Manuscript Number:

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Article Type: Research Article

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Abstract: The objective of this research was to study the kinetics of grinding of an anhydrous paste based on hazelnut and cocoa, in stirred ball mills by means of particles size determination and rheological analysis. Grinding was carried out in a pilot refiner (30 °C, 72 rpm, 60 kg of 5.5-mm diameter stainless steel balls) with 10 kg of paste. The grinding kinetics was described in terms of the cumulative oversize fraction by the second order solution of the population balance model allowing the estimation of the first and the second Kapur constants as a function of particle size class. The flow curves of refined pastes were successfully modeled with the Casson rheological model and can be explained by the theory of dense suspensions. Further studies are however necessary to develop a model for the description of the rheological behavior as a function of solid packing fraction and shear rate.

Highlights

- A population balance approach proved adequate to model grinding kinetics
- The first and second Kapur constants were estimated and regressed on size class
- Casson model describes the pseudoplastic behavior of the refining paste
- The packing fraction of the refining paste was related to its rheological behavior
- Grinding affected mainly the rheology of the pastes

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TITLE

Modeling Grinding Kinetics of Fat Based Anhydrous Pastes

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Abstract

The objective of this research was to study the kinetics of grinding of an anhydrous paste based on hazelnut and cocoa, in stirred ball mills by means of particles size determination and rheological analysis. Grinding was carried out in a pilot refiner (30 °C, 72 rpm, 60 kg of 5.5-mm diameter stainless steel balls) with 10 kg of paste. The grinding kinetics was described in terms of the cumulative oversize fraction by the second order solution of the population balance model allowing the estimation of the first and the second Kapur constants as a function of particle size class.

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Introduction

Fat based anhydrous pastes used for the preparation of ice creams are close to nut based spreads for the recipe, but they are not spreadable across a wide temperature range and become more flowable than a spread at 20-25 °C (Birkett, 2009). They could also resemble a filling cream, that is generally fat and sugar based, and represents an important component in different confectionary foods, in which provides taste, texture and adhesion of the baked items (Miele et al., 2015).

Cream processing requires a solid particle size reduction operation, called refining and/or grinding. Its main goal is to obtain a desired solid particle size, specific for each product. During grinding, the tailings of large particles absorb part of the mechanical energy, causing an increase in surface energy and a decrease in particle size. A limit condition is reached when the finest particles agglomerate and release part of surface energy, greatly reducing the grinding efficiency (Li et al., 2017). Another quality attribute of the refined paste is its viscosity which is affected by grinding. Excessive grinding results in higher viscosity of the paste and may require the addition of expensive viscosity modifiers and/or dispersant phase to adjust its value to the target for the specific application.

Very few studies have dealt so far with food refining by means of stirred ball mills (Alamprese et al., 2007; Lucisano et al., 2006; Hennart et al., 2012; Fidaleo et al. 2017a; Fidaleo et al., 2017b) and even fewer studies have focused on modeling aspects. In particular, Fidaleo et al. (2017b) developed a mathematical model of refining of a hazelnut and cocoa based anhydrous paste in stirred ball mills. The model was able to predict the effect of key parameters - grinding media diameter and mass, rotation speed, recycle flow rate and temperature - on the refining kinetics, determined by the fineness of the paste as measured by a digital micrometer, at different process scales.

Thus, considering the lack of scientific knowledge on the modeling of food refining in stirred ball mills, the objective of this research was to study the kinetics of grinding of an anhydrous paste based on hazelnut and cocoa, in stirred ball mills by means of particles size determination and rheological analysis.

2. Theoretical aspects

The kinetics of batch grinding can be described by using the population balance model that considers the change in the quantity of particles in each size class as a function of the grinding time (Varinot, Berthiaux, & Dodds, 1999). It corresponds to the following set of differential equations of mass balance over discrete size intervals:

$$\frac{dm_i(t)}{dt} = -S_i m_i(t) + \sum_{j=1}^{i-1} S_j b_{ij} m_j(t) \quad (1)$$

where t is the grinding time; i is the size index (varies between 1, smaller class size, and n , larger class size), m_i is the mass fraction of particles bounded by size-indexes $i-1$ and i (for example, particles passing and retained on two adjacent sieves in a standard mesh series); the selection function S_i is the rate of grinding of the i -th class of particles; the breakage function b_{ij} is the fraction of daughter particles of i -th size when j -th size particles are broken.

