

# Forward and Inverse Problems of Supercritical Extraction of Oil from Polydisperse Packed Bed of Ground Plant Material

A. G. Egorov<sup>a</sup>, A. A. Salamatin<sup>a</sup>, and R. N. Maksudov<sup>b</sup>

<sup>a</sup> Kazan (Volga Region) Federal University, Kazan, Russia

<sup>b</sup> Kazan National Research Technological University, Kazan, Russia

e-mail: egorov2@ksu.ru

Received January 28, 2013

**Abstract**—The problem of determining the overall extraction curve for the supercritical fluid oil extraction from polydisperse layer of ground oilseed granules was solved analytically using the shrinking core model. The functional dependence obtained for bi-disperse approximation of the packed bed describes the results of known experiments with high accuracy. Ways to solve the inverse problem of determining the size distribution function for particles of granular layer based on experimental overall extraction curves are discussed.

**DOI:** 10.1134/S0040579514010011

## INTRODUCTION

New technologies for extracting components from ground plant materials based on supercritical fluid extraction (SFE) are superior to the traditional industrial methods in the quality of the final product and ecology of the process [1, 2]. This generates an increased interest in mathematical modeling the SFE from the granular layer of the ground plant material.

The entire SFE model must include two submodels, i.e., an outer macroscale model that describes the transport processes in the extractor apparatus containing granular layer and an inner model, in which kinetics of oil extraction from the single particle in the layer is presented. The first submodel is usually formulated [3–7] as a model of the ideal exclusion reactor with the possible consideration of longitude dispersion. The second submodel suggests the schematization of the shape and structure of the particles in the layer and concretization of the processes of dissolution and diffusional transfer inside the particle.

The granular layer usually is described in a monodisperse approximation, while the concept of shrinking core is often used for the development of inner model [3–6]. Based on this, the inner oil-containing zone (core) and peripheral transport zone are identified in the particle. The core radius decreases over time due to the diffusional release of the oil containing in the core through the transport zone into the inter-particle space. The oil concentration in the core remains constant. The extraction process finishes when the core radius becomes zero.

The application of the SC-model to calculate the extraction processes from oilseeds of different cultures (see the works cited above) showed that the shrinking core scheme in general correctly describes the extraction dynamics from the layer of granular particles.

However, the pronounced two-step character of the extraction process with the high initial rate of extraction followed by the sharp drop in the oil yield was observed in a series of experiments [7–9]. The adequate description of these effects suggests the expansion of the SC model for the case of polydisperse granular layer [6, 7].

In this work, the set-up of the respective problem is suggested in a form of a system of equations with an integrodifferential operator determined by the particle size distribution function. An analytical solution of the system is presented. Testing of the model is conducted for the extended set of the known experimental data. The way for the solution of the inverse problem of determination of the distribution function using experimental oil yield curves are discussed.

## PROBLEM SET UP

The SFE process is realized through filtration of supercritical fluid, usually supercritical carbon dioxide, through the granular layer of particles of ground plant material. The oil contained in plant cells dissolves in the fluid saturating granules, diffuses to their surface, and is transported by the fluid to the outlet cross-section of the reactor through the porous channels of the layer. The particles have a characteristic size of approximately 1 mm, and each contains  $10^3$ – $10^5$  plant cells. The particle shape in the granular layer can be different depending on the type of the material. In this work, we restrict our consideration to two cases, i.e., spherical particles and flat particles with a thickness of significantly less than their longitudinal size. Special interest in flat particles is caused by two reasons aside from practical considerations. First, in this case, the obtained calculation formulas are the most simple and

illustrative. Secondly, the oil extraction dynamics from the layer of polydisperse particles of any shape in a wide and practically important time range is described by the same asymptotic equations as for the flat particles.

Here,  $t$  is time,  $z$  is the space coordinate calculated from the cross section of the input along the extractor axis,  $m$  is porosity of the granular layer, and  $v$  is the rate of fluid filtration,  $a$  is the particle size equal to the radius of the spherical particle and the half-thickness of flat particles,  $f$  is the density, and  $F$  is the particle size distribution function. According to the definition, the value  $dF = f(a)da$  is a volumetric fraction of particles with size from  $a$  to  $a + da$ . The mass concentration of oil in supercritical fluid in pore space is designated as  $C$  and equilibrium concentration in solution at given pressure and temperature is designated as  $\theta_*$ . The ratio of the initial oil mass stored in the particle to its volume is denoted as  $\theta_0$ . Let us restrict our consideration to the typical case of particles with high oil contents when  $\theta_0 \gg \theta_*$ .

According to the shrinking core model [3–6], two zones are identified each moment in the particles of the packed bed. The oil content in the plant cells of the core  $0 < r < R(t)$  is  $\theta_0$ , equilibrium concentration in the solution is  $\theta_*$ . Oil in the cells of the transport zone  $R(t) < r < a$  is fully exhausted, and the solution concentration changes from  $\theta_*$  at the mobile border  $r = R(t)$  to the lesser value  $\theta_a$  on the surface of the grain  $r = a$ . The concentration drop  $\theta_* - \theta_a$  is a driving force of the oil diffusional transport from the core to the particle surface. It was established in [5] that the diffusional resistance of the transport zone is much higher than in the border zone of the filtering flow at the particle surface. This allows  $\theta_a$  to be identified with  $C$ . It was also shown there that the diffusion process for the particles with high oil content is quasistationary, due to which the rate of the core border movement and the density of the diffusional oil flow  $q$  from the grains into the pore space in each single moment of time are proportional to the concentration difference  $\theta_* - C$  as follows:

$$\theta_0 \frac{\partial R}{\partial t} = -q \left( \frac{a}{R} \right)^{n-1}, \quad q(t, z, a) = \frac{D_{\text{eff}}}{a - R} \left( \frac{a}{R} \right)^{(1-n)/2} (\theta_* - C).$$

Here,  $D_{\text{eff}}$  is the effective diffusion coefficient, index  $n$  is equal to 1 or 3 for flat or spherical particles, respectively.

