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TECHNOLOGY OF SPECIALTY FATS BASED ON PALM STEARIN

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Розроблена нова технологія модифікування жирів, яка дозволяє шляхом ферментативного етанолізу одержати жири спеціального призначення (кулінарні, хлібопекарські та для молочної промисловості). Такі жири за показниками якості відповідають вимогам нормативних документів і, крім того, збагачені фізіологічно-активними інгредієнтами – етиловим ефірами жирних кислот, які краще засвоюються організмом людини і зменшують ресинтез жиру

Ключові слова: алкоголіз, пальмовий стеарин, етиловий спирт, фермент, етилові ефіри, жир спеціального призначення

Разработана новая технология модифицирования жиров, которая позволяет путем ферментативного этанолиза получить жиры специального назначения (кулинарные, хлебопекарные и для молочной промышленности). Такие жиры по показателям качества соответствуют требованиям нормативных документов и, кроме того, обогащены физиологически-активными ингредиентами – этиловыми эфирами жирных кислот, которые лучше усваиваются организмом человека и уменьшают ресинтез жира

Ключевые слова: алкоголиз, пальмовый стеарин, этиловый спирт, фермент, етиловые эфиры, жир специального назначения

1. Introduction

To date, there is imbalance in the nutritional needs of the population of Ukraine and in the world as a whole, the essence of which is that the diet is dominated by high calorie products that enter the body when eating the food with high content of fat and simple carbohydrates. This way of consuming food leads to the deterioration in the population health, occurrence of diseases of the cardiovascular system and premature aging.

The relevance of the work in this direction is linked to the fact that, since the products of oil and fat industry refer to the goods of mass demand, creating new domestic technologies and designs with respect to dietary fats with healthcare and prophylactic and functional properties can be an efficient solution to this problem.

2. Analysis of scientific literature and the problem statement

Oil and fat industry of Ukraine produces wide range of specialty fats, but there is a significant amount of fats among them that contain spatial isomers of natural unsaturated fatty acids (trans-isomers). They are formed in large volumes during hydrogenation of vegetable oils for obtaining solid and half-solid fat product. Reducing the content of trans-isomers in oil and fat products is a worldwide trend, linked to

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the discovery of the role of the trans-isomers in the development of cardiovascular diseases. In this connection, the main directions of design of technology of oil-fat products today are reducing the content of trans-isomers, drawing fatty acid and acylglycerol content of oil and fat product near to a "perfect" fat, improving functional and technological properties [1].

It was found that the trans–isomers of fatty acids deepen the deficit of essential fatty acids and significantly reduce their positive effect even at adequate consumption. Therefore, the World Health Organization (FAO/WHO) defined that the consumption of any quantity of industrial trans-isomers of fatty acids was harmful for health and recommended reducing the level of their consumption down to 1 % of the daily calorie ration. There is neither safe bottom limit nor upper tolerant intake for the trans-isomers of fatty acids, and it is not possible to set acceptable daily consumption level for the trans-isomers [2].

Alternative ways to change physical and chemical indicators of fatty raw material and obtaining fats with predetermined characteristics that do not contain trans-isomers of fatty acids are the processes of fractionation, transesterification and blending [3]. These processes are researched sufficiently enough. A new way of modifying the fats can be a process of ethanolysis, which in scientific and technical literature is more researched in terms of obtaining biodiesel fuel from technical raw fat [4, 5]. This process can also be applied to modify food fatty raw material and obtain the product with different functional and technological properties. Modification of fats by the specified way would involve restructuring of active fractions of the fats (acyl groups), namely, the conversion of triacylglycerols into the ethyl esters of fatty acids, which are better digested by human body and, at the same time, contribute to the reduction of fat resynthesis.

The task of expanding the range of fats that do not contain trans-isomers can also be successfully solved through a wider use of palm oil and its fractions and fully hydrated vegetable oils. Tropical oils and their fractions are traditionally used in the production of foodstuffs. But changing lifestyles and new requirements to the consumed products in terms of health benefits and ease of use lead to the necessity of new forms of using tropical oils.

Palm stearin is a solid fraction of palm oil, which is created in the process of fractionation after crystallization at a certain temperature, it has firm consistency with the content mostly of palmitic and stearic fatty acids, which predetermines melting temperature of 50–54 °C, it is the source of natural solid fats that do not contain trans-isomers of fatty acids. Palm stearin is used as a formulation ingredient in the products with various fat composition (margarine and fat products), for the process of transesterification and for manufacturing the products with technical purposes [6].

