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REFINING KINETICS OF FAT BASED ANHYDROUS CREAMS

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Refining Kinetics of Fat Based Anhydrous Creams

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Abstract

Anhydrous pastes defined as a complex system consisting of several solid particles dispersed in a continuous fluid (oil) or in a semi-solid phase as cocoa butter, (Birkett, 2009).

Refining of anhydrous pastes in a stirred ball mill was characterized in terms of energy use and product viscosity, particle size and sensory characteristics. With special milling power of 0.03 kW/Kg of paste, the fineness of partical interest 22.4 and 30.4mm, was reached in 225-150min, respectively (Fidaleo, 2017). The pastes showed a pseudoplastic behavior, as zero shear rate viscosity was around 1000 Pa·s, for the low refined samples, increasing until values between 1000 and 10000 Pa·s, for the samples more refined. The particle size distribution (PSD) curves obtained by laser diffractometry were unimodal, with D_{90} higher than digital micrometer reding but with a good coorelation, R = 0.85.

2. INTRODUCTION

2.1 Filling creams and pastes

The cream could be defined as a complex formula made of different solid particles (sugar, cocoa powder, milk whey, milk powder, etc.) dispersed in a continuous fluid (oil). The quality, quantity, and type for each ingredient used in a formula, particularly fats, affect the creams rheological and textural properties and also the flow parameters. (Glicerina et al., 2013).

The water content in the cream influences the shelf life, technological properties and the intended use of the product; in this case, we focused on anhydrous pastes to study in the second part the shelf life for the product. Bakery filling creams are used in various baked goods. Creams are important components in different confectionary foods, in which they provide taste, texture, and adhesion of the baked items (Miele et al., 2015). From a processing viewpoint, these creams belong to the categories: heavy creams, light creams, and creams with water. Pralines, truffles, nougat, are the names frequently given to fat-based fillings and centers. These fillings are used with chocolate, biscuits, wafer, cakes to provide an enormous variety of products. These products can be made suitable for all markets, from the premium market to the low cost, high volume market (Birkett, 2009).

A filling is usually called ‘cream’. In some countries ‘creams’ are called ‘cremes’, in others ‘fillings’. The amount of cream in a sandwich ranges from about 17 to 36% with an average amount of 26%.

2.1.1 Ingredients

Sweet creams are basically sugar and fat mixtures; even if also other ingredients are included in the recipe and they influence many characteristics of the final product. There is also non-sweet cream used as fillings. The basic cream cannot have icing sugar as its main ingredient, so non-sweet powders like milk powders, cheese powder, maltodextrin, starch, and cracker dust must be used as bulking agents with the fat. These powders do not dissolve in the mouth as readily as sugar so it is necessary to have higher fat content in the cream to make them more palatable. The flavoring agents, apart from bottled liquids, include meat extract powders, dried utilized yeast and monosodium glutamate (Manley, 2001). The quality of the fat and the type of sugar largely determine the eating quality.

Sugar is generally the main ingredient of fat-based fillings and confectionery products. Highly refined white sugar is 99.9% sucrose, a non-reducing disaccharide (Birkett, 2009). The greater the quantity of sugar in the cream recipe the harder and ‘drier’ will be the cream, the larger the sugar crystal size the more gritty will be the cream in the mouth. It is not necessary to have the sugar particle size as small in creams as in chocolate because the cream is mixed with biscuit while eating. Thus, a maximum sugar particle size of about 40 μm will be acceptable for sugar in creams.

The fat content has an enormous effect on the sensory and rheological properties of fat-based fillings. Generally, the fat content is about 30% of the filling but it can be up to about 60%. Since fat is the continuous phase

in a fat-based filling, the viscosity of the filling decreases as the fat content increases. The type of fat that is used affects the sensory properties of the filling, its compatibility with the other components of the product and the shelf life of the product. There are different ways to categorize filling fats. Generally, three types of fat can be used: polymorphic filling fats, non-lauric (cocoa butter), suited for covering with chocolate or super coating composed of cocoa butter equivalents; non-polymorphic, non-lauric filling fats, such as aerating filling fats with a density of 0.6 g cm^{-3} and; non polymorphic, lauric filling fats, based upon coconut and palm kernel oil. Fat based upon hydrogenated rapeseed, soyabean oil, and palm fractions have been used successfully as filling fats for many years because of their excellent oxidative stability, speed of solidification, direct crystallising in the β' form, but they had a high trans content. In the last years, the use of filling fats composed of interesterified blends of palm fractions and palm kernel oil fractions have increased significantly (Birkett, 2009). Basically, the consistency of cream is determined by the solids content of the fat. Clearly, the higher the temperature the lower will be the fat solids and the softer will be the cream. The cream has to be soft at the time of stenciling or depositing, but firm at the time of eating. Furthermore, the cream will taste better if the fat in the cream melts quickly in the mouth and has a very small fraction of solids that melt above body temperature. If there are high amounts of high-melting solids in the fat a waxy film will be left in the mouth. The best fats for creams are, therefore, those with a very steep melting curve, which release sugar and flavors. The lauric fats, coconut and palm kernel oils, and their blends are commonly used. These fats melt

rapidly and draw latent heat from the mouth to give an attractive cool eating sensation. The hardness of cream, at ambient temperature, is also affected by the crystal size of the fat. Fats that have been mechanically agitated, while cooling, have small free crystals and are said to be plasticized. Fats which cool passively from the liquid are much firmer at ambient temperature because the crystals have grown together in an interlocked form. Thus, if there is a big difference between the temperature of the fat and the ambient temperature, at the sandwiching time the cream will be firmer than if the temperature difference is small. In addition, if the cream is significantly aerated this will also make the cream softer when the cream cools (Manley, 2001). Sugars do not chemically react with fats, but they impart product's rheological characteristics (Helstad, 2006).

Most fat-based fillings contain some milk component, often a milk powder, in order to have good flavor and texture. A simple fat and sugar mix are not generally considered to be acceptable. In order to meet specific industry requirements, many milk powders may be used, such as whole or skimmed milk powder, cream powder, demineralized whey powder. Lecithin is the most frequently used emulsifier in fat-based fillings because it gives the filling an acceptable viscosity with less fat and to bind water if it is present. Lecithin can be sourced from soy, rape, and sunflower (Birkett, 2009). This emulsifier speeds the mixing of the cream but tends to give softer creams after cooling.

Also, flavors can be added to the formulation. There is a great range of cream flavors. Brown 'chocolate' creams are the most popular and vanilla

and ‘creamy’ vanilla the next. Others include fruit flavors such as lemon, orange, strawberry, and raspberry. The chocolate creams are flavored with cocoa or cocoa mass (milled roasted cocoa beans, the precursor of chocolate). The creamy vanilla creams have skimmed or full cream milk powder to mellow the vanilla flavor and the fruit-flavored creams include bottled fruit extracts or oils together with an appropriate amount of fruit acid (citric, tartaric or malic) to give tartness. In all cases, the optimum effect is achieved if color is added to ‘suggest’ the flavor. The flavor may be enhanced with small quantities of salt which has a very fine particle size (Manley 2001). Vanilla extract is a spice that has been traditionally used in fat-based fillings, at concentrations up to 0.05% (Birkett, 2009).

2.2 Anhydrous pastes

Anhydrous pastes defined as a complex system consisting of several solid particles dispersed in a continuous fluid (oil) or in a semi-solid phase (cocoa butter).

Anhydrous pastes are spreadable products, generally used as they are in baked products, wafers, coextruded biscuits, ice cream industries. Those anhydrous pastes are generally characterized by a medium-high caloric power because of the high content of fat. In fact, many pastes are made of powdered milk, dehydrated cream, and a mix of solid fat.

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 liquid than a spread at 20-25 °C, due to the composition of their lipid fraction (Birkett, 2009).

Anhydrous creams are usually refined in plants within which the cream is subjected to high shear stresses. They have a water content of less than 1% which guarantees the microbiological stability of the product and their shelf-life is about 24 months.

2.3. Refining process

Cream/paste processing requires a solid particle size reduction operation, called refining and/or grinding. Its main goal is to decrease the solids to a specific particle size that depends on the specific product (Fidaleo et al., 2017). It is well known, for example for chocolate and chocolate-based products, that the size of the largest solid particles has a direct influence on rheological (flow properties) and sensory (mouthfeel grittiness) properties. Solid size reduction in a cream/paste is achieved through refining, a unit operation mostly carried out with roll refiners (Beckett, 1999), in five-roll mills and very often with pre-refining in three-roll refiners (Loncarevic et al. 2017). For small productions, stirred ball mills are becoming common alternatives in the confectionery industry, for refining of chocolate mass and in the production of cream products and chocolate-like products (Pajin et al., 2011). Stirred ball mills were introduced at the beginning of the 20thcentury in the refining of paintings and were later applied to the mining and powder industries (Alamprese et al., 2007). A ball mill is a jacketed vertical or horizontal cylinder equipped with paddle mixers. About

60–80% of the void volume is filled with the grinding media, typically balls made up of stainless steel, steel, ceramic or other materials. Agitation of the product and the grinding media in the tank by the rotating shaft with arms results in impact and shearing actions that determine the reduction of the solid particles of the product as well as their homogeneous dispersion. The product can also be recycled through the ball mill several times (Alamprese et al., 2007; Lucisano et al., 2006; Pajin et al., 2011). During this process of mixing, grinding, and recirculation, the size of the solid particles was reduced and their surface gets wrapped by the fat phase (Petkovic et al., 2013), conferring to the cream its rheological and textural properties. 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). As reported by Afoakwa (2007), if 90% of the particle size is smaller than 30 μm, the cream is homogeneous and the separation of the lipid fraction phases is inhibited. Moreover, particle size should be less than 25 μm to ensure that the papillae do not perceive the graininess of the particles and to obtain the right palatability. However, very few studies have dealt so far with food refining by means of stirred ball mills (Fidaleo et al., 2017).