Eq. (1) can also be written in cumulative form as:

$$\frac{dR_i(t)}{dt} = -S_i R_i(t) + \sum_{j=1}^{i-1} R_j(t) [S_{j+1} B_{ij+1} - S_j B_{ij}] \quad (2)$$

where $B_{ij} = \sum_{k=i+1}^n b_{kj}$ is the cumulative breakage function representing the probability of fragments from a particle of size x_j to have a size less than x_i and $R_i(t) = \sum_{j=1}^i m_j(t)$ is the mass fraction of particles greater than x_i .

Use of Eq.s (2) requires knowledge of the functions B_{ij} and S_i which are all the more difficult to obtain the higher the precision required, as this implies a larger number of classes (Berthiaux et al., 1996). It has been shown (Kapur and Agarwal, 1970) that Eq.s (2) admit the following approximate solutions, the so called G-H solutions:

$$R_i(t) = R_i(0) \exp\left(k_i^{(1)} t + k_i^{(2)} \frac{t^2}{2!}\right) \quad (3)$$

where $k_i^{(1)}$ and $k_i^{(2)}$ are lamed parameters called the first and the second Kapur constant, also indicated with G_i and H_i , respectively. These equations can be easily applied to

experimental results to simulate $R_i(t)$ for each class of size x_i of particles. In fact, compared to Eq.s (2), they contain only two unknown parameters, $k_i^{(1)}$ and $k_i^{(2)}$, which can be easily computed from a limited amount of experimental data. The main drawback of Eq.s (3) is that $k_i^{(1)}$ and $k_i^{(2)}$ do not have a direct physical meaning while S_i and b_{ij} or S_i and B_{ij} in Eq.s (1) or (2), respectively, do. This is probably the reason why many studies, such as (Hennart et al., 2012) used the first order approximation of Eq. (3) (where $k_i^{(2)}$ is assumed to be zero) for grinding kinetics modeling. In fact, under this circumstance, $k_i^{(1)}$ corresponds to S_i , the selection function, from which the breakage function can be calculated as $b_{ij}=(S_{i-1}-S_i)/S_j$ (Hennart et al., 2012; Berthiaux et al., 1996). In any case, it has been shown that even from $k_i^{(1)}$ and $k_i^{(2)}$ values estimated by using Eq.s (3), it is possible to back calculate breakage functions (Purker, Agrawal, & Kapur, 1986).

By fitting Eq.s (3) to the R_i -vs- t experimental data, both $k_i^{(1)}$ and $k_i^{(2)}$ values can be estimated for each size class x_i . Several equations have been proposed to represent $k_i^{(1)}$ as a function of the particle size x_i . In this work we used the following functional form (Varinot et al., 1999) to express both $k_i^{(1)}$ and $k_i^{(2)}$ dependence on x_i :

$$k_i^{(j)} = \frac{kx_i^\alpha}{\left[1 + \left(\frac{x_i}{x^*}\right)^\Lambda\right]} \quad (4)$$

where k , α , x^* and Λ are fitting parameters while j indicate the first ($j=1$) or the second ($j=2$) Kapur constant.

For $x_i \ll x^*$, assuming $\Lambda > 0$, Eq. (4) reduces to another equation that has been proposed to express $k_i^{(1)}$ as a function of x_i (Berthiaux et al., 1996; Hennart et al., 2012):

$$k_i^{(j)} = kx_i^\alpha \quad (5)$$

As far as flow rheological properties, an anhydrous paste can be considered a dispersion where cocoa, sugar, nut and milk solids are dispersed in a liquid phase made up of oil and nut and cocoa fats. Its flow behavior can be associated to that of food suspensions (Servais et al., 2002). The Cross, Carreau and Quemada-Casson models have been used to describe

the rheological data of apparent viscosity as a function of shear rate for many food dispersions (Rao, 2007).

The Quemada model (Fang et al., 1997) is a viscosity equation for dispersed systems based on zero-shear, η_0 , and infinite-shear, η_∞ , viscosities, and a structural parameter λ dependent on the shear rate. For highly concentrated dispersed systems η_∞ is generally much lower than η_0 , so that $\eta_\infty/\eta_0 \ll 1$ and the dispersion may have a yield stress. Under this circumstance the Quemada model reduces to the Casson model:

$$\eta^{1/2} = \left(\frac{\sigma_0}{\dot{\gamma}} \right)^{1/2} + (\eta_\infty)^{1/2} \quad (6)$$

where σ_0 is the Casson yield stress and η_∞ is the infinite-shear viscosity, also called the Casson plastic viscosity.

