

Supercritical fluid extraction of soybean oil from the surface of spiked quartz sand - modelling study

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Summary

The extraction of soybean oil from the surface of spiked quartz sand using supercritical CO₂ was investigated. Sand as solid was used; it is not porous material so the internal diffusion does not exist, all the soluble material is in the surface of the particles. Sovová's model has been used in order to obtain an analytical solution to develop the required extraction yield curves. The model simplifies when the internal diffusion can be neglected. The external mass transfer coefficient was determined by fitting the theoretical extraction curve to experimental data. According to the external mass transfer coefficient, a new *Sherwood* correlation was developed in terms of the dimensionless groups: *Reynolds* and *Schmidt* number. It was found that this correlation give superior results when compared to experimental data.

Keywords: supercritical fluid extraction, soybean oil, modelling, *Sherwood* correlation

Introduction

Supercritical fluid extraction is a powerful separation technique and is very common for the extraction of oil. It is good alternative to conventional separation methods thanks to the favourable properties of supercritical fluids. The motivation for the development of supercritical fluid technology is a result of increasing cost of energy, awareness about pollution control, and the performance demands of specialized new materials. Carbon dioxide (CO₂) is the most commonly used fluid for supercritical extraction and it can be easily recycled. Supercritical fluid extraction can be applied from analytical scale up to large industrial scale. Supercritical fluid technology have experienced the rapid advances (Lang and Wai, 2001; Brunner, 2005; Pourmortazavi and Hajmirsadeghi, 2007; Sahena et al., 2009; Temelli, 2009).

For successful extraction, solubilities of the extracted compounds need to be taken into account. Also mass transfer resistances due to the structure of the raw material and to the specific location of the compounds to be extracted can also play a relevant role. The complex interplay between thermodynamics (solubility) and kinetics (mass transfer) has to be understood to properly perform supercritical fluid extraction (Reverchon and De Marco, 2006). Brunner (1984) explored the

basic variables that influenced the mass transfer of solutes and provided the basis for several other modelling studies involving oilseed. Mathematical modelling of complex phenomena is important from economic point of view. Mathematical models are required for scale up procedure from laboratory to pilot and industrial plant. However, such predictions require the establishment of model which can predict phase behaviour, equilibrium, solubility, adsorption, desorption, mass and heat transfer and others (Norhuda and Mohd Omar, 2009).

Several researchers used supercritical CO₂ to extract the oil from soybean seeds using supercritical fluid extraction (Friedrich and List, 1982; Friedrich and Pryde, 1984; Hong et al., 1990; Taylor et al., 1997; Nodar et al., 2002; Artz et al., 2005; Jokić et al., 2012). Supercritical CO₂ extraction of soybean oil was investigated also in this study but oil was adsorbed on the sand particles used as solid and non porous material. Extraction curve was analyzed by well known Sovová's model (Sovová, 1994) simplified by neglecting internal diffusion of oil. The main point of this study was to analyze external mass transfer of supercritical extraction by fitting theoretical extraction curve to experimental data. According to these results new equation between *Sherwood*, *Reynolds* and *Schmidt* number was proposed.

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Materials and methods

Material

Supercritical fluid extraction was performed on the soybean cultivar "Ika" created at the Agricultural Institute Osijek in Croatia in 2009. The quartz sand used to be mixed with oil was provided by a Hungarian company called SPEKTRUM-3D KFT. Reagent-grade *n*-hexane (Reanal Ltd., Budapest) was used for laboratory Soxhlet-extraction. The CO₂ used for pilot plant extraction was 99.5 % (w/w) pure and supplied by Linde Gas Hungary Co. Ltd. (Budapest). Moisture content of soybean was determined by oven drying to constant weight at 105 °C (AOAC, 2000) and noted as percentage (11.02± 0.11 %).