The equation describing distribution of oil concentration  $C$  dissolved in supercritical fluid on its filtration through the bed layer in the regime of expanded extraction front assumes the form:

$$v \frac{\partial C}{\partial z} = q_s = (1 - m) \int_0^\infty q(t, z, a) \frac{A(a)}{V(a)} f(a) da. \quad (1)$$

Here,  $q_s$  is the density of the source of oil coming from the grains to the pore space in a volume unit of the bed layer, and  $A(a)$  and  $V(a)$  are surface area and volume of the grain with the size  $a$  ( $A/V = n/a$ ). Second-degree terms that describe the capacitive and dispersion effects in the pore space essential only during the short-term initial stage of extraction [5, 6] are dropped in the equation for convective oil transfer (1).

As a result, the inner and outer SFE submodels for a polydisperse packed bed layer are transferred to the system of two equations relative to unknown functions  $R(t, z; a)$  and  $C(t, z)$  as follows:

$$\begin{aligned} \theta_0 (a - R) \left( \frac{R}{a} \right)^{(n-1)/2} \frac{\partial R}{\partial t} &= -D_{\text{eff}} (\theta_* - C), \\ v \frac{\partial C}{\partial z} &= -(1 - m) \theta_0 \int_0^\infty \frac{\partial}{\partial t} \left( \frac{R}{a} \right)^n f(a) da \end{aligned} \quad (2)$$

with the following initial and boundary conditions:

$$R(0, z; a) = a, \quad C(t, 0) = 0. \quad (3)$$

The suggested model (2), (3) contains constants accepted as a given  $\theta_*$ ,  $\theta_0$ ,  $D_{\text{eff}}$  and density of particle size distribution  $f(a)$ . The density of particle size distribution can be determined from either the results of sieve analysis or alternative granulometric measurements. The equilibrium concentration  $\theta_*$  depending on the conditions of extraction (temperature, pressure, material composition) can be estimated *a priori* using, for example, a known Del Valle equation [13] for the average solubility of oils in supercritical  $\text{CO}_2$  and refined further according to the slope of the linear initial part of the curve of the oil yield after extractor on conducting an experiment [5, 6]. The initial load  $\theta_0$  of the extractive oil that also depend on experimental condition are determined [5, 6] by the asymptote of the overall extraction curve at large times. Finally, the effective diffusion coefficient that can change in a wide range depending on material type is an adaptation parameter of the model. It is a function of extraction parameters and the chosen extractant, and is determined from the conditions of the best fit of experimental and calculated curves of the oil yield.

**Analytical solution of the problem.** Let us introduce a dimensionless parameter to solve problem (2) and (3) as follows:

$$y(t, z) = \frac{v}{L(1 - m)\theta_0} \int_0^t C(t, z) dt,$$

which represents the accumulated oil extracted by the time  $t$  from the part of the packed bed layer  $[0, z]$  normalized to the initial oil mass in the entire reactor of the  $L$  height. Let us also determine the dimensionless analogues of the rest of the parameters by normalizing

$z$  to  $L$ , normalizing time  $t$  to  $t_{sc}$ , and normalizing  $a$  and  $R$  to  $a_{sc}$  without changing symbols as follows:

$$t_{sc} = \frac{L(1-m)\theta_0}{v\theta_*}, \quad a_{sc} = \sqrt{\frac{2nL(1-m)D_{eff}}{V}}.$$

The time scale  $t_{sc}$  represents the entire time of complete oil extraction from the reactor with the particles of infinitesimally small size, and the grain scale  $a_{sc}$  corresponds to the particle size, at which this time will double, as will be shown below.

By integrating the equations (2) over time considering condition (3), we obtain

$$\frac{\partial y}{\partial z} = \int_0^{\infty} s f(a) da, \quad s(t, z, a) = 1 - \left(\frac{R}{a}\right)^n, \quad (4)$$

$$\varphi(s) = (t - y)/a^2. \quad (5)$$

The  $\varphi(s)$  function is determined in the interval  $0 < s < 1$  and is represented by the following expression:

$$\varphi(s) = \begin{cases} s^2, & n = 1 \\ 3(1 - (1 - s)^{2/3}) - 2s, & n = 3. \end{cases}$$

The  $\varphi(s)$  monotonously increases from zero at  $s = 0$  to one at  $s = 1$  for both types of particles. Let us denote the function inverse to  $\varphi$  by  $S$ . By inverting (5) and substituting the result in (4), the following ordinary integrodifferential equation for the function  $y(t, z)$  is obtained:

$$\frac{\partial y}{\partial z} = \int_0^{\infty} S\left(\frac{t - y}{a^2}\right) f(a) da. \quad (6)$$

The time  $t$  in this equation plays role of the parameter. The  $S(\varphi)$  function appearing in (6) is formally replaced by zero and one in the range  $\varphi < 0$  and  $\varphi > 1$ , respectively. The solution to Eq. (6) is presented as quadratures taking into consideration the second condition in (3) at  $y(t, 0) = 0$

$$z = \int_{t-y}^t \frac{d\tau}{k(\tau)}, \quad k(\tau) = \int_0^{\infty} S\left(\frac{\tau}{a^2}\right) f(a) da. \quad (7)$$

