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The rheological component as an influencing factor in the technique of formulating natural fats

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Abstract

Currently, the volume of studies on the *manifestations of fat flow* has increased. The fat considered as a *solid-elastic biopolymer* (palm oil), thermodynamically unstable, consists of: 1. *continuous phase*, formed by the elastic network of unsaturated lipids; 2. *discontinuous phase* of solid crystals. Crystallization, polymorphism and crystal size / geometry are flow phenomena influenced by the fatty acid species that form triglycerides and that pose problems in food processing induced by post-crystallization processes. Therefore, the topic is relevant for the sector of minimally invasive fat processing technologies. *Predictive* tests were performed on the conditions of fractional crystallization, starting from the following hypothesis: it is considered that the particles (dS, dO (S - stearin, O - olein)), which sediment depending on the *two separation methods* (*fractional crystallization in gravitational force field, centrifugal*), accessed in the paper, are spherical. Sedimentation occurs at the same rate as in suspension. The operation covers all areas of sedimentation: laminar, intermediate and turbulent. The imposed conditions allow the determination of the following parameters:**a)** the ratio d_s/d_o for both forms of sedimentation; **b)** critical diameters d_{cS}, d_{cN} for sedimenting particles.

Keywords: palm oil, lipids, dry fractionation, fractional crystallization, physical formulation, rheological behavior, flow areas, critical diameters

1. Introduction

Currently, it is recognized that the *process of lipid crystallization* is one of the physical properties that cause problems, through the phenomenon of *polymorphic transition*, the formation of solid lipid agglomerates with a maximum content of saturated fats (solids), which may be incompatible with certain operations. / processes of *transformation / formulations / product formation*. The possibilities of current lipid formulation are multiple: hydrogenation, interesterification, fractional distillation, molecular distillation, etc., all of which allow the chemical or physico-chemical "*formulation*" of natural fats according to the intended purpose [1, 2, 3, 4].

The operation has some peculiarities:

1. *wet crystallization* with the addition of surfactants (and detergents) and / or solvents;
2. *dry fractional crystallization* (*without the intervention of other substances*), separation process on physical principles, for which we can say the intervention of two factors (operating parameters):

    a) temperature;

    b) rheological component and / or behavior.

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The *dry fractional crystallization* process can be combined with physical separation technologies (settling, sedimentation, filtration, mixing, pressing, or combinations) in which, in addition to temperature and inter- and intramolecular attraction forces, the rheological component specific to each molecular species of lipids in the mixture that physically require separation operations can act. This component must be related to the separation / sedimentation velocities, as a result of the intervention of forces of a nature specific to the physical separation operations (gravitational, centrifugal, pressure).

The purpose of the operation of fractional crystallization and physical separation is to separate the initial lipid mixture into its constituent phases: **a)** *fluid* component (liquid), ***olein***; **b)** *solid* component (with low fluidity), ***stearin***. Depending on the purpose pursued, which conditions the accessed operating parameters, with influences on the state of aggregation of the continuous phase (*intervention moment of the rheological component*), determines the choice of the separation scheme (*olein pathway / stearin pathway*). The process can be applied to a wide range of natural vegetable and animal fats (palm oil, coconut oil, extra virgin olive oil, lard, tallow, milk fat, etc.).

The *crystallization phenomenon* is a complex one, influenced by a series of factors (temperature, time, speed, forces of action), and the mode of management and control determines the quality of the finished products. These are generators of crystal dimensions and formation of *polymorphic* crystal networks / structures ($\alpha \rightarrow \beta' \rightarrow \beta$) ($\beta$ has the highest thermomechanical stability, with parallel triclinic faces). The cause explains the presence of different melting intervals, but also of *flow patterns* mutually influenced by the nature of the triglycerides in the initial mixture.

