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Study opportunities on using the natural lipid substitutes resulted by dry fractionation in obtaining bakery products (bread)

Georgiana Felicia Bustan[1], Oana Maria Costar[1], Adela Nistorescu-Mihalca[2], C. G Fora.[1], A. Riviș[1], P. B. Rădoi[1], A. Rinovetz[1*]

[1]1Banat's University of Agricultural Sciences and Veterinary Medicine "King Michael I of Romania" from Timisoara, Faculty of Food Engineering, 300645-Timisoara, Romania, CaleaAradului 119, Romania, Phone: +40-256-277327; Fax: +40-256-277261
[2]SC Prospero SRL, Str. Luncani 24, Timisoara, Romania, Phone: +40 256 219 644

Abstract

The elaboration of lipid products with colloidal properties, ***structurally and functionally*** modified, other than the starting base, with structural role in the integrated product and by micellar carriers in ensuring the health status, is relatively recent, being the result of accepting the idea that: the food has determinant role in the prophylaxis and therapy of certain conditions. The paper addresses two aspects: **1**- ***methods of lipid modification*** (simple mixing, hydrogenation, inter-esterification, ***fractionation***), continuously optimized, by scientific understanding of the physico-chemical-colloidal processes. In general terms "***fractionation***" describes the processes of ***fractional crystallization of triglycerides*** (with the major influence parameters represented by duration and temperature), from a lipid mixture, in order to eliminate structures with high melting range and their ***mechanical separation***; **2**- ***integration of some lipid fractions (oleins)*** in the manufacturing process of bakery products (bread) on a classical technology. In a narrow sense, ***dry fractionation*** is the process by which natural or already modified oils and fats are separated into *solid/liquid* (***stearine***/***olein***) fractions. The main qualitative-sensorial and physico-chemical aspects of the oils were evaluated as integrated axillary material, with collidal properties and the finished product (bread), which allows the final conclusions to be drawn favorable or not, to the variants of the analyzed samples, based on a selective specialized study, and finally proposed technological flow. The bibliographic study allowed the synthesis of new conclusions and the elaboration of new ideas that fit in the area of food engineering concerns.

Keywords: natural lipid, unit operation, lipid modification, fractional crystallization, dry fractionation, bakery products.

1.Introduction

The *common property* of lipids is *solubility*. However, there are many problems to be fully defined. The *FDA* modified the definition of lipids based on solubility as a common property, with - "*total lipids of higher organic acids expressed as triglycerides*" - to determine the *caloric index*, because the solubility and size of the hydrocarbon chain of the higher organic acids directly influence the data [1]. Lipids are of great biological value as component parts of foods, which, by their physico-chemical properties (reactivity, structure and energy equivalent of approximately 39 kJ / g of fat), give them *nutritional, organoleptic and textural qualities*, which particularize numerous food products. In most cases, lipids, in addition to the role of *transmembrane transporters* in the biological functions of the cell, also have a technological role for all organic and inorganic components [2].

The major sources of dietary fat are *vegetable oils* and *animal fats* (pork lard, fish, beef, sheep, etc.). The *functional-structural specificity* of lipids in the human body determines a differentiated diet and contributes in a complex system to the overall metabolism of all the nutritional constituents.

Corresponding address: alexandrurino@yahoo.com

Lipid polymorphism, the morphology of the crystalline structure and the mode of micellar aggregation, can lead to a modification of the structure of the crystalline network, which results in changes in the rheological properties ("*hardness*").

Researches on the conditions for the modification of the "*hardness*" of lipids have shown that ***dry fractionation modification***, induces the modification of the polymorphic structure and viscosity [3].

Hippolyte Mège Mouries, (**1869**), is considered the *pioneer* of the process of ***dry fractionation*** of animal fat, based on the assumption that "*butterfat should be found in animal fat*". By fractionating the beef broth, he obtained a layer of liquid fat, which he called *oleo-margarine* or *tallow olein*. After mixing this lipid fraction with the skimmed milk, a solid product called "*economic butter*" followed, and later "*MOURIES margarine*" [4, 5].

The ***dry fractionation*** process *induces modifications / formulations* of the physical properties of the raw material (lipid mixtures), lipid fractions, or the finished product.

By ***fractional crystallization***, fats may be enriched in certain triglycerides, or unwanted components may be removed. This process can also be used to remove fractions of saturated triacylglycerides or rich in high melting *trans* isomers. For the separation of the solid fractions with a fine microcrystalline structure, the cooling process is closely monitored, as it is associated with crystallization over limited temperature ranges [6].

