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FOOD COMPOSITIONS BASED ON WALNUT OIL (*Juglans regia L.*) RESISTANT TO OXIDATIVE DEGRADATION

253.06 - BIOLOGICAL AND CHEMICAL TECHNOLOGIES IN THE FOOD INDUSTRY

Summary of the doctoral thesis in technical sciences

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The doctoral thesis and the summary can be consulted at the the library of the Technical University of Moldova on the National Agency for Quality Assurance in Education and Research website (www.anacip.md).

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CONCEPTUAL ELEMENTS OF THE RESEARCH

Nowadays, the concept of a balanced diet from the point of nutrients content is scientifically argued and influences the policy of European countries in the field of improving the quality of population life. One of the most effective ways to ensure healthy nutrition is to apply foods and food supplements rich in bioactive compounds as widely as possible. We stand out foods fortified with essential polyunsaturated fatty acids among different types of functional products.

Important theoretical and practical assessments, regarding the fact that essential polyunsaturated fatty acids have a beneficial effect on human health, have conditioned to conduct the investigations of the selection of natural sources of lipids, rich in biologically active compounds, in order to use them in food compositions.

Walnut oil is a quality final product, competitive on local and foreign markets, with an increased biological value due to the concentration of essential polyunsaturated fatty acids ω-3, ω-6 higher than 70g / 100g oil [1]. Modern trends are oriented towards the use of walnut oil in alimentation in various forms of food compositions of vegetable and animal origin. But due to the lack of specialized technologies for processing nuts into finished foods and methods to prevent their degradation, currently, it is produced only walnut kernels and relatively small quantities of walnut oil in the Republic of Moldova [2].

The storage and use of lipids in the form of walnut oil is a complex technological problem due to the irreversible oxidative changes of polyunsaturated fatty acids. Thus, this resulted in the fact that walnut oil is practically not used for obtaining new quality foods. Extending the shelf life of walnut oil will help to expand the range of food products. It will lead to the increasing of nuts volume production, stimulate the development of the food industry, and attract new investments. It is also assumed that the health of the citizens of the Republic of Moldova will improve due to the amelioration of their diet with polyunsaturated fatty acids [3, 4].

Because of the above, it was planned to conduct scientific research in order to obtain new knowledge about the physicochemical, functional properties of walnut oil, the use of this oil in the elaboration of compositions and processes of new final products.

Based on these facts, the purpose of the work is the realization of theoretical and experimental research in order to elaborate food compositions of W/O emulsions type based on walnut oil, ensuring the stability and high biological value of the final product.

The need to prevent the process of oxidative degradation of polyunsaturated fatty acids is one of the most complicated problems related to ensuring the stability of food compositions based on walnut oil. The following scientific hypothesis was formulated to contribute to the solution of this problem:

- *the oxidation prevention of walnut oil polyunsaturated fatty acids in food compositions can be ensured by the formation of W/O emulsion with a determined ratio between polyunsaturated and saturated fatty acids.*

To achieve the research purpose and to verify the scientific hypothesis, the following **objectives** were formulated:

1. The determination of possible ways to prevent the oxidative degradation of walnut oil polyunsaturated fatty acids in food compositions;
2. The influence evaluation of saturated and unsaturated fatty acids on the stability and texture of food compositions with walnut oil;
3. The analysis of antioxidants impact on the prevention of oxidative degradation of polyunsaturated fatty acids in walnut oil;
4. The elaboration of composition and technology for obtaining new foods in the form of W/O emulsion, as *spread*, based on dairy products and walnut oil;
5. The evaluation of nutritional value and physicochemical properties of spreads with walnut oil;
6. The establishment of shelf life and optimal storage period of the final product.

The research methodology includes a series of analytical, instrumental procedures and techniques for determining the quality indicators of lipid compositions.

Scientific novelty and originality. For the first time, it was scientifically argued and experimentally demonstrated the possibility of the prevention of oxidative degradation of walnut oil polyunsaturated fatty acids in food compositions by the combination of walnut oil lipids and dairy fats in the form of emulsions.

The solved scientific problem includes the determination of the most important physicochemical, nutritional, and technological properties of compositions based on walnut oil and the identification of optimal and efficient conditions for their technological processing and use.

The theoretical significance consists in improving the research methods of walnut oil quality, obtaining the scientific results that demonstrate the possibility of stabilization of lipid compositions with a high content of polyunsaturated fatty acids and the formation of functional foods based on them.

The applicative value of the work consists in arguing the methodology of walnut oil using for the obtaining of various food products with a high content of polyunsaturated fatty acids, especially in food compositions of emulsion type.

Implementation of scientific results. The results of the scientific research were published in journals listed in Scientometric databases, in collections of symposia, and were discussed during debates at national and international scientific conferences. Invention patent No.1281 „*The method of obtaining the mix of spreadable fats based on sweet cream*” was obtained.

Approval of results. The main results of the thesis were communicated and discussed at national and international scientific conferences and symposia such as technical-scientific conferences of collaborators, doctoral students, and students, Chisinau (2014, 2019); international conference „Modern Technologies in the Food Industry”, Chisinau (2018); international scientific conference of young scientist and students, Kyiv (2016, 2017); international scientific conference of young scientist and students, Mogilev (2016); international scientific and practical conference „Biotechnology: experience, traditions and innovations”, Kyiv (2016, 2018); national symposium „Creation opens the Universe”, Chisinau (2015-2018); international symposia and invention fairs: „EURO INVENT-2018”, Iasi, Romania; „PRO INVENT – 2019”, Cluj-Napoca, Romania; „INFO INVENT – 2019”, Chisinau.

The most relevant results of the thesis were presented in the national magazine „Journal of Engineering Science”, Chisinau (2019, 2020) and recognized foreign magazines „Journal of Food and Packaging Science, Technique and Technologies”, Plovdiv (2016) and „Ukrainian Food Journal”, Kyiv (2019).

The results of scientific research were also discussed and presented in the reports of the national project 5.817.02.30A „Methodological and technical developments for the modernization of walnut processing technology (Juglans regia L.) with the use of biologically active components in functional foods” and the international one, supported by the World Scholarship Program of the World Federation of Scientists based in Geneva, Switzerland.

Summary of thesis compartments. The work consists of four chapters. The first part represents the review of the literature, the analysis of the current state of the thesis topic issue. The second chapter includes a brief description of the materials and methods of analysis. And there are obtained scientific results and their analysis presented in chapters 3 and 4. The thesis concludes with practical conclusions and recommendations.

Keywords: polyunsaturated fatty acids, antioxidants, dairy fats, food emulsions, spread.

THESIS CONTENT

1. Walnut oil - nutritional and technological aspects

The first chapter represents the analysis of bibliographic sources and aims at the most valuable achievements regarding the development of manufacture technologies of food compositions based on walnut oil stable to oxidative degradation.

By studying the characteristics of walnut oil, it has been shown that it has healing properties and is of great interest for use as a lipid base for the formulation of W/O type food emulsions with increased biological value. Lipid oxidation is one of the most important processes of the deterioration of lipid-containing foods. This process can be inhibited both by antioxidants and by the formation of lipid compositions with a determined ratio between unsaturated and saturated fatty acids. At the end of the first chapter, the purpose and objectives of the research are formulated.

2. Research materials and methods

Chapter 2 characterizes raw materials used for the research, methods for determining the physicochemical, microbiological, and technological indices, as well as the methodology of statistical processing of experimental data.

The main objects of study are the samples of walnut kernel oil („Cogalniceanu” and „Calarashschi” varieties) from the harvests of 2014-2018, obtained by cold pressing in industrial and laboratory conditions [5], as well as food emulsions (spreads) based on them [6]. Different dairy and vegetable products, purchased in the commercial networks of the Republic of Moldova, and auxiliary components (antioxidants, saturated fatty acids, lecithin emulsifier), approved for use in food [7], were used for the research of physicochemical, structural, and sensory properties of experimental samples, as well as for the technological elaborations.

Standard methods, approved for use in the food industry, and modern instrumental methods of analysis (gas chromatography at „Kristallux4000M”, IR spectroscopy at „SPECORD M-80”, UV-Vis spectroscopy at „HACH-LANGE DR-5000”, instrumental test for accelerated lipid oxidation at „892 Professional Rancimat”, and the CIELab method at the colorizer.org program), were used in the experimental research.

The analysis of the microstructure of the W/O emulsions was performed using the „Biolam” and „Motic DMB 5-5” optical microscopes (with a digital camera). The assessment of the sensory properties of the experimental samples was performed by tastings [8].

Various mathematical methods for analyzing experimental data were applied in the research, including the Box-Hunter method (Full Factorial Experiment with two and three factors, FFE 2^2, and FFE 2^3) [9]. The construction of state diagrams of ternary compositions also refers to mathematical methods. The research results were processed using statistical methods [10].

3. Physico-chemical stability of walnut oil

Chapter 3 describes the particularities of walnut oil obtaining and presents the results of the analysis of its quality and chemical composition. The stability of walnut oil to oxidative degradation is analyzed depending on the influence of the following factors: natural antioxidants („in situ” extracts of carrot and green tea leaves), synthetic antioxidants (octyl gallate, ascorbyl palmitate, DL-α-tocopherol), water and saturated fatty acids.

3.1. Physico-chemical characteristics of walnut oil

The main object of the research was the oil obtained by the cold pressing of walnuts of the „Cogalniceanu” variety. In-shell walnuts were broken by hand, the kernels were removed and crushed. The oil was separated from chopped walnuts under the action of a gradually increasing external pressure (from 5 to 50 MPa) so that the temperature didn`t exceed 27°C [11]. The yield of extracted walnut oil was 40.7 ± 1.4%.

Walnut kernel lipids have a low content of saturated fatty acids (9.18%), and polyunsaturated fatty acids make up almost 83% of total fatty acids (Table 1). The walnut oil obtained in the research is considered fresh, as its peroxide index is much lower than the maximum permissible value (3.30 ± 0.13 mmol/g oil), and the aldehyde content is insignificant (0.53 ± 0.09 c.u.).