3. OBJECTIVE:

The Particle size and rheological properties of creams and pastes, produced and very used by confectionery and bakery companies, play an important role in consumer choice, purchasing decisions and final consumption. The particles must be not even too small because they would make the pasta too viscous and uniformly distributed in the continuous phase. Excessive grinding results in a 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.

Starting from all those considerations, the objective of the experimental thesis was to study the kinetics of grinding of an anhydrous paste in stirred ball mills, and, at the same time, to determine the most suitable refining time to achieve the best properties of cream and make it acceptable for consumers.

In order to reach those objectives, the present thesis was divided into two parts:

1. Preliminary characterization of calorimetric properties and oxidative stability during the refining process;

2. Refining kinetics by means of Granulometric analysis and viscosity determination of pastes at different refining times (from 0 to 300 min).

As first, it was verified if the process condition eventually affected both thermal properties of the cream, by means of calorimetric analysis (DSC),

and primary oxidation indices, such as acidity and peroxide values, by means of chemical determinations. After that, during the refining of the cream, at different times, refined pastes were sampled over time and analyzed for granulometric properties by means of Mastersizer particle analyzer, and rheological characteristics by using Rheometer.

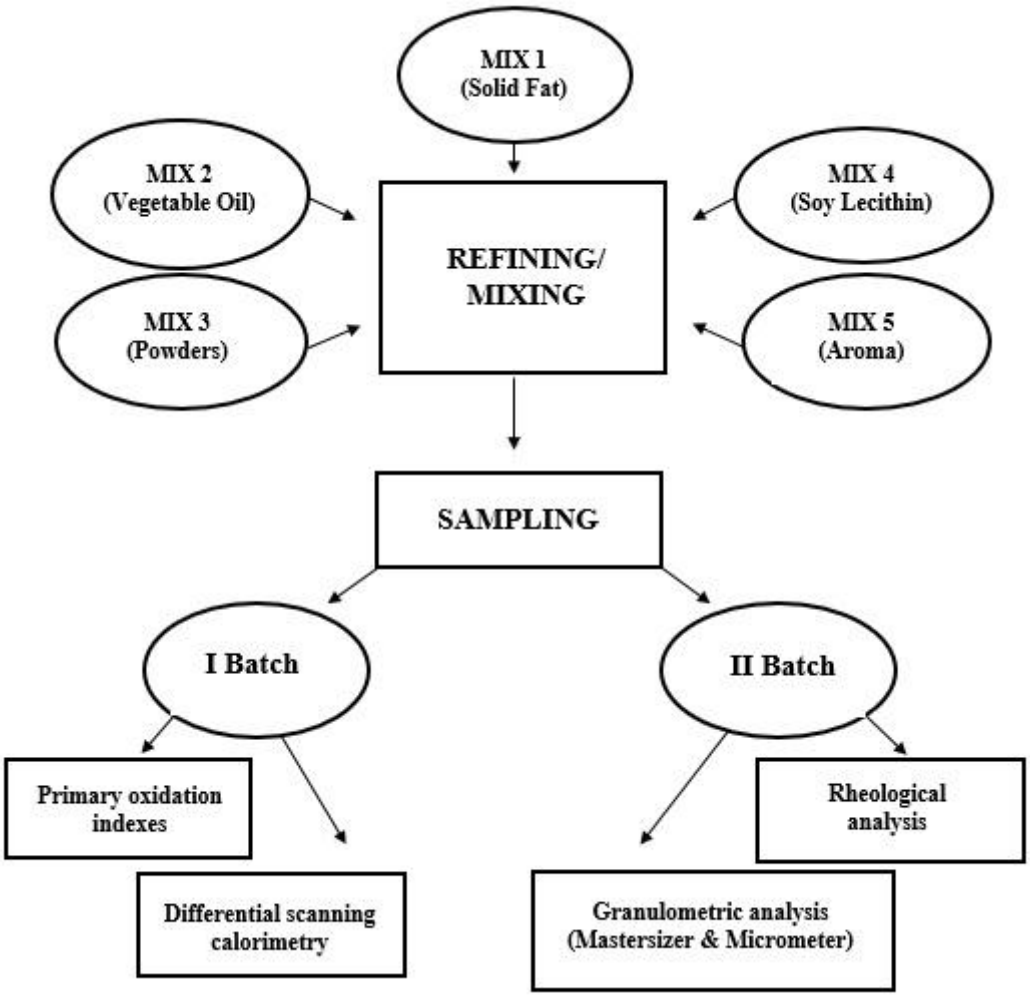

Figure 1: Experimental design

4. MATERIALS AND METHODS:

4.1 Materials

The ingredients used for anhydrous paste production were supplied by the manufacturer MAC 3 (San Clemente (RN), Italy). Five mixes to produce a batch of 10 kg were used:

1. MIX 1 → cocoa butter + palm fat, which represent the component of solid fats at room temperature; allow to give structure and consistency to the product;

2. MIX 2 → sunflower oil (promotes good resistance to oxidation) + vegetable oils (sunflower, palm) + hazelnut paste. This mix is the fat component, liquid at room temperature, allows to give the right spreadability to the final product;

3. MIX 3 → sugar + glucose syrup + skim milk powder + whole milk powder + lactose + powdered cream + dextrin malt + milk proteins;

4. MIX 4 → soy lecithin, this emulsifier has the function of being at the interface between the solid phase (powders) and the liquid phase (oil) allowing an effective mixing; it also performs a mild antioxidant action;

5. MIX 5 → aromas, to enhance flavor and characteristic smell to the product.

Table 1 shows the list of ingredients, allergens and the chemical-physical and nutritional information of the finished product.

Table 1: Ingredients and nutritional value of the final product

Chemical / physical characteristics	**Nutritional information**	**100g of product**
Humidity: max 1.5%	Energy	85 Kcal
Fats: 39%	Fat	39g
Ash: max 1.5%	Saturated fat	8.3g
	Carbohydrates	45g
	Protein	0.14g
	Sugars	46g
	Salt	

4.2. Paste preparation

A stirred ball mill was used for mixing and refining the cream (Micron20, Selmi s.r.l., Italy), with a capacity of 70 kg, a mass flow of 10 kg / h and a power of 4 kW. The mill consists of a cylindrical tank containing ± 60 kg of spheres (12 mm of diameter), a vertical shaft with horizontal arms that allows the movement of the balls and a pump for product recycling; all parts of the mill are made of stainless steel. The mill is also equipped with a temperature control system that allows us to monitor the temperature and keep it constant throughout the production. The process was carried out in batch mode with 10 kg of product to be refined.

The refining parameters have been set on the mill display (the set temperature is 50 ^{o}C for the machine) which allows us to keep the cream temperature constant at 45 °C, an increase in temperature can occur due to the rotational and translational movement of the balls mixer during the processing phase, generate friction and increase the total entropy of the

system. Another parameter that must be set is the refining time, this parameter has been set from time to time based on the times that we need, according to the experimental plan.

The different mixes were added in the refining machine as following:

1. Dissolve MIX 1 separately on a heating plate and/or in a pan in a water bath.

2. Load in refiner MIX 1 and MIX 2.

3. Then gradually insert MIX 3.

4. Insert MIX 4 (1/3 beginning, 1/3 half, 1/3 fine refine, micron of arrival 23-24μm).

5. Finally, insert MIX 5.

The total refining time of the cream is about 5 hours (300 minutes).

Several samples were taken at different refining times, 0 (which corresponds to the time after the addition of all the ingredients in the refining batch), 5, 10, 15, 20, 30, 40, 60, 70, 90, 120, 150, 180, 210, 240, 270 and 300 min.

The quantity of sample that taken from the machine was such as not to affect refining. The cream after being produced was stored in containers and under controlled temperature conditions, at 25°C.

Figure 2: Paste preparation

Pastes were prepared two times: first, pastes were preliminarily characterized; after about a month from the preparation of the first batch, another 10 kg of paste were produced and characterized to study grinding kinetics.

4.3 Paste preliminary characterization:

The paste after 0, 5, 10, 15, 20, 30, 40, 60, 70, 90, 120, 150, 180, 210, 240, 270 and 300 min of refining time were analyzed. Each analysis was replicated three times.

4.3. 1. Differential scanning calorimetry (DSC)

In order to model the heat transfer phenomena which take place during paste storage, predictive correlations of the paste thermophysical properties as a function of temperature are needed (Cogne et al, 2003).

A differential scanning calorimetric (DSC Q200, TA Instrument, USA) was used to determinate the melting points of the pastes. Paste has been

undergoing under thermal properties which allow assessing the optimum temperature to store the cream. The samples at time 0 and 300 minutes of refining were subjected to calorimetric analysis. Before being analyzed, the samples were weighed (8 mg of cream) in aluminum capsules, which were then sealed. Two replicates were done for each sample and following thermal history has been applied:

- Isotherm 60 °C for 1 minute;
- Cooling at 10 °C / min up to -80 °C;
- Isotherm at -80 °C for 30 minutes;
- Heating at 10 °C / min up to 60 °C.

