial depletion is aimed at, decreasing filtration velocities still can be used to shorten the extraction procedure. It could be done at maximum v-values for the initial extraction stage, i.e. $v >> 1$, $t \to 0$. For example, for flat particles, if criterion (8) is fulfilled, the solvent could be pumped with the rate of $v = 0.5t^{-0.5}$. In this case the outlet concentration is $c(1,t) = 1$ and the yield is

$Y = \int_0^t 0.5t^{-0.5}dt > t$ for $t < t_+ = 1$, while the full depletion time remains equal to unity (see black thin line on Figure 1 – OEC for $v = 0.5t^{-0.5}$ and $F = a^2$). This scenario was not considered in [7]. Numerical simulations show that the same conclusion is true for spherical particles.

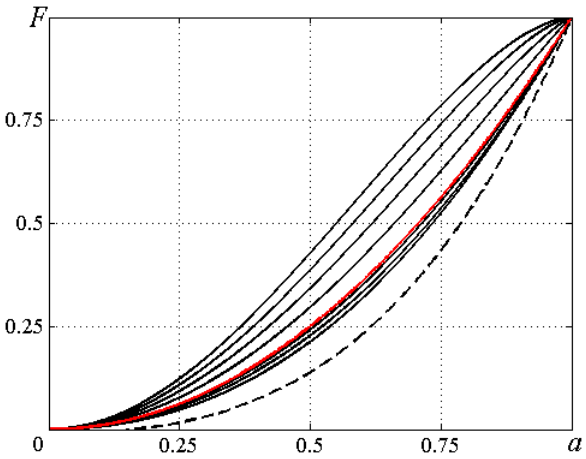

Figure 3: Optimal domain boundaries of ODFs for different $v(t)$ -dependencies in case of flat particles (solid lines) and spherical particles (dashed line).

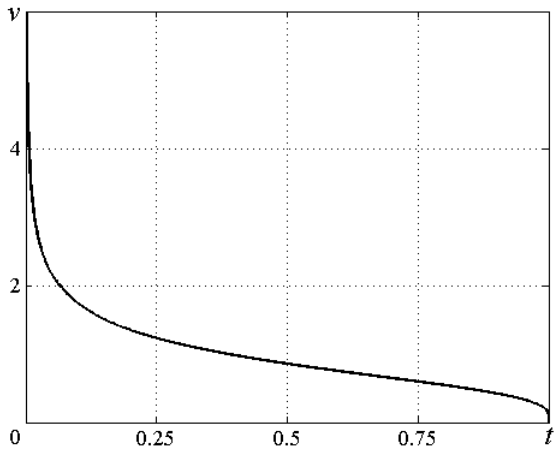

Figure 4: Time-dependent filtration velocity (9) for spherical particles which extends optimal domain of ODFs to the dashed boundary shown in Figure 3.

CONCLUSION

The spatially inhomogeneous (polydisperse) packed beds of ground plant material, described by packing function χ, and variable-in-time filtration rates could be used to significantly intensify the extraction process and reduce the full depletion time of packed beds.

The LMS packed beds are shown to be optimal to minimize the full depletion time t_+ and deliver the maximum current yield of the solute in the course of the extraction process.

At a constant filtration velocity, there exists an optimal domain of ODFs for which LMS packs provide the minimum extraction time $t_+ = 1$ (i.e. t_{sc}). Computational experiments show that variable-in-time monotonically decreasing filtration rates can be introduced to essentially extend the optimal domain of ODFs. Within the optimal domains of ODFs there is no need to finely grind all the plant material.

The extraction model (4)-(7) and the optimization approach implicitly involve the extractor's dimensions and other technological parameters in the optimization procedure.

REFERENCES

[1] SCHÜTZ, E., Chemical Engineering Technology, Vol. 30, **2007**, p. 685.

[2] SHARIF, K.M., RAHMAN, M.M., AZMIR, J., MOHAMED, A, JAHURUL, M.H.A, SAHENA, F., ZAIDUL, I.S.M., Journal of Food Engineering, Vol. 124, **2014**, p. 105.

[3] GOTO, M., ROY, B.C., HIROSE, T., The Journal of Supercritical Fluids, Vol. 9, **1996**, p. 128.

[4] EGOROV, A.G., MAZO, A.B., MAKSUDOV, R.N., Theoretical Foundations of Chemical Engineering, Vol. 44, **2010**, p. 642.

[5] EGOROV, A.G., SALAMATIN, A.A., MAKSUDOV, R.N., Theoretical Foundations of Chemical Engineering, Vol. 48, **2014**, p. 39.

[6] EGOROV, A.G., SALAMATIN, A.A., Russian Mathematics, Vol. 59, **2015**, In press.

[7] FIORI, L., CALCAGNO, D. COSTA, P., The Journal of Supercritical Fluids, Vol. 41, **2007**, p. 31.