Tab.1. The polyunsaturated fatty acid composition of walnut kernel oil, “Cogâlniceanu” variety, 2015 harvest, determined by gas chromatography, P > 99,9%

Name of fatty acids	Mass fraction of fatty acids, %
C 18:2 (linoleic), ω-6	11,62
C 18:3 (γ-linolenic), ω-6	61,98
C 18:3 (α-linolenic), ω-3	8,88
C 20:2 (eicosadienoic)	0,20
C 20:3 (eicosatrienoic), ω-3	0,03
C 22:2 (cis-13,16-docosadienoic)	0,23
Total	**82,93**

It was observed that the quality of walnut oil correlated with the parameters of the IR spectra, and the signals, which confirm the change in the quality of walnut oil, were manifested in the samples with a short shelf life. The peaks of functional -C–O- groups of the superior aliphatic ester (at 1100 cm^{-1}, 1170 cm^{-1} and 1230 cm^{-1}), characteristic only for oils, were highlighted, as well as peaks of terminal $-CH_3$ groups (at 1395 cm^{-1}), which depend on the content of C:18 chain fatty acids and can serve to confirm the identity of oil compositions.

It is known that the lipid self-oxidation mechanism includes chain reactions, which are initiated by the formation of radicals by releasing the hydrogen atom from the methylene group ($-CH_2-$), adjacent to the double bond of unsaturated fatty acids [1]. The formation of peroxides and hydroperoxides occurs by fixing the oxygen molecule to the radical (-CH●-) of the unsaturated fatty acid chain and the addition of the hydrogen atom to the peroxide radical (Figure 1).

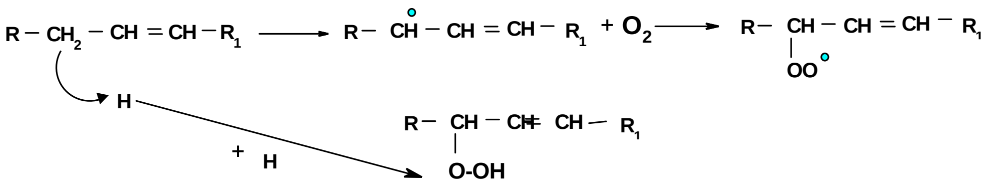


Fig.1. Schematic presentation of peroxides and hydroperoxides formation

For these reasons, the intensities of the absorption bands of the $-CH_2-$ group in the oil spectrum should reduce at oil peroxidation, while the signals of the -CH= group, for example, ν_{C-H} at 3010 cm^{-1}, should remain intact. By converting the values of transmittances (T) into optical densities (absorbances, A), the ratio A_{3010} / A_{2920} (Figures 2, 3) was calculated for walnut oils (WO) with a different period of storage:

- for WO $_{\text{freshly pressed}}$: $\frac{A_{3010}}{A_{2920}} = 0{,}562;$
- pentru WO $_{\text{2 months}}$: $\frac{A_{3010}}{A_{2920}} = 0{,}621.$

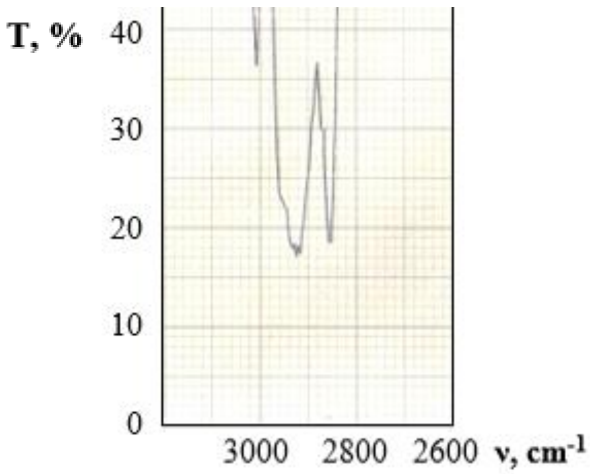


Fig.2. Fragment of the IR spectrum of the WO $_{\text{freshly pressed}}$: valence oscillations of C-H bonds

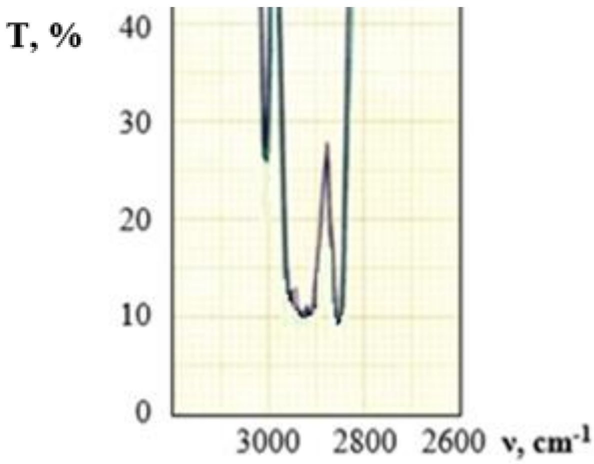
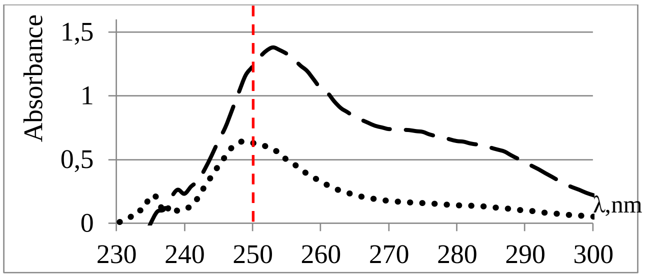


Fig.3. Fragment of the IR spectrum of the WO $_{\text{2 months}}$: valence oscillations of C-H bonds

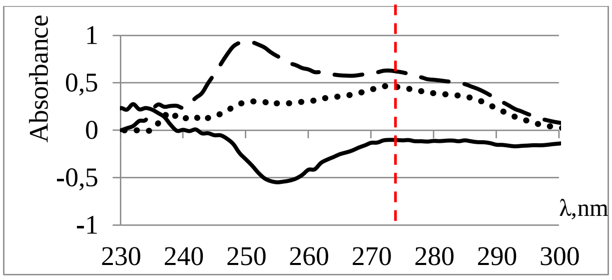
We consider that these differences in absorbance values could serve to determine the degree of walnut oil freshness, because the ratio of optical densities A_{3010}/A_{2920} increases as a result of the oil oxidative degradation.

The degree of freshness and, in general, the quality of the walnut oil can also be determined by the analysis of its UV-Vis spectra, especially by calculating the differences between the spectra of walnut oils (WO) with different period of storage and between walnut oil and sunflower oil (SFO). Thus, spectra similarity of oils, with a certain period of storage, was observed in the 240-270 nm wavelength range (Figure 4). It may indicate oxidation or another type of degradation of vegetable lipids.



WO industial – WO TUM
WO TUM (1 year) – WO TUM (fresh)

Fig.4. Differences between the spectra of walnut oils (1:80 dilution, solvent and reference - chloroform)



WO industial – SFO
WO TUM (fresh) – SFO
WO TUM (1 year) – SFO

Fig.5. Differences between the spectra of walnut oils and sunflower oils (1:80 dilution, solvent and reference - chloroform)

The spectra of walnut oils obtained industrially by local producers are similar to the spectra of walnut oil obtained at TUM and kept one year in darkness at (3 ± 2)ºC (Figure 4). These spectra show a higher absorbance than the spectra of freshly obtained walnut oil at 250 nm wavelength, which may indicate that the oxidative degradation of the respective lipids has taken place. The peak, characteristic for sunflower oil and commercial walnut oils, was observed at 275 nm wavelength (Figure 5), which may mean that technological processes, other than the cold pressing, were applied to obtain these products.

We consider that the UV-Vis spectroscopy method can serve both for the post-factum identification of the technologies based on which the oil batches were produced and for highlighting some signs of vegetable lipids degradation. It is a prospective research method of the quality of virgin oils, but it needs further development.

3.2. The analysis of walnut oil stability in the presence of natural antioxidants

The full factorial experiment (FFE 2^2) was planned to analyze the stability of walnut oil in the presence of oily extracts from carrot (16.52 mg/100g oil of β-carotene, X_1 factor) and green tea leaves (95.71 mg / 100g oil of chlorophyll „a", X_2 factor).

Based on the obtained extracts, three series of samples were formed, A and B series – mixtures of walnut oil and natural antioxidants in different proportions (Table 2) and C series – control – without walnut oil. Sunflower oil served as a background in composition formation.

Tab.2. Proportions between the components of lipid compositions

Nr. of exper./ Factor	Oily extract of β-carotene, ml		Oily extract of green tea, ml		Walnut oil „TUM", ml	Sunflower oil, ml	Total, ml
B 1	+	1	+	1	6	2	10
B 2	+	1	-	0,5	6	2,5	10
B 3	-	0,5	+	1	6	2,5	10
B 4	-	0,5	-	0,5	6	3	10

The spectra change dynamics were studied over a month. The peak at 269 nm wavelength (Figure 6), which suffers essential changes while storing the walnut oil, was selected from the spectra of the series.

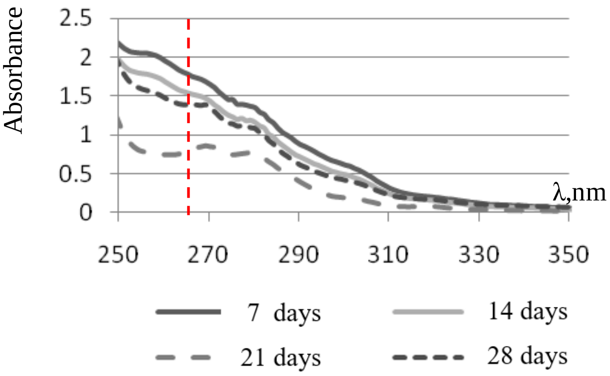


Fig.6. Spectra of compositions of vegetable oils fortified with biologically active compounds, B1 series

The kinetic curves of obtained lipid compositions were constructed in the coordinates $A_{269} = f(\tau)$ in order to determine the influence coefficients (Table 3), which can quantitatively characterize the influence of lipid extracts of antioxidants on the stability of walnut oil.

Thus, the stability of the compositions is observed in the first two weeks of storage, representing a period of lipid stabilization with natural antioxidants. The oily extract of green tea (factor β_2) manifests the most pronounced stabilizing effect in this period.

Tab.3. Values of influence coefficients, B series

Period, days	Influence coefficients, A_{269}			
	β_0	β_1	β_2	β_{12}
7	**1,407**	**0,163**	**0,043**	0,086
14	**1,336**	**-0,104**	**0,169**	**0,081**
21	**0,834**	*-0,032*	0,059	0,006
28	**1,307**	0,105	0,080	*-0,094*

To evaluate the influence of the natural extract of antioxidants on the structure of emulsions based on walnut oil, systems consisting of: the apolar phase – walnut oil (Oil) plus the oily extract of green tea leaves (Extract) and the polar one – water, were obtained.