The relative viscosity of a concentrated solid suspension can be related to its solid volume fraction (ϕ) through equations of the form of Krieger and Dougherty's equation, originally proposed for rigid sphere suspensions (Wildemuth and Williams, 1984):

$$\eta_r = \frac{\eta}{\eta_s} = \left(1 - \frac{\phi}{\phi_m} \right)^{-[\eta]\phi_m} \quad (7)$$

where ϕ_m is the maximum packing volume fraction of the solids, η_r and η_s are the paste reduced viscosity and the dispersant viscosity, respectively, and $[\eta]$ is the intrinsic viscosity that can be assumed equal to 2.5 if the particles or build-up aggregates are spherical.

The a priori prediction of the maximum packing fraction, ϕ_m , for a system of particles depends on its geometric arrangement. Suspensions of monomodal spheres self-assemble to form a so-called random close-packed (RCP) arrangement with a ϕ_m of about 0.63 (McGear, 1961). For multimodal systems, it is more difficult to arrive at a theoretical value of ϕ_m . Qualitatively, small spheres may fit into the spaces between packed large spheres thus increasing ϕ_m , and according to Eq. (7), decreasing the viscosity of the suspension. Rheological experiments with bimodal, multimodal, and polydisperse systems show that at

136 equal total particle volume fraction, the viscosities of multimodal systems are lower than
137 for their monodisperse counterparts.

3. Experimental

3.1 Materials

The following formulation with reference to 100 g of hazelnut and cocoa based anhydrous paste was used: sugar (31 g), vegetable oils (27 g), ice sugar (14 g), cacao powder (11 g), hazelnut paste (8 g), milk powder and derivatives (7.5 g), other (0.9 g), lecithin (0.6 g) (Fidaleo et al., 2017b). The solids volume fraction of the product (volume of solids divided by the volume of paste), ϕ , is an important material property of suspensions since it is related to flow behavior. An approximation of ϕ can be obtained from the mass of the main ingredients (m_i) and their density (ρ_i):

$$\phi = \frac{m_s/\rho_s + m_c/\rho_c + m_m/\rho_m + m_h/\rho_h}{m_s/\rho_s + m_c/\rho_c + m_m/\rho_m + m_h/\rho_h + m_o/\rho_o + m_l/\rho_l + m_{oh}/\rho_{oh}} \quad (8)$$

where m_s is the sugar mass, m_c the cacao mass, m_m the milk solids mass, m_h the hazelnut solids mass, m_l the lecithin mass, m_o the vegetable oil mass, m_{oh} the hazelnut oil mass, while ρ_s , ρ_c , ρ_m , ρ_h , ρ_l , ρ_o and ρ_{oh} are the corresponding densities (Taylor et al., 2009; van der Vaart et al., 2013). The densities of the materials at 20°C are as follows: sugar, 1426 kg/m³; cacao solids, 1350 kg/m³; lecithin, 893 kg/m³ (van der Vaart et al., 2013); milk solids, 1480 kg/m³ (Berlin and Pallansch, 1963); hazelnut paste solids, 916 kg/m³ (Ozdemir and Akinci, 2004).; seed oil, 900 kg/m³. The hazelnut paste was assumed as made up of 60% oil and 40% solids (Ozdemir and Akinci, 2004). The solids volume fraction estimated by Eq. (8) was equal to 0.568, thus close to that of a typical milk chocolate (with 30% w/w fat) of 0.575.

3.2 Sample preparation

For cream production, a stirred ball mill was used (model Micron 20, Selmi s.r.l, Modena, Italy) with 60 kg of 5.5-mm diameter stainless steel balls. Ingredient weight was set on 10 kg, according to manual specifications of the instrument. Speed rate was fixed (72 rpm) and the temperature was controlled (30±2°C). The circulation of the product during refinement was maintained by a dual-purpose volumetric pump. Sampling was carried out from 0 to 120 min during the grinding process.

3.3 Particle size distribution

The particle size distribution (PDS) was analyzed by using a Mastersizer laser diffraction particle size analyser equipped with Hydro 3000 dispersion unit (Malvern Instruments, Worcestershire, UK) (Armini et al., 2018). For each cream, two different replicates were analyzed and for each replicate, 15 measurements were performed.

The fineness of the pastes was also determined by using a digital micrometer (Fidaleo et al., 2017b).