Determination of particle size distribution with sieving

Soybeans were grounded and sieved using a vertical vibratory sieve shaker (Labortechnik GmbH, Ilmenau, Germany) for 20 min. About 200 g loading were used at each sieving. The raw material size distribution was determined using a nest of 9 sieves of aperture sizes 1.4, 0.8, 0.63, 0.5, 0.4, 0.315, 0.2, 0.1 and 0.05 mm. The mass of fragments remaining on each sieve after sieving was used to calculate the distribution of fragments, which was then normalized in respect of the total mass. For evaluation of sieve analysis results the Rosin-Rammler-Bennett (RRB) distribution (Allen, 1981) was chosen. The percentage by mass of particles (*R*) greater than screen size (*d*) is given as:

$$R = 100 \exp \left[- \left(\frac{d}{d_0} \right)^n \right] \quad (1)$$

where

*d*₀ represents the particle size corresponding to the 36.8 % of the cumulative probability distribution (size constant), and *n* controls the shape of the distribution (uniformity coefficient). The function of the sum of sieve residue (*R*) was fitted to the experimental data by changing the representative particle size *d*₀ and the uniformity coefficient *n*, minimizing the sum of the mean square error using STATISTICA 8.0 software (Stat Soft Inc., USA).

The quartz sand with the same particle size distribution like soybeans was prepared for the second part of experimental work.

Determination of the initial and remain oil content

The initial oil content was measured by traditional laboratory Soxhlet-extraction with *n*-hexane. About

30 g of ground material was extracted with about 250 mL solvent, until totally depleted. The whole process took 16 h. The measurement was done in triplicate. The average of the initial oil content for three replicates was 20.08 ± 0.14 %.

In order to check the amount of remain oil in the sand further Soxhlet experiments have been done.

Supercritical fluid extraction

The first part of experimental work was related to supercritical fluid extraction of oil from soybeans in order to obtain the soybean oil which were used for second part of experimental work. Different solvent mass flow rates were investigated. The high pressure pilot plant equipped with 5 L volume extractor vessel (delivered by NATEX Austria), used for extraction of soybean oil is described in detail elsewhere (Rónyai et al., 1998). The extraction was carried out at 400 bar and 40 °C. The operating parameters in the separator were 40 bar and 20 - 25 °C. The accumulated product samples were collected and weight at certain time intervals. The CO₂ flow rate was measured by a Mikro Motion RFT 9729 type mass flow meter. The extraction was carried on until the amount of the product sample, collected for 1 h decreased to under 0.1 % of the raw material. The height and the diameter of the extractor basket were *h*_E = 0.585 m, *d*_E = 0.098 m, respectively. The experimental conditions for supercritical fluid extractions of soybean oil are given in Table 1.

Table 1. Experimental conditions of the supercritical fluid extraction of soybean oil

Experiment*	<i>m</i> _s (g)	<i>m</i> _f (kg/h)
Run 1	1004.3	14.125
Run 2	1002.4	9.103
Run 3	1003.4	11.354
Run 4	1003.0	9.053
Run 5	1002.5	6.551
Run 6	1000.7	9.092
Run 7	1001.3	4.065

*Conditions: *T*_E=40 °C; *P*_E=400 bar; *d*₀= 0.394 mm

Furthermore, supercritical fluid extraction of soybean oil from the surface of spiked quartz sand was the second part of the experiment. The quartz sand was mixed with soybean oil (10 % w/w) previously obtained by supercritical fluid extraction. This proportion was selected in order to obtain a homogeneous well mixed sample. The sand and oil have formed the raw material. Total of 12 experiments related to supercritical fluid extraction of soybean oil from the surface of spiked quartz sand have been done, some of them were parallel

experiments with the same solvent flow rate, and the other were carried out in different mass flow conditions in order to compare this effect in the extraction yield curves. Five experiments were done with different packed column height. Distribution of the particle size of crushed soybeans (in the first part of the experiment) and quartz sand (in the second part of the experiment), determined by Rosin-Rammler-Bennett's model (Eq. (1)), was identical. The experimental conditions for supercritical fluid extraction of soybean oil from the surface of spiked quartz sand are given in Table 2.

Table 2. Experimental conditions for the supercritical fluid extraction of soybean oil from the surface of spiked quartz sand

Experiment*	m_s (g)	\dot{m}_f (kg/h)
Run 1	1638.9	9.128
Run 2	1643.3	8.996
Run 3	1644.4	9.033
Run 4	1643.6	11.588
Run 5	1644.5	14.056
Run 6	1644.3	6.539
Run 7	1644.4	4.068
Run 8	2088.5	9.147
Run 9	2087.6	4.080
Run 10	2093.3	14.089
Run 11	2095.9	14.001
Run 12	2089.0	4.116