Dry fractional crystallization is the ***simplest and most economical*** process of separation on ***green principles*** (***physical process***), as opposed to the fractionation with detergent or solvent, because substances with a toxicogenic potential are not involved, which subsequently require laborious removal procedures. The process consists in the ***controlled crystallization of the oil or fat*** melt, by carefully *monitoring the cooling temperature*, followed by the ***mechanical / physical separation*** (***gravitational / centrifugal sedimentation***) of the solid fraction (***stearin***) from the liquid (***olein***).

The ***dry fractionation*** process for a natural lipid mixture can be structured as presented in Figure 1.

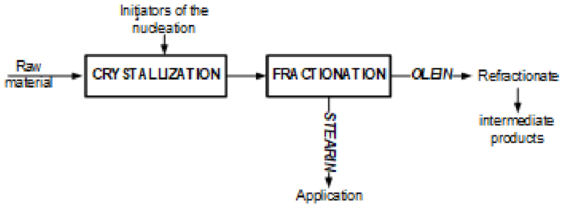

Figure 1. General block diagram of ***dry fractionation*** of natural fats and oils.

Current techniques allow ***modification / correction*** of one or more characteristics of natural lipids so that they become nutritionally and / or functionally appropriate to a particular purpose / product ("tailor-made lipids" or "designer lipids"). Obviously, the products resulting from these transformations may differ significantly from the initial sources [7].

The main objectives for the modification of oils and fats are: **1**. to obtain products with intermediate physico-chemical characteristics that are not present in the structural range of natural fats (stronger or softer, with faster or slower melting, modified color, etc.) ; **2**. obtaining a product similar to the existing one, but at a reduced price; **3**. oxidation stability; **4**. optimizing palatability; **5**. expanding the assortment of nutritionally superior products by reducing saturated higher acids, trans isomers and increasing the concentration of polyunsaturated ones [7,8].

In ***practice***, *dry fractionation* accesses three variants of different fractionation operations based on the association of crystallization and separation: **1**. winterization (crystallization of the solid fraction, followed by gravitational separation under refrigeration conditions); **2**. dewaxing (variant of winterization, aims to eliminate small quantities of waxes from vegetable oils rich in unsaturated higher acids resulting in liquid fractions with a high degree of clarity at low temperatures); **3**. pressing (separating the fluid fraction from the solid one by means of pressure). The resulting fractions were referred to as "***humanized***" or "***de-stearized***" fats [7].

The advantages of the dry fractionation process are: **1**. *natural process* (without the addition of additives, chemicals or solvents); **2.** *reversible* (physical process without molecular changes); **3**. "***green***" (non-polluting, without waste); **4**. *maintaining organoleptic properties* (taste, aroma); **5**. *economic*.

*Due to the versatility of the **dry fractionation process**, in the current practice we find a wide range of applications of this operation on the basis of natural lipids and synthesis*.

The classic bread-making technology involves five phases: **1**. receiving and storing raw and auxiliary materials; **2**. preparation of raw materials and auxiliaries before the actual manufacturing technology; **3**. dough preparation; **4**. dough processing; **5**. baking; **6**. cooling / storage / delivery of finished product. For the preparation of the dough, two variants can be technologically adopted: a. *direct* by simultaneously mixing all the components and obtaining the dough, followed by fermentation, portioning and baking; b. *indirect* - it involves obtaining the dough in two or three phases, followed by fermentation, portioning and baking (1. preparation of leaven and dough; 2. preparation of leaven, dough or preparation of "*fresh-dough*") [9, 10, 11,12].

By the ***indirect method***, better quality bread is obtained (with pleasant taste and odor, well developed porosity core with thin-walled pores). The resulting dough presents a greater technological flexibility, being able to intervene during the manufacturing process to remove any mistakes. *Advantage*: use of a small quantity of yeast. *Disadvantage*: the increase in the number of technological operations and machines (dosing, kneading and fermentation repeating with each preparation), the increase of the manufacturing cycle, due to the increase of the total duration of fermentation.

Through the ***direct method***, the manufacturing process is simplified, reducing at the same time, the number of machines (especially tanks, mixers). It also reduces the manufacturing cycle. *Disadvantages*: obtaining lower quality bread (due to improper taste and core structure, as well as increased yeast consumption).