Considering that  $S \equiv 1$  at  $a < \sqrt{\tau}$ , and integrating the expression for  $k(\tau)$  by parts

$$k(\tau) = \int_{\sqrt{\tau}}^{\infty} S\left(\frac{\tau}{a^2}\right) f(a) da + \int_0^{\sqrt{\tau}} f(a) da = - \int_{\sqrt{\tau}}^{\infty} F(a) dS\left(\frac{\tau}{a^2}\right),$$

we finally obtain by the substitution of integral variable

$$k(\tau) = \int_0^1 F\left(\sqrt{\frac{\tau}{\varphi(s)}}\right) ds. \quad (8)$$

The dimensionless curve overall extraction  $Y$  (OEC) from the reactor  $Y(t) = y(t, 1)$  is of main practical interest. From the general solution (7), we obtain

$$1 = \int_{t-Y}^t \frac{d\tau}{k(\tau)}. \quad (9)$$

The initial OEC slope and its limiting value  $Y(\infty)$  equal to one. Let us denote the duration of the initial linear stage of the extraction by  $t_-$  and the time of complete extraction—by  $t_+$ .

The concentration of outgoing fluid from the reactor equals to equilibrium at  $t < t_-$ . The duration of the initial stage  $t_-$  is determined by the conditions

$$1 = \int_0^{t_-} \frac{d\tau}{k(\tau)}. \quad (10)$$

All oil in the reactor is extracted at  $t > t_+$ , and  $Y(t) = 1$ . Hence, the complete extraction time is given by the condition

$$1 = \int_{t_+-1}^{t_+} \frac{d\tau}{k(\tau)}. \quad (11)$$

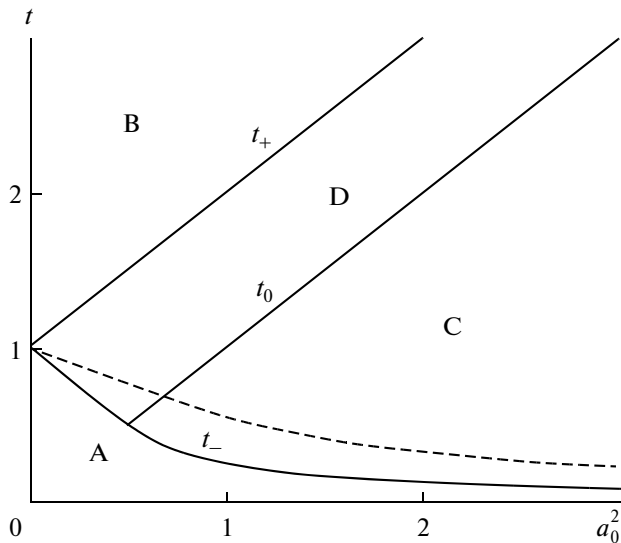
It can be seen from (8) that  $k \leq 1$ ; hence, for (11) to be valid, it is necessary that  $k(\tau) \equiv 1$  at  $\tau > t_+ - 1$ . As a result, the integral function in (8) must be identical with one at  $\tau > t_+ - 1$  and any  $s$ ,  $0 < s < 1$ . In other words, the condition  $F(a) \equiv 1$  must be valid at  $a > \sqrt{t_+ - 1}$ , and, hence, the complete extraction time is determined by the maximum grain size  $a_{max}$  as follows:

$$t_+ = 1 + a_{max}^2.$$

**Monodisperse media.** Distribution function for monodisperse medium consisting of identical particles of the size of  $a_0$  is represented by the Heaviside function  $F(a) = H(a - a_0)$ . For flat particles from (8), we have  $k = \min(1, \tau^{1/2} a_0^{-1})$  considering the fact that  $\varphi(s) = s^2$ . The calculation of the time of completion of the linear extraction stage according to Eq. (10) yields

$$t_- = \begin{cases} 1 - a_0^2 & a_0^2 < 0.5 \\ 0.25a_0^{-2} & a_0^2 > 0.5. \end{cases}$$

The curves  $t = t_-(a_0)$ ,  $t = t_+(a_0) = 1 + a_0^2$ , together with the curve  $t = t_0(a_0) = a_0^2$ , divide the plane  $(t, a_0)$  into four subareas (solid lines in Fig. 1). The linear stage of extraction occurs in area A; here,  $Y = t$ . Extraction is completed in the area B, and  $Y = 1$ . The



**Fig. 1.** Scheme of the process in  $(t, a_0)$  plane for monodisperse layer of flat and spherical particles: A—saturated area; B—area of complete extraction; C, D—regions of complete exhaustion.

OEC of nonlinear extraction in areas C and D is described by the equations

$$(t, a_0) \in C: Y(t) = \frac{\sqrt{t}}{a_0} - \frac{1}{4a_0^2};$$

$$(t, a_0) \in D: Y(t) = t - \left( \frac{t-1+a_0^2}{2a_0} \right)^2.$$

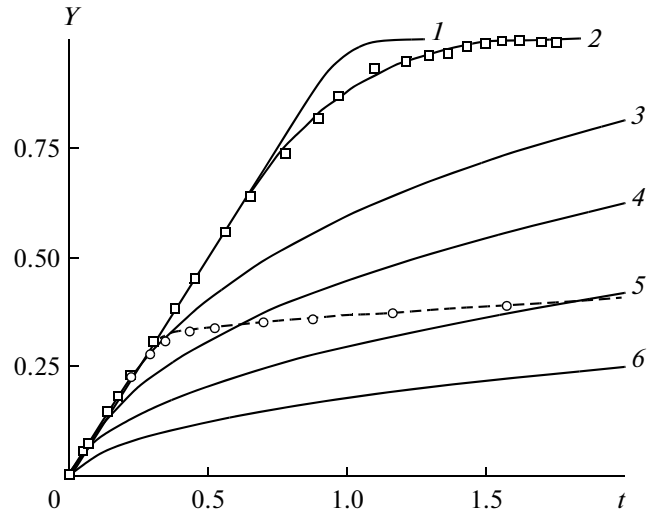
It can be tested that the  $Y(t)$  curve and its first derivative are continuous at the borders of the subareas.

