Seed Oil Supercritical Extraction: Charge Granulometric Distribution And Modeling

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A theoretical investigation on the influence of the granulometric distribution of milled seeds on the seed oil extraction was performed. In the literature various models predicting the seed oil supercritical extraction kinetic were detailed: even if the milled substrate presents a like-Gaussian particle distribution, these models simplified this distribution in an unique mean dimension. Often the particles were assumed to have a spherical shape and the Sauter mean diameter (Smd in the following) was the most utilized mean dimension. In the present investigation the limits of this approximation were analyzed.

At first the behavior of the extraction kinetic in relation to variations in the granulometric distribution of the milled substrate was analyzed in test cases. The seed charge was considered split into two granulometric classes with identical weight fraction (50% and 50%) and with identical Smd: the differences arising from using various combinations of particle diameters were analyzed. The approximation of using the Smd resulted in a slight under-estimation of the extraction yield just after the beginning of the extraction, and in an overestimation in the following of the process.

Then the model was used considering a real granulometric distribution of grape crushed seeds. This distribution took into consideration a set of several diameters (from 0.05 mm to 2.90 mm). In this case, the maximum percentage difference between the outputs of the simplified Smd model and the outputs of the 'granulometric' model was found equal to 8%.

INTRODUCTION

Supercritical fluids extraction was studied by several authors and some of them developed mathematical extraction models. First Bulley *et al.* [1], Lee *et al.* [2] and Fattori *et al.* [3] proposed a model in which the mass transfer resistance was considered to be present only in the solvent phase. King and Catchpole [4] considered the variations of the transport coefficient as a function of the degree of extraction, using a shrinking core model. Particles were assimilated to spheres and a transport coefficient was established for every spherical shell. Goto *et al.* [5], Sovovà [6] and Sovovà *et al.* [7, 8] considered a process in which the charge of the extractor was constituted by particles, whose solid phase was divided between broken and intact cells. Consequently, an immediately available fraction of oil (the so called free oil fraction) and another slowly available one (the tied oil fraction) were present. Reverchon and Marrone [9] proposed an extraction model in which there were two differential terms, for the free and the tied oil fraction, respectively. Furthermore, some authors suggested simplified models with analytical solution.

All resolutive equation systems considered homogeneous dimension particles, using the Sauter mean diameter, evaluated from the particle granulometric distribution, as an input for the mathematical extraction model. This could be an efficacious simplification when milled seeds have actual homogeneous dimensions. However, considering all the particles having the same diameter could bring to small modeling errors.

In this work new mass balances were developed in order to consider the contribute of all granulometric classes to the extraction process.

Granulometric distributions with the same Sauter mean diameter were implemented to examine the influence of small or big unhomogeneity of the particles. These can affect the distribution of the oil, even at the beginning of the extraction (that is the initial condition on the partition of free and tied oil) and during the process, because of the smaller transport coefficient related to the tied oil fraction.

Then the analysis moved to consider real granulometric distributions relevant to milled grape seeds. Also in this case, the extraction kinetic modeled considering the whole granulometric distributions was compared with the extraction kinetic modeled considering its mean value (Smd).

THE MODEL

The system of equations modified to consider the whole granulometric distribution was the one suggested by Reverchon and Marrone [9, 10]. The model evolved from the description of intact and broken cells proposed by Sovovà [8], in which the oil was present in the vegetable substrate as free and tied oil. The model was described in detail in [11].

Differential mass balances of the oil inside the extractor and of the free and tied oil utilized in this study are reported in Table 1. The substrate (milled seed particles) was considered to be composed by N granulometric classes. The subscript 'j' indicates the granulometric class considered.

Table 1: The Marrone-Reverchon model [9, 10] modified to take into account the different granulometric classes. Mass balances of total solute, free oil phase and tied oil phase.

$$\varepsilon\cdot\rho_f\cdot\frac{\partial C}{\partial t}+\varepsilon\cdot u\cdot\rho_f\cdot\frac{\partial C}{\partial z}-\varepsilon\cdot\rho_f\cdot D_{Ax}\cdot\frac{\partial^2 C}{\partial z^2}+\sum_{j=1}^{N}\left((1-\varepsilon)\cdot\phi_{t,j}\cdot\rho_{s,j}\cdot\frac{\partial F_j}{\partial t}\cdot\omega_j\right)+\sum_{j=1}^{N}\left((1-\varepsilon)\cdot\phi_{f,j}\cdot\rho_0\cdot\frac{\partial\psi_j}{\partial t}\cdot\omega_j\right)=0 \qquad (1)$$

$$(1-\varepsilon)\cdot\phi_{f,j}\cdot\rho_0\cdot\frac{\partial\psi_j}{\partial t}\cdot\omega_j=-k_{e,j}\cdot a_j\cdot K_\psi\cdot(C_0-C) \qquad j=1,N \qquad (2)$$

$$(1-\varepsilon)\cdot\phi_{t,j}\cdot\frac{\partial F_j}{\partial t}\cdot\omega_j=-k_{i,j}\cdot a_j\cdot\left(F_j-K_{f,j}C\right) \qquad j=1,N \qquad (3)$$