4.3.2. Primary oxidation indices

In order to obtain initial information on the oxidative stability of the newly produced paste, the free fatty acid content and peroxide value, due to primary oxidation, were performed.

Sample at 0, 90, 150, 300 minutes of refining were analyzed (Figure 3). 10g of paste, placed in a plastic falcon, were centrifuged for 20 minutes at 10000 rpm (Universal Centrifuge Z 326, Hermle, Germany) to obtain the separation of the lipid phase. The supernatant was recovered and was subjected to a further centrifuge (14000 rpm for 10 min) to eliminate any solid residues. The analyzes were conducted at room temperature on the freshly extracted oil.

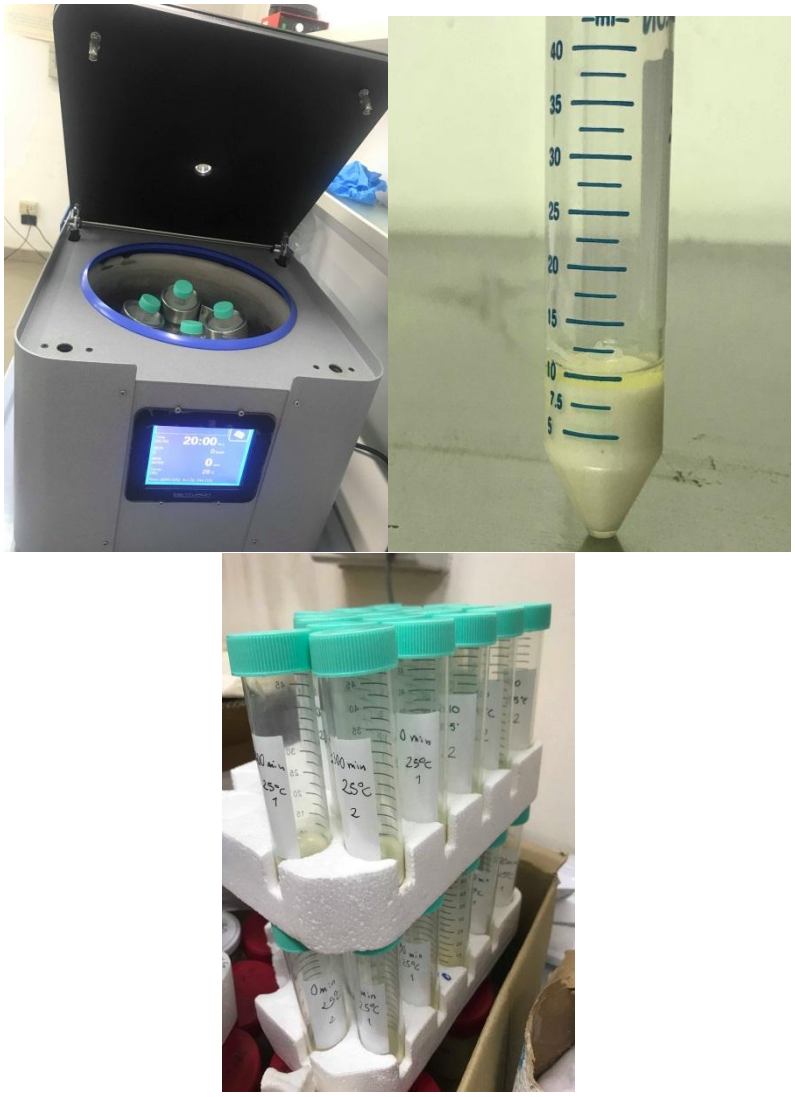

Figure 3: Oil separation by Centrifuge instrument.

The acidity of lipid phase was determined by titration with NaOH in ethanol/ether, using phenolphthalein as an indicator. At the end of the titration, the percentage of oleic acid was determined using the following formula:

% acidity (in oleic acid) = V * N * (P / 1000) * (100 / m) = (V * N * P / 10 * m)……(1)

V = is the volume, in milliliters, of the solution of sodium hydroxide used;

N = is the concentration of the sodium hydroxide solution used;

P = is the oleic acid equivalent weight = 282

m = the weight, in grams, of the sample used for the analysis.

The number of peroxides is expressed as the milliequivalents of peroxide oxygen combined in a kilogram of oil. Its determination involves treating an oil sample with a potassium iodide solution.

The iodine released by the reaction of the iodide with the peroxide compounds is back-titrated with a solution of sodium thiosulphate in the presence of starch as an indicator. The calculation of the number of peroxides is carried out at the end of the titration using the following formula:

Number of peroxides ($meqO_2$/kg oil) = (V x N x 1000) / m…….. (2)

V = is the number of mL of the sodium thiosulphate solution used for the test.

N = is the normality of the sodium thiosulphate solution used for titration.

m = the weight in g of the substance to be analyzed.

4.4 Paste characterization:

4.4.1. Particle size measurement

An electronic digital micrometer (Metrocontrol Srl, Casoria NA) and a Mastersizer laser diffraction analyser were used for measuring particle size. The digital micrometer is the most recent innovation in micrometer technology. Digital micrometers are able to take extremely accurate measurements; most can measure to 0.0005 inches and 0.001mm.

The micrometer is a high precision caliper, it is a measurement tool widely used in production since it allows having immediate information on the size of the particles present in the sample, but is not able to provide information on particle distribution. All cream samples were subjected to this analysis. After the calibration of the instrument, a quantity of sample was placed on the fixed part of the instrument and the mobile part was screwed until the screw met resistance, at that point, the size of the particles found in the sample was read on the instrument's display. Micrometer measurements were performed online (during refining) at 45 °C and after conditioning the samples for 24 hours at 25 °C. For each sample, 5 measurements were performed.

A Mastersizer laser diffraction particle size analyser equipped with Hydro 3000 dispersion unit (Malvern Instruments, Worcestershire, UK) was used. The operating principle of this instrument is light scattering, laser diffraction for the precise and rapid measurement of particle distributions, with a measuring range ranging from 0.01 to 3500 µm.

Before performing the analysis, it was necessary to set a specific operating procedure for the type of sample analyzed.

The parameters set were:

- Type of particles: non-spherical
- The type of dispersant: sunflower oil
- Stirring speed: 1500 rpm
- Obscuration: 10 – 30%

All the samples (about 0.1 g of paste) at different refining times were analysed at environmental temperature (20±2°C).

The dispersant used is a common sunflower seed oil with a refractive index of 1,496, chosen so that the sugar present in the sample subjected to analysis does not dissolve, making the measurement more efficient (Do et al., 2007; Glicerina et al., 2014b; Afoakwa et al., 2009; Aidoo et al., 2014; Belščak- Cvitanović et al., 2015; Fidaleo et al., 2017).

For each paste, three different replicates were analysed and for each replicate, 20 measurements were performed. Several indices of the PSD based on the volume of particles were estimated, including the D_{10}, $D_{50,}$ and D_{90}, respectively (Glicerina et al. 2014b).

4.4.2. Rheometer analysis:

The viscosity of cream samples was determined by a Modular Advanced Rheometer System (HAAKE MARS, ThermoScientific, Waltham, USA*)* with controlled deformation, equipped with a vane tool geometry (diameter 22mm, length 16 mm, distance 8.5 mm). Viscosity measurements were carried out in a flow rate range ($\gamma^{\cdot}$) between 0.01 and 100 s^{-1}, which is the most relevant interval for the study of rheological properties and texture of food products (Vizireanu et al., 2011).

4.5 Data analysis

The thermograms obtained by calorimetric analysis were processed with the TA Universal Analysis software (TA Instruments, USA).

The granulometric characterization of the samples was quantified using the Mastersizer 3000 software and the data were expressed in terms of D_{10}, $D_{50,}$ and D_{90}. From this data, it was possible to quantify the percentage volumes of particles corresponding to all the granulometric classes present in each sample (Afoakwa et al., 2009).

The flow curves were fitted according to the rheological Power Law model which is represented in the following as:

$$\dot{\eta} = K \cdot (\dot{\gamma})^{n-1} \qquad (3)$$

where ɳ is the viscosity (Pa·s), K is the consistency index (Pa·s^n), $\dot{\gamma}$ is the shear rate (1/s) and n is the dimensionless flow behavior index. In order to measure the goodness of fit, the regression coefficient (R^2) was determined.

One-way analysis of variance (ANOVA) and multiple comparisons (Duncan) were used to evaluate if differences among the sample means were statistically significant ($p \leq 0.05$). The statistical software SPSS for Windows, version 17.0 was used for data analysis (SPSS Inc., Chicago, IL, USA).

5. RESULTS AND DISCUSSION:

5.1. Differential scanning calorimetry (DSC)

From the thermogram of each sample the start (T_{ON-SET}), end ($T_{END-SET}$) and peak melting (Tpk) temperatures were calculated, and the specific enthalpy (ΔH, expressed in J / g of fat).

As we can see in figure 4, for the samples at 0min refining time, the fusion started at -56.03 °C and ended around 3.59 °C; with a peak around -27.41 °C, while the fusion enthalpy was about 23.8 J / g of fat, as well as at 300min of refining , the fusion started at -56.03 °C and ended around 6.4 °C; with a peak around -30.43 °C, while the fusion enthalpy was about 23.9 J / g of fat.