By its structural-mechanical properties and composition, palm stearin can partially replace hydrogenated vegetable oils, which are characterized by high content of trans–isomers of fatty acids. Specificity of the composition of palm stearin, high content of high melting triacylglycerols and limited content of the low melting ones, limits possibilities of its wider use in foodstuffs [7]. According to the Malaysian Council of palm oil producers, palm stearin can be used only in 40 % of all fat-containing food products [8].

The raw material for the production of modified specialty fats can also be fully-hydrogenated vegetable oils, such raw materials do not contain trans-isomers, they have altered physical and chemical parameters and are promising in terms of modification.

It is known that the fats in the digestive tract of a human body are exposed to hydrolytic splitting. Metabolic transformation of traditional oil involves the hydrolysis stage that is catalyzed by the enzyme – pancreatic lipase with formation of free fatty acids (FFA) and 2-monoacylglycerols (2-MAG), which are then absorbed in the intestine, resulting in the synthesis of triacylglycerols (TAG) by metabolic way with 2-MAG. If the product of hydrolysis is the 1-monoacylglycerols, then in the process of metabolism they disintegrate into glycerol and FFA, and are absorbed by the cells of the intestine, bypassing the next resynthesis of TAG. As a result, excessive amount of fat particles in the blood serum is not produced in the process of digestion because they are deposited in the cells of adipose tissue [9].

To expand the areas of application of palm stearin in fat-containing foodstuffs, it is proposed to modify it by the method of alcoholysis of fats. In particular, by processing part of acylglycerols of fats into ethyl esters and incomplete acylglycerols by fermentative ethanolysis, we propose obtaining a range of fats for special purposes. Unlike the known fats, these fats will contain certain amount of ethyl esters of fatty acids.

Ethyl esters of fatty acids can be assigned to a group of functional food ingredients. Medicinal product "Linetol" is known to have been used, which consists of a mixture of ethyl esters of fatty acids of linseed oil [10, 11]. Application of ethyl esters of linseed oil in human nutrition provides a decrease in the concentration of cholesterol and triacylglycerols in the blood serum. Their ability to prevent the formation of atherosclerotic plaques in the blood vessels of elastic type and the development of dystrophic changes in liver and kidneys, necrotic processes in myocardium, were experimentally established [12, 13]. Ethyl esters of fatty acids have better digestibility, especially for elderly people, and do not contribute to the resynthesis of fat in a human body.

Now the oil and fat and related industries face acute task of obtaining fats that will not only comply with official documentation and standard requirements, but will also be able to apply in other sectors of the food industry, which desperately need high-quality and inexpensive raw materials, therefore, this issue remains rather relevant. Improving the technology of the use of fatty products, in particular, palm stearin, in the production of oil and fat products, means a significant advantage, namely: providing the required amount of solid fat without the use of hydrogenated fats or reducing their amount to a minimum.

Taking into account the needs of the population of Ukraine in the functional food, this technology can become an important contribution to solving the problem of recovery and increase in the life expectancy of the population of Ukraine.

3. The purpose and objectives of the study

The aim of this work is to develop a method of obtaining a new type of specialty fats by way of fermentative alcoholysis.

To achieve the set goal, the following tasks are to be solved:

– to determine rational conditions of obtaining specialty fats;

– to study the composition and properties of the products of fermentative ethanolysis of fatty raw material;

– to identify ways of applying the obtained products of the synthesis.

4. Materials and methods of the study of the process of modification, the composition and properties of the products of ethanolysis of palm stearin

Industrial sample of palm stearin was used in the research. The data on fatty acid composition of palm stearin are presented in Table 1.

Table 1

Fatty acid composition of palm stearin

Fatty acids	A range of values [14]	Industrial sample
Lauric acid ($C_{12:0}$), %	0,1–0,3	0,24
Myristic acid ($C_{14:0}$), %	1,1–1,7	1,36
Palmitic acid ($C_{16:0}$), %	49,8–68,1	60,75
Palmitoleic acid ($C_{16:1}$), %	0,05–0,1	–
Stearic acid ($C_{18:0}$),%	3,9–5,6	4,89
Oleic acid ($C_{18:1}$), %	20,4–34,4	27,06
Linoleic acid ($C_{18:2}$), %	5,0–8,9	5,42
Alpha-linolenic acid ($C_{18:3}$), %	0,1–0,5	–
Arachidonic acid ($C_{20:0}$), %	0,3–0,6	0,28

For carrying out the processes of modification we used lipolytic enzyme Lipozyme TL IM, the drug lipase, immobilized on granular silica gel, manufactured by Novozyme (Denmark).