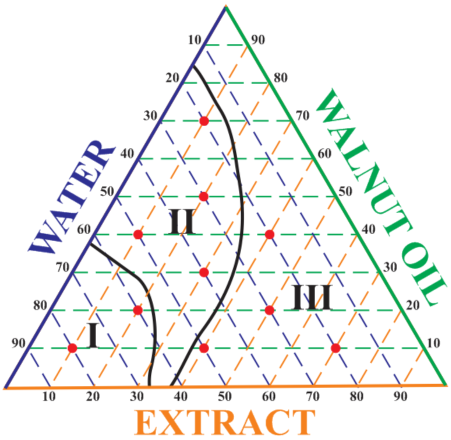


Fig.7. Initial phase state of the system Green tea extract - Walnut oil - Water

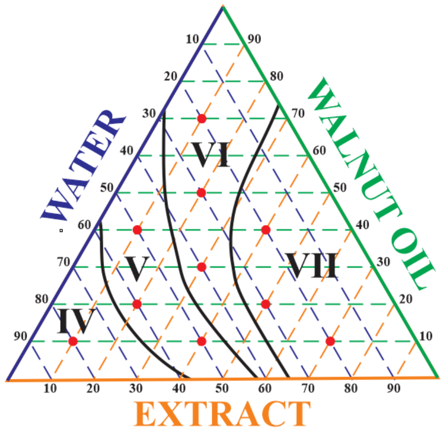


Fig.8. Aggregate stability of the system Green tea extract - Walnut oil - Water

Three regions with different phase states were highlighted (Figure 7). Region III corresponds to the formation of W/O emulsions. These emulsions are formed in a wide range of Extract concentrations, 40...100%. Instead, the range for Walnut oil is much narrower, 85...100%. Thus, the analysis of the phase diagram demonstrates that the green tea oily extract structurally stabilizes the W/O emulsions.

The evaluation in time of the „Green tea extract – Walnut Oil – Water" system (Figure 8) determined four areas of stability, which increased "from water to oil": region IV (<1min.), region V (2…5 min.), region VI (5…7 min.), region VII (> 7 min.). Therefore, the oily green tea extract exerts a pronounced stabilizing effect of W/O emulsions, the most stable system having an aqueous phase content of up to 30% [12].

3.3. The analysis of walnut oil stability in the presence of synthetic antioxidants

The modification dynamics of the properties of walnut oil compositions with different concentrations of synthetic antioxidants were studied over 75 days, the samples being kept in darkness at (23 ± 2)ºC. The experimental probes were prepared according to the FFE 2^3 plan for the following influence factors: octyl gallate, OG, X_1 (25...75mg/kg); ascorbyl palmitate, AAP, X_2 (16.7...50 mg/kg); DL-α-tocopherol, DLTP, X_3 (65...195 mg/kg). The added weight of antioxidants was calculated so as to comply with the requirements on the maximum permissible concentrations of each type of antioxidant (OG: DLTP: AAP = 100 : 300 : 500) [13].

After 14 and 60 days of sample storage, the values of peroxide indices (IP) were analyzed, elaborating the regression equations, which reflect the influence of factors (antioxidants) on the stability of the compositions.

$$\mathbf{\widehat{IP}_{D14} = 3{,}06X_0 - 0{,}54X_1 - 0{,}24X_2 - 0{,}39X_3 + 0{,}27X_{12} + 0{,}12X_{13} + 0{,}19X_{123}}, \qquad (1),$$

where: the value $\widehat{IP}_{D14}$ represents the mathematical expectation of the model, "predicted" after excluding the insignificant factor $\beta_{23}X_{23} = 0{,}08\ X_{23}$; $\mathbf{\Delta\beta = 0{,}11}$ for q = 5%, $\mathbf{\Delta\beta = 0{,}16}$ for q = 1%.

$$\mathbf{\widehat{IP}_{D60} = 11{,}46X_0 - 0{,}79X_1 + 1{,}73X_2 - 1{,}42X_{12} - 1{,}64X_{13} + 1{,}24X_{23} - 0{,}83X_{123}}, \qquad (2),$$

where: the value $\widehat{IP}_{D60}$ represents the mathematical expectation of the model, "predicted" after excluding the insignificant factor $\beta_3X_3 = 0{,}34\ X_3$; $\mathbf{\Delta\beta = 0{,}58}$ for q = 5%, $\mathbf{\Delta\beta = 0{,}85}$ for q = 1%.

In equation (1) the value of the central coefficient $\beta_0 = 3.06$ is less than the respective value of IP for walnut oil, which was untreated with antioxidants (3.30 ± 0.13 mmol/g oil). Thus, the deoxidizing action of the system is confirmed (OG + DLTP + AAP).

According to equation (2), the X_2 factor (DLTP) has a "bad" influence on the lipid system, significantly contributing to the increase of the peroxide index of the composition with walnut oil after 60 days. The X_3 factor (AAP) no longer acts directly, because its influence coefficient does not exceed the error value of the experiment ($\beta_3 = 0.34 < \Delta\beta_{5\%} = 0.58$). The possible cause of this phenomenon is that ascorbyl palmitate has been consumed in 2 months. Only the X_1 factor (OG) of all the generating factors has a weak but positive influence on the peroxide index.

The *p*-anisidine indices (IPA) of the walnut oil compositions with antioxidants were determined over 75 days of storage (equation 3), after the values of peroxide indices significantly increased in the analyzed samples, basing on the hypothesis that the accumulation of secondary oxidation products in lipids begins after the formation of peroxides [14].

$$\mathbf{\widehat{IPA} = 2{,}039X_0 + 0{,}197X_2 - 0{,}093X_{13} - 0{,}069X_{23}} \qquad (3),$$

where: the value $\widehat{IPA}$ represents the mathematical expectation of the model, "predicted" after excluding the insignificant factors, X_{13} factor being significant with $\mathbf{\Delta\beta = 0{,}092}$ for q = 22%, but X_{23} factor – with $\mathbf{\Delta\beta_{23} = 0{,}063}$ for q = 35%.

In equation (3), DLTP has a significant positive value, which means a "bad" influence on the stability of the compositions. The overall negative ('good') impact on the IPA of the antioxidant pairs, (OG + AAP) and (DLTP + AAP), was also observed.

Therefore, the antioxidant activity increases in DLTP < AAP < OG series in walnut oil compositions. The use of DLTP to stabilize lipid compositions is not efficient. The system of two antioxidants, OG + AAP, has a synergistic stabilizing action.

3.4. The analysis of the stability of the Walnut oil-Water-Antioxidant system

Fat-soluble antioxidants are surfactants, respectively, they concentrate on the oil/water interface. Therefore, the analysis of the overall influence of antioxidants and water on the stability of walnut oil is of interest while obtaining emulsion-type food systems.

Samples of walnut oil with different concentrations of water (0.0...0.3%) and n-Octyl Gallate antioxidant (0.0...0.2 mg/g) were prepared according to the FFE 2^2 plan (Table 4). The obtained compositions were placed in disposable ampoules, which were sealed, ensuring the absence of air access. The ampoules were stored in darkness and opened only directly at the time of measurement.

Tab.4. The FFE 2^2 experiment plan for the formation of compositions of Walnut oil – Water – Octyl gallate system

Factor		Composition, N							
		1		2		3		4	
Walnut oil, g	X_0	+	20	+	20	+	20	+	20
Water, %	X_1	-	0	+	0,3	-	0	+	0,3
n-Octyl Gallate (OG), mg	X_2	-	0	-	0	+	2	+	2
Interaction	X_{12}	+		-		-		+	

The analysis of the kinetics of the lipid oxidation process was performed by evaluating the change of peroxide indices, IP (Figure 9).

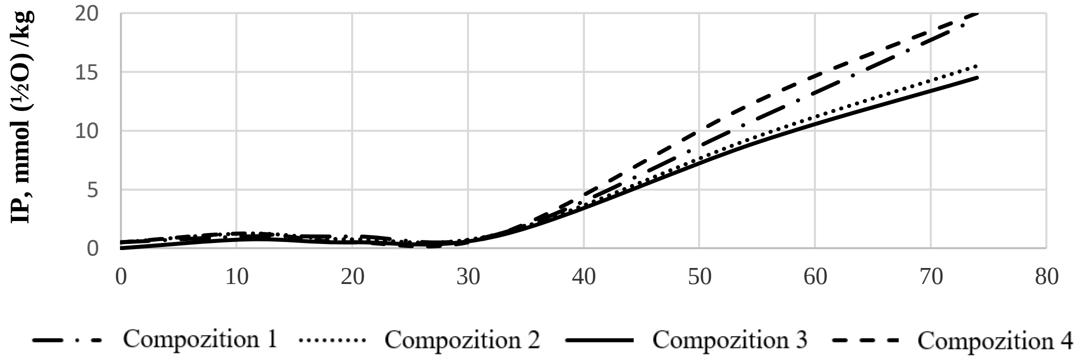


Fig 9. Comp arative analysis of the oxidation dynamics of Walnut oil – Water – Octyl gallate system

Based on the analysis of Figure 9, the dehydrated walnut oil without antioxidant (composition 1) and the one saturated with water and antioxidant (composition 4) have the highest values of the peroxide index after 70 days of samples storage. In oil, saturated with water and without antioxidant (composition 2), water extracts hydroperoxides and interferes with their decomposition products, thus, partially prevents oxidation [15]. The most stable is the dehydrated composition containing octyl gallate (composition 3). Therefore, when there is a risk of storing walnut oil compositions stabilized with antioxidants at high temperatures (for example, during the summer), it is recommended to perform their dehydration in advance [16].

3.5. The influence of fatty acids on the texture of compositions with walnut oil

The influence of saturated and monounsaturated fatty acids on the stability of walnut oil compositions was evaluated using the Rancimat method (Table 5).

Tab.5. Induction time for vegetable lipids at 120ºC

Vegetable fats	Ratio of unsaturated / saturated fatty acids	Induction time (IT), h	Stability time (ST), h	ST-IT, h
Cocoa butter [17]	0,77	9...15	-	-
Palm oil [17]	1,02	7…12	-	-
Walnut oil	12,33	1,92	2,56	0,64
Cocoa butter + Walnut oil (1:1)	6,55	2,33	3,34	1,01
Palm oil + Walnut oil (1:1)	6,68	3,14	3,84	0,70
Oleic acid + Walnut oil (1:1)	-	0,79	1,40	0,61

Although the content of saturated fatty acids in cocoa butter is higher than in palm oil [18, 19], the mixture of palm oil with walnut oil manifests the longest induction time. But the period from the appearance of the first volatile products of oxidation (induction time) until complete lipid degradation (stability time) is more prolonged for the mixture of cocoa butter with walnut oil. The presence of monounsaturated fatty acids in the composition accelerates the oxidation of walnut oil, the induction time of the blend with oleic acid being 2.4 times shorter than that of pure walnut oil. The possible cause of these phenomena is related to the physical state of the aggregation of analyzed vegetable fats, which, in turn, depend on their chemical structure.