Thus, recent research has focused on understanding the *physical phenomena* involving the crystallization of lipids, in an attempt to obtain effective solutions to *optimize*, *stabilize* or *modify* this process, depending on the nature of the raw material and subsequent application in the technological manufacturing process [5]. A major role is played by the temperature, pressure and size of the force of action that must always be adjusted for each path and stage of separation [6]. In the case of centrifugal separation, relatively high yields of olein of 75-80%, but low in solids (stearin) can be obtained. In the field of activity of gravitational and centrifugal drills, for the two separate ones (solid / liquid), of different densities, mutually insoluble (quality given by the different solidification / melting intervals), different *sedimentation rates* are generated, which determines the separation of phase. *It is applied to solids with diameters larger than 0.005 mm and a concentration in the liquid phase of 2-40%* [7, 8].

2.Materials and methods

In the present paper, the *non-hydrogenated palm oil* was chosen as a study model, which was followed by the behavior and modification directed at *fractional crystallization* and physical gravitational and centrifugal force field separation. The raw material considered as a *solid-elastic, thermodynamically unstable biopolymer* consists of:

(1) *continuous phase*, formed by the elastic network of unsaturated lipids;

(2) *discontinuous phase* of solid crystals.

As a preliminary processing, the sample, initially solid, is carefully melted at a temperature of 75°C to "*destroy the crystallization memory*". The operating parameters are shown in Table 1.

Table 1.Operating parameters accessed in the physical separation of palm oil

No. crt.	Sedimentation method	Operating parameters			Separation stage (T)
		Time [h]	Temperature [ºC]	Angular speed [rpm]	
1	gravitational	12	35		1
		12	25		2
		12	15		3
2	centrifugal	3	35	3400	1
		3	25	3400	2
		3	15	3400	3

As a mode of operation, the separation in stages, following the ***olein path*** was adopted. For each separation step, two distinct products were obtained: (1) ***olein (O)*** - the separated liquid fraction at the top of the container: (2) ***stearin (S)*** - the crystallized solid fraction deposited at the bottom of the container. From the liquid phase (olein (***O1***)), a second sample is formed which is further separated.

To determine the density (***ρ***), the pycnometric method was chosen (fast and suitable for small amounts of sample), and to determine the viscosity (***η***), the Höppler method [9].

3.Results and discussions

The phenomenon of fractional crystallization and mechanical separation is a complex one, dependent on a series of mechanisms, in which an important role is played by the *fractional crystallization* of the solid from the liquid mass, with the formation of supermolecular networks and finally *lipid formulations*. The role of non-lipid elements (sometimes initiators of nucleation) is to change the nature of the interactions between structural components, being *plasticizing* and / or "*braking*" factors for the redistribution of triglycerides in various phases of the technological process. Although, a number of studies have been conducted in this field, the ***operating parameters*** remain the factors responsible for the functional directions directed for the resulting fractions. The evolution of physical separation techniques confirms that a monitored refrigeration coupled simultaneously with the *separation of phases by gravity and / or centrifugal force field*, can be an efficient, economical way to obtain new characters for the finished product.

The crude raw material and the obtained fractions (olein / stearin (lipid substitutes)) were physico-chemically evaluated. The obtained data were recorded in Table 2.

By going through the profile literature of the flow / separation / sedimentation models, in the field of unitary operations in the food industry, attempts were made to *predict / determine* the conditions of fractional crystallization. The operation covers all areas of sedimentation: laminar, intermediate and turbulent, conditions that allow the determination of the following parameters: (**a**) the d_S/d_O ratio for both forms of sedimentation; (**b**) critical diameters d_{cS}, d_{cN} for sedimenting particles. Under the imposed conditions, the sedimentation rates for the two particles and in both cases of fractionation, are equal ($w_O=w_S$). Below are calculation examples for the case of the first fractionation step, for both cases (gravitational and centrifugal), starting from the raw material, respecting the imposed conditions. Subsequently, the data obtained were centralized in table 3. Thus: (**1**) for the *laminar domain*, the d_S/d_O ratio is determined from the sedimentation rate according to *Stokes*' law; (**2**) for the *intermediate domain*, the d_S/d_O ratio is determined from the sedimentation rate according to the *Allen* equation; (3) for the *turbulent domain*, the dS / dO ratio is determined from the sedimentation rate after *Newton* [10-17].