For the modification of fatty materials, the restructuring of the fats is proposed, namely, of their active parts (acyl groups), with obtaining the derivatives of fatty acids that have functional properties. The purpose of this adjustment is to convert triacylglycerols (fats) into the ethyl esters of fatty acids, which are better absorbed by a human body and reduce the resynthesis of fat.

The method of modification of fatty raw material is based on the reaction of ethanolysis. The reaction scheme is in Fig. 1 [15].

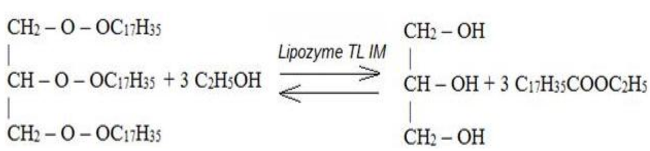

Fig. 1. Reaction of obtaining ethyl esters of fatty acids

The vast majority of specific lipases influence extreme 1.3-ester bonds of the triacylglycerols, while the reaction with central 2-bond is difficult, which reduces the output of the final product by a third. This obstacle can be reduced through the use of the phenomenon of acyl-migration of acyl groups of triacylglycerols from position 2 into the free position 1 or 3, followed by the reaction with 1.3-regiospecific lipase. Acyl-migration can be induced by using lipases, immobilized by ion-exchanging polar resins, for example, by anionite in the case of Lipozyme IM, or by adding silica gel to the reaction medium. The output of ethyl esters increases up to 90 % [16].

To determine the component structure of the obtained products of synthesis – monoacylglycerols (2-MAG), diacylglycerols (DAG), triacylglycerols (TAG), ethyl esters of fatty acids (EEFA), we used the gas chromatograph CP-3800 (Varian), equipped with a flame ionization detector, a system of electronic control of gas flows, universal injector for the introduction of samples in the modes with and without separation of flows, autosampler (CP-8410 Varian) and the computer software "Galaxy".

We used capillary column MET-Biodiesel (length of 14 m, internal diameter of 0.53 mm, thickness phases of 0.16 μм) with the length, before the column, of 2 m, internal diameter of 0.53 mm; flow rate of 2.5 ml/min, the coefficient of flow distribution of 20:1, the temperature of the injector of 390 °C, the temperature of the detector (PID) of 400 °C, injected volume of 1.0 ml.

5. Results of the study of the composition and properties of the products of ethanolysis of palm stearin

The research aimed at creating functional products based on palm stearin and expanding the area of its application was conducted using enzyme technology. Functional purpose to the products of synthesis is provided by the component – ethyl esters of fatty acids, which are better absorbed by a human body and reduce the resynthesis of fat.

We used enzyme preparation as a catalyst in the process of alcoholysis, which is a product of protein nature, and this affects the conditions of the process. In particular, the temperature of the process, this is an important indicator. According to the recommendations of the manufacturer, the temperature of the process for optimal performance of the enzyme must be maintained within the range of 60–70 °C; the amount of the enzyme preparation Lipozyme TL IM should reach 12 % by mass of the fatty acids in the composition of triacylglycerols.

The influence of the conditions of fermentative alcoholysis of palm stearin by ethyl alcohol on the degree of its conversion into ethyl esters of fatty acids was defined. Rational conditions of the process were identified:

– the amount of the enzyme Lipozyme TL IM – 12 % by mass of fatty acids;

– mole ratio of fatty acid : ethyl alcohol – 1:3;

– the temperature of the process – 60 °C;

– duration of the process – 13 hours at constant stirring.

The samples were taken every hour and the melting point of the reaction mixture was determined. The experimental data of kinetics of the process of fermentative alcoholysis of palm stearin is in Fig. 2.

It was found that in the reaction of alcoholysis of palm stearin, when using ethyl alcohol as a reagent in the presence of lipolytic enzyme, there occurs a change of physical and chemical indicators (including the melting temperature decrease) and of the composition of the reaction mixture, due to accumulation of ethyl esters and incomplete acylglycerols. This feature makes it possible to obtain fats with predetermined composition and properties, by terminating the process at a certain stage.