The composition of palm oil consists essentially of saturated fatty acids with a longer aliphatic chain than in cocoa butter. Basing on the formula (4), the average lengths of the carboxylic chain (LC) of unsaturated fatty acids (taking into account% of fatty acid of the total saturated fatty acids), which enter the compositions of palm oil [18] and butter cocoa [19]:

$$L_{cc} = \frac{\sum L_{cc,i} \times \omega_i}{100\ \%}, \quad (4)$$

where: $L_{cc,\,i}$ – the number (proportional to length) of carbon atoms in the saturated fatty acid chain; ω_i – the mass part of the acid.

From the calculations made, it was established that the average length of the carboxylic chain of palm oil is longer than that of cocoa butter - 16.16 and 15.25, respectively. Thus, the stabilizing potential of palm oil can be explained not only by the gross amount of saturated fatty acids but also by the 'quality', i.e. their chemical structure, including the chain length.

In the food industry, solid vegetable lipids are used in combination with liquid oils to obtain different types of spreads (spreads). The melting point of these compositions must be similar to that of dairy fat, in the range of about 30 ± 5°C [20], while the melting point of walnut oil is equal to –18°C [21]. To optimize the composition of vegetable lipid mixtures and to minimize the concentration of saturated fatty acids, it was proposed to use a pure saturated fatty acid with a long aliphatic chain.

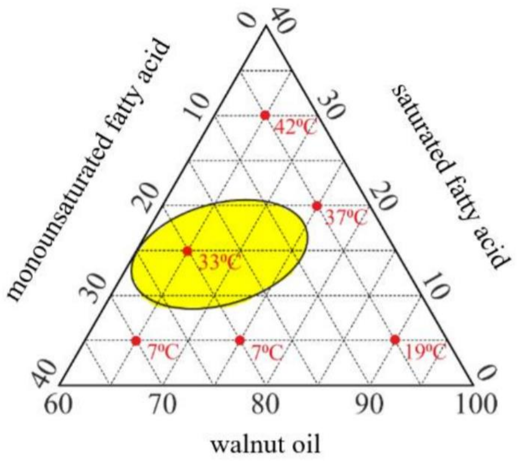


Fig.10. Diagram of system Walnut oil - Monounsaturated fatty acid - Saturated fatty acid

The Gibbs-Roseboom diagram was constructed for determining the melting temperatures at the landmarks for the compositions with 60…90% walnut oil, 5…30% stearic acid, and 5…30% oleic acid (∑ = 100). Analysis of the diagram of Walnut oil–Pure monounsaturated acid–Pure saturated acid system (Figure 10) shows that walnut oil becomes a product with a spreadable texture and a melting temperature similar to that of dairy fat (33 ± 2°C) in compositions with 60...75% walnut oil, 10...25% oleic acid, 10...20% stearic acid. Thus, the solid composition of walnut oil can be obtained by combining it with 15% saturated fatty acid with a carboxylic chain length equal to 18 [22].

4. The elaboration of compositions and technology for obtaining spread-type foods based on walnut oil

Chapter 4 sets out the technological aspects of the elaboration of food compositions with walnut oil resistant to oxidative degradation. The principles of obtaining spreads based on dairy fats and vegetable lipids are described, elaborating their technological production schemes and arguing the quality and high biological value of the final products.

4.1. The designing of compositions and technology for obtaining spread-type foods based on walnut oil

The development of new technologies for obtaining products balanced by composition provides, among other things, the adjustment of their lipid fractions to an optimal ratio between saturated fatty acids (SFA), monounsaturated (MUFA), and polyunsaturated (PUFA) [23, 24].

Butter, a fatty product used every day, represents an emulsion of W/O type, solid at room temperature. The transformation of the texture of butter from solid to semi-solid state at t = 30...37°C is due to the content of SFA > 40% of total fat [1]. According to the chemical composition, butter shows nutritional value, especially energic one, but the PUFA content is only 2...6% of total fat [25, 26]. The biological value and quality of butter can be improved by significantly increasing the content of polyunsaturated fatty acids in its composition of butter. To this end, the development of technology for obtaining spread-type food compositions based on dairy lipids and walnut oil was initiated.

Spread foods fall into the category of products obtained from the mixture of vegetable and/or animal fats with a total fat content between 62% and 80% [6, 27]. Based on the data obtained previously, that the food emulsion of W/O type is more stable in the system with an aqueous phase content of up to 30% (Figure 8) and, taking into account the traditional preferences of consumers, it was agreed that the total lipids content in spreads should be between 70 and 75%. And due to the fact that in order to obtain the solid texture of the product, the content of saturated fatty acids in total fat must be higher than 40%, it was proposed to develop the technology of spreads obtaining that would contain more than 50% of dairy fats.

The spread structure must be similar to butter and represent an emulsion of W/O type with a melting temperature between 27...36ºC. The main chemicals that can influence the "in vivo" function of the product are saturated and polyunsaturated fatty acids, proteins, and water (Figure 11). Thus, the spread quality is influenced by the composition and fatty acids content, the presence of non-fatty additives, the type of emulsion, and, last but not least, the lipid phase used, which determines the melting temperature, product hardness, its spreadability, and other structural and rheological characteristics [24].

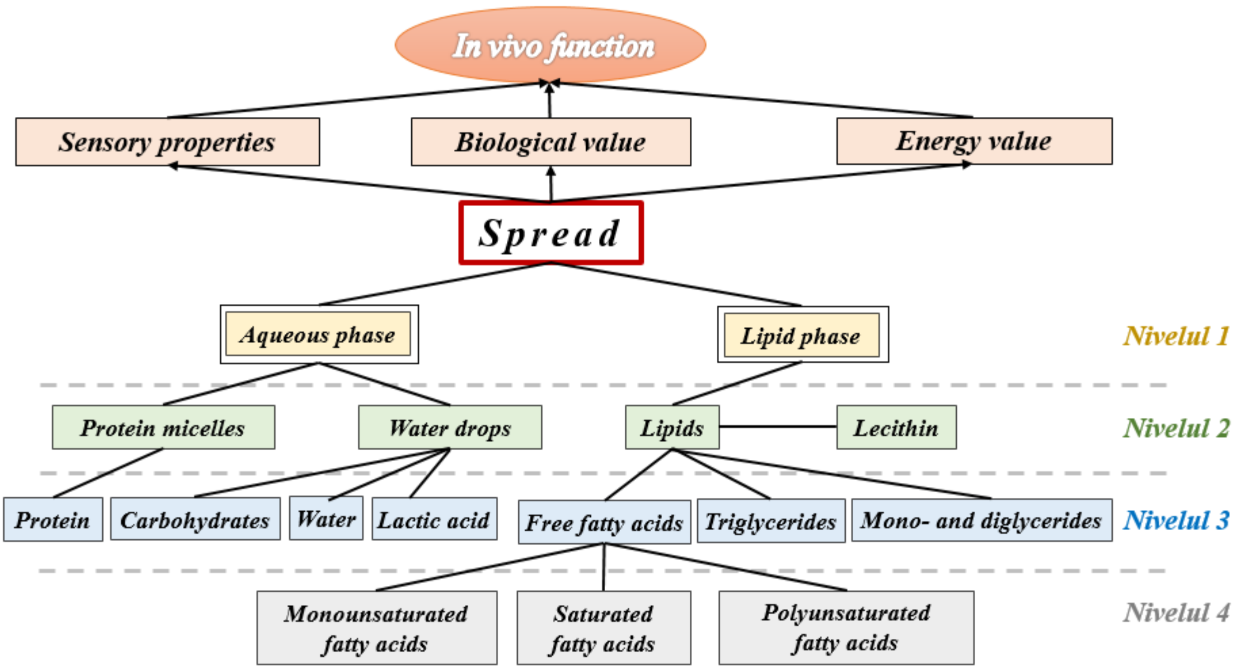


Fig.11. The scheme of the structure of the spread containing walnut oil

The aim formulated was to obtain the spread with the concentration of walnut oil not less than 20% of the total fat content, maintaining sufficient antioxidant stability of the product within the realization of *production – distribution – sale – consumption* chain. Thus, the high biological potential of the spread must be ensured both in the process of obtaining and at the product store.

The stability of butter as a W/O emulsion depends on the efficiency and the speed of the process of separating the lipid fraction from sweet cream (O/W emulsion), which represents a determining factor in obtaining spreadable products. To choose the method of obtaining spreads based on dairy fats and vegetable lipids, two ways of lipid phase concentrating were analyzed: by the process of beating the sweet cream with a fat content of up to 40% and by the transformation of sweet cream with high-fat content.

To normalize the emulsion lipid content and to formate the vegetable compositions based on walnut oil, skimmed milk was used as a source of the aqueous phase. Besides, to ensure the structural and antioxidant stability of the spreads, the soy lecithin emulsifier was introduced in their recipes, contributing to the fine dispersion of water droplets in the lipid fraction of the product [28].

4.2. The elaboration of spreads based on the mix of emulsions with high-fat content

In the first stage, the technology of obtaining spreads based on sweet cream with 72.5 ± 0.5% fat, skim milk, walnut oil, and emulsifier was tested.

Preliminary studies have shown that the use of walnut oil as such in the formulation of spreadable mixtures negatively influences the texture and thermostability of the final product. Therefore, modified vegetable oil was used as vegetable lipids, representing the blend of walnut oil with stearic acid (85:15, the ratio being identified as optimal according to Figure 10) with a melting temperature of 30 ± 1°C [22], within the experimental research on the obtaining of spreads based on the mixture of emulsions with high-fat content.

The amount of lecithin necessary to obtain the spreads based on the mixture of dairy and vegetable lipids was investigated depending on the concentration of walnut oil in the product composition and the value of the thermostability of obtained samples. It has been established that the negative effect of increasing the concentration of walnut oil in the emulsion lipid phase on the thermostability of the spread can only be partially compensated by increasing the concentration of lecithin [29]. The average recommended amount of emulsifier for the production of spread containing walnut oil is 0.2...0.3% lecithin in the total mass of the product.