Materials and methods

The study proposes the *use / integration in the classic bread making process*, of ***structured lipids (oleins)***, from pork lard, *fractionated dry in a centrifugal force field*. The preliminary pork lard was melted at 65°C, brought to room temperature and intensively homogenized, followed by dry fractionation (fractional crystallization and mechanical separation (centrifugal)). The fractionation operation was conducted in two stages according to the proposed technological scheme for which the speed (3400 rpm) and duration (175 min) were kept constant and the duration varied (figure 2). In order to obtain the bread with the addition of ***olein*** as a result of the ***dry fractionation*** of the lard, the ***direct method*** (without leaven) was chosen. Other materials: flour, water, yeast, salt, sugar, olein figure (Figure 3). Reagents (Sigma-Aldrich, Merck) of analytical purity.

Results and discussions

Preliminary tests for the separation of pork lard have led to the observation that the operating parameters have a decisive influence on the efficiency of dry fractionation. The centrifugal separation leads to the formation of two distinct phases: *upper fluid* ("*oily*" - ***olein***) yellow and *lower solid* (***stearin***), with high viscosity. It can be admitted with sufficient accuracy that the two phases belong: the upper one (***olein***) - mostly unsaturated lipid fractions, fluids / liquids, and the lower one respectively (***stearin***) - mostly saturated lipids, crystallized solids. Based on these preliminary observations and after setting the operating parameters (figure 2), the actual fractionation of the pork lard was started, accessing two fractionation stages, according to the scheme proposed in figure 2. Finally from the basic material (pork lard) resulted in two oleins (***olein I, olein II***) and two stearins (***stearin I, stearin II***). From the observations generated by the determination of some physical-chemical quality indicators, both for the pork lard and for the resulting ***liquid fractions (oleins)***, we can say that each oleic fraction has different properties (Table 1).

The resulting values represent technological benchmarks that can monitor the fractionation operation itself in the direction of obtaining (separating) the lipid assortment required by the subsequent food technology practice and the current technological progress requires and demands new directions for valuing the functional potential of the resulting lipid fractions.

Based on these considerations, as well as the study in the literature, the aim was to ***integrate oleins*** as an emulsifier in the process of making white flour bread in a *direct system* (without maia). As a comparative model, we went to the manufacture of bread samples without and with refined sunflower oil, marketed. Sensory analyzes were performed on the resulting samples and geometric and physical parameters were determined: length (L), width (l), height (h), volume (V), mass (m) density (ρ). The data are subsequently corroborated with the physico-chemical indicators of the olines. Figures 4 and 5 show the bread samples in the following order:

- ***Sample A** – basic recipe without lipid addition* (m = 990 g);
- ***Sample B** – with the addition of commercially refined sunflower oil* (m = 1020 g);
- ***Sample C** – with the addition of olein I* (m = 1024 g);
- ***Sample D** – with the addition of olein II* (m = 1028 g).

Sensory analysis of the samples was carried out using the *dot-scale method*, by questioning 10 people who examined organolepticly from each sample (external appearance, interior, consistency and behavior at chewing, smell, taste, color) whose conclusions were recorded in the table and interpreted comparatively by the graphical method.

The results of the sensory analysis (arithmetic mean and maximum score) are presented in Table 2 and Table 3 and graphically interpreted, comparatively, in Figure 6.

Figure 4. Bread samples.

Figure 5. Presentation of bread samples in section.

The results of the sensory analysis show that the bread samples to which the sunflower oil ***(sample B), olein I (sample C) and olein II (sample D)*** were added, showed a maximum sensory score of admissibility decreasing from 17.5 ÷ 11.4.

The assortments of breads ***fortified with olein***, proved to be on the limit of sensory admissibility, obtaining less than ***14*** points for sample ***D***.

The defects of sensory quality were due to the modified taste and smell induced by the strong self-oxidation processes characteristic of lipids. From the values of the quality indicators determined for oleins, we can observe a correlation of those of acidity (***AI***) and iodine number (***CI***), with the characteristic taste and odor of the auto-oxidation processes due to the presence of the free higher organic acids and the increase of the unsaturation degree of oleins. However, from the sensory characterization it can be observed that the sample ***D*** received a maximum score compared to the other samples and a satisfactory puncture related to the external aspect compared to the measurable dimensions, resulting: length (**16.5 cm**); width (**11.5 cm**); height (**13 cm**). We can say that the two lipid fractions (olein I and II), integrated in the manufacturing process, exert influence on the geometrical and physical growth parameters. It also correlates with the masses, respectively the densities of the analyzed samples (table 2). The density of samples ***C*** and ***D*** decreases, correlated with the increase in the volume of samples, especially differences in samples with olein.