3.4 Rheological properties

Viscosity of cream samples, as well as that of the vegetable oil used and the supernatant liquid obtained by centrifugation of the refined paste, was determined by a Modular Advanced Rheometer System (Haake MARS, Thermo Scientific, Waltham, USA), equipped with a vane tool geometry (diameter 22mm, length 16 mm, distance 8.5 mm). The viscosity curves were measured as a function of increasing shear rate (0.01-100 s⁻¹) at 30°C. Three replications for each sample were performed.

3.5 Determination of solid bed density and maximum packing fraction

For solid bed density (SBD) determination, a known weight of samples (≈10 g) was placed in 50-ml centrifuge tubes. The tubes were placed in a thermal oven (Universal Oven, Memmert, Schwabach, Germany) at 30 °C for two hours before being centrifuged at 10000 rpm for 20 minutes. The Solid bed density of the samples was calculated as the ratio of the mass of solids in the suspension to the volume of solid bed after centrifugation.

The maximum packing fraction (ϕ_m) was calculated by considering the PSD of each paste as based on a mixture of spheres with n different diameters, D_i , and corresponding volumetric fractions, X_i . For n-component mixtures of spheres, Lee (1970) proposed the following equations:

$$(\phi_p)_i = \sum_{j=1}^{j=n} \phi_{ij} \cdot X_j \quad (9)$$

$$\sum_{j=1}^{j=n} X_j = 1 \quad (10)$$

where:

- ϕ_p is a function that predicts ϕ_m ;

- i and j refers to the particles with diameter D_i and D_j , respectively;

$$\phi_{ij} = \begin{cases} 0.639 + \frac{\phi_{\max}\left(\frac{D_i}{D_j}\right) - 0.639}{0.265}, & D_i \geq D_j \\ 0.639 + \frac{\phi_{\max}\left(\frac{D_j}{D_i}\right) - 0.639}{0.735}, & D_i < D_j \end{cases}$$

- $\phi_{\max}(D_i/D_j)$ is the maximum volume fraction of binary mixtures with diameter ratio D_i/D_j .

The maximum volume fraction of binary mixtures as a function of diameter ratio, $\phi_{\max}(D_i/D_j)$, was calculated starting from the data reported in the paper of Lee (1970). The data from Fig. 1 of the paper, labeled as corrected data series, were fitted by the probit 4P nonlinear model implemented in JMP software (v. 14.2.0) and the obtained regression equation was used to estimate the maximum volume fraction for a given diameter ratio. The fitting was excellent with R^2 , RMSE and mean relative error equal to 0.998, 0.0038 and 0.34%, respectively. ϕ_m was then calculated as the smallest value of ϕ_p determined by Eq. (9).

3.6 Data analysis

Several indexes of the PSD based on the volume of particles were estimated, including the percentiles, D_{10} , D_{50} , and D_{90} , and the oversize fraction, R_i , that is the fraction of particles having size greater than x_i , the lower limit of the particle size class i .

ANOVA and Fisher's method with $\alpha=5\%$ were applied on data to compare both PSD parameters and fineness of pastes by using JMP statistical software release 14.2.0, (SAS Institute, Cary, NC, USA). Where necessary, data were transformed (Box-Cox transformations) to minimize variance differences among samples and submitted to ANOVA.

The rheological data of viscosity as a function of shear rate were fitted by JMP statistical software by using the weighed least squares method (with the inverse of squared experimental viscosities as weights). The oversize as a function of time data, the Kapur constants as a function of particle size data and the volumetric packing factor as a function of diameter ratio for binary systems data were fitted by the least squares method by using JMP software.

220 A Matlab (The MathWorks, Inc., MA, USA) script was developed to calculate ϕ_m
221 according to Eq. (9) and it was validated on four PSDs (rectangular, triangular, etc.)
222 described by Lee (1970).

3. Results and Discussion

3.1 Particle size distribution and fineness data

The PSD curves of anhydrous pastes as a function of grinding time are reported in Fig. 1. Before grinding ($t=0$ min), the paste presented a tri-modal PSD with particle sizes ranging from 0.8 to about 800 μm . After 5 min of grinding ($t= 5$ min), the peak relative to the larger particles became a shoulder, and after 20 min ($t= 20$ min) the distribution could be considered almost unimodal, even if a left small shoulder, corresponding to particles with sizes between 0.8 and 1.7 μm , was still observed in PSD curves.