Similar results are valid for spherical particles. The  $(t, a_0)$  is divided by the curves  $t = t_-(a_0)$ ,  $t = t_+(a_0)$ ,  $t = t_0(a_0)$  into four subareas exactly as above. The  $t_+(a_0)$  and  $t_0(a_0)$  dependences remain the same as for flat particles. The  $t = t_-(a_0)$  dependence (dashed line in Fig. 1) is defined as  $t_- = 1 + a_0^2(1 - \kappa)$ , where  $\kappa = 3\ln 3 - \pi/\sqrt{3} = 1.482$ . It is presented in parametric form at  $a_0^2 < \kappa^{-1}$ .

$$t_- = \frac{\phi(s)}{\phi(s)}, \quad a_0^2 = \frac{1}{\phi(s)}, \quad 0 < s < 1,$$

$$\phi(s) = -3\ln \left[ \left( \frac{1}{2} + (1-s)^{1/3} \right)^2 + \frac{3}{4} \right]$$

$$+ 2\sqrt{3} \arctan \left[ \frac{2}{\sqrt{3}} \left( \frac{1}{2} + (1-s)^{1/3} \right) \right] + 3\ln 3 - \frac{2\pi}{\sqrt{3}}.$$



**Fig. 2.** OEC for monodisperse granular layer of spherical particles with size  $a = 0.5$  (1),  $0.9$  (2),  $2$  (3),  $3$  (4),  $5$  (5),  $9$  (6). Squares indicate OEC from tomato seeds, [9]; circles indicate OEC from apricot kernels [10]; dashed line shows solution for bimodal granular layer.

As with flat particles,  $Y = t$  and  $Y = 1$  in the areas A and B, respectively. The OEC is described by the following equations in areas C and D:

$$(t, a_0) \in C: Y(t) = t - a_0^2 \phi \left\{ \Phi \left[ S \left( t a_0^{-2} \right) - a_0^{-2} \right] \right\},$$

$$(t, a_0) \in D: Y(t) = t - a_0^2 \phi \left\{ \Phi \left[ (t-1) a_0^{-2} + \kappa - 1 \right] \right\}.$$

Here,  $\Phi$  denotes a function inverse to  $\phi$ .

A series of OECs for monodisperse granular spherical material is presented in Fig. 2. The different curves relate to particles of different size  $a$ .

The OECs curves are in good agreement with separate experimental observations [3–5]. The results of experiments on the extraction of oil from tomato seeds ground to a size of 0.25 mm from [9] are presented by squares in Fig. 2 as an example.

On the other hand, in many cases, the monodisperse approximation cannot describe the available experimental material, and clearly demonstrates a two-phase time course of the OEC. One of the typical experimental OEC [10] that represent oil extraction from apricot kernels is presented in Fig. 2 by circles.

Naturally, effort must be made to describe the similar curves based on the assumption of the bimodality of the particle size distribution considering that the density of the particle distribution  $f(a)$  has two local maxima with one located in the area of low  $a$  values and another in the area of large  $a$  values. Let us denote these media as bimodal.

**Bimodal media.** The density of the particle size distribution for bimodal media can be presented as

$$f(a) = \alpha f_1(a) + (1 - \alpha) f_2(a),$$

where  $\alpha$  and  $1 - \alpha$  represent contributions of small and large fractions, and  $f_1$  and  $f_2$  are their distribution densities. The specific argument values of  $f_1$  are significantly less than 1, and the values of  $f_2$  are significantly larger. Hence, in expression (7), which defines the  $k(\tau)$  functions as follows:

$$k = \alpha \int_0^{\infty} S\left(\frac{\tau}{a^2}\right) f_1(a) da + (1 - \alpha) \int_0^{\infty} S\left(\frac{\tau}{a^2}\right) f_2(a) da$$

the values of the first integral in the right part are defined by the character  $S(\varphi)$  at  $\varphi \rightarrow 1$ , and the values of the second are defined at  $\varphi \rightarrow 0$ . Considering that  $S(1) = 1$ ,  $S(\varphi) \approx \sqrt{n\varphi}$ , at  $\varphi \rightarrow 0$ , we obtain

$$k(\tau) \approx \alpha + (1 - \alpha) \frac{\sqrt{n\tau}}{a_0}, \quad a_0^{-1} = \int_0^{\infty} f_2(a) \frac{da}{a}. \quad (12)$$

The  $a_0$  value represents an average particle size of the large fraction calculated from the ratio of the total volume of all particles to their surface area.

Note that it was actually assumed when deriving equation (12) that  $\tau \ll a_0^2$ . Hence, the use of Eq. (12) in expressions (9) and (10) that present the general solution of the problem is only acceptable for a much shorter time interval than  $a_0^2$ . For bimodal media  $a \gg 1$ , and SFE is usually carried out on the order of several dimensionless time units. In this case the substitution of (12) in (9) and (10) is justified.