According to the documents, regulating the oil and fat industry in Ukraine, specialty fats include confectionery fats, culinary, bakery fats and those for dairy industry.

These types of fat products are in accordance with DSTU 4335:2004 "Fats: confectionery, culinary, bakery and for dairy industry. General technical specifications". Organoleptic and physical-chemical parameters of the fats in accordance with DSTU 4335:2004 are included in Table 2.

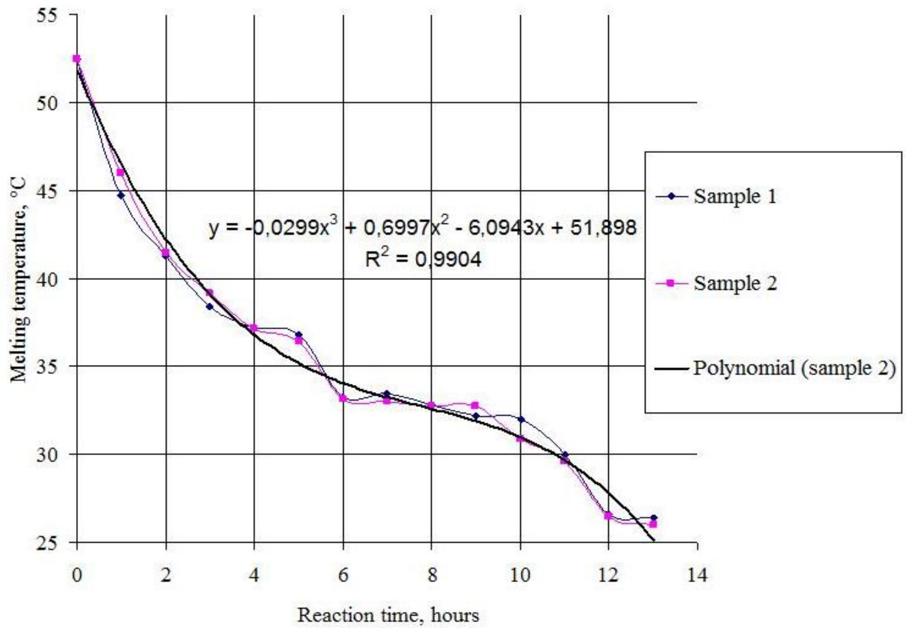

Fig. 2. Kinetics of melting temperature of palm stearin during the reaction of alcoholysis

Important physical-chemical indicators of specialty fats that are included in the foodstuffs are the melting point, hardness and content of solid phase in the defined range of temperatures. Melting temperature of a fat phase determines the fusibility of a product, which characterizes the fullness of fat melting at the temperature of a human body.

By studying the kinetics of melting temperature of palm stearin, it was found that after a certain time period, the indicator of melting temperature corresponded to the requirements of the normative documentation (DSTU 4335:2004) on the specialty fats. The correspondence of characteristics of the fatty products to the requirements of the normative documentation is presented in Table 3.

Thus, one can confirm that in 5 hours, according to the melting temperature indicator, we obtained confectionery fat and fat for dairy products; in 6 hours, this fat corresponded to the culinary and confectionary fat, and fat for dairy products; in 13 hours – to the bakery fat.

Table 2

Organoleptic and physical-chemical parameters of specialty fats in accordance with DSTU 4335:2004

Name of the indicator	Standard for fats			
	Culinary	Confectionery	Bakery	For dairy products
Smell and taste	Pure, in case of introduction of animal fats and aromatic additives, characteristic for these additives	Pure taste, characteristic for fat, without additional flavour and smell	Pure taste. The smell of the added flavoring	Pure taste. The smell of the added flavoring
Colour	From light-yellow to yellow	From white to light-yellow	From light-yellow to yellow	From light-yellow to yellow
Consistency	Homogeneous, hard, plastic or ointment-like	Homogeneous, hard, fragile	Homogeneous, movable (measured at temperature 16 °C)	Homogeneous, hard, plastic or ointment-like. Bulkiness allowed.
Mass fraction of fat, %, not less than	99,70			
Mass fraction of moisture and volatile substances, %, not higher than	0,30			
Acid number, mg CON/g, not higher than	0,4		0,5	0,4
Melting point, °C	28,00–36,00	28,00–39,00	17,00–27,00	32,00–38,00
Temperature of hardening, °C	–	Not lower 29	Not higher 15	–
Peroxide number, ½ O mmol/kg – at the dispatch from the enterprise	5,00			
Mass fraction of solid triacylglycerols at 20 °C, %	25–45	25–80	25–35	26–34
Hardness by Kaminsky, at temperature of 15°C, g/cm	–	150–850	–	80–180
Mass fraction of nickel, mg/kg, not higher than	0,5			