Fig. 1

Table 1 reports the percentiles of the PSD and the fineness, as result of the micrometer measurements, of paste during grinding. It can be observed that increasing the grinding time resulted in a statistically significant negative effect on D_{90} and on the other percentiles. D_{90} values highly correlated with micrometer readings, as reported in the literature (Fidaleo et al., 2017). Pastes refined for 90 and 120 min were not statistically different for fineness but were different for almost all the percentiles of PSD, even if the differences were very small. However, after already 120 minute the average particle size was around 16 μm , so it was not convenient to move on with the grinding process for this type of product.

Table 1

Fig. 2 reports the oversize R_i as a function of grinding time for several size classes of particles (only 10 size classes of 31 classes analyzed).

Fig. 2

The oversize fraction of particles of small size classes did not change much or tended to stabilize as a function of time while for large size classes it dropped to zero after a small grinding time. This behavior required to filter the R_i data before using them with Eq. (3). R_i -vs- t data were fitted by using Eq. (3) to obtain $k_i^{(1)}$ and $k_i^{(2)}$ estimates for each size class x_i , as reported in Fig. 3. For small size classes the estimated second Kapur coefficients $k_i^{(1)}$ were not statistically different from zero, thus a first order model was

adequate to describe the data. For fittings of intermediate size classes, both $k_i^{(1)}$ and $k_i^{(2)}$ coefficients were statistically different from zero, so the second order model was necessary to describe the data.

$k_i^{(1)}$ values were negative for all the size classes studied and increased in absolute value as x_i increased. $k_i^{(2)}$ values were positive and increased with the size class. The ratio between $k_i^{(1)}$ and $k_i^{(2)}/2!$ values for each size class x_i was about constant and equal to 314 ± 18 min.

In the literature, Eq. (4) was suggested to express the first Kapur constant, $k_i^{(1)}$ (Varinot et al., 1999), but in the present work the same equation was also applied for $k_i^{(2)}$ data. The estimated unknown parameters are reported in Table 2. Interestingly, α , x^* and Λ estimates did not differ much between the first and the second Kapur function as could be expected from the constancy of the ratio $k_i^{(1)}/(k_i^{(2)}/2!)$.

Table 2

Estimated parameters were also used to reconstruct the experimental $k_i^{(1)}$ and $k_i^{(2)}$ values (see the continuous lines in Fig. 3). By using Eq. (4) to express the dependence of $k_i^{(1)}$ and $k_i^{(2)}$ on the size class x_i with the estimates of their unknown parameters as reported in Table 2 and substituting it into Eq. (3), an equation for the grinding kinetics was obtained and allowed a good reconstruction of the Ri-vs.-t curves reported in Fig. 2.

Fig. 3

3.2 Rheological properties

Pastes withdrawn at different refining times exhibited a shear thinning behavior (pseudoplastic), that is their apparent viscosity (η) was a decreasing function of the shear rate ($\dot{\gamma}$), as shown in Fig. 4. Furthermore, at the lowest shear rate tested (0.011 s^{-1}) the

apparent viscosities differed greatly among the samples while at the highest shear rate (70.90 s^{-1}) they tended to coincide and to be much smaller.

Fig. 4

As shown in Fig. 4, the experimental apparent viscosity data as a function of shear rate are quite well described by the Casson model, the mean relative error between the experimental and predicted data of each paste ranging from 3.6 to 7.7%. The model parameters estimated by the weighted least squares method are reported in Table 3.

Table 3

While the yield stress increased remarkably as a function of time, η_{∞} seemed to increase as well but to a much lesser extent. Both σ_0 and η_{∞} values are in line with the values measured at 40°C reported by Taylor et al. (Taylor et al., 2009) for chocolate made up of crumb (a dried mixture of milk powder, sugar and cocoa solids) and sunflower oil (20 to 70 Pa and 4 to 15 Pa s, respectively) and dry mix milk, crumb, dark and white chocolate (0.5 to 20 Pa and 1 to 10 Pa s, respectively).

The oil used to prepare the pastes as well as the supernatant liquid obtained by centrifugation of the refined paste behaved as a Newtonian fluid (constant viscosity) in the shear rate range of $0.89\text{-}89 \text{ s}^{-1}$ with viscosities of 42.0 ± 0.4 and $45.4\pm3.0 \text{ mPa s}$, respectively. It is worth noting that these viscosity values are coincident with the viscosity of cocoa butter at 40°C which behaves as a Newtonian fluid with a viscosity of 45 mPa s (Taylor et al., 2009). This allows to compare the rheological behavior at 30°C of the paste under study with that of molten chocolate at 40°C .