It is also worth mentioning that the obtained expression (12) for  $k(\tau)$  is identical to the one for a bimodal medium that consists of two types of flat particles: one of negligibly small size (fraction  $\alpha$ ) and other with size  $a_0$  (fraction  $1 - \alpha$ ). This is explained by the fact that the mobile exhaustion front only penetrates the large particle for a small distance relative to their size at times  $\tau \sim 1$ . The extraction process is only determined by the total surface area of the particles. The geometry of granules does not affect the process, and the front movement remains flat.

The substitution of (12) into (9) results in the following implicit expression for OEC  $Y(t)$  at  $t_- < t \ll a_0^2$ :

$$\ln\left(\frac{1 + \varepsilon\sqrt{t - Y}}{1 + \varepsilon\sqrt{t}}\right) + \varepsilon(\sqrt{t} - \sqrt{t - Y}) = \frac{\varepsilon^2 \alpha}{2}, \quad (13)$$

$$\varepsilon = \sqrt{n} \frac{1 - \alpha}{a_0 \alpha}.$$

By expanding  $Y$  into a power series of the small parameter  $\varepsilon$ , we obtain

$$Y = \alpha + \frac{2}{3} \varepsilon (t^{3/2} - (t - \alpha)^{3/2}) + O(\varepsilon^2). \quad (14)$$

Similar calculations for the completion time of the linear stage of extraction result in the following expression

$$t_- = \alpha + \frac{2}{3} \varepsilon \alpha^{3/2} + O(\varepsilon^2). \quad (15)$$

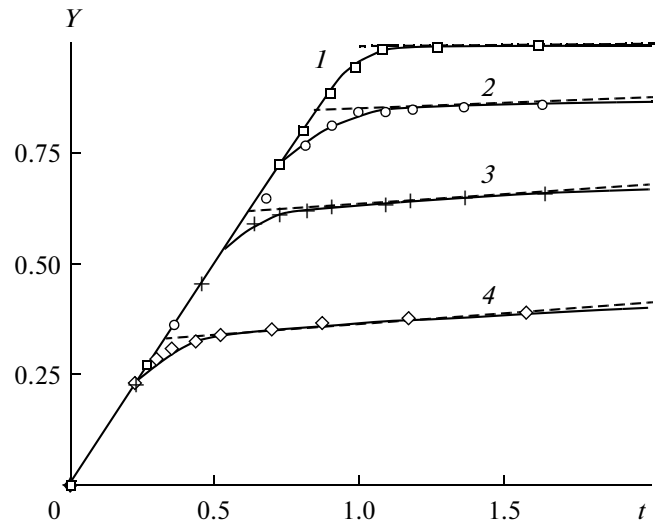


Fig. 3. Kinetics of oil SFE from apricot kernels [10] for particles with diameter  $d = 0.4$  (1),  $0.8$  (2),  $0.92$  (3),  $1.5$  (4) mm. Markers represent experimental data; solid lines show general theory of bimodal granular layer; dashed lines show asymptotic approximation.

Asymptotic equations (13)–(15) represent the complete solution of the SFE of oil from the bimodal granular layer. The characteristic shape of the solution is presented in Fig. 2 by a dashed line. This line corresponds to values  $\alpha = 0.28$ , and  $a_0 = 13.44$ . It can be seen that the suggestion of the bimodal character of the bed layer explains the observed character of experimental dependencies completely.

## COMPARISON WITH EXPERIMENT

Let us consider the known experimental data on the kinetics of the oil SFE process from apricot kernels [10] and pumpkin [8] and sunflower [7] seeds. Four experiments were performed in [10] and [8] when determining the OEC for layers with different sizes of particles, and five such experiments were performed in [7]. The experiments in [7] were conducted in an extractor with a total load of 34 g at a pressure of 28 MPa, temperature 313 K, and fluid flow of 10 g/min. The respective values in [8] were 3.25 g, 30 MPa, 313 K, 1.8 g/min and, in [10], they were 5 g, 45 MPa, 325 K, 3 g/min.

Let us briefly present the used treatment method and interpretation of the experimental data on the example of oil extraction from apricot kernels [10]. Experiments 1–4 were performed on different fractions with particle diameter  $d$  of 0.4–1.5 mm, separated from the ground material with sieve analysis (Table 1). The results of measurements are presented in Fig. 3 by dots.

The equilibrium concentration  $\theta_*$  and initial oil stores  $\theta_0$  were determined according to [5, 6] by the initial slope of the OEC and its asymptote ( $t \rightarrow \infty$ ) for

**Table 1.** Composition and particle size of fractions used in calculations

[10]	Experiment number	1	2	3	4	
Apricot	Diameter of particle in large fraction $d$ , mm	0.4	0.8	0.92	1.5	
	Contribution of small fraction $\alpha$	0.98	0.81	0.56	0.28	
	Diameter of particle in small fraction $d_1$ , mm	0.054	0.066	0.054	0.054	
[8]	Experiment number	1	2	3	4	
Pumpkin	Diameter of particle in large fraction $d$ , mm	0.45	0.84	1.34	1.93	
	Contribution of small fraction $\alpha$	0.94	0.84	0.44	0.31	
	Diameter of particle in small fraction $d_1$ , mm	0.028	0.028	0.028	0.028	
[7]	Experiment number	1	2	3	4	5
Sunflower	Diameter of particle in large fraction $d$ , mm	0.312	0.488	0.545	0.563	1.2
	Contribution of small fraction $\alpha$	0.87	0.65	0.58	0.53	0.265
	Diameter of particle in small fraction $d_1$ , mm	0.038	0.036	0.04	0.04	0.04