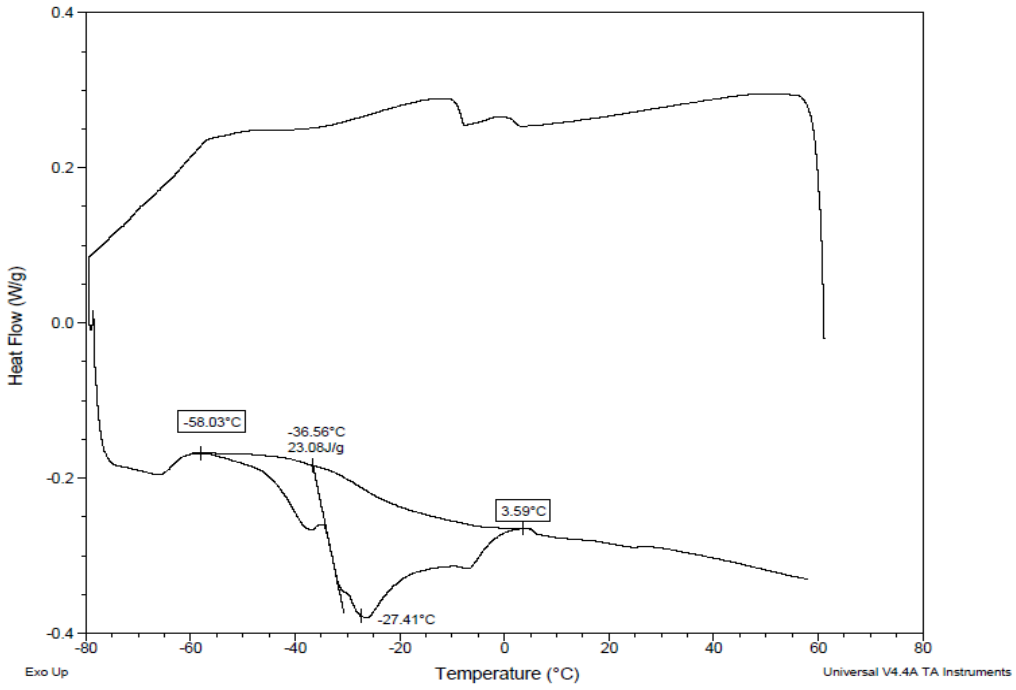

Figure 4a: Paste thermogram of paste after 0 min of refining time.

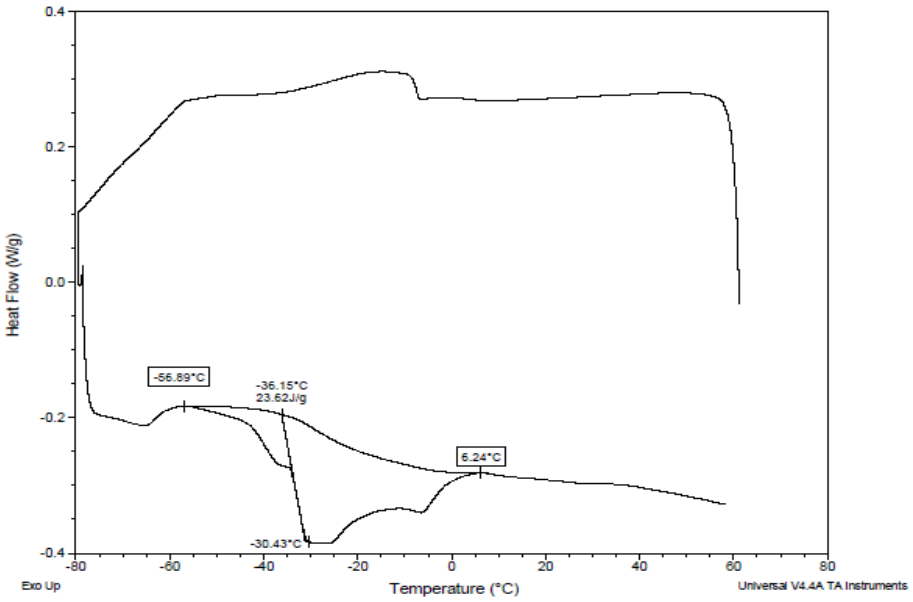

Figure 4b: Paste thermogram of paste after 300min of refining time.

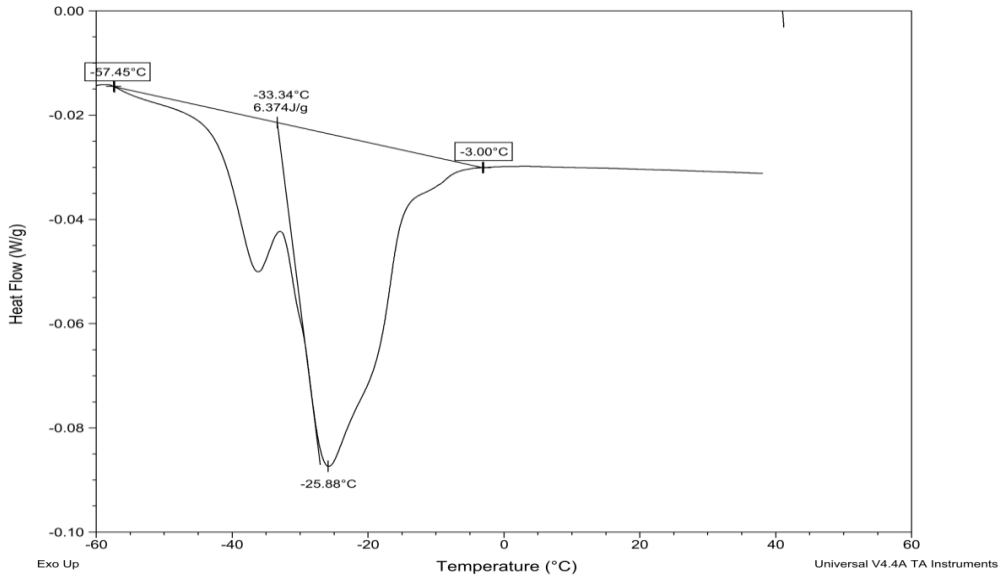

Figure 5a: Sunflower oil thermogram.

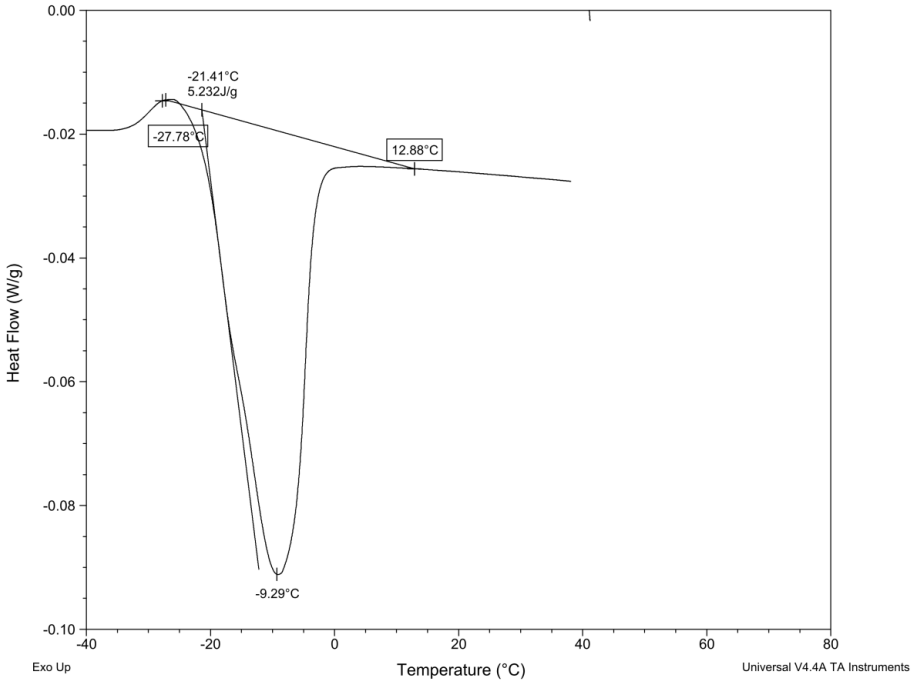

Figure 5.b: Hazelnut paste thermogram.

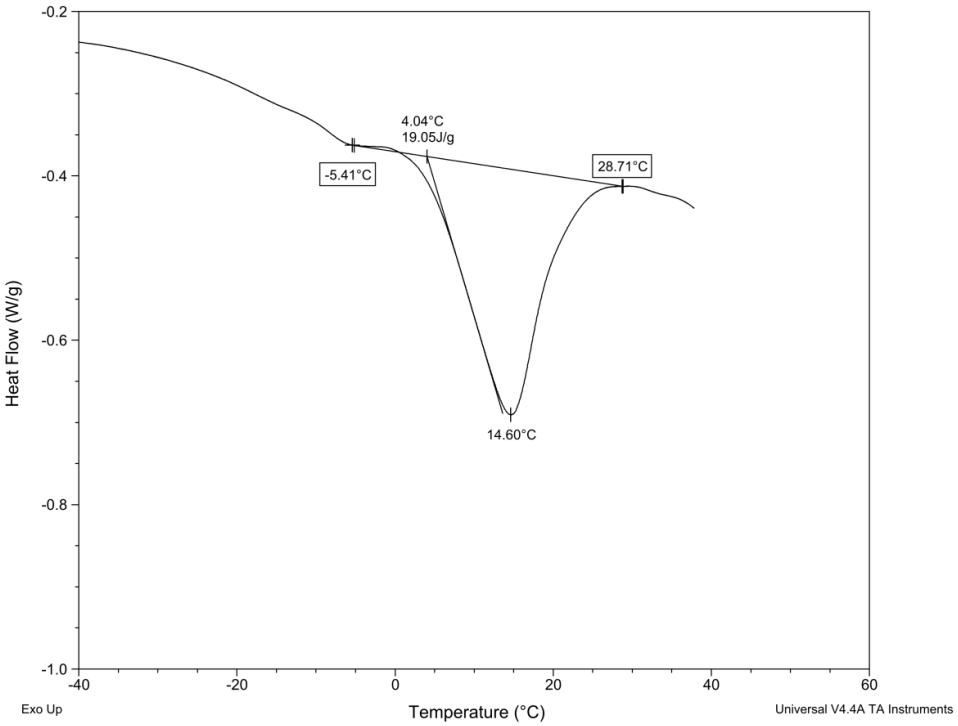

Figure 5c: Palm oil thermogram.