In the equation system proposed by Reverchon and Marrone, all terms were evaluated considering the Sauter mean diameter. To investigate the influence of a whole granulometric distribution on the behavior of the extraction kinetic, all diameter dependent parameters and variables were identified (ϕ_f, Re, ϕ_t, Sh, ρ_s, k_e, a, $k_i(t\to\infty)$). For a detailed description of these and other model parameters refer to [11, 12].

Also the axial dispersion coefficient is a function of the particle diameter: $D_{Ax}=f(\mathrm{Re})$. But D_{Ax} is a property of the extractor bed and not of the single particles; hence, to evaluate it, the Sauter mean diameter and the correlation proposed by Funazukury *et al.* [13] were used.

To solve the system of Eqs (1)-(2)-(3), 2N+1 initial conditions and two boundary conditions were necessary. The boundary conditions were the same of the original model [9, 10, 11]. One hypothesis of the model was that the solute (oil), at the beginning of the extraction, saturates the solvent ($C(z,0)=C_0$). According to Reverchon and Marrone [9, 10], the solvent saturation was due to the free oil dissolution. The initial condition relevant to the free oil ($\psi_{0,j}$) can be written considering that the free oil in the particles before entering the extractor has to be equal to the oil that saturates the solvent plus the quantity of oil remaining within the particles, when those are closed inside the extractor autoclave, Eq. (4):

$$\sum_{j=1}^{N} \rho_0 \cdot (1-\varepsilon) \cdot \phi_{f,j} \cdot \omega_j = \varepsilon \cdot \rho_f \cdot C_0 + \sum_{j=1}^{N} \psi_{0,j} \cdot \rho_0 \cdot (1-\varepsilon) \cdot \phi_{f,j} \cdot \omega_j \tag{4}$$

The value of the fraction of free oil content to free oil content in untreated seeds at the beginning of extraction ($\psi_{0,j}$) was considered to be constant ($\psi_{0,j} = \overline{\psi}_0$): it was expected that all the granulometric classes contribute to the same extent to the solvent saturation.

From Eq. (4), the initial conditions on the free oil was deduced to be Eq. (5):

$$\psi_{0,j} = \overline{\psi}_0 = \overline{\psi}(z,0) = \frac{\rho_0(1-\varepsilon) \cdot \sum_{j=1}^{N} (\phi_{f,j} \cdot \omega_j) - C_0 \varepsilon \rho_f}{\rho_0(1-\varepsilon) \cdot \sum_{j=1}^{N} (\phi_{f,j} \cdot \omega_j)} = 1 - \frac{1}{K_\Psi} \frac{\varepsilon}{1-\varepsilon} \frac{\rho_f}{\sum_{j=1}^{N} (\phi_{f,j} \cdot \omega_j)} \tag{5}$$

The initial conditions relevant to the tied oil concentration was obtained writing the total oil as the sum of the free oil of all the classes plus the tied oil of all the classes, and assuming that the oil of each class was proportional to its weight fraction, Eqs. (6) and (7):

$$\rho_e Y_\infty \omega_j = \rho_0 \cdot \phi_{f,j} \cdot \omega_j + F_{0,j} \cdot \rho_{s,j} \cdot \phi_{t,j} \cdot \omega_j \tag{6}$$

$$F_{0,j} = F_j(z,0) = \frac{\rho_e \cdot Y_\infty - \rho_0 \cdot \phi_{f,j}}{\rho_{s,j} \cdot \phi_{t,j}} \tag{7}$$

RESULTS

Constant Sauter mean diameter distribution analysis

It was developed a survey on the differences between several granulometric distributions with identical Smd, split into two classes with identical weight fractions (50 % and 50 %). The following couples of particle diameters were considered: 0.55 and 0.7704 mm; 0.49 and 0.93 mm and 0.40 and 1.623 mm. Two Gaussian distributions, respectively with variance $\sigma = 0.12$ and $\sigma = 0.2$, centered in the Smd value, were also constructed. The variances were selected arbitrarily. These data were used to analyze the accuracy of an extraction model, when it considers a mean value for the particle diameters (such as the Sauter mean one) instead of the real granulometric distribution.