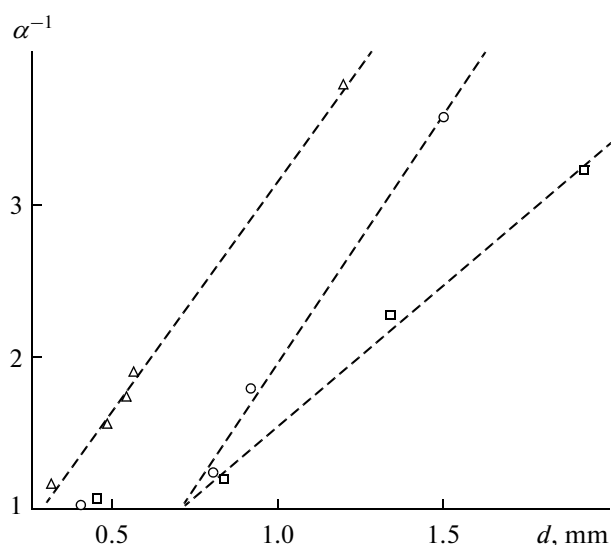
a load with particles of the smallest size; they comprise  $\theta_* = 14.5 \text{ kg/m}^3$  and  $\theta_0 = 345 \text{ kg/m}^3$ .

Despite the prior fractionation of the granular layers and their apparent mono dispersity, the experimental OEC have well pronounced two-stage character even in this case as can be seen in Fig. 3. Hence, all calculations were conducted based on the assumption of a bimodal layer. The size of particles  $d$  in the large fraction was preset the same as in experiments, and the contribution of the small fraction  $\alpha$  was found from the condition of the best fit of the asymptotic equations (13)–(15) and the experimental data. Another adaptation parameter, the coefficient of effective diffusion, was selected for each series of experiments with an identical type of raw material. For example, even the asymptote approximation (14), (15) (dashed lines in Fig. 3) describes all experimental curves quite satisfactorily for apricot stones at optimal values of the  $\alpha$  parameter presented in Table 1 and  $D_{\text{eff}} = 3.9 \times 10^{-12} \text{ m}^2/\text{s}$ . An almost ideal fit with the experiment (solid line in Fig. 3) is provided by the general theory of the bimodal granular layer, which allows one to additionally consider and select the size of the small fraction that is set equal to zero in (14), (15). In this case, the model OEC were calculated according to Eqs. (8), (9) with bidisperse distribution density  $f(a) = \alpha\delta(a - a_1) + (1 - \alpha)\delta(a - a_0)$ . The values of the effective particle diameter of the small fraction  $d_1$  corresponding to the dimensionless parameter  $a_1$  are presented in Table 1. It is interesting to note that the  $d_1$  hardly changes from series to series and comprises two to three diameters of plant cells.

Good agreement of the model OEC and experimental data similar to Fig. 3 is observed when the results from [7, 8] are processed using the bidisperse approximation. The equilibrium concentration and initial oil stores were  $\theta_* = 6.6 \text{ kg/m}^3$ ,  $\theta_0 = 121 \text{ kg/m}^3$

in [7] and  $\theta_* = 7.7 \text{ kg/m}^3$ ,  $\theta_0 = 212 \text{ kg/m}^3$  in [8]. Effective diffusion coefficient was equal to  $D_{\text{eff}} = 1.2 \times 10^{-12} \text{ m}^2/\text{s}$  for pumpkin seeds and  $D_{\text{eff}} = 0.5 \times 10^{-12} \text{ m}^2/\text{s}$  for sunflower seeds. The rest of the parameters are presented in Table 1.

The way of possible emergence of the fraction of small particles in uniform layers prepared with the sieve analysis of the seeds is of interest. Different mechanisms are discussed in the literature, e.g., the attachment of dust on large particles due to adhesion and mechanical factors [6], mechanical damage of the particle surface in the process of grinding [11, 12], and



**Fig. 4.** Dependence of small fraction contribution on particle diameter of the main fraction of the layer: triangles indicate sunflower seeds, circles indicate apricot kernels, squares indicate pumpkin seeds.

others. In any case, the contribution of the small fraction must be determined by the specific surface area of the main fraction (large particles). The higher the specific surface area (i.e., the smaller the diameter  $d$  of the large particles), the higher the contribution of the small fraction. The data presented in Table 1 confirm this suggestion. Moreover, as can be seen in Fig. 4, in all cases, the corresponding dependence can be presented as follows:

$$\alpha^{-1} = \max\left(1, 1 + \frac{d - d_0}{d_*}\right).$$

The approximation parameters  $d_0$  and  $d_*$ , together with  $D_{\text{eff}}$  and  $d_1$ , depend only on the type of material, not on the degree of grinding. These four universal constants entirely determine the oil SFE process for the particular type of raw material. These parameters for apricot kernels and pumpkin and sunflower seeds are summarized in Table 2.

### ANALYSIS OF INVERSE PROBLEM

The limited duration of the considered SFE processes does not allow for further detalization of the fraction composition of the granular layer on the basis of OEC. Only the subsurface layer of large particles participates in the extraction process at these time scales, all granules behave similarly independent on their size. Nevertheless, identification of the fraction composition becomes possible in principle at the sufficiently long duration of the process. Subsequently, the inverse problem of reconstructing the particle distribution function  $F(a)$  from the experimental OEC  $\{Y(t), 0 < t < \infty\}$  can be considered.