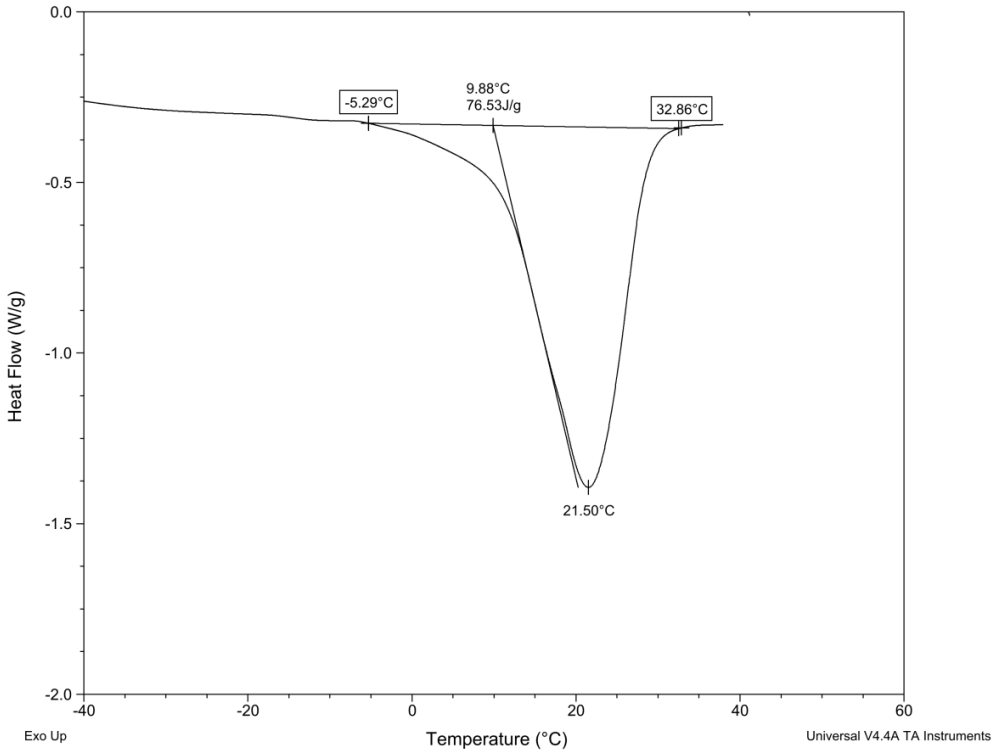

Figure 5d: Cocoa butter thermogram.

There was no effect of the refining time on thermal paste properties. Those properties were only affected by the fat type used. In fact, comparing figure 4 with figure 5 it is clear that pastes presented a $T_{ON\text{-}SET}$ close to that of sunflower oil and a $T_{END\text{-}SET}$ close to that of cocoa butter and palm oil, showing that a small fat amount was still melting at environmental temperature.

5. 2.Oxidation indices

Pastes after 0, 90, 150, and 300 minutes of refining were analyzed and the results were reported in table 2. There was no effect of the refining process on those indices, as expected. Acidity values varied from 0.75 to 0.84%. Peroxide values were around 26-27 $meqO_2/kg_{oil}$. Starting from those

results, also for the next paste production the reefing process was stopped after 300 min.

Table 2: Acidity and peroxide results.

	Replicate	Refining time (min)			
		0	90	150	300
Acidity%	1	0.8156	0.854	0.7935	0.7406
	2	0.7992	0.8265	0.8155	0.7703
	Average	0.8074	0.84025	0.8045	0.75545
Peroxide ($meqO_2/kg_{oil}$)	1	26.2845	25.727	25.944	26.453
	2	25.9216	25.961	24.947	26.938
	Average	26.10305	25.844	25.4455	26.6955

5.3.Granulometric analysis

The granulometric distribution of the pastes is the characteristic that most correlated to the structure and texture properties. In order to study the refining kinetics; the particle size distribution of the cream samples was acquired by laser diffraction.

The particle size distributions relating to different refining time from 0 to 300 min were presented in figure 6-7-8.

As shown in figure 6 below, from 0 – 40 min, the PSD curve presented a almost unimodal distribution that decreased progressively as the peak became higher and moved towards values of smaller dimensions during refining, showing a small left shoulder.

After 40 min of refining, the size of the solid particle ranged from 1.6 - 76 micrometers; from 40 to 180 min, as it is shown in figure 7, the left shoulder was higher, moving towards values of PSD smaller.

Then, (figure 8) the distribution of particle size after 180min was almost constant, so from a granulometric point of view could be useless to continue refining after 180min.

As stated by Bolenz and Manske (2013), unimodal PSD curves are more typical for ball mill refining products, meanwhile, many roller milled products presented a multimodal PSD curve. Those authors studied the effect of fat content during grinding on PSD and flow properties of milk chocolate. The PSD curves obtained for chocolate, refined in ball mills, were unimodal and not affected by fat content. Unimodal distributions in ball mills were also observed by Bolenz, Holm, and Langkrar (2014) in the refining of milk chocolate.

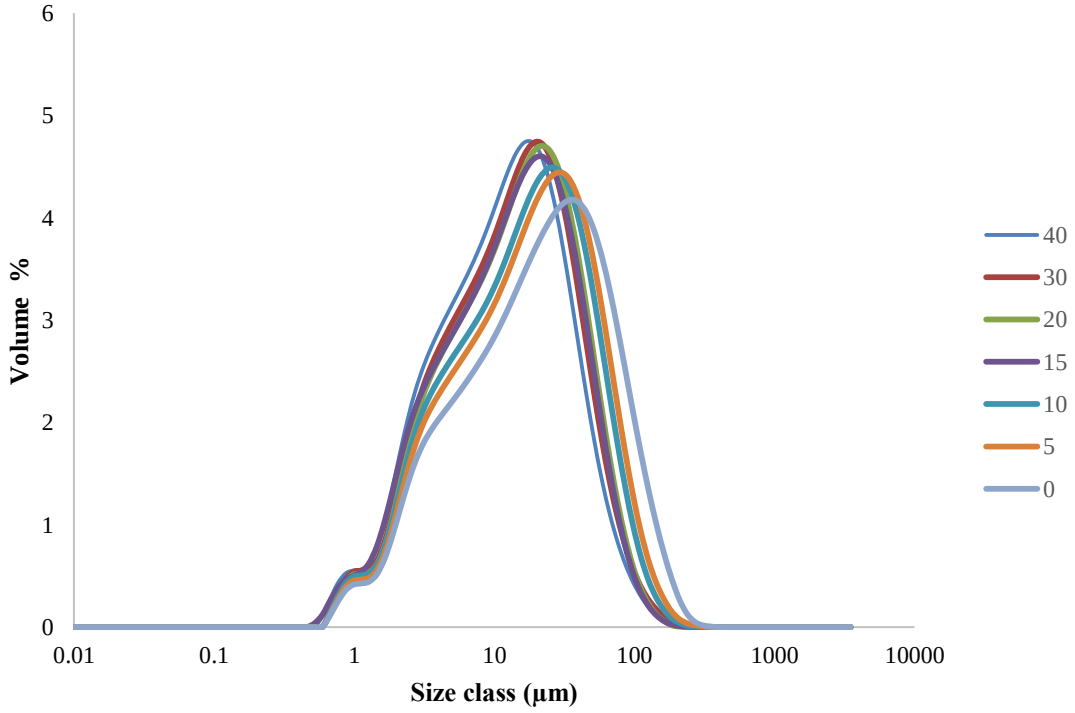

Figure 6: PSD of paste stored at 25 °C after 0, 5, 10, 15, 20, 30,40 min of refining.