Stokes	***Allen***	***Newton***
$\frac{d_{S1}^2}{d_{O1}^2}=\sqrt{\frac{(\rho_{O1}-\rho_{UP})}{(\rho_{S1}-\rho_{UP})}}$	$\frac{d_{S1}}{d_{O1}}=\left(\frac{\rho_{O1}-\rho_{UP}}{\rho_{S1}-\rho_{UP}}\right)^{\frac{0,714}{0,142}}$	$\frac{d_{S1}}{d_{O1}}=\left(\frac{\rho_{O1}-\rho_{UP}}{\rho_{S1}-\rho_{UP}}\right)$

Table 2. Comparative evolution of physico-chemical indicators for raw material (palm oil) and liquid / solid separates

Formulation operation	***separate (symbol)***	***Indicators***		***Separation steps***	***Sedimentation parameters***		
		d_{50}^{50} [g/mL]	**η** [Pa·s]		**time [h]**	**temperature [ºC]**	**angular velocity [rpm]**
Raw material	UP	0.8675	0.1068				
Gravitational sedimentation	O_1	0.906	0.03913	1	12	35	
	S_1	0.8865	0.04017				
	O_2	0.8960	0.03349	2	12	25	
	S_2	0.8813	0.03397				
	O_3	0.8764	0.02630	3	12	15	
	S_3	0.8805	0.02689				
Centrifugal sedimentation	O_{11}	0.8932	0.03517	1	3	35	3400
	S_{11}	0.9190	0.06362				
	O_{22}	0.8862	0.02717	2	3	25	3400
	S_{22}	0.9210	0.03230				
	O_{33}	0.8781	0.01653	3	3	15	3400
	S_{33}	0.8711	0.01925				

d_{50}^{50} – density; η- dynamic viscosity.

Table 3. Values obtained for the critical diameters from the conditions imposed for separation

Separation steps	**Sedimentation**													
	Gravitational							**Centrifugal**						
	d_S/d_O			$d_{cS} \cdot 10^{-3}$ [m]		$d_{cO} \cdot 10^{-3}$ [m]		d_S/d_O			$d_{cS} \cdot 10^{-4}$ [m]		$d_{cO} \cdot 10^{-4}$ [m]	
	Stokes	**Allen**	**Newton**	**Stokes**	**Newton**	**Stokes**	**Newton**	**Stokes**	**Allen**	**Newton**	**Stokes**	**Newton**	**Stokes**	**Newton**
1	1.423	1.554	2.026	12.445	326.175	9.825	259.875	0.707	0.805	0.5	5.79	153.153	7.28	192.654
2	0.636	0.568	0.405	5.04	132.363	6.81	178.8	0.51	0.656	0.26	4.14	109.5	3.66	97.02
3	1.12	1.15	1.251	11.37	300.76	4.873	128.89	0.732	0.677	0.536	7.571	200.277	4.232	114.345

The critical diameter for the sedimenting particles (***stearin*** (S) / ***olein*** (O)), are determined according to *Stokes* and *Newton*'s law (d_{cS}, d_{cN}), as follows:

Stokes	***Newton***
$d_{cS1} = 2{,}62 \cdot \sqrt[3]{\frac{\eta_{UP}^2}{\rho_{UP} \cdot (\rho_{S1} - \rho_{UP}) \cdot g}}$	$d_{cS1} = 69{,}3 \cdot \sqrt[3]{\frac{\eta_{UP}^2}{\rho_{UP} \cdot (\rho_{S1} - \rho_{UP}) \cdot g}}$
$d_{cO1} = 2{,}62 \cdot \sqrt[3]{\frac{\eta_{UP}^2}{\rho_{UP} \cdot (\rho_{O1} - \rho_{UP}) \cdot g}}$	$d_{cO1} = 69{,}3 \cdot \sqrt[3]{\frac{\eta_{UP}^2}{\rho_{UP} \cdot (\rho_{O1} - \rho_{UP}) \cdot g}}$