This demonstrates that the studied lipid colloidal system (oleins), plays a major role in the formation of the gluten structure, affirmed also by the sensory values recorded for the inner aspect, consisting of the increase of the porosity of the core (maximum registering for sample ***D***), but the rancid odor persists. An important factor and not to be neglected, is the *polymorphic* form in which the lipid system crystallizes, as well as their stability due to the different heat treatments along the processing path. The geometric shape of the lipid crystals can also induce the growth of the bread through the conjugated action on the gluten network.

These statements are also supported graphically (Figure 6). For color, a gradual decrease of the score granted to this parameter is observed, which can be explained by the baking time, which for samples ***C*** and ***D*** (with ***olein***), was not sufficient. Probably this shortcoming can be corrected by extending the baking time. The strong odor of rancidity, which is minimal (score ***1.15***) for sample ***D***, is also accentuated by the heat treatment of the baking operation, since the high temperatures favor the degradation of the lipids resulting in aldehydes with characteristic odor of rancid.

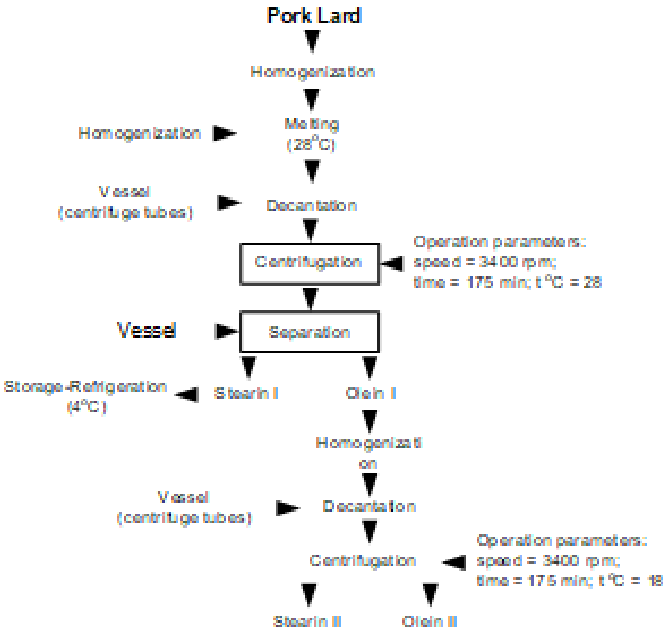

Figure 2. Block diagram of dry fractionation of pork lard

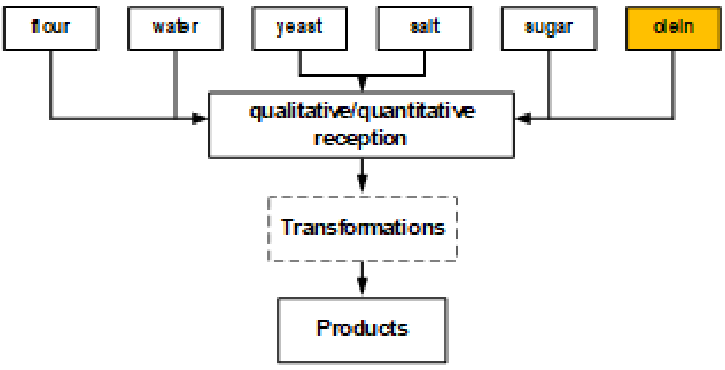

Figure 3. Proposed block scheme for the manufacture of bread with the addition of olein from pork lard

Table 1. The values of the physical and chemical indicators corresponding to the analyzed samples (average values)

Crt.no	Physico-chemical characteristics	M. U.	Pork lard	Olein I	Olein II
1	IA[1)]	[mg KOH/g]	2.2	0.22	0.3
2	IS[2)]	[mg KOH/g]	198.2	198.7	197.2
3	IE[3)]	[mg KOH/g]	196	198.4	196.9
4	CI[4)]	[g I_2/100 g]	79.82	63.2	64.52
5	Color index [5)]	[mg I/100 mL]	4	5	7
6	Melting range [6)]	[°C]	35.7	28	18
7	Solidification interval [6)]	[°C]	29	8	6.5
8	Water[7)]	[%]	0.9725	0.0816	0.0822
9	(n_D^{50})[8)]	-	1.4492	1.452	1.466
10	d_{40}^{40} [9)]	[g/mL]	0.9070	0.9142	0.9094

[1)] AI – acidity index; [2)]IS – saponification index; [3)]IE – ester index; [4)]CI – the iodine value (Wijs method); [5)] Color index at t=50°C; [6)] the average value of the initial and final melting / solidification interval; [7)] drying in the oven; [8)] n_D^{50} – refractive index determined at 50°C; [9)] d_{40}^{40} - density, at the temperature of 40°C.