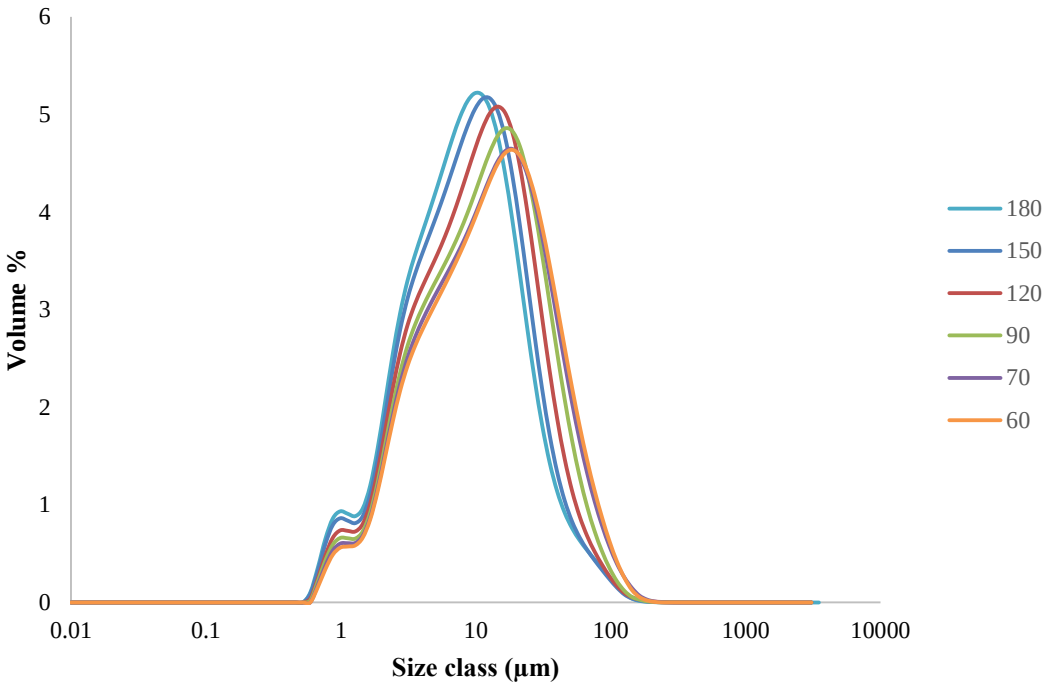

Figure 7: PSD of paste stored at 25 °C after 60, 70, 90, 120, 150, 180min of refining.

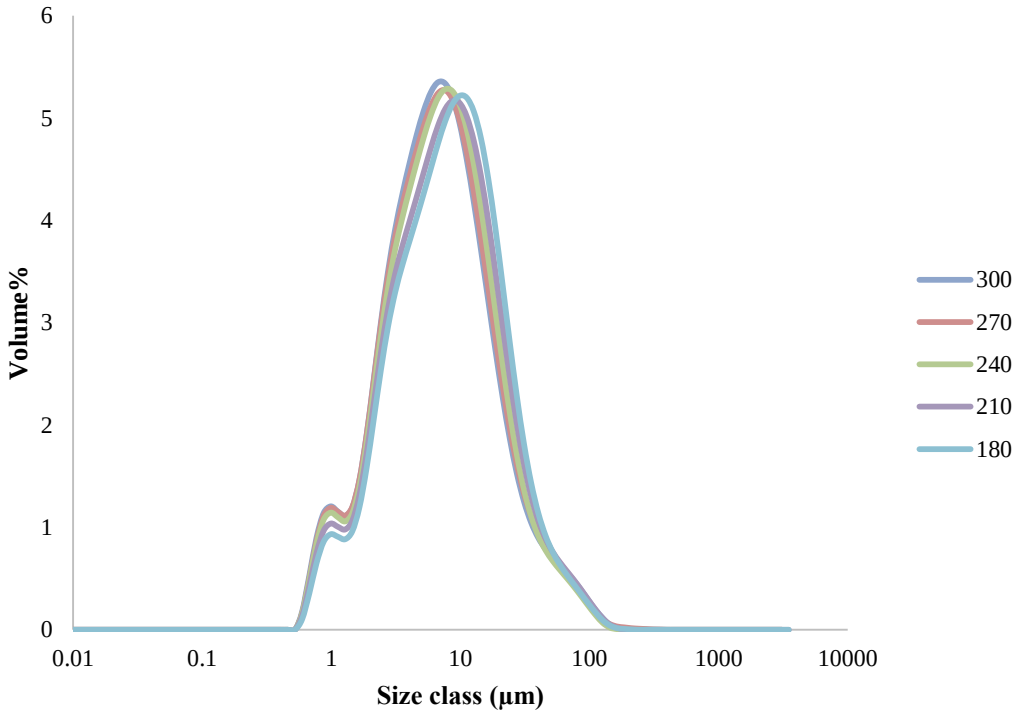

Figure 8: PSD of paste stored at 25 °C after 180, 210, 240, 270, 300 min of refining.

In table 3 the D_{10}, D_{50} and D_{90} values (average ± standard error) from PSD curves were reported, as well as its fineness (φ), measured through a digital micrometer. Digital micrometer measurements were performed both online (at 45 °C) to check how the not fat solid particles varied during the refining time and at 25 °C to verify how all the particles varied during the refining process. From the statistical analysis, it came out that all those parameters significantly varied during refining times. In particular, they decreased over time with fast speed rate at the beginning (until 20 min of refining); then they decreased gradually with a low speed rate. In particular, the D_{90} from 120 to 300min of refining time was almost constant. Fineness measured at 25 °C was close to that measured online, even if those values were a little bit higher than the other ones because of a small amount of fats that were solid at 25 °C.

Table 3: PSD parameters (D_{10}, D_{50}, D_{90}) and fineness (□) of pastes during refining time.

Refining time (min)	□ (45 °C)	D_{10}	D_{50}	D_{90}	□ (25 °C)
0	80.40 ± 2.713^{g}	3.5500 ± 0.03^{k}	22.933 ± 0.16^{o}	87.800 ± 0.60^{l}	84.40 ± 3.370^{i}
5	66.00 ± 1.581^{f}	3.2667 ± 0.029^{j}	18.366 ± 0.47^{n}	64.700 ± 2.11^{k}	72.60 ± 2.421^{h}
10	62.80 ± 9.167^{f}	3.1733 ± 0.067^{ij}	17.533 ± 0.37^{m}	61.300 ± 1.33^{j}	68.60 ± 1.568^{h}
15	44.40 ± 2.542^{e}	3.1733 ± 0.028^{ij}	16.500 ± 0.11^{l}	55.967 ± 0.58^{hi}	57.40 ± 1.400^{g}
20	38.80 ± 2.672^{de}	3.0967 ± 0.27^{hi}	15.4667 ± 0.03^{k}	51.533 ± 0.28^{gh}	55.60 ± 1.631^{g}
30	31.80 ± 1.356^{cd}	3.1667 ± 0.166^{gh}	14.633 ± 0.08^{j}	49.33 ± 0.69^{gh}	43.00 ± 1.140^{f}
40	29.20 ± 1.241^{bc}	3.000 ± 0.03^{gh}	14.100 ± 0.23^{i}	47.600 ± 1.36^{g}	42.00 ± 0.949^{f}
60	23.60 ± 0.400^{abc}	2.9667 ± 0.02^{fg}	13.9667 ± 0.12^{hi}	49.367 ± 0.21^{g}	39.00 ± 0.894^{ef}

70	23.40 ± 1.778^{abc}	2.9000 ± 0.05^{f}	13.4667 ± 0.06 ^{h}	47.700 ± 0.28^{f}	35.40 ± 0.400^{de}
90	23.80 ± 1.393^{abc}	2.7900 ± 0.025^{e}	12.5000 ± 0.10^{g}	41.433 ± 0.12^{e}	31.20 ± 0.490^{cd}
120	20.40 ± 1.435^{ab}	2.6333 ± 0.01^{d}	11.100 ± 0.00^{f}	35.400 ± 0.26^{d}	28.20 ± 0.633^{c}
150	24.40 ± 1.720^{abc}	2.4600 ± 0.01^{cd}	9.633 ± 0.01^{e}	30.567 ± 0.08^{d}	26.60 ± 1.470^{c}
180	20.60 ± 1.327^{ab}	2.3467 ± 0.006^{bc}	8.8567 ± 0.01^{d}	28.833 ± 0.14^{cd}	27.20 ± 0.663^{c}
210	18.80 ± 1.068^{a}	2.2067 ± 0.037^{b}	8.233 ± 0.09^{c}	28.133 ± 0.42^{bc}	28.40 ± 2.015^{c}
240	20.00 ± 1.141^{a}	2.0967 ± 0.088^{ab}	7.5567 ± 0.08^{b}	25.600 ± 0.05^{a}	26.80 ± 1.594^{c}
270	20.80 ± 1.772^{ab}	2.0400 ± 0.025^{a}	7.2900 ± 0.08^{ab}	26.233 ± 0.54^{ab}	21.80 ± 0.800^{b}
300	17.80 ± 0.735^{a}	2.0100 ± 0.076^{a}	6.9600 ± 0.11^{a}	24.767 ± 0.37^{a}	13.80 ± 0.860^{a}

Values in the same column followed by different letters differ significantly at P<0.05 level (Duncan's method).