To correlate the rheological properties of the pastes with their degree of refining, the solid bed densities of the pastes were determined experimentally (Mongia, and Ziegler, 2000) and the values of ϕ_m were calculated through the algorithm developed by Lee (1970) starting from the PSD of the pastes. Both ϕ_m and SBD decreased as a function of milling time, from 0.759 to 0.716 and from 1145 to 1077 kg m^{-3} , respectively, with a similar trend. This can be explained by considering that the PSD of the pastes becomes narrower as milling proceeds, resulting in a decrease of the packing capability of the solids. Do et al. (2007) studied the effect of PSD on the rheological properties of chocolate models

consisting of sugar and a cocoa butter equivalent. They simulated different PSDs by mixing different proportions of sugar with two different solid sizes (fine and coarse). The D_{90} of their dispersions varied between 27 (fine fraction) and 107 μm (coarse fraction) and the ϕ_m that they estimated varied between 0.691 and 0.751, respectively. Based solely on the D_{90} , the fine fraction of the abovementioned dispersions would correspond to the paste under study refined for 60 min while the coarse one with the unrefined paste for which we estimated values of ϕ_m of 0.724 and 0.789, respectively, thus very close to the ones estimated by the cited authors.

There is a vast literature that relates ϕ_m to the viscosity of suspension systems and shows that it is possible to optimize the PDS of a suspension to increase ϕ_m and thus reduce the viscosity. This concept has been applied also to the case of chocolate (Bolenz et al., 2014; Do et al., 2007). In the case of melted chocolate, efforts have been devoted to optimizing the PSD, at a given volume fraction of solids, for example by mixing coarse and fine solid particles, to increase ϕ_m and thus decreasing the viscosity of the product, avoiding or limiting the addition of cocoa butter and viscosity modifiers (lecithin or other emulsifiers). It is also known that excessive grinding of chocolate solid particles results in viscosity increase and thus particle size distribution analysis is considered important to control the grinding process in order to avoid overgrinding.

Eq. (7) does not show any explicit dependence of η on shear rate. One way to include the shear dependence of suspension viscosity is to assume that ϕ_m changes with shear rate as a result of microstructure modification, in particular agglomeration and deagglomeration phenomena. For example, Wildemuth and Williams (1984) derived a relationship where ϕ_m is a function of shear stress (σ) and monotonically increases from $\phi_{m,0}$ at $\sigma = 0$ to $\phi_{m,\infty}$ as $\sigma \rightarrow \infty$. When substituted into an appropriate η_r versus ϕ/ϕ_m relationship, such as Eq. (7), the result is a model that gives viscosity as a function of solid volume fraction and shear stress. Windhab (2000), on the other hand, used the concept of fluid immobilization and applied Eq. (7) by substituting the solid volume fraction ϕ with an effective solid volume fraction that was expressed as a function of shear rate and other parameters.

We applied Eq. (7) to each couple of values of relative viscosity and corresponding shear rate and estimated ϕ_m through a non-linear equation solver using a value of ϕ of 0.568 and $[\eta]=2.5$. As shear rate increased from 0.011 to 89.233 s^{-1} , ϕ_m increased from

0.570 to 0.588 or 0.569 to 0.583, respectively for the pastes refined for 15 or 120 min. The geometric ϕ_m , estimated by the algorithm of Lee (1970) (Table 1), was equal to 0.759 and 0.716 for the pastes refined for 15 or 120 min, respectively. The disagreement between the values of ϕ_m estimated by using Eq. (7), that is from rheological data, and those calculated from the algorithm proves that the pastes under study were characterized by a high degree of interaction that likely resulted in loose structures that immobilized a large part of the fluid phase and that persisted even at the highest shear rates studied. In fact, if the particles were fully dispersed and non interacting, by using Eq. (7) with $\phi_m = 0.716-0.759$ pertaining to the PSD of pastes refined for 120-15 min, respectively, the relative viscosity of the pastes can be calculated as 16.7-13.6, much smaller than the values presented by the pastes, in the range of 145 to 52456. However, the relative viscosities at the highest shear rate tested are closer to the prediction values than the relative viscosities at low shear rates. So, it seems that at infinite share the relative viscosities tend to approach the values predicted by Eq. (7). This is consistent with the idea that the viscosity of concentrated suspensions is made up of two terms, hydrodynamic and structural viscosity (Lee, 1970). The hydrodynamic viscosity is independent of the rate of shear and represents the limiting viscosity at high rates of shear. On the other hand, the structural viscosity gives non-Newtonian effects as a function of the rate of shear. Thus Eq. (7) represents only the hydrodynamic viscosity. From these data, it seems that the effect of refining on the rheological behavior is due more to the reduction of the particle diameter and thus to the increase of the specific surface area of particles than to the reduction of the packing ability of the particles. In fact, by increasing the specific surface of particles the interaction between particles also increases and thus the probability of agglomerate formation increases. Consequently, refining seems to influence more the structural viscosity than the hydrodynamic viscosity.