Let us rearrange Eqs. (8) and (9) as follows:

$$G(t) = G(t - Y) + 1, \quad (16)$$

$$\int_0^1 F\left(\sqrt{\frac{t}{\varphi(s)}}\right) ds = \frac{dt}{dG(t)}. \quad (17)$$

This allows one to determine the function  $G(t)$  from the given OEC  $Y(t)$  based on functional equation (16), followed by the determination of the required distribution function from the integral equation (17) by calculating the  $dG/dt$  derivative.

It follows from (17) that, at  $t > t_+$ ,  $dG/dt \equiv 1$ . The dependence  $G(t)$  is determined with the accuracy of the integration constant. Let us set  $G(t) = t$  at  $t > t_+$  considering this arbitration. The calculation of  $G(t)$  at  $t < t_+$  does not pose a problem. The corresponding calculation scheme is illustrated in Fig. 5. The function  $y(t) = t - Y(t)$  presented there is equal to zero at  $t < t_+$ , coincides with  $y(t) = t - 1$  at  $t > t_+$ , and grows monotonously in the segment  $[t_+, t_+]$ .

Let us assume that it is necessary to calculate  $G$  at a certain point  $t_0$ . According to (16),  $G(t_0) = G(t_1) - 1$ ,

**Table 2.** Approximation parameters for processing of experimental data

Raw material	$D_{\text{eff}}, \text{m}^2/\text{s}$	$d_1, \text{mm}$	$d_0, \text{mm}$	$d_*, \text{mm}$
Apricot	$3.9 \times 10^{-12}$	0.054	0.71	0.31
Pumpkin	$1.2 \times 10^{-12}$	0.028	0.71	0.54
Sunflower	$0.5 \times 10^{-12}$	0.038	0.29	0.34

where  $t_1 = t_0 + Y(t_0)$  (see Fig. 5). By continuing this procedure, we obtain

$$G(t_0) = G(t_1) - 1 = \dots = G(t_k) - k = t_k - k.$$

Due to finiteness of  $t_+$  it will require a finite number of steps  $k$  to reduce the calculation of  $G(t_0)$  to calculation of  $G(t_k)$  at  $t_k > t_+$ .

Let us further consider the procedure for solution of integral equation (17) for the case of flat particles at  $\varphi(s) = s^2$ . By substituting the integral variable in (17), we obtain

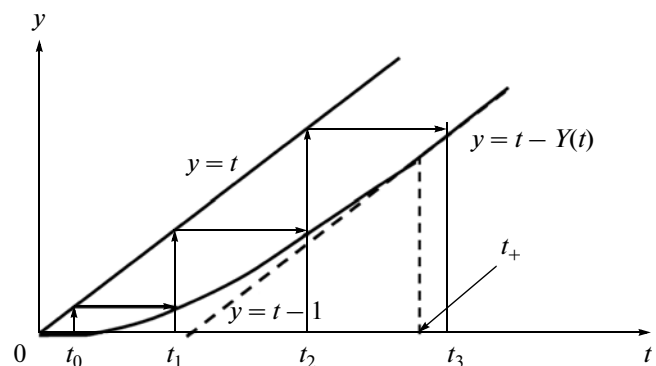
$$\int_{\sqrt{t}}^{\infty} F(a) \frac{da}{a^2} = \frac{dt}{\sqrt{td}G(t)}.$$

By differentiating this equation, we ultimately obtain

$$F(a) = -2a^2 \frac{d}{da} \left( \frac{da}{dG(a^2)} \right). \quad (18)$$

The ill-posed character of the inverse problem is obviously demonstrated by the need for the double differentiation of the  $G(t)$  function, which is specified by the experiment.

The problem of solving the integral equation (17) in the case of spherical particles is similar in nature to the ill-posed procedure (18); however, it requires the application of special numerical iteration methods.



**Fig. 5.** Scheme for calculating the  $G(t)$  function.

The discussion of this problem is beyond the scope of this work.

## CONCLUSIONS

The generalization of the mathematical model of the supercritical extraction in the framework of shrinking core scheme for the case of the polydisperse granulated layer of ground plant material was conducted in this work. The analytical solution of the problem of calculating the oil-yield curve was found.

The consideration of the fraction polydispersity of the layer provides the almost ideal agreement of the model with the known experimental data. It is sufficient to calculate the SFE processes that are limited in duration (at the finite intervals of the dimensionless time) in the bidisperse approximation. The adaptation of the model to the three types of raw material showed that the contribution of the small fraction was proportional to the specific surface area of the granulated layer, and the size of its particles corresponded to a few (two to three) diameters of the cells of plant material independent on the degree of grinding. Asymptotic dependencies (13) and (14)–(15) can be used to assess OEC.

Description of longer experiments requires a higher degree of detalization of the particle size distribution function of the porous granulated layer. In connection with this, the inverse problem of determining the fractional composition of the layer by the experimental OEC was presented. The problem was reduced to solving the integral equation and was considered to be poorly posed. The analytical solution was found for flat particles. Special numerical iterative procedure is suggested for the general case. The preliminary calculation experiments show that the integral operator for flat particles can be used in this procedure as an effective preconditioner, which significantly increases the rate of its convergence.