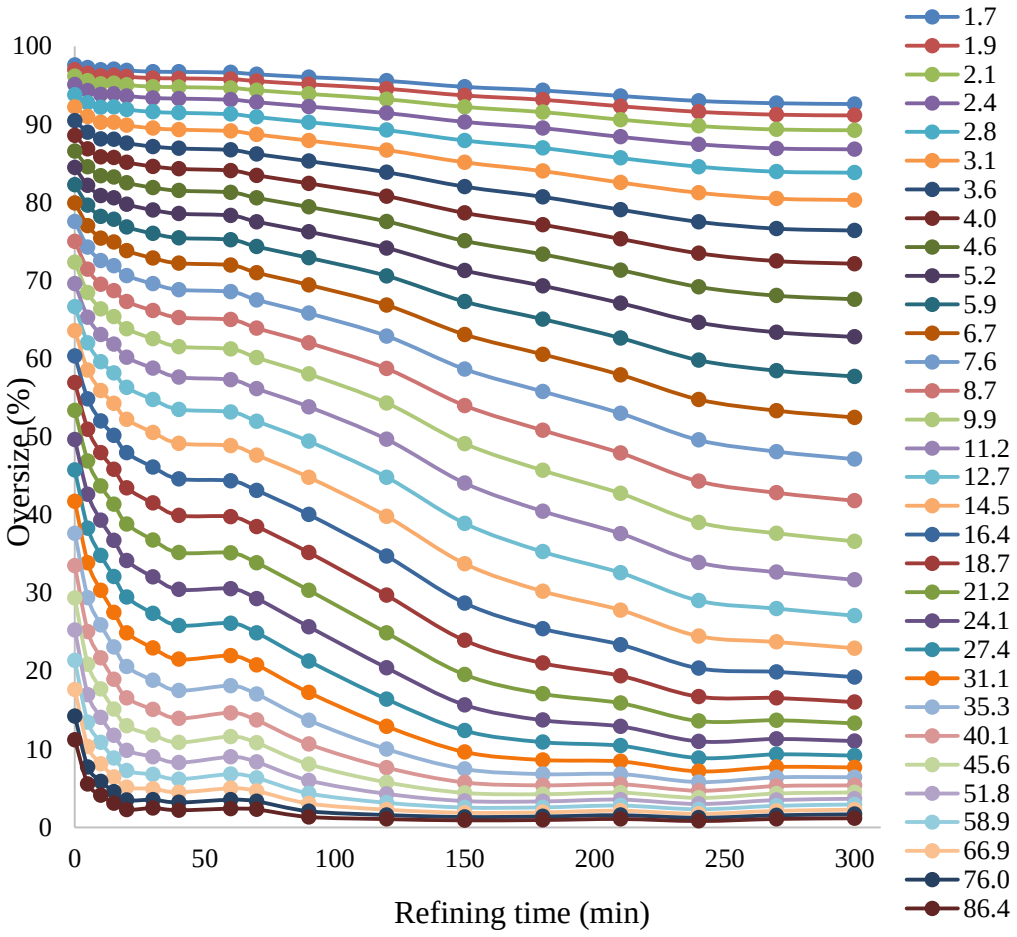

Figure 9: Cumulative oversize fraction as function of refining time for different size classes (From 1.7 to 86.4 μm).

As can be seen on figure 9, the cumulative frequency, as a function of refining time, remained constant for the very small particles; the small ones (max 10 μm) were a little bit reduced during the first 60 minutes and then rapidly decreased until 240 minutes. For medium particles (from 10 to 35 μm) there was a continuous decrease during the whole refining process. Finally, for coarser particles, there was a very fast reduction only during the first 40 minutes of refining.

The correlation of the D_{90} values with the fineness, for this type of product, has already been highlighted by Beckett (2008), showing that the values of D_{90} were slightly higher than the micrometric readings. In this study, as we can see in figure 10, y = 1.03 and R^2 = 0.84, so there was a good correlation between those parameters.

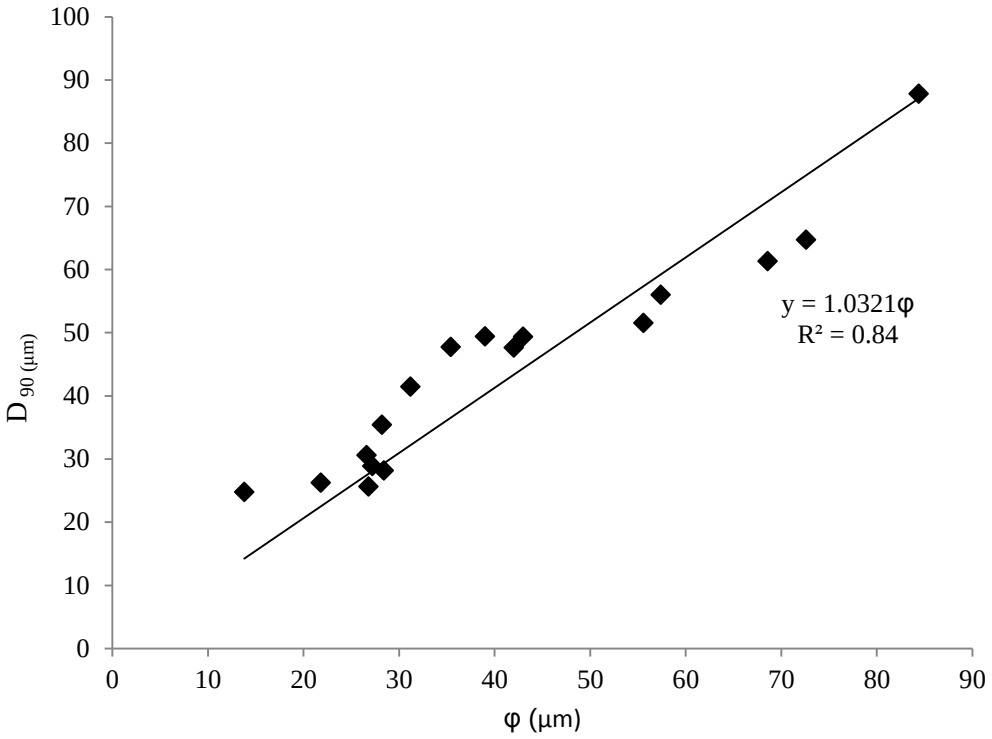

Figure 10: D_{90} values vs fineness (φ)

D_{90} values were higher than the micrometer measurements. This is consistent with the results of Fidaleo et al., (2017), who refined an anhydrous chocolate paste in an industrial ball mill. The samples obtained at 195 and 225 min of milling presented statistically different D_{90} mean values equal to 37.6 and 35.2 μm, respectively and a fineness of 24 and 22 μm. Our results are also consistent with Bolenz et al. (2014) and Bolenz and Manske (2013); they refined white chocolate in ball mills until a

micrometer value of 22 μm was reached and estimated for their samples D_{90} ranging from 28.14 to 30.50 μm. As underlined by Glicerina et al. (2014) and Pieri, Bittelli, and Pisa (2006) this may be due to the fact that the laser diffraction method considers the solid particles as spheres while they may be more similar to flat particles, like disks. Thus, the micrometer method estimates a figure linked to the thickness of the flat particles, that is their smallest dimension, which in chocolate seems to correlate better with consumers acceptability compared to the other particle dimensions because once in the mouth particles will tend to orient along their flattest axis (Pugh, 2014).

5.4. Rheological analysis

To study the effect of the refining time on the viscosity of the creams, for all the samples the curves of apparent viscosity vs shear rate were acquired. The experimental results obtained were shown in Figures 11(a-b).

All samples showed a pseudo-plastic behavior, in fact, the apparent viscosity of the pastes decreased as the shear rate increased; the viscosity increased as a function of the refining time; the zero shear rate viscosity was around 1000 Pa·s, for the low refined samples, increasing until values between 1000 and 10000 Pa·s, for the samples more refined.

During the first three hours, there was no effect of refining on viscosity, as shown in figure 11a, but after 3 hours of refining, there was a clear of refining on zero shear rate viscosity, even if at high shear rate those differences were reduced.

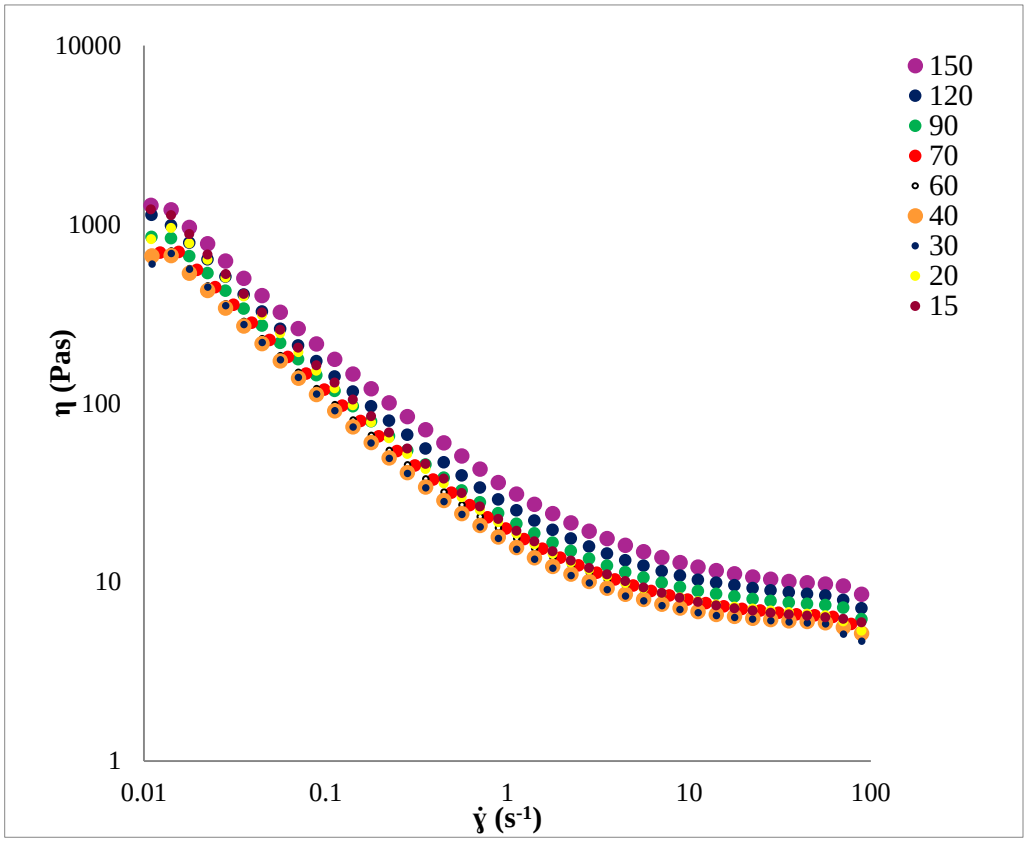

Figure 11.a Apparent viscosity of the cream after 15, 20, 30, 40, 60,70,90,120,150 minutes of refining