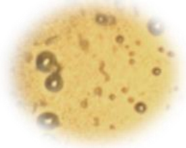
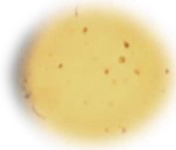
The concentration of lipids in the compositions is achieved by the method of transforming the high-fat O/W emulsion into W/O type, without the essential change of the total fat content in the final product.

According to the current study of the technologies used in the production of spreads based on dairy fats and vegetable lipids [23, 28], three methods of a spreadable product obtaining have been identified.

Method № 1 includes the step of forming the vegetable emulsion from modified walnut oil, water, and emulsifier. Subsequently, this emulsion is mixed with dairy lipids, being then subjected to thermo-mechanical treatment until the formation of the butter texture. When performing Methods № 2 and 3, the emulsification process of the composition takes place after mixing all the components heated to a temperature of 55°C, the addition of the ingredients being realized in a different order.

The analysis of the described methods was fulfilled by obtaining spreads with 71...74% of total fat, including 50% of modified walnut oil. The equivalent ratio between vegetable and dairy lipids was chosen to comparate the characteristics of spread samples produced by different methods (Table 6). Following the analysis of the physicochemical, organoleptic properties and the microscopic structure of the products, it was established that the spread obtained by Method № 3 possess the best characteristics by consistency (compact, homogeneous), thermostability (0.70 ± 0.04), melting temperature (32.5 ± 0.2°C) and texture.

Tab.6. Characteristics of spreads obtained by different methods based on the mix of emulsions with high-fat content

Characteristics	Method № 1	Method № 2	Method № 3
Color (on the surface and in section)	 White, uniform throughout the mass, with characteristic luster	 Yellowish white, uniform throughout the mass, with characteristic luster	 Yellowish white, uniform throughout the mass, with characteristic luster
Appearance	Continuous surface, without air gaps and impurities		
Consistency (at 10-12°C)	Unctuous, compact, homogeneous	Creamy, homogeneous	Unctuous, compact, homogeneous
Smell	Pleasant, with less pronounced butter flavor		
Taste	Of sweet cream with a hint of walnut and a slight residual taste of tallow		
Fat content, %	72,3 ± 0,2	72,2 ± 0,1	72,4 ± 0,2
Water content, %	25,2 ± 0,2	25,3 ± 0,1	25,1 ± 0,2
Thermostability coefficient	0,62 ± 0,04	0,58 ± 0,03	0,70 ± 0,04
Melting temperature, °C	32,5 ± 0,3	31,5± 0,5	32,5 ± 0,2
The structure under a microscope			

However, the use of walnut oil modified with stearic acid in spreads with 50% of vegetable lipids from total fats leads to the manifestation of a slightly residual taste of tallow. It was proposed to study the impact of different concentrations of modified walnut oil in spread composition (<50% of total fat) on the characteristics of the final product (Table 7).

Tab.7. Physico-chemical characteristics of spreads based on the mix of emulsions with high-fat content and different ratio between dairy and vegetable lipids

Dairy fat content,% of total fat	Modified walnut oil content,% of total fat	Fatty acid composition,% of total fatty acids			ω6:ω3 ratio		Thermo-stability coefficient
		SFA	MUFA	PUFA			
50	50	42,9	20,0	36,4	32,5:3,9	8,4	0,70±0,02
60	40	47,0	22,6	29,6	26,4:3,2	8,4	0,88±0,01
70	30	51,0	25,3	22,8	20,3:2,4	8,4	0,88±0,01
80	20	55,0	27,9	16,0	14,3:1,7	8,4	0,93±0,01

According to the data presented in table 7, the use of modified walnut oil (15% stearic acid) in the proportion of 20…50% in spread obtaining leads to the improvement of its nutritional and biological value as a result of increased content of polyunsaturated fatty acids and, respectively, reduced concentration of saturated fatty acids.

The samples with 20...40% of vegetable lipids from the total fats show the unctuous, homogeneous consistency, the good values of the thermostability coefficient (0.88...0.93), and the ratio SFA: PUFA = 1.5...4, which fits the concept of "balanced fat" [23, 24].

Despite the fact that even at spreads with the minimum amount of modified walnut oil (20%) the optimal ratio between saturated and polyunsaturated fatty acids is ensured, these samples do not correspond from a sensory point of view, having a barely perceptible hint of tallow taste due to the presence of stearic acid in the composition of the product. For these reasons, it was necessary to identify technological solutions to ensure the structural, rheological, nutritional as well as organoleptic properties of the spread containing walnut oil.

4.3. The elaboration of spreads based on the mix of emulsions with a fat content of up to 40%

The method of spread obtaining was developed, which presumes the formation of W/O emulsions through the beating process of the mix of 35...40% of dairy lipids and walnut oil in the form of O/W emulsion (Figure 12).

The spread production within industrial conditions assumes three control points: at the obtaining of different types of emulsions (O/W and W/O) and the final product validation. The duration of the production cycle depends on the volume of processed raw material and on average constitutes 8-12 hours. The yield of the final product is 45...50%.

The elaborates method of obtaining spreads with an increased content of polyunsaturated fatty acids was described within the invention patent "*The method of obtaining the mix of spreadable fats based on sweet cream*" [30].

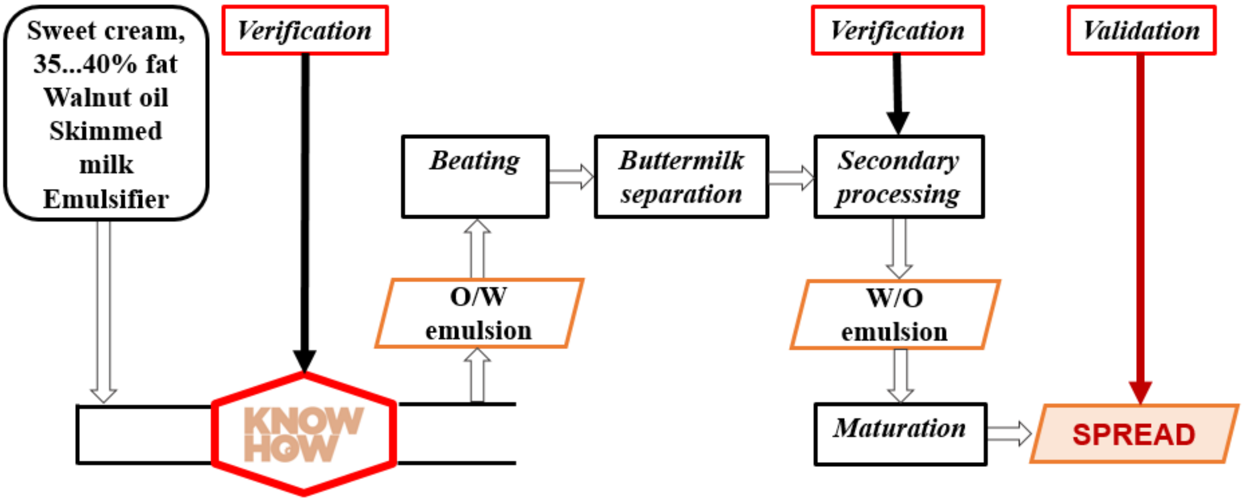


Fig.12. General scheme of the spread manufacturing process according to the invention patent, No. 1281, 2018.09.30.

To determine the optimal quantities of walnut oil in spread composition based on the mix of emulsions with a fat content of up to 40%, samples with 20 and 30% of walnut oil from total fats were prepared.

The influence of the amount of walnut oil on the organoleptic properties of the spreads was analyzed by a team of 7 tasters with the necessary skills according to ISO 22935/2015 [8]. For comparison, the sensory characteristics of the industrial spread, 72.5% fat, were evaluated in parallel (Table 8).

Tab.8. Evaluation of sensory indicators of spreads

Sensory indicators	Spread with 30% walnut oil of total fat	Spread with 20% walnut oil of total fat	The industrial spread
Appearance	4,57 ± 0,58	4,57 ± 0,58	4,86 ± 0,41
Consistency	4,00 (unanimously)	4,86 ± 0,41	5,00 (unanimously)
Smell	4,67 ± 0,57	4,71 ± 0,53	4,71 ± 0,53
Taste	4,67 ± 0,57	4,86 ± 0,41	4,67 ± 0,57
Punctaj mediu	**4,48± 0,54**	**4,75 ± 0,49**	**4,82 ± 0,44**

The data in Table 8 show that the spread with 30% of walnut oil was depreciated by slightly soft consistency, although the average score per product being a value of about 4.5, which means minimal deviations from sensory requirements. Nuances of rancid taste were noted in the industrial product. From the experimental samples, spread with 20% of walnut oil obtained the highest average score per product, being favorably appreciated for the pleasant aroma of sweet cream with a discreet flavor of walnut oil.

Tab.9. Physicochemical characteristics of the spreads based on the mix of emulsions with a fat content of up to 40% and different ratio between dairy and vegetable lipids

Dairy fat content,% of total fat	Walnut oil content,% of total fat	Fatty acid composition,% of total fatty acids			ω6:ω3 ratio		Thermo-stability coefficient
		SFA	MUFA	PUFA			
70	30	46,9	25,6	26,5	23,70:2,80	8,38	0,78±0,02
80	20	52,3	28,2	18,4	16,49:1,96	8,43	0,83±0,02

Analyzing the thermostability coefficient of the spreads with 20% and 30% walnut oil of total fats (Table 9), we observe that its values decrease with increasing the concentration of walnut oil in the product composition but remain within satisfying limits (0.78...0.83) [25]. The SFA : PUFA ratio of experimental samples varies between 1.8...2.8, which fits the concept of „balanced fat” where SFA : PUFA = 3...4: 1...2 [23, 24].

Thus, by performing the method of producing spreads based on the mixt of emulsions with a fat content of up to 40% (figure 12), final products with the PUFA content of about 15...30% of the total fatty acids (Table 10) can be obtained.

Tab.10. Characteristics of the spreads based on the mix of emulsions with a fat content of up to 40%

№	Characteristics	Values for spreads with walnut oil
1	Lipids, % *which includes*	71...74
	polyunsaturated fatty acids, %	15...30
	the ω3 and ω 6 ratio	5...10
2	Water, %	23... 27
3	Proteins, %	<1
4	Glucides, %	<1,5
6	Melting temperature,°C	30…32
7	Thermostability coefficient	0,80 ± 0,05
9	Taste and smell	of sweet cream with a pleasant remnant taste of walnut oil
10	Consistency (at 10-12ºC)	compact, plastic, homogeneous, with a glossy surface in section
11	Color	pale yellow, uniform throughout the mass

The spread with 20% of walnut oil of the total fats based on the mix of emulsions with a fat content of up to 40% was analyzed using a microscope to determine how the presence and incorporation of walnut oil lipids contribute to product structure (figure 13). To determine the polarity of the spread phases, water-soluble (polar) dye, methylene blue, and fat-soluble (non-polar) dye, sudan III, were added at different stages of sample preparation.