*Conditions: $T_E=40$ °C; $P_E=400$ bar; $d_0=0.397$ mm

Mathematical modelling

For the mathematical description of the extraction curves the Sovová model (Sovová, 1994) was used. The Sovová model is suitable to describe the extraction of crushed seeds with fluid in plug flow. This model assumes the existence of two mass transfer coefficients, one in the solvent phase and one in the solid one, and neglects the accumulation of the solute in the fluid phase. Furthermore, the Sovová model attributed the existence of different regimes in the extraction to the fact that a part of the solute is trapped in intact cells, while the other part is contained in broken cells at the particle surface as a result of the milling. Supercritical fluid extraction process, in this case, can be divided into three periods, the first one being controlled by convection in the fluid phase, the last one controlled by diffusion in the solid, and an intermediary period when the diffusion mechanism starts, operating combined with convection.

In the case of the supercritical fluid extraction of soybean oil from the surface of spiked quartz sand, the simplified form of Sovová model was obtained according to the following assumptions:

- A steady state is present;
- Axial dispersion is negligible;
- The sand is not porous material so the internal diffusion will not exist; all the soluble material is at the surface of the particles;
- Isothermal process;
- Isobaric process;
- Physical properties of the supercritical fluid are constant;
- No interaction between sand (solid) and oil exists.

According to given assumptions above, the parameter $q=1$; which means that all the soluble material is at the surface of the particles and the equation can be simplified. The dimensionless length coordinate, which shows the margin between the two different parts, can be simplified as following:

$$Z_k = \frac{1}{S} \ln \left[1 + \frac{1}{q} \left\{ \exp \left[S \left(\vartheta - \frac{q}{Q} \right) \right] - 1 \right\} \right] = \vartheta - \frac{1}{Q} \quad (2)$$

After ϑ_k time the soluble material is completely extracted from the external surface and the equation gets the following form:

$$\vartheta_k = \frac{q}{Q} + \frac{1}{S} \ln \{ 1 - q [1 - \exp(S)] \} = \frac{1}{Q} + 1 \quad (3)$$

For determining the dimensionless extraction yield curves the following equations can be used:

$$\frac{Y_E}{x_0} = \vartheta [1 - \exp(-Q)] \quad \text{if} \quad \vartheta < \frac{1}{Q} \quad (4)$$

$$\frac{Y_E}{x_0} = \vartheta - \frac{1}{Q} \exp[Q \vartheta - Q - 1] \quad \text{if} \quad \frac{1}{Q} \leq \vartheta < \frac{1}{Q} + 1 \quad (5)$$

$$\frac{Y_E}{x_0} = 1 \quad \text{if} \quad \vartheta \geq \frac{1}{Q} + 1 \quad (6)$$

where the main dimensionless variables of Sovová's model are defined as:

$$Z = \frac{h}{H} \quad (7)$$

$$\vartheta = \frac{t}{\tau} \quad (8)$$

and the dimensionless model parameters (τ , Q) are given by Eqs. (9) - (10).

$$\tau = \frac{m_s x_0}{\dot{m}_f y^*} \quad (9)$$

$$Q = \frac{m_s k_f a_p \rho_f}{\dot{m}_f (1 - \varepsilon) \rho_s} \quad (10)$$

$$a_p = \frac{6}{d_{sv}} (1 - \varepsilon) \quad (13)$$

where τ is the minimal extraction time (the time of the extraction, if the saturated solution leaves the extractor), which is necessary for the creation of dimensionless time (ϑ). The solubility of soybean oil y^* (kg/kg) were determined by an empirical equation in function of temperature and pressure (Valle and Aguilera, 1988). For determination the viscosity η , which is necessary for calculation of *Reynolds* and *Schmidt* numbers, empirical equation proposed by Vesović et al. (1990) was used. The infinite-dilution molecular diffusion coefficient D_{12} in supercritical CO₂ was determined using a predictive equation based on the rough-hard-sphere theory (Eaton and Akgerman, 1997). The density of the CO₂ (ρ_f) was calculated using the Bender equation of state (Ghazouani et al., 2005). The density measurement of the solid raw material (ρ_s) using an air pycnometer is described in detail elsewhere (Nagy et al., 2008).