Thus, it seems that the flow characteristics of the grinded pastes can be explained by the theory of dense suspensions. Further studies are however necessary to develop a model for the description of the rheological behavior as a function of solid packing fraction and shear rate.

4. Conclusions

Modeling results show that the population balance approach described in the literature in dry or wet grinding of non-food materials in various types of mills can be used successfully to characterize the grinding process in a stirred ball mill of a food product made up of several type of solids (cocoa, sugar, hazelnut) dispersed in a fat phase. The G-H model was successfully used to describe the grinding kinetics of particles in each size class. The first and second Kapur functions were well fitted with a four-parameter model and allowed excellent reconstructions of the oversize (R_i) as a function of time (t) for each size class.

The rheological properties of the grinded pastes were well described by the Casson model. The increase of the apparent viscosity as a function of refining time can be only partly explained by the decrease of the geometric solid packing fraction which affects the hydrodynamics viscosity. Most likely, the system is characterized by a high degree of particle interactions, that increases as the particle size reduces, thus increasing the structural viscosity of the paste.

Acknowledgments

The authors thank MEC3-OPTIMA SRL (San Clemente, Italy) for supplying the ingredients to prepare the hazelnut and cocoa based paste and Mr. Carlo Vanni (MEC3-OPTIMA SRL) for his collaboration and useful discussions.

Nomenclature

Symbols

- b_{ij} : breakage function of class sizes i and j
 B_{ij} : cumulative breakage function of class i and j
 D_i : diameter of particles in class size i (m)
 D_{10}, D_{50}, D_{90} : 10th, 50th and 90th percentiles of PSD
 f : paste fineness as measured by micrometer
 $k_i^{(1)}$: first Kapur constant
 $k_i^{(2)}$: second Kapur constant
 k : empirical coefficient in Eq. (4) and (5)
 m_i : mass of particles in class size i
 R_i : cumulative weight fraction oversize x_i
 S_i : selection function for class size i
 t : time
 x^* : empirical coefficient in Eq. (4)
 X_i : volume fraction of particles in class size i

Greek symbols
 α : empirical coefficient in Eq.s (4) and (5)
 $(\phi_p)_j$: function predicting ϕ_m
 $\dot{\gamma}$: shear rate
 $[\eta]$: intrinsic viscosity, $\lim_{\phi \rightarrow 0} (\eta - \eta_s) / (\eta_s \phi)$
 Λ : empirical coefficient in Eq. (4)
 X_j : volume fraction of solid in size class i
 η_∞ : viscosity at infinite shear rate, parameter in Eq. (6)
 η : paste viscosity
 η_r : paste reduced viscosity, η / η_s
 η_s : dispersant viscosity
 ρ_i : density of component i
 σ_0 : yield stress, parameter in Eq. (6)
 ϕ : volume fraction of solids in the paste

431 ϕ_{ij} : binary coefficients
432 ϕ_m : maximum packing volume fraction of the solids in the paste
433 $\phi_{\max}(D_i/D_j)$: maximum packing volume fraction of the solids in binary mixtures with
434 diameter ratio D_i/D_j .
435

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1 **Figure captions**

2 **Figure 1.** Particle size distribution of pastes at different grinding times: 0 (——),
3 5 (---), 15 (— — —), 30 (————), 60 (— — —), 90 (———) and 120 (——) min.

4 **Figure 2.** Cumulative oversize fraction (R_i) as function of grinding time for different size
5 classes (x_i): ■, 5.2 μm ; ●, 9.9 μm ; ▲, 16.4 μm ; □, 21.2 μm ; ○, 27.4 μm ; △, 35.3 μm ; x,
6 45.6 μm . The points indicate the actual measurements while the continuous lines
7 correspond to the model predictions obtained by Eq. (3) and Eq. (4) together with the
8 parameter values reported in Table 2.