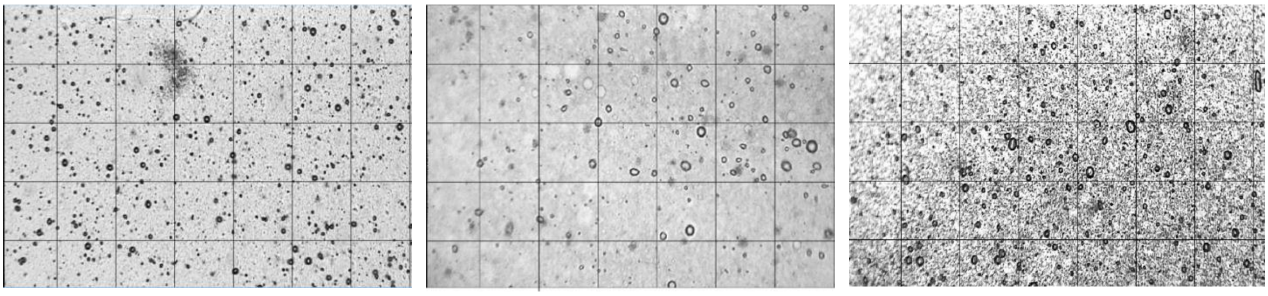


Fig.13. Images of the spread with 20% walnut oil under the Motic microscope with the cell dimensions of 100x100 µm, where different dyes were applied for analysis:
A) sudan III, B) methylene blue, C) sudan III & methylene blue

Images of the microstructure of spreads containing walnut oil (Figure 13) show that the processed product represents an emulsion in which water droplets and air inclusions are dispersed in the structured continuous lipid phase (Figure 14). The dimensions of the water droplets are between 7 and 13 µm, which are uniformly dispersed in the lipid phase. This confirms that, following the beating process of the emulsion mix with lipid content of up to 40%, there was not only the composition viscosity increase, due to the agglomeration of lipid globules, but the inversion of the product phases [12].

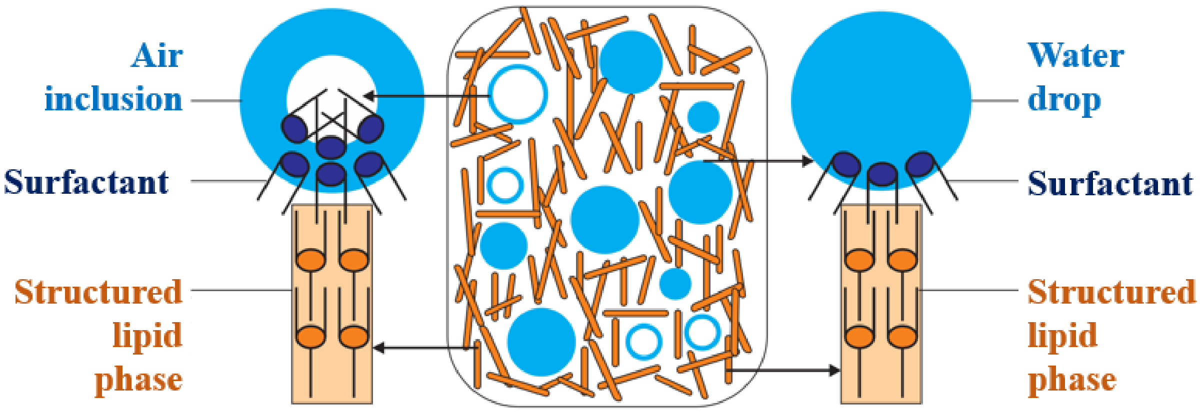


Fig.14. The schematic representation of the microstructure of spread containing walnut oil:
polar (●) and non-polar (—) parts

According to the data in point 3.2, enriching the composition of spreads with extracts of natural antioxidants of β-carotene and chlorophyll "a" contributes to slowing down the oxidative degradation of polyunsaturated fatty acids in walnut oil from walnut oil. At the same time, in addition to the antioxidant effect, the extracts show the properties of dyes, which can negatively influence the appearance of the final product, causing an intense unnatural color.

The color intensity of the spread samples based on the blend of emulsions with a fat content of up to 40% was studied by the CIELab method (Table 11), β-carotene being chosen as the basic pigment for analysis because it is more compatible with the traditional color of spreads than the green pigment of α-chlorophyll.

Tab.11. Determining the color intensity of spreads by the CIELab method

Spread samples	Butter 	Spread with 20% of walnut oil 	Spread containing *β*-caroten 
ΔE	0 (witness)	5,3	18,1

The data in Table 10 indicates that 23.1 mg/kg product of the oily extracts of β-carotene intensifies the spread coloration in 3-4 times more than walnut oil. The decrease of carotenoids in the composition of the spread is not relevant in terms of ensuring the product antioxidant stability. For this reason, the examination of the influence of synthetic antioxidant presence on the shelf life of spreads was planned to be verified.

4.4. The assessment of the stability and shelf life of spreads

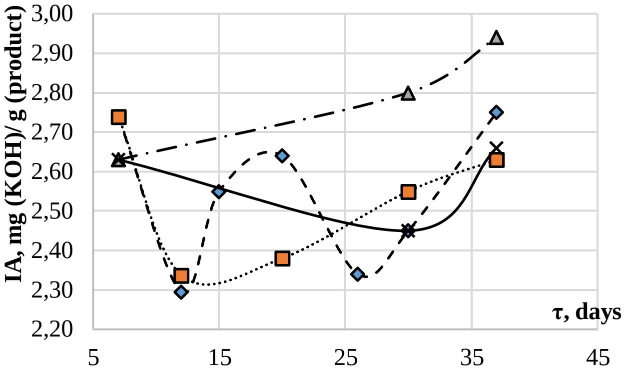
To determine the influence of the increased content of polyunsaturated fatty acids on the stability of the product, two series of spread samples with 20% walnut oil of total fat were prepared, one of which was additionally stabilized with 250 mg/kg of antioxidant L-ascorbic acid 6-palmitate [7]. The obtained samples were packed in aluminum foil, 10-40 g each, and stored at temperature regimes: t = (3 ± 2) ºC and t = – (6 ± 3) ºC. The shelf life of the spreads containing walnut oil was determined according to the physicochemical, structural, organoleptic, and microbiological stability of the product.

The analysis of Figure 15 shows that the obtained spreads are stable against oxidative degradation of up to 40 days. The curve of oxidation product formation is more evident in the samples without antioxidants (figure 15 - B, C), which may mean that the rate of peroxide accumulation and their transformation into oxidation by-products is higher in pure samples. It was also established that the changes of physicochemical properties of the samples kept at t = (3 ± 2) ºC are more visible than at the ones stored at t = – (6 ± 3)ºC but are not critical for the quality of final products.

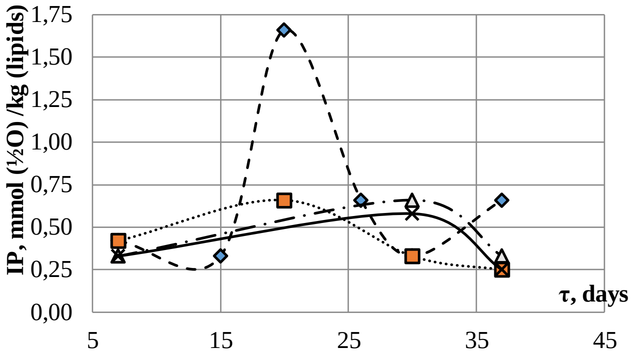
The changes of spreads sensory properties, manifested by the decrease of product plasticity, were found along with the appearance of the first signs of water droplets coalescence (figure 16). The lipid phase creaming was established after 30 days of keeping the spreads at t = (3 ± 2)ºC and after 37 days of their storing at t = – (6 ± 3)ºC.

That is, taking into account the data obtained by the dynamic evaluation of physicochemical changes, which took place in the spread samples (figure 15), we conclude that the temperature regime influences more on the stability of spreads organoleptic and structural properties than on the speed of their oxidative degradation.

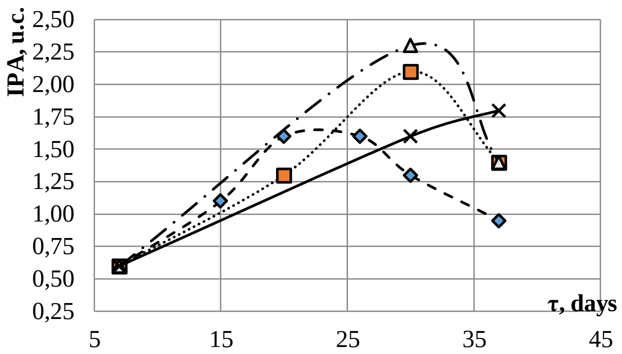
Dynamics evaluation of the microbiological stability of the spreads was performed for samples with a mass of 10.0 ± 0.5 g. The permissible limit of the number of mesophilic aerobic and facultative anaerobic microorganisms was exceeded in products kept at a temperature of t = (3 ± 2)ºC after 10 days from the beginning of the experiment, while the spreads stored at a temperature of t = – (6 ± 3) ºC were recognized as harmless up to one month (Figure 17). Based on the fact that the analysis was performed for samples with a mass of 10.0 ± 0.5 g each, we conclude that the time till microbiological risk appearance, respectively, the shelf life of spreads in a consumer package (50-1000g) can be doubled [25].