## DESIGNATIONS

$A(a)$ —surface area of granule with size  $a$ ,  $m^2$ ;  
 $a$ —particle size equal to the radius in the case of spherical particles and half-thickness in the case of flat particles,  $m$ ;  
 $a_{\max}$ —maximum size of granules,  $m$ ;  
 $a_{sc}$ —particle size scale,  $m$ ;  
 $C$ —mass concentration of oil solution in supercritical fluid in the pore space,  $kg/m^3$ ;  
 $D_{\text{eff}}$ —effective diffusion coefficient in granules,  $m^2/s$ ;  
 $d$ —particle diameter of large fraction,  $m$ ;  
 $d_1$ —particle diameter of small fraction,  $m$ ;  
 $F$ —size distribution function;  
 $f$ —density of volumetric size distribution function,  $m^{-1}$ ;

$L$ —height of the reactor,  $m$ ;  
 $m$ —porosity of the granular layer;  
 $q$ —density of the oil diffusional flow from granules of the size  $a$  into a pore space,  $kg/(m^2 s)$ ;  
 $q_s$ —total density of the oil diffusional flow from granules in the bed into pore space,  $kg/(m^2 s)$ ;  
 $R$ —core radius of the particle,  $m$ ;  
 $t$ —time,  $s$ ;  
 $t_{sc}$ —time scale,  $s$ ;  
 $t_-$ —duration of the linear extraction stage,  $s$ ;  
 $t_+$ —total extraction time,  $s$ ;  
 $V(a)$ —volume of the granule of size  $a$ ,  $m^3$ ;  
 $v$ —rate of the fluid filtration,  $m/s$ ;  
 $Y$ —dimensionless overall extraction curve;  
 $y$ —accumulated oil yield from the  $[0, z]$  layer normalized to the initial oil load of the reactor;  
 $z$ —coordinate measured from the inlet cross section along the extractor axis,  $m$ ;  
 $\alpha$ —contribution of the small fraction;  
 $\delta$ —Dirac delta function,  $m^{-1}$ ;  
 $\theta_0$ —ratio of the initial oil load in the particle of the granular layer to its volume,  $kg/m^3$ ;  
 $\theta_a$ —concentration on the surface of the granule,  $kg/m^3$ ;  
 $\theta_*$ —equilibrium concentration of oil in supercritical  $CO_2$  (at given pressure and temperature),  $kg/m^3$ .

## SUBSCRIPTS AND SUPERSSCRIPTS

$n$ —index is equal to 1 or 3 for flat and spherical particles, respectively.

## REFERENCES

1. Donelian, A., Carlson, L.H.C., Lopes, T.J., and Machado, R.A.F., Comparison of extraction of patchouli (*Pogostemon cablin*) essential oil with supercritical  $CO_2$  and by steam distillation, *J. Supercrit. Fluids*, 2009, vol. 48, no. 1, p. 15.
2. Rout, P.K., Naik, S.N., Rao, Y.R., Jadeja, G., and Maheshwari, R.C., Extraction and composition of volatiles from *Zanthoxylum rhesta*: comparison of subcritical  $CO_2$  and traditional processes, *J. Supercrit. Fluids*, 2007, vol. 42, no. 3, p. 334.
3. Goto, M., Roy, B.C., and Hirose, T., Shrinking-core leaching model for supercritical fluid extraction, *J. Supercrit. Fluids*, 1996, vol. 9, no. 2, p. 128.
4. Doker, O., Salgin, U., and Calimli, A., Modeling of extraction of  $\beta$ -carotene from apricot bagasse using supercritical  $CO_2$  in packed bed extractor, *J. Supercrit. Fluids*, 2004, vol. 28, no. 1, p. 11.
5. Maksudov, R.N., Egorov, A.G., Mazo, A.B., et al., Mathematical model of oil-plant seeds extraction by supercritical carbon dioxide, *Sverkhkrit. Flyuidy: Teor. Prakt.*, 2008, vol. 3, no. 2, p. 20.



6. Egorov, A.G., Mazo, A.B., and Maksudov, R.N., Extraction from a polydisperse granular layer of milled oilseeds with supercritical carbon dioxide, *Theor. Found. Chem. Eng.*, 2010, vol. 44, no. 5, p. 642.
7. Fiori, L., Supercritical extraction of sunflower seed oil: experimental data and model validation, *J. Supercrit. Fluids*, 2009, vol. 50, no. 3, p. 218.
8. Salgin, U. and Korkmaz, H., A green separation process for recovery of healthy oil from pumpkin seed, *J. Supercrit. Fluids*, 2011, vol. 58, no. 2, p. 239.
9. Roy, B.C., Goto, M., and Hirose, T., Extraction rates of oil from tomato seeds with supercritical carbon dioxide, *Jpn. J. Chem. Eng.*, 1994, vol. 27, no. 6, p. 768.
10. Ozkal, S.G., Yener, M.E., and Bayindirli, L., Mass transfer modeling of apricot kernel oil extraction with supercritical carbon dioxide, *J. Supercrit. Fluids*, 2005, vol. 35, no. 2, p. 119.
11. Sovova, H., Rate of the vegetable oil extraction with supercritical CO<sub>2</sub>. I. Modeling of extraction curves, *Chem. Eng. Sci.*, 1994, vol. 49, no. 3, p. 409.
12. Reverchon, E. and Marrone, C., Modeling and simulation of the supercritical CO<sub>2</sub> extraction of vegetable oils, *J. Supercrit. Fluids*, 2001, vol. 19, no. 2, p. 161.
13. Del Valle, J.M. and Aguilera, J.M., An improved equation for predicting the solubility of vegetable oils in supercritical CO<sub>2</sub>, *Ind. Eng. Chem. Res.*, 1988, vol. 27, no. 8, p. 1551.

*Translated by L. Brovko*