Figure 1 displays the outputs of the model, relevant both to the Sauter mean diameter and to the granulometric distributions above detailed. To facilitate the lecture of the chart, one of the two curves relevant to a Gaussian distributions (the one with $\sigma = 0.12$) was removed; actually, this curve showed a trend very similar to the one of the other.

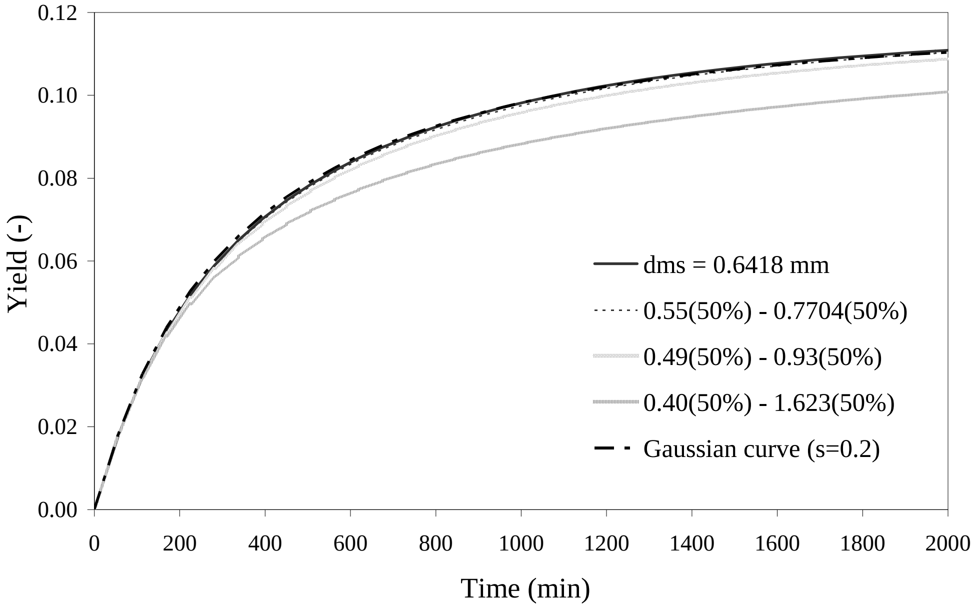
Figure 1 shows the typical trend of an extraction process. It is evident the first linear part of the curves, in which the yield is essentially due to the free oil extraction, and subsequently the smoother one, related to the extraction of the tied oil and to the complete exhaustion of the matrix.

All the curves overlap in their initial part: the solvent exits the extractor saturated by the solvent. Then, in the central part of the extraction, the yields tend slightly to differentiate.

Figure 1 shows that the trend of the 'Gaussian'-curve and of the '*0.55 mm (50%) – 0.7704 mm (50%)*'-curve is very similar to that of the *Smd*-curve. This is due to the fact that the differences between the granulometric distributions in these cases are fairly small. In the first part of the curve, the 'Gaussian'-curve lays over the *Smd*-curve, because of the presence of a greater quantity of free oil in the smallest particles. When this easily available solute contribute is exhausted, the influence of the bigger particles causes a slackening on the extraction yield and consequently the 'Gaussian'-curve lays under the one pertaining to the Sauter mean diameter.

The other two curves represented in Figure 1 tend always to lay under the Sauter mean diameter curve. In particular, the '*0.40 mm (50%) – 1.623 mm (50%)*'-curve yield is very different from the others. The gap between the two granulometric classes and the Sauter mean diameter is the greatest in this case. This fact brings repercussions to the kinetic of the process, causing a slower advancement of the extraction.