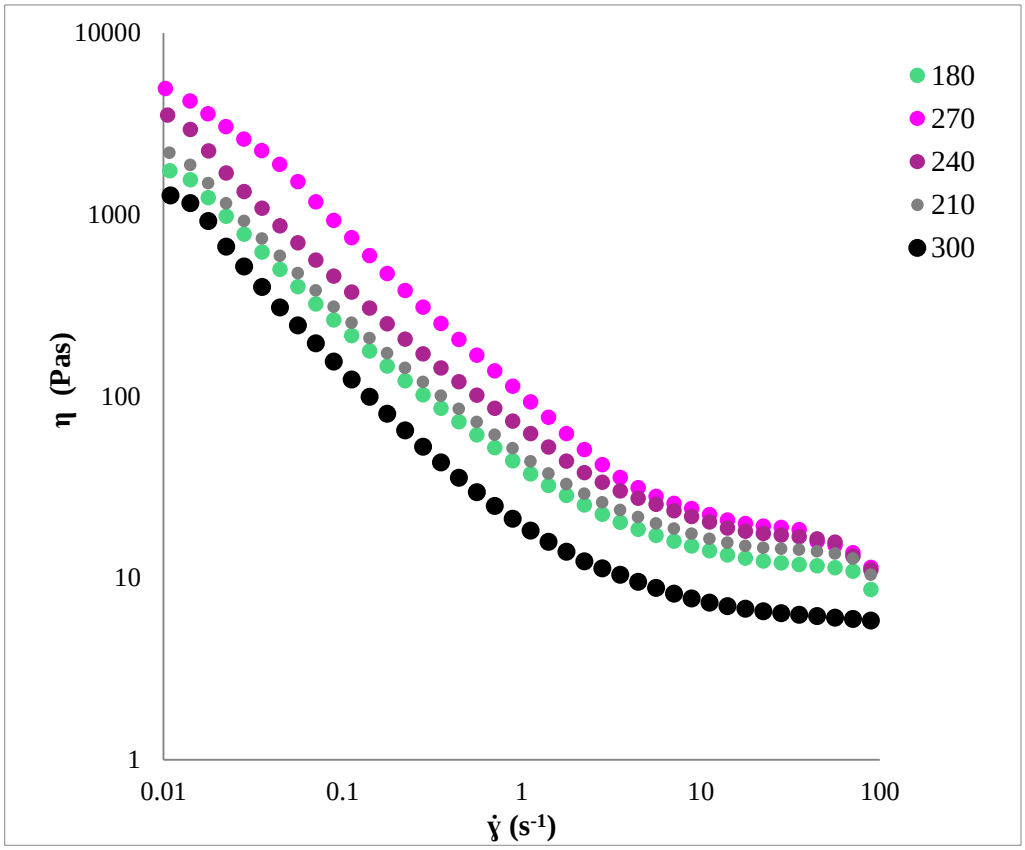

Figure 11.b Apparent viscosity depending on the frequency of the cream after 3hours of refining time.

In table 4 the estimated k and n parameters from viscosity curves in a reduced shear rate range (2-50 s^{-1}) were reported. As reported in table 4, there was an increase of the consistency index (K) as the refining time increased too, especially after 120 min of refining, and at the same time, the flow index (n) was reduced. The values of R^2 were close to 1 for all the samples.

This behavior can be explained by the structural breakdown of the molecules due to the hydrodynamic forces generated and to the increased alignment of the constituent molecules (Izidoro et al. 2008).

Table 4: Flow rate and index of consistency of the cream according to the refining time.

Refining time (min)	n	K ($Pa \cdot s^n$)	R^2
15	$0.77863 \pm 0.00083^{cde}$	$13.5933 \pm 0.11866^{abc}$	0.9944 ± 0.000067^{b}
20	0.79716 ± 0.0048^{def}	13.616 ± 1.731^{abc}	0.9951 ± 0.00070^{b}
30	0.8156 ± 0.0013^{f}	11.258 ± 0.0232^{a}	0.9950 ± 0.00020^{b}
40	0.8135 ± 0.00097^{f}	11.4864 ± 0.1647^{a}	0.9947 ± 0.00012^{b}
60	0.80886 ± 0.00068^{f}	12.951 ± 0.1190^{ab}	0.9950 ± 0.00033^{b}
70	0.80256 ± 0.00086^{ef}	13.029 ± 0.1153^{ab}	0.9956 ± 0.00058^{b}
90	$0.79073 \pm 0.0014^{cdef}$	15.778 ± 0.1287^{abc}	0.9949 ± 0.00088^{b}
120	$0.77986 \pm 0.00320^{cde}$	18.721 ± 0.4272^{bc}	0.9951 ± 0.00034^{b}
150	0.7713 ± 0.0110^{cd}	19.346 ± 1.6869^{c}	0.9947 ± 0.00030^{b}
180	0.76146 ± 0.00296^{bc}	26.979 ± 0.9933^{d}	0.8363 ± 0.78333^{a}
210	0.77286 ± 0.00159^{cd}	30.807 ± 1.444^{d}	0.9924 ± 0.00046^{b}
240	0.73583 ± 0.00439^{b}	41.498 ± 2.335^{e}	0.9919 ± 0.00020^{b}
270	0.66413 ± 0.0206^{a}	54.828 ± 1.9030^{f}	0.9730 ± 0.0011^{b}
300	0.6485 ± 0.0228^{a}	73.379 ± 5.711^{g}	0.9686 ± 0.0251^{b}

Values in the same column followed by different letters differ significantly at $P<0.05$ level (Duncan's method).

These indices have allowed us to evaluate the rheological behavior of the creams by offering an easy way to interpret the result. The consistency index increasing and the flow index decreasing as the refining time increased was already highlighted by Fidaleo et al. (2017) and others. This behavior was in line with the rheological behavior of solid dispersions such as chocolate (Birkett, 2009). Loncarevic et al. (2016) used a laboratory ball mill to produce a spreadable cocoa cream with different refining degree and containing varying amounts of lecithin of different origins (sunflower, rapeseed and soy lecithin). The authors found Casson viscosity increased with the increase of milling time. This was reported also by Afoakwa, Paterson, and Fowler (2008) who investigated the effects of particle size

distribution and composition on the rheological properties of dark chocolate, where it was observed that an increase in particle size resulted in a decrease in Casson plastic viscosity. For what regards the magnitude of the flow model parameters obtained, the composition of the product under study in terms of fat, cocoa, hazelnut paste, sugar, and lecithin is similar to cocoa spreads (Di Monaco et al., 2008). However, the type of fat may differ and this results in different rheological parameter values, as reported by Glicerina et al. (2013) who found that increasing the level of hydrogenated fats in nut spreads results in increased consistency and apparent viscosity.

6. Conclusion

The objective of the thesis was to characterize one type of anhydrous creams, refined in a ball mill, by means of granulometric distribution, rheological properties, and calorimetric properties, and it has been achieved.

The particle size distribution curves obtained from the cream samples showed a unimodal trend, typical for ball mill refining products. From the study of the granulometric parameters, it emerged that the optimal time around the right degree of refining can be obtained after about 180 minutes of refining if a paste with a fluid-like behavior is required. After 180 minutes of refining, the fineness reached a value of 28.8 μm and assumed an asymptotic trend afterward, making it difficult to obtain a further reduction of particle size by prolonging the refining time. Meanwhile, the apparent viscosity mainly varied after 200 minutes of refining, and a paste with a solid-like behavior was achieved.

However, the quality and rheological properties of creams are affected by a number of factors, such as the type and different amounts of fats. Our results highlighted that when a paste contains both oils and solid fat, the refining kinetic was slower than that of a cream that contains only oil as the fat phase.

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تطوير عوامل انتاج الكريما القائمه على الدهون

اعداد

محمد سلامة

إشراف

سامر مدلل

نيكوليتا ميلي

الملخص

تُعرف الكريما اللامائية بأنها نظام معقد يتكون من عدة جسيمات صلبة معلقة في سائل مثل (الزيت) أو في مرحلة شبه صلبة مثل زبدة الكاكاو. تم اعادة تكرير الكريما اللامائية في ماكنة الطحن التي تميزت من حيث استخدام الطاقة ولزوجة المنتج وحجم الجسيمات والخصائص الحسية، بسبب قوة الطحن الخاصة التي تبلغ 0.03 كيلو وات / كغ من الكريما، وصلت نعومة المنتج 22.4 و30.4 ملم، في 225–150 دقيقة، على التوالي.

كانت النتائج ايجابية وتم الحصول على نتائج ذات فائدة كبيرة للمصانع، حيث أظهرت الكريما سلوكًا يسمى pseudoplastic، حيث كانت اللزوجة عند الصفر حوالي 1000 باسكال، بالنسبة للعينات المكررة في وقت قصير، وزادت حتى القيم بين 1000 و10000 باسكال، للعينات الأكثر وقتا للتكرار. كانت منحنيات توزيع حجم الجسيمات (PSD) التي تم الحصول عليها بواسطة قياس حيود الليزر أحادية الوسائط ، بالرغم من انه تم وجود D90 أعلى من قراءه الميكرومتر الرقمي ولكن مع معدل جيد حيث كان يساوي R = 0.85.