A) Dynamics of spread acidity index (IA), 3.5 being maximum acceptable limit (MAL)



B) Dynamics of the peroxide index (IP) of lipid phase separated from spread, 10.0 being MAL



C) Dynamics of the p-anisidine index (IPA) of lipid phase separated from spread, 3.0 being MAL

Fig.15. The evaluation of spread stability against oxidative degradation during storage:

- spread, t = (3±2)ºC
- spread + antioxidant, t = (3±2)ºC
- spread, t = – (6±3)ºC
- spread + antioxidant, t = – (6±3)ºC

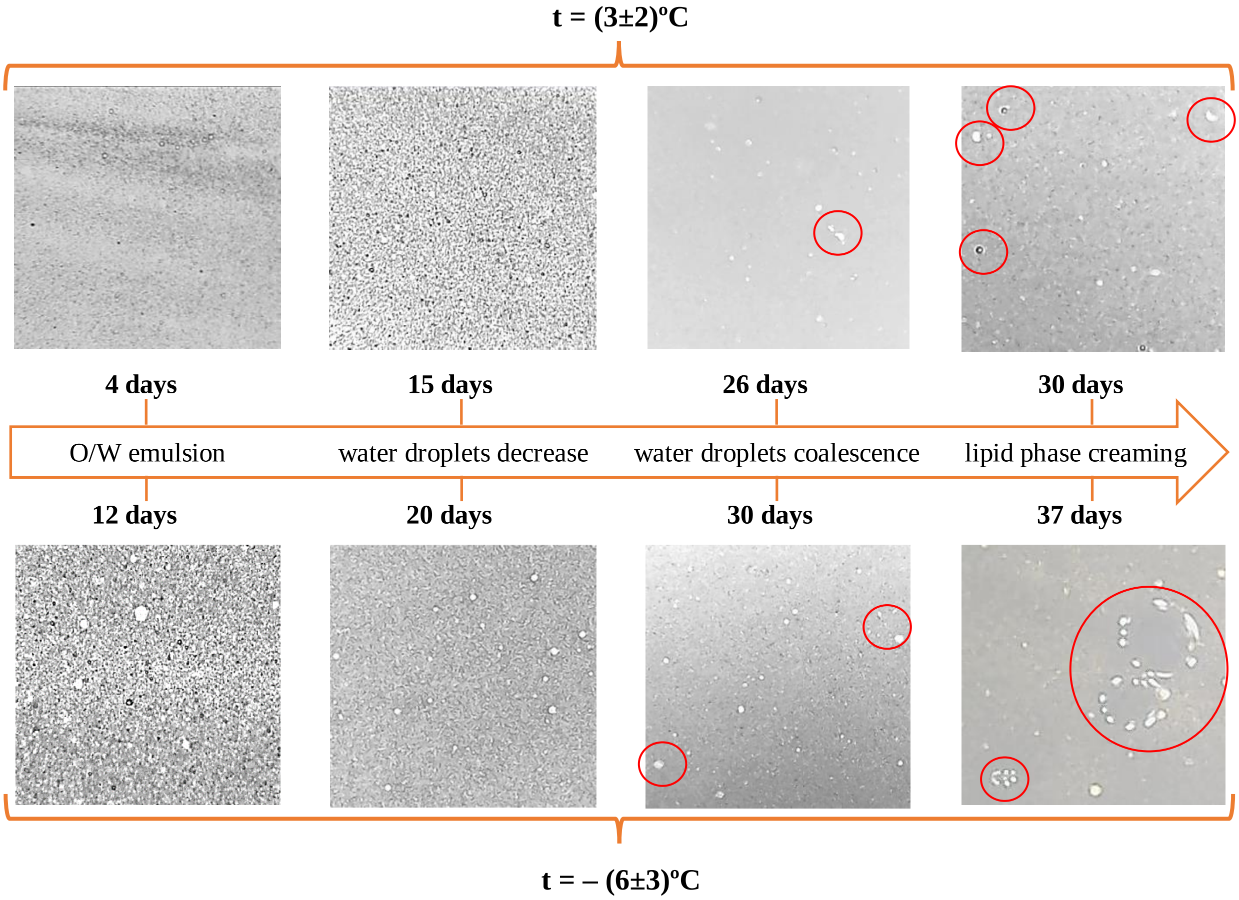


Fig.16. The aggregative stability of the microstructure of spread containing walnut oil

The main criterion in determining the shelf life of spreads, obtained by the newly elaborated method, is the speed of the product microbiota development (figure 17). That is, despite expectations, the main risk at storing lipid compositions, based on the mix of emulsions of animal and vegetable origin, is not the instability caused by oxidation characteristic for walnut oil, but the influence of microbiological and technological factors caused by the presence of dairy products and high water content in the spread [31].

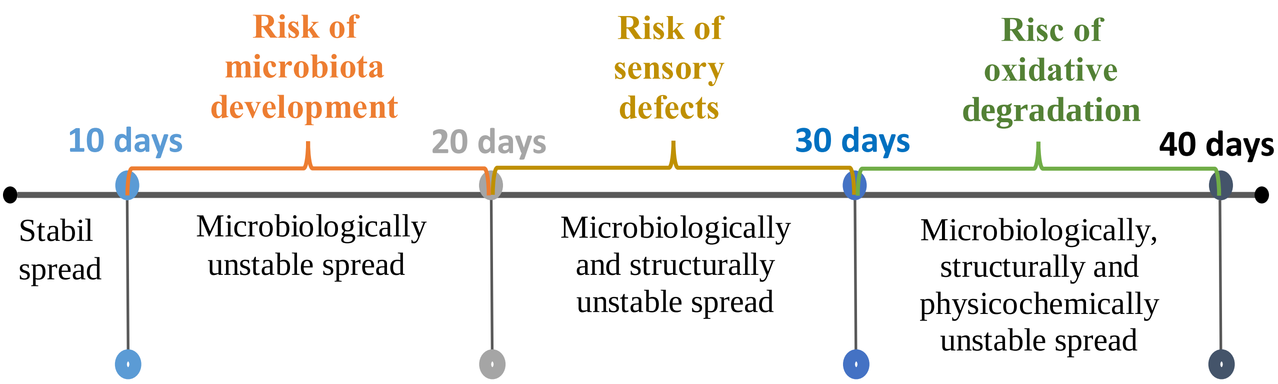


Fig.17. Scheme of physicochemical, structural and microbiological risks that influence the shelf life of spreads with walnut oil kept at t = (3 ± 2)°C

GENERAL CONCLUSIONS AND RECOMMENDATIONS

The theoretical and experimental research carried out in the thesis led to the formulation of the following **conclusions**:

1. For the first time, the technological principle of preventing the oxidative degradation of walnut oil polyunsaturated fatty acids was scientifically argued by forming W/O emulsion-type compositions with the saturated fatty acids of dairy lipids.

2. It was determined, that the lipid composition consisting of *walnut oil: dairy fat*, in the ratio *1 : 4*, represents the basis of the homogeneous and stable texture of the spread-type product.

3. It has been established that blocking the oxidation process of polyunsaturated fatty acids in walnut oil in the presence of antioxidants depends on their activity expressed in the following series: DL-α-Tocopherol (E 307) <Ascorbyl Palmitate (E 304) <Octil Gallat (E 311).

4. Theoretical and experimental research has shown that the processing of the mix of dairy fat and vegetable lipids in the form of O/W emulsion into W/O one by the beating process gives the final products physicochemical and nutritional properties characteristic for spread-type foods.

5. It was determined that the obtained spreads containing walnut oil have a butter-like structure, a melting temperature of 30...32°C, thermostability coefficient of 0,85 ± 0,05, compact, plastic and homogeneous consistency, uniform straw yellow color, and sweet cream flavor with a pleasant remnant aftertaste of walnut oil, but the content in ω3 and ω6 polyunsaturated fatty acids are up to 8 times higher than in the classic butter.

6. It has been established that among the factors determining the shelf life of spreads containing walnut oil, namely physicochemical, sensory and microbiological changes, the most significant risk represents the microbiological alteration of the product. It has been determined that the recommended period of storage for spreads at a temperature of (3 ± 2)ºC is up to 10 days and at a temperature of (– 6 ± 3)ºC up to 30 days.

7. The process for obtaining spreads based on sweet cream and walnut oil with a high content of ω3 and ω6 polyunsaturated fatty acids, between 19…46% of total fat, was elaborated and patented.

Recommendations:

- Spreads containing walnut oil, intended to be stored for more than one month at a temperature of (3 ± 2)ºC, are recommended to be supplemented with 250 mg/kg antioxidant L-ascorbic acid 6-palmitate.
- The industrial manufacture of spreads can be carried out on the technological lines of butter production, taking into account that the hygienic conditions, the assembly of the technological lines should correspond to the technology of spreads obtaining.
- It is foreseen the elaboration of the Technological Regulation for obtaining the spreads, which is adapted to the technical conditions of the technological line of butter processing.

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OWN PUBLICATIONS ON THE THESIS

1. Articles in scientific journals

- **RADU, O.** Peculiarities of walnut oil state in some food emulsions. In: *Journal of Engineering Science.* Vol. XXVII, № 1, 2020, pp. 69 - 74. ISSN 2587-3474.
- **RADU, O.**, POPESCU, L., TATAROV P., BAERLE, A. Factors that determine the shelf life of a butter-like spread based on walnut oil. In: *Journal of Engineering Science.* Vol. XXVI, № 3, 2019, pp. 119 - 124. ISSN 2587-3474.
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2. Articles in the scientific collections of international conferences

- **RADU, O.** The study of walnut oil (*Juglans regia L.*) oxidative stabilization by saturated fatty acids. In: *Proceedings of International Conference 'Modern Technologies in the Food Industry'*, October 18-20, Chisinau, 2018, pp. 272-275. ISBN 978-9975-87-428-1
- **RADU, O.**, BAERLE, A., TATAROV, P., POPOVICI, C. Aggregative stability of emulsions containing walnut oil. In: *Proceedings of International Conference 'Modern Technologies in the Food Industry'*, October 18-20, Chisinau, 2018, pp. 230-231. ISBN 978-9975-87-428-1
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- **RADU, O.**, ROŞCA, I. Ocenka podlinnosti i kachestva masla greckogo orekha metodom infrakrasnoj spektroskopii. {The evaluation of the authenticity and quality of walnut oil by the method of infrared spectroscopy} In: *International scientific conference of young scientist and students*, April 28-29, Mogilev, 2016, pp. 238. ISBN 978-985-6985-60-0
- POPOVICI, C., BAERLE, A., **RADU, O.,** TATAROV, P. Radical Scavenging Capacity of Walnut Oil: Effect of some Antioxidants on Storage Period. In: *International scientific conference of young scientist and students*, April 13-14, Kyiv, NUFT, Part I, 2016, pp. 339

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- SANDULACHI, E., **RADU, O.**, FUIOR, A. Estimation of apical necrosis in *Juglans regia L.* walnuts harvested in Moldova. In: *Proceedings of International Conference 'Modern Technologies in the Food Industry'*, November 1-3, Chisinau, 2012, Part II, pp. 295-300. ISBN 978-9975-80-646-6