Table 2. The results of the sensory analysis as arithmetic mean and the maximum score for the bread samples analyzed

Feature evaluated	Average score			
	Sample A	Sample B	Sample C	Sample D
Exterior shape and appearance	3.05	3.05	1.85	2.45
Interior appearance	2.55	2.5	2.75	3
Consistency and behavior in chewing	2.6	2.75	2.15	1.55
Smell	2.8	2.9	2.45	1.15
Taste	3.25	3.3	2.95	1.4
Color	2.9	2.9	2.5	1.85
Max points	17.5	17.4	14.65	11.4

Table 3. Geometrical and physical characteristics

Sample	Geometric feature			Physical feature		
	length (L) [cm]	width (l) [cm]	height (h) [cm]	volume (V) [cm^3]	mass (m) [g]	density (ρ) [g/cm^3]
A	15.5	11.5	12	2139	990	0.4628
B	16	12	11.5	2208	1020	0.4619
C	16	11.5	12.5	2300	1024	0.4452
D	16.5	11.5	13	2466.75	1028	0.4167

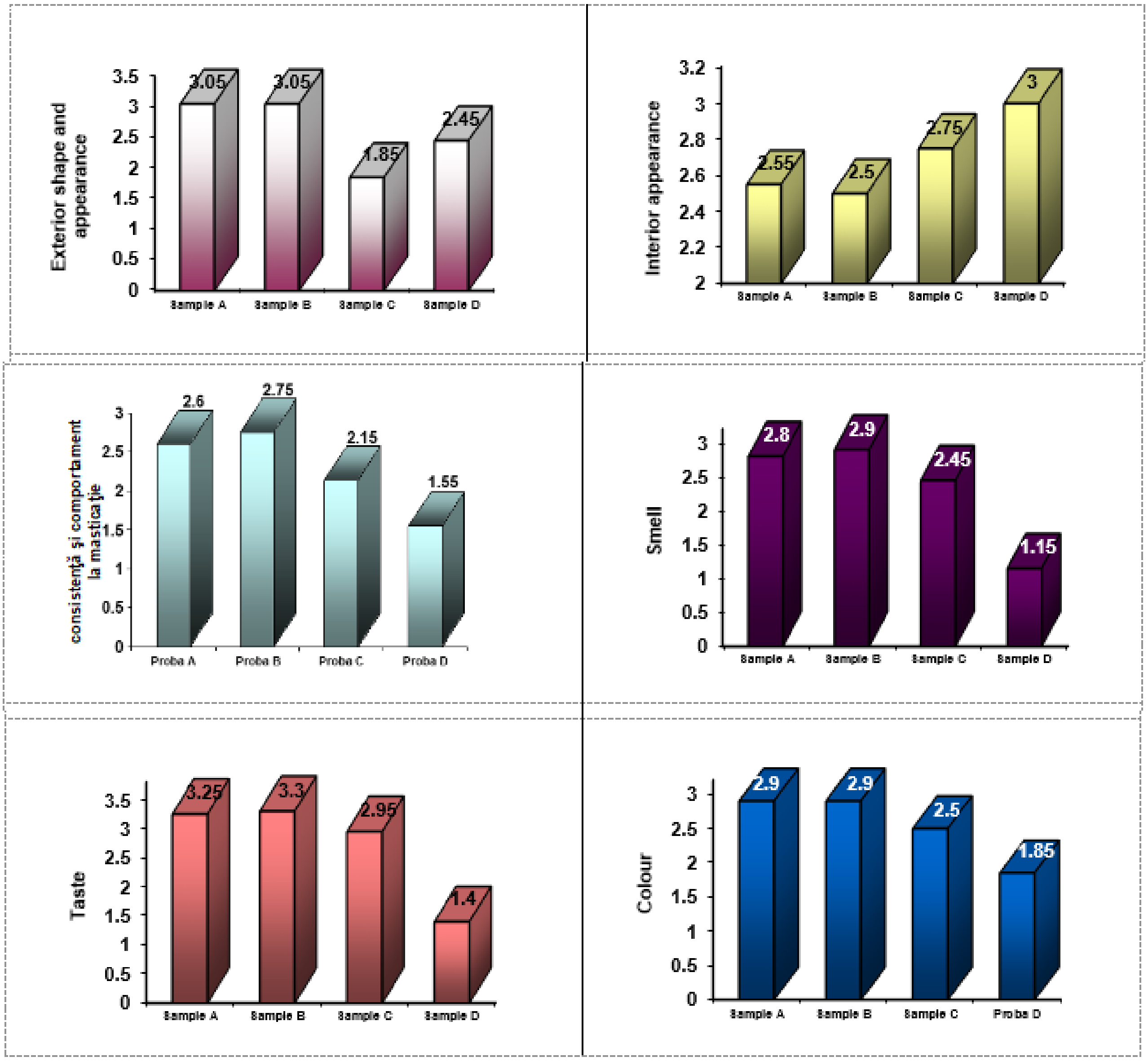

Figura 6. Comparative values for the evaluated sensory characteristic

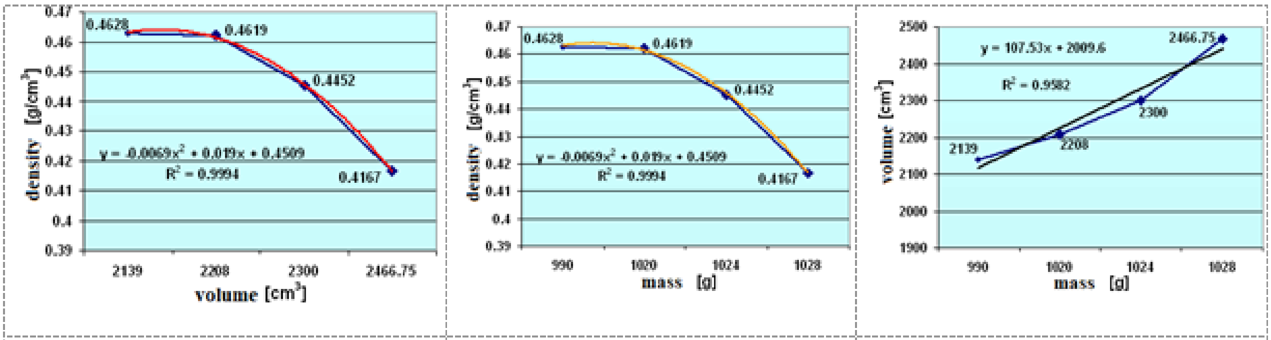

Figure 7. Comparative evolution of geometric and physical parameters for the studied samples

We can say that, besides the quality of the materials entered in the system, the time / temperature parameter, is a determining factor in obtaining food products with ***modified lipids***, more easily digestible by the body. The accessed lipid system (***oleins***), by its character, can be a factor of transport of nutritional biological utilities integrated in the micellar matrix.

In order to verify the hypotheses previously formulated, in the case of the evolution area of the geometric and physical parameters (volume, mass, density), their mathematical-graphical interpretation of the experimental data was resumed (figure 7), which confirms the correctness of the hypotheses previously formulated by the high values of of the linear correlation coefficient R for the volume dependence of the sample mass and parabolic for the dependence between density / volume and density / sample mass. In all three cases, the correction coefficient R is very close to the unit.

4. Conclusions

New trends in the field of *food diets* require a mutual response from food technologies, which have a common basis: excessive urbanization and new stressors generated by it, for which the human body cannot emit an effective immune response. This has led to the introduction of new "***green***" processing technologies to obtain "*more humanized*" raw materials, with beneficial effects on the body. The paper highlights the importance of the controlled/monitored physical changes, with an important role in reformulating the natural lipid mixture with direct influence on the final characters of the finished product (bread).

The topic addressed is one of actuality and perspective, with real impact on the development of new foods with health benefits and by integrating lipid systems with functions other than the basic material. This requires a careful physical-chemical "*structural*" approach, for a better knowledge of phenomena and new characters, conditioned by the structural elements of the food matrix. The data obtained must be correlated with the action of the *processing parameters* specific to the technological, sequential operations, which form the process as a whole.

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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