After determination of the RRB model parameters (d_0, n) the surface–volume mean diameter of the packed bed was calculated using Eq. (11).

$$d_{sv} = \frac{1}{1/d_0 \Gamma(1 - 1/n)} \quad (11)$$

where $\Gamma(w)$ is gamma function, which can be evaluated as:

$$\Gamma(w) = \int_0^\infty e^{-u} \cdot u^{(w-1)} du \quad (12)$$

The specific surface area of a packed column (a_p) can be determined by:

The specific void fraction (ε) is given as:

$$\varepsilon = 1 - \frac{\delta}{\rho_s} \quad (14)$$

The bulk density (δ) was obtained from the bulk volume and the weight of the raw material loaded in the extractor basket.

Values of τ can be determined from the measured and empirically estimated parameters mentioned above, whereas Q parameter was fitted to the experimental curves.

Results and discussion

The external mass transfer does not depend only on superficial fluid velocity but also on diameter of solid particles. Related to this fact the sand with the same particle size distribution like soybeans was prepared for experimental work.

The obtained parameters for η, ρ_f and D_{12} together with calculated *Reynolds* number ($Re = u_s \cdot d_{sv} \cdot \rho_f / \eta$) for all experimental conditions of extraction of soybean oil from the surface of spiked quartz were given in Table 3 together with the values of the minimum extraction time τ defined by the Eq. (9). The fitted parameter Q , the mass transfer coefficient in the fluid phase and *Sh* number in the different extraction experiments are also shown in Table 3. The values of *Reynolds* number were in the range from 0.4008 to 1.3883, and τ was in the range 3216-15532 seconds depending on the experimental conditions of extraction. The calculated value for viscosity was $1.07 \cdot 10^{-4}$ Pa·s, diffusion coefficient $5.45 \cdot 10^{-9}$ m²/s, density of the fluid phase 957.2 kg/m³ and according to that values *Schmidt* number ($Sc = \eta / D_{12} \cdot \rho_f$) was calculated to be 20.59.

Table 3. The fitted parameter Q , the mass transfer coefficient in the fluid phase, *Sh* and *Re* number in the different extraction experiments

Experiment	u_s (m/s)	<i>Re</i> (-)	τ (s)	Q (-)	k_f (m/s)	<i>Sh</i> (-)
Run 1	0.00035	0.8995	4885	0.822	$1.70 \cdot 10^{-7}$	0.0089
Run 2	0.00035	0.8865	4959	0.791	$1.61 \cdot 10^{-7}$	0.0085
Run 3	0.00035	0.8869	4965	0.758	$1.55 \cdot 10^{-7}$	0.0081
Run 4	0.00045	1.1419	3867	0.747	$1.96 \cdot 10^{-7}$	0.0103
Run 5	0.00054	1.3851	3216	0.961	$3.05 \cdot 10^{-7}$	0.0160
Run 6	0.00025	0.6444	6877	0.853	$1.26 \cdot 10^{-7}$	0.0066
Run 7	0.00016	0.4008	11056	1.211	$1.11 \cdot 10^{-7}$	0.0058
Run 8	0.00035	0.9013	6815	1.167	$1.73 \cdot 10^{-7}$	0.0091
Run 9	0.00016	0.4019	15532	1.684	$1.11 \cdot 10^{-7}$	0.0058
Run 10	0.00054	1.3883	4554	1.324	$3.00 \cdot 10^{-7}$	0.0159
Run 11	0.00054	1.3796	4486	1.363	$3.09 \cdot 10^{-7}$	0.0162
Run 12	0.00016	0.4056	15179	1.584	$1.05 \cdot 10^{-7}$	0.0055

The new mass transfer coefficient in the fluid phase (k_f) was determined from the fitted Q parameter (Eq. (10)). From the calculated mass transfer coefficient in the fluid phase, *Sherwood* number (Sh) was obtained according to the following equation:

$$Sh = \frac{d_{sv} \cdot k_f}{D_{12}} \quad (15)$$

which represents the mass transfer between the surface and the fluid. The values of external mass transfer coefficients were in the range from $1.05 \cdot 10^{-7}$ to $3.09 \cdot 10^{-7}$ m/s.