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- **RADU, O.** The statistical analysis of walnuts lot quality. In: *Technical - Scientific Conference of Collaborators, Doctoral Students and Students, Technical University of Moldova*, March 26-29, 2019. Chisinau, 2019, Part I, pp. 511-512. ISBN 978-9975-45-587-9
- **RADU, O.**, BAERLE, A., ROŞCA, I. Particularităţile spectrale ale uleiurilor vegetale fortificate cu substanţe biologic active naturale. {Spectral particularities of vegetable oils fortified with natural biologically active substances} In: *Technical - Scientific Conference of Collaborators, Doctoral Students and Students, dedicated to the 50th Anniversary of T.U.M.*, October 20-21, Chisinau, 2014, Part II, pp. 73-76. ISBN 978-9975-45-382-0
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- **RADU O**., CAPCANARI T. Uleiul din semințe de struguri – produs de perspectivă în fabricarea alimentelor funcționale. {Grape seed oil – a perspective product in the production of functional foods}. In: *Technical - Scientific Conference of Students and Doctoral Students*, November 15-17, Chisinau, 2012, Part II, pp. 99-102. ISBN 978-9975-45-251-9
- FUIOR, A., SANDULACHI, E., **RADU, O.** Incidenţa microbiană a nucilor *Junglas regia L.* {The microbial incidence of *Junglas regia L.* walnuts}. In: *Technical - Scientific Conference of Students and Doctoral Students*, November 15-17, Chisinau, 2012, Part II, pp. 67-68. ISBN 978-9975-45-251-9
- **RADU O.,** SANDULACHI E., FUIOR A. Microorganisme izolate din nucile (*Juglans regia L.*) recoltate de pe sol. {Microorganisms isolated from nuts (*Juglans Regia L.*) harvested from the ground}. In: *Technical - Scientific Conference of Students and Doctoral Students*, November 15-17, Chisinau, 2012, Part II, pp. 69-70. ISBN 978-9975-45-251-9

4. Invention patents and other intellectual property objects

- **RADU, O.**, POPESCU, L., TATAROV P., BAERLE, A. *Procedeu de obţinere a amestecului de grăsimi tartinabile pe bază de smântână dulce*. {*The method of obtaining the mix of spreadable fats based on sweet cream*}. Invention patent No. 1281. Date of decision publication: 2018.09.30. BOPI No. 9/2018

ANNOTATION

Radu Oxana: Food compositions based on walnut oil (*Juglans regia L.*) resistant to oxidative degradation, Ph.D. thesis in technology, Chisinau, 2020.

Thesis structure: The thesis consists of an introduction, 4 chapters, general conclusions and recommendations, bibliography from 233 titles, 7 appendices. The basic text includes 103 pages, 50 figures, and 57 tables.

Keywords: polyunsaturated fatty acids, antioxidants, dairy fats, food emulsions, spread.

The purpose of the work: the realization of theoretical and experimental research in order to elaborate food compositions of W/O emulsions type based on walnut oil, ensuring the stability and high biological value of final product.

Objectives: the determination of possible ways to prevent the oxidative degradation of walnut oil polyunsaturated fatty acids in food compositions; the influence evaluation of saturated and unsaturated fatty acids on the stability and texture of food compositions with walnut oil; the analysis of antioxidants impact on the prevention of oxidative degradation of polyunsaturated fatty acids in walnut oil; the elaboration of composition and technology for obtaining new foods in the form of W/O emulsion, as *spread*, based on dairy products and walnut oil; the evaluation of nutritional value and physicochemical properties of spreads with walnut oil; the establishment of shelf life and optimal storage period of final product.

Scientific novelty: for the first time, it was scientifically argued and experimentally demonstrated the possibility of the prevention of oxidative degradation of walnut oil polyunsaturated fatty acids in food compositions by the combination of walnut oil lipids and dairy fats in the form of emulsions.

Solved scientific problem: the determination of the most important physicochemical, nutritional and technological properties of compositions based on walnut oil and the identification of optimal and efficient conditions for their technological processing and use.

Theoretical significance: the improvement of research methods of walnut oil quality, the obtaining of scientific results that demonstrate the possibility of stabilization of lipid compositions with a high content of polyunsaturated fatty acids and the formation of functional foods based on them.

Applicative value: the methodology of walnut oil using for the obtaining of various food products with a high content of polyunsaturated fatty acids, especially in food compositions of emulsion type, was argued.

Implementation of scientific results: publications in journals and symposium collections, results discussion within debates on national and international scientific conferences (19 scientific papers); invention patent No. 1281 „The method of obtaining the mix of spreadable fats based on sweet cream”.

ADNOTARE

Radu Oxana: Compoziţii alimentare pe baza uleiului de nucă (*Juglans regia L.*) rezistente la degradări oxidative, teză de doctor în ştiinţe tehnice, Chişinău, 2020.

Structura tezei: teza constă din introducere, 4 capitole, concluzii şi recomandări, bibliografie cu 233 titluri, 7 anexe. Textul de bază conține 103 pagini, inclusiv 50 de figuri și 57 de tabele.

Cuvinte-cheie: acizi graşi polinesaturaţi, antioxidanți, grăsime lactată, emulsii alimentare, spread.

Scopul lucrării: realizarea cercetărilor teoretice şi experimentale privind elaborarea compoziţiilor alimentare de tip emulsii A/U pe bază de ulei de nucă, asigurând stabilitatea și valoarea biologică ridicată a produsului finit.

Obiectivele lucrării: determinarea căilor posibile de prevenire a degradării oxidative a acizilor grași polinesaturați ai uleiului de nucă în mediile alimentare; studiul influenței aciziilor graşi nesaturaţi și saturaţi asupra stabilității și texturii compoziţiilor alimentare cu ulei de nucă; analiza impactului antioxidanților asupra prevenirii degradării oxidative a acizilor graşi polinesaturaţi ai uleiului de nucă; elaborarea compoziţiei şi tehnologiei de obţinere a alimentelor noi sub formă de emulsii A/U, de tipul *spread*, pe baza produselor lactate și uleiului de nucă; aprecierea valorii nutritive și proprietăților fizico-chimice ale spread-urilor cu ulei de nucă; stabilirea termenului de valabilitate și duratei de păstrare a produsului finit.

Noutatea şi originalitatea ştiinţifică: pentru prima dată a fost argumentată științific și demonstrată experimental posibilitatea prevenirii degradării oxidative a acizilor grași polinesaturați ai uleiului de nucă în compozițiile alimentare prin combinarea lipidelor uleiului de nucă și grăsimilor lactate sub formă de emulsii.

Problema ştiinţifică soluţionată: stabilirea celor mai importante proprietăţi fizico-chimice, nutritive şi tehnologice ale compozițiilor pe bază de ulei de nucă şi identificarea condiţiilor optimale şi eficiente de procesare tehnologică şi de utilizare a acestora.

Semnificaţia teoretică: perfectarea metodelor de cercetare a calității uleiului de nucă, obţinerea rezultatelor ştiinţifice care demonstrează posibilitatea de stabilizare a compozițiilor lipidice cu un conținut înalt de acizi grași polinesaturați și formarea pe baza acestora a unor produse alimentare funcționale.

Valoarea aplicativă a lucrării: a fost argumentată metodologia de utilizarea a uleiului de nucă la obținerea diferitor produse alimentare cu un conținut ridicat de acizi grași polinesaturați, în special în compoziții alimentare sub formă de emulsii.

Implementarea rezultatelor ştiinţifice: publicații în reviste, culegeri ale simpozioanelor, discutarea rezultatelor în cadrul dezbaterilor la conferinţele ştiinţifice naţionale şi internaţionale (19 lucrări științifice); brevetul de invenţie nr.1281 „Procedeu de obţinere a amestecului de grăsimi tartinabile pe bază de smântână dulce”.

АННОТАЦИЯ

Раду Оксана: Пищевые композиции на основе масла грецкого ореха (*Juglans regia L.*), устойчивые к окислительной деградации, диссертация на соискание ученой степени доктора технических наук, Кишинэу, 2020.

Структура диссертации: диссертация состоит из введения, 4 глав, выводов и рекомендаций, списка литературы из 233 ссылок, 7 приложений. Работа изложена на 103 страницах, включая 50 рисунок и 57 таблиц.

Ключевые слова: полиненасыщенные жирные кислоты, антиоксиданты, молочный жир, пищевые эмульсии, спред.

Цель работы: проведение теоретических и экспериментальных исследований для разработки пищевых композиций типа эмульсии В/М на основе масла грецкого ореха, обеспечивая стабильность и высокую биологическую ценность конечного продукта.

Задачи работы: определение возможных способов предотвращения окислительной деградации полиненасыщенных жирных кислот масла грецкого ореха в составе пищевых продуктов; изучение воздействия ненасыщенных и насыщенных жирных кислот на стабильность и текстуру пищевых композиций с маслом грецкого ореха; анализ влияния антиоксидантов на предотвращение окислительной деградации полиненасыщенных жирных кислот в масле грецкого ореха; разработка состава и технологии получения новых продуктов питания в виде эмульсий В/М, типа *спред,* на основе молочных продуктов и масла грецкого ореха; оценка пищевой ценности и физико-химических свойств спредов с маслом грецкого ореха; установление срока годности и оптимального пеориода хранения конечного продукта.

Научная новизна: впервые была научно аргументирована и экспериментально продемонстрирована возможность предотвращения окислительной деградации полиненасыщенных жирных кислот масла грецкого ореха в составе пищевых композиций путем комбинирования липидов масла грецкого ореха и молочных жиров в виде эмульсий.

Научная проблема, решенная в исследовании: определение важнейших физико-химических, питательных и технологических свойств композиций на основе масла грецкого ореха и выявление оптимальных и эффективных условий их технологической обработки и использования.

Теоретическая значимость: совершенствование методов исследования качества масла грецкого ореха, получение научных результатов, демонстрирующих возможность стабилизации липидных композиций с высоким содержанием полиненасыщенных жирных кислот и формирования на их основе функциональных пищевых продуктов.

Практическая значимость работы: была аргументирована методология использования масла грецкого ореха для получения различных продуктов питания с высоким содержанием полиненасыщенных жирных кислот, особенно в пищевых композициях в виде эмульсий.

Внедрение научных результатов: публикации в журналах и сборниках симпозиумов, обсуждение результатов в рамках дискуссий на национальных и международных научных конференциях (19 научных работ); патент № 1281 «Способ получения спреда на основе сладких сливок».

RADU OXANA

FOOD COMPOSITIONS BASED ON WALNUT OIL (*Juglans regia L.*) RESISTANT TO OXIDATIVE DEGRADATION

253.06 - BIOLOGICAL AND CHEMICAL TECHNOLOGIES IN THE FOOD INDUSTRY

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