In the case of centrifugal force separation, it is necessary to replace the gravitational acceleration (***g***) with centrifugal acceleration (***a_c***), from the equations previously stated, as follows:

$$a_C = r \cdot \omega^2 ;\ \omega = \frac{2 \cdot \pi}{60} \cdot N$$

where: a_c – centrifugal acceleration, [m/s^2]; r – distance (radius) of the particle from the axis of rotation, [m]. The chosen values: r = 0,18 m; N – centrifugal speed. N = 3400 [rpm]; ω – angular velocity, [rpm]. ω = 3400 rpm was chosen

$$\omega = \frac{2 \cdot \pi}{60} \cdot N = 355{,}866\ [\text{rpm}]$$

$$\Rightarrow a_C = r \cdot \omega^2 = 0{,}18 \cdot (3400)^2 = 22795{,}31\ [\text{m/s}^2]$$

In the same calculation method the results are obtained for the other separation stages (T) (tab. 1), knowing that for each sedimentation stage, for the two separation modes, the physical properties of the separating suspension (ρ_m) are modified, thus: (1) for gravitational T2 $\rho_m = \rho_{O1}$, and for centrifugal $\rho_m = \rho_{O11}$ (tab. 2); 2. for gravitational T3 $\rho_m = \rho_{O2}$, and for centrifugal $\rho_m = \rho_{O22}$ (tab. 2). The viscosities are chosen in the same way (tab. 2). The results of the calculations are presented in Table 3. The sign (-), which appeared as a difference, resulting from the difference in density in steps 2 and 3 of separation, was neglected.

Comparing the evolution of the ratio of diameters and critical diameters, it results that the separation by sedimentation of stearin particles from the suspension mass, in both forms of separation (gravitational / centrifugal), takes place in the *laminar flow range*.

Overall, the experimental data obtained and the calculations performed, allow the formulation of the following statements regarding the differences of the sedimentation operation given by the nature of the forces acting on the two separates. To these are added the property of lipids to crystallize conditionally by the nature of triglycerides and the melting-solidification interval, as follows:

(1) the lipid mixture represents a complex system with multiple interactions due to the simultaneous presence of mono-, di-, triglycerides and the presence free fatty acids, which generate crystallized fractions;

(2) through the phenomenon of polymorphism, the presence of hydrogen bonds, Van der Waals type interactions, sedimentation, is manifested with restraint to the phenomena of gravitational field flow;

(3) the sometimes modest but still visible difference between the resulting values (tab. 3), between the lipid separates, lead to the idea that the appropriate choice of the separation parameters is decisive in the change in the desired direction of the product quality;

(4) obtaining high yields and efficiencies of separation by gravitational and / or centrifugal sedimentation can be achieved only by thorough research at the laboratory scale, research that allows later the formulation of behavioral predictions that can be transposed on an industrial scale, respecting laboratory constraints.

4. Conclusions

From the obtained data it confirms that the rheological behavior (manifested by the differentiated flow), proves to be responsible together with the operating parameters (temperature, duration, centrifugal separation speed) for the separation efficiency.

Most food products are *not ideal*, they are dependent on sedimentation on the hydrodynamic effort (flow, centrifugation, filtration, settling, melting-solidification, etc.). Viscosity as a common property of fluids opposes the flow of neighboring layers in relative motion (centrifugation, filtration, etc.), by inducing tangential stresses, depending on the thermodynamic state of the system.

It demonstrates that the separation by physical methods of a lipid system is a complex process in which the phenomena of flow, solid / liquid fractional crystallization, but also the technical performance of the accessed separation procedures are manifested simultaneously.

Compliance with Ethics Requirements. Authors declare that they respect the journal's ethics requirements. Authors declare that they have no conflict of interest and all procedures involving human or animal subjects (if exist) respect the specific regulation and standards.

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