The *Sherwood* number is normally written as a function of the *Reynolds* and the *Schmidt* number. Bird et al. (2002) suggested that data of Sh , Sc and Re are generally correlated in the form as in Eq. (16):

$$\log(Sh/(Sc^{0.33})) = \log(const) + pow1 \cdot \log(Re) \quad (16)$$

According to the calculated Sh numbers and with the Re and Sc dimensionless numbers, the new Sh correlation plotting $\log(Re)$ versus $\log(Sh/Sc^{0.33})$ was derived. Linear regression was used to determine the constant coefficient and the required power of the Re number from the straight line of slope. In this way, the new *Sherwood* correlation has been developed and has a following form (Eq. (17)):

$$Sh = 0.0039Re^{0.78}Sc^{0.33} \quad (17)$$

From Fig. 1 can be seen an excellent agreement between the experimental and simplified Sovová model calculated values for the dimensionless oil yield (experimental runs 3, 6 and 10 are chosen for the comparison).

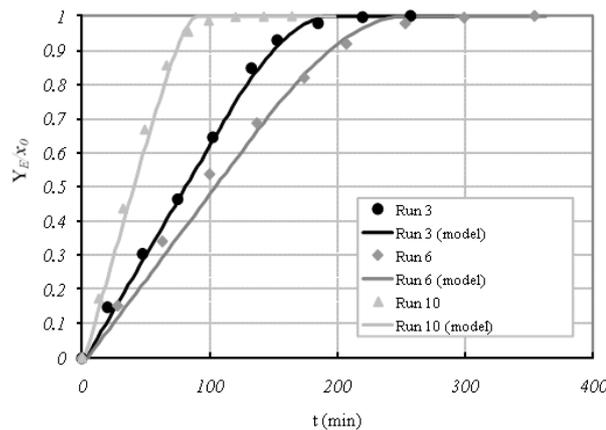


Fig. 1. Experimental and model extraction curves obtained for selected experiments

Table 4 show the calculated values of *Sherwood* number and external mass transfer coefficient for the extraction of oil from soybeans using supercritical CO₂ whose experimental conditions are given in Table 1. The values of *Sherwood* number were calculated using the new *Sherwood* correlation (Eq. (17)), and the

external mass transfer coefficient k_f was calculated from the Eq. (15). It can be seen that the value of the external mass transfer coefficient ranged from $1.44 \cdot 10^{-7}$ to $2.61 \cdot 10^{-7}$ m/s, except in the case where was used small CO₂ flow rate (4.065 kg/h), where the value of external mass transfer coefficient was $9.89 \cdot 10^{-8}$ m/s.

Table 4. Calculated values of *Sherwood* number and external mass transfer coefficient for the extraction of oil from soybeans using supercritical CO₂

Experiment	u (m/s)	Re (-)	Sh^* (-)	k_f (m/s)
Run 1	0.00054	1.3794	0.0136	$2.61 \cdot 10^{-7}$
Run 2	0.00035	0.8889	0.0097	$1.85 \cdot 10^{-7}$
Run 3	0.00044	1.1087	0.0115	$2.20 \cdot 10^{-7}$
Run 4	0.00035	0.8841	0.0096	$1.85 \cdot 10^{-7}$
Run 5	0.00025	0.6398	0.0075	$1.44 \cdot 10^{-7}$
Run 6	0.00035	0.8879	0.0096	$1.85 \cdot 10^{-7}$
Run 7	0.00016	0.3969	0.0051	$9.89 \cdot 10^{-8}$

* Sh values are determined using the new *Sherwood* correlation (Eq. 17)

In the literature, some papers are related to the development of new *Sherwood* correlation during the supercritical fluid extraction (Eqs. 18-28):

$$Sh = 2 + 1.1Re^{0.6}Sc^{0.33} \quad (\text{Wakao and Funazkri, 1978}) \quad (18)$$

$$Sh = 0.38Re^{0.83}Sc^{0.3333} \quad (\text{Tan et al., 1988}) \quad (19)$$

$$Sh = 0.2548Re^{0.5}Sc^{0.3333} \quad (\text{King et al., 1997}) \quad (20)$$

$$Sh = 0.206Re^{0.8}Sc^{0.3333} \quad (\text{Puiggene et al., 1997}) \quad (21)$$

$$Sh = 1.309 - 0.258Re^{-0.0023}Sc^{0.463} \quad (\text{Mongkholkhajornsilp et al., 2005}) \quad (22)$$

$$Sh = 1.661 - 0.517Re^{-0.014}Sc^{0.333} \quad (\text{Mongkholkhajornsilp et al., 2005}) \quad (23)$$