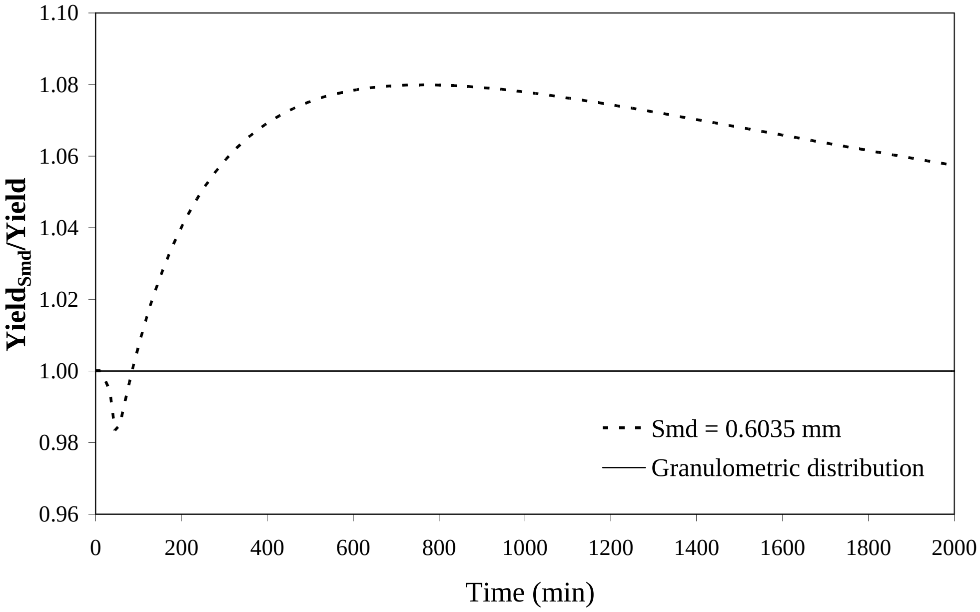
Figure 1: Constant Sauter mean diameter chart.



Sauter mean diameter and the real granulometric distribution

The model built was also used to evaluate the extraction yield relevant to a real granulometric distribution and to compare it to the one obtained using the Sauter mean diameter (Figure 2). In Figure 2, in order to facilitate the reading of the modeling results, a dimensionless extraction yield was plotted as the ratio between the yield relevant to the Smd and the yield related to the granulometric distribution.

Figure 2: Sauter mean diameter and real granulometric distribution.



The granulometric distribution was previously [12] experimentally evaluated and, in a weight fraction versus diameter diagram, it followed an asymmetric bimodal distribution trend. Except for the initial part of the extraction process, to consider the Sauter mean diameter as an approximation of the real granulometric distribution of particles, caused an overvaluation of the actual trend of the extraction process. The maximum deviation was 8% and occurred at about 10 hours since the beginning of the extraction.

From what discussed in the preceding paragraphs, the deviations of a simplified extraction model, in which a mean value of diameter is used, depends on the variability of diameters that constitute the real granulometric distribution: the greater is this variability, the greater will be the percentage error on the extraction yield.

CONCLUSION

In the modeling of extraction processes the substrate is in the general case considered as composed by particles having all a unique dimension, which is chosen as representative of the whole of the particles. This particle average dimension is normally the Sauter mean diameter. In this study, by means of a model capable to take into account the whole granulometric distribution of the substrate, we showed to which extent this simplification is valid.

The approximation results to be acceptable when the difference in the particle dimensions is not too large; granulometric distributions centered in their mean value (like Gaussian distributions) can be well represented by a dimensional average value. Nevertheless, in particular cases, the simplification leads to loss in accuracy. In these cases, the availability of a model capable to consider the whole granulometric distribution allows to achieve better results.

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NOTATIONS

a	specific surface of the solid [1/m]
C	solute concentration in the solvent in terms of mass of solute per unit mass of solvent [kg/kg]
C_0	solute concentration in the solvent at the beginning of extraction (saturation value) [kg/kg]
D_{Ax}	axial dispersion coefficient [m^2/s]
d_p	particle diameter [m]
F	solute concentration in the solid in terms of mass of solute per unit mass of non-soluble solid [kg/kg]
F_0	solute concentration in the solid at the beginning of extraction [kg/kg]
k_e	external mass transfer coefficient [m/s]
k_i	internal mass transfer coefficient [m/s]
K_f	equilibrium constant between the tied-oil phase and the solvent [-]
K_Ψ	equilibrium constant between the free-oil phase and the solvent [kg/m^3]
N	number of granulometric classes [-]
Re	Reynolds number[-]
Sh	Sherwood number [-]
t	time [s] (or [min])

u	interstitial velocity of the solvent [m/s]
z	axial coordinate in the extractor [m]
Y	extraction yield [-]
Y_∞	asymptotic extractable oil yield [-]

Greek letters

α	free oil parameter
ε	voidage of the extraction bed [-]
ϕ_f	fraction of the particle volume filled by the free-oil phase [-]
ϕ_t	fraction of the particle volume filled by the tied-oil phase [-]
ρ_f	density of the solvent [kg/m^3]
ρ_0	density of the vegetable oil [kg/m^3]
ρ_s	density of the non-soluble solid [kg/m^3]
Ψ	fraction of free oil content to free oil content in untreated seeds [-]
Ψ_0	fraction of free oil content to free oil content in untreated seeds at the beginning of extraction [-]
$\overline{\Psi}_0$	mean value of the ratio between free oil content and free oil content in untreated seeds at the beginning of extraction [-]

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