9 **Figure 3.** First ($k_i^{(1)}, \circ$) and second ($k_i^{(2)}, \square$) Kapur constants as a function of size class (x_i).
10 Dots represent the constants estimated by fitting the experimental data with Eq. (3) applied
11 to each size class while the continuous lines represent predictions by using Eq. (4) and the
12 parameter estimates reported in Table 2.

13 **Figure 4.** Apparent viscosity (η) as a function of shear rate ($\dot{\gamma}$) for pastes refined for 15
14 (□), 30 (■), 60 (○), 90 (●) and 120 (△) min. Symbols refer to experimental data while
15 continuous lines to model predictions obtained by Eq. (6) together with the parameter
16 values reported in Table 3.

17

Figure 1

Figure 2

Figure 3

Figure 4

1 **Tables**

2

3 **Table 1:** Fineness (f) and particle size distribution parameters (D_{10} , D_{50} , D_{90}) of pastes at
4 different grinding times (mean $\pm$ standard deviation).

Time (min)	f (μm)	D_{10} (μm)	D_{50} (μm)	D_{90} (μm)
0	118.67 $\pm$ 1.85 ^a	2.67 $\pm$ 0.02 ^a	13.72 $\pm$ 0.29 ^a	95.45 $\pm$ 2.75 ^a
5	87.33 $\pm$ 2.40 ^b	2.67 $\pm$ 0.03 ^a	12.72 $\pm$ 0.11 ^b	71.84 $\pm$ 1.02 ^b
15	56.00 $\pm$ 3.21 ^c	2.31 $\pm$ 0.07 ^b	10.12 $\pm$ 0.22 ^c	46.82 $\pm$ 0.43 ^c
30	34.33 $\pm$ 0.88 ^d	2.24 $\pm$ 0.02 ^b	8.75 $\pm$ 0.06 ^d	33.42 $\pm$ 0.41 ^d
60	23.33 $\pm$ 0.66 ^e	2.012 $\pm$ 0.007 ^c	7.12 $\pm$ 0.01 ^e	22.42 $\pm$ 0.09 ^e
90	17.33 $\pm$ 0.88 ^f	1.795 $\pm$ 0.002 ^d	6.246 $\pm$ 0.006 ^f	18.20 $\pm$ 0.04 ^f
120	16.67 $\pm$ 0.33 ^f	1.644 $\pm$ 0.002 ^e	5.751 $\pm$ 0.005 ^g	16.32 $\pm$ 0.07 ^g

5

6 **Table 2.** Point estimates of the unknown parameters of Eq. (4) obtained through nonlinear
7 regression of the first and second Kapur constants, $k_i^{(1)}$ and $k_i^{(2)}$, as a function of x_i .

Parameter	Unit	$k_i^{(1)}$	$k_i^{(2)}$
k	$\text{min}^{-1} \mu\text{m}^{-\alpha}$ or $\text{min}^{-2} \mu\text{m}^{-\alpha}$	$-5.85 \cdot 10^{-4}$	$3.91 \cdot 10^{-6}$
α	Dimensionless	1.29	1.24
x^*	μm	96.28	94.16
Λ	Dimensionless	1.76	3.80
RMSE	min^{-1} or min^{-2}	$9.04 \cdot 10^{-4}$	$3.71 \cdot 10^{-6}$
DFE	Dimensionless	27	27

9

10 RMSE and DFE refer to the root mean square error of regression and its degrees of
11 freedom, respectively.

Table 3: Rheological parameters of the Casson model (yield stress, σ_0 , and viscosity at infinite shear rate, η_∞), solid bed density (SBD) and maximum volume fraction ($\phi_{\max}$) for pastes refined for different amounts of time.

Time (min)	η_∞ (Pa s)	σ_0 (Pa)	SBD (kg m ⁻³)	$\phi_{\max}$ (-)
15	5.87± 0.21	10.98±0.31	1145±21	0.759
30	7.72±0.22	11.42± 0.28	1094±53	0.739
60	8.34±0.20	15.11±0.30	1088±3	0.724
90	8.14±0.17	20.59±0.31	1087	0.718
120	8.03± 0.15	25.42±0.33	1077	0.716

Data represent mean±standard error (for model parameters), mean±standard deviation (for replicated SBD measurements) or the algorithm estimated value ($\phi_{\max}$).