$$Sh = 0.541 - 0.133Re^{0.5}Sc^{0.333} \quad (\text{Mongkholkhajornsilp et al., 2005}) \quad (24)$$

$$Sh = 3.173Re^{-0.06}Sc^{-0.85} \quad (\text{Mongkholkhajornsilp et al., 2005}) \quad (25)$$

$$Sh = 0.085Re^{-0.298}Sc^{0.333} \quad (\text{Mongkholkhajornsilp et al., 2005}) \quad (26)$$

$$Sh = 0.135Re^{0.5}Sc^{0.33} \quad (\text{Mongkholkhajornsilp et al., 2005}) \quad (27)$$

$$Sh\{1 + 1.5(1 - \varepsilon)\} = 0.035Re^{0.5}Sc^{0.33} \quad (\text{Hong et al., 2005}) \quad (28)$$

but so far there is no published scientific papers related to *Sherwood* correlation during the supercritical extraction of vegetable oils from the surface of non-porous material. Therefore, a significant scientific contribution of this research is in the possibility of the estimation of external mass transfer coefficient in the case of supercritical extraction of oil from the surface of non-porous material, especially in the scale up of the results from the laboratory to industrial scale.

The closest comparison of the results obtained from this study was made with the results obtained by Hong et al. (1990). In the model proposed by Hong et al. (1990), the extraction rates were constant during the initial extraction period where the film resistance controls the rates, and then, the rates shifted to time-dependent diffusion controlling the mass transfer mode. According to the authors of this model, for each period of extraction was carried out individually mass transfer calculations, and the results were combined on the basis of the observed mass transfer data. The resulting values of external mass transfer coefficient during the supercritical extraction of soybean oil published by Hong et al. (1990) are similar to the values of k_f obtained in this work.

Conclusions

According to the external mass transfer coefficient during the supercritical extraction of soybean oil

from the surface of quartz sand, the new *Sherwood* correlation was developed. The importance of the new *Sherwood* correlation is in the estimation of the external mass transfer coefficient in the case of supercritical extraction of oil from the surface of non-porous material, especially in the scale up of the results from the laboratory to industrial plant.

Future research should include the valorization of the obtained new *Sherwood* correlation on the extraction of other vegetable oils by supercritical CO₂ from the surface of non-porous material.

Nomenclature

a_p	specific interfacial area (m ² /m ³)
D_{12}	diffusion coefficient (m ² /s)
d	screen size (mm)
d_E	diameter of the extractor basket (m)
d_{sv}	surface–volume mean diameter (mm)
d_0	representative particle size, where $R=36.8\%$ (mm)
h	length coordinate of the bed (m)
H	total length of the bed (m)
h_E	height of the extractor basket (m)
k_f	mass transfer coefficient in the fluid phase (m/s)
k_s	mass transfer coefficient in the solid phase (m/s)
\dot{m}_f	mass flow of the fluid (kg/s)
m_s	amount of the raw material (g)
n	uniformity factor (-)
q	soluble fraction in the surface of the particles (-)

Q	dimensionless model parameter (-)
P_E	extraction pressure (bar)
R	sum of sieve residue (%), from the sieve experiments
Re	Reynolds number (-)
S	dimensionless model parameter (-)
Sc	Schmidt number (-)
Sh	Sherwood number (-)
t	time (s)
T_E	extraction temperature (°C)
u	variable of gamma function
u_s	supercritical velocity (m/s)
w	variable of gamma function
x_0	initial oil concentration in the solid phase (kg/kg)
y^*	solubility of oil in CO ₂ (kg/kg)
Y_E	extraction yield (kg extract/kg solid matrix)
Z	dimensionless length coordinate (-)
Z_k	dimensionless length coordinate of the margin between the two extraction parts (-)

Greek letters

Γ	gamma function
δ	bulk density of raw material (kg/m ³)
ε	void fraction in bed (m ³ /m ³)
η	viscosity of the fluid phase (Pa·s)
ϑ	dimensionless time (-)
ϑ_k^q	dimensionless time when the soluble material runs out from the external surface (-)
ρ_f	density of the fluid phase (kg/m ³)
ρ_s	density of the solid phase (kg/m ³)
τ	minimal extraction time (s)

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