Table 3

Characteristics of obtained fatty products in accordance with DSTU 4335

The duration of the process (melting point)	Culinary 28,00–36,00 °C	Confectionery 28,00–39,00 °C	Bakery 17,00–27,00 °C	For dairy products 32,00–38,00 °C
5 hours (36,4–36,8 °C)	–	+	–	+
6 hours (33,1–33,3 °C)	+	+	–	+
13 hours (26,4–26,6 °C)	–	–	+	–

Another important indicator of fats that differentiates the area of application is hardness. The hardness of fat raw materials, which is determined (in accordance with normative documentation) at 15 °C, characterizes one of the most important properties of solid fats and oils – the attribute to acquire necessary structure at a certain temperature. The higher the content of the solid fraction in this fat, the higher is its hardness. The content of the solid phase within the temperature range from 5 to 35 °C defines the plasticity of fatty products, which describes the property of the fat, under the influence of mechanical action, to change the shape without breaking the whole, i. e., the property to maintain the shape after discarding the load. A fat with necessary plasticity does not change in a wide range the ratio of solid and liquid acylglycerols. Thus, high elastic-plastic properties of a product are determined by the composition of its solid fraction, which is heterogeneous and enters liquid state in a wide range of temperatures [14].

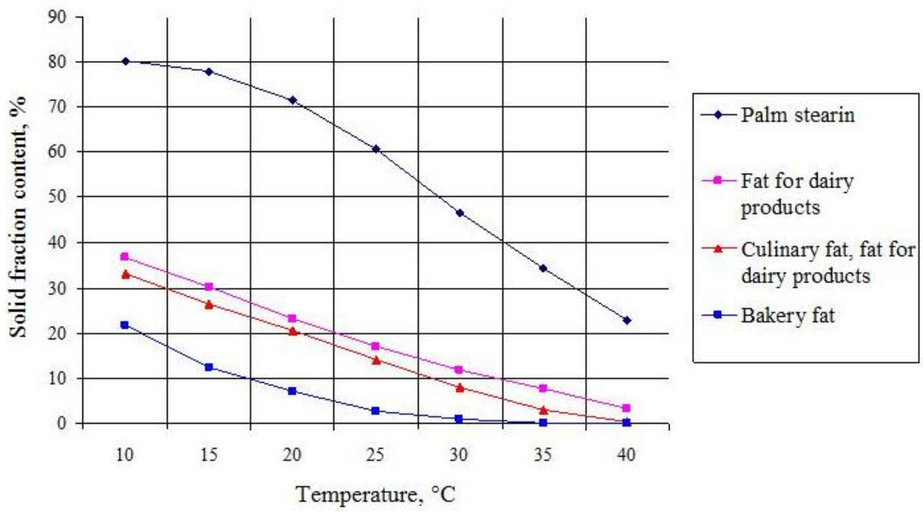

Fig. 3. Results of the study of the content of TTG by the NMR method

All received fatty products were analyzed by the Kaminsky device and the indicator of hardness was specified according to DSTU 4463:2005. Thus, it was established that for the sample after 5 hours of the reaction, the hardness at 15 °C was 101–108 g/cm, after 6 hours – 88.7–97,0 g/cm; the assessment was not performed for a fatty product after 13 hours of the reaction, because its consistency was plastic and, according to the normative documentation, this indicator is not standardized. Analyzing the obtained results for the compliance with the applicable regulatory document, we can conclude that, according to the indicators of melting temperature and hardness, fatty products have the following purposes:

– after 5 hours of the reaction – fat for dairy products;
– after 6 hours – culinary fat and dairy products;
– after 13 hours – bakery fat.

Apart from the classical determination of the hardness of obtained fatty foods (by the Kaminsky device), this indicator was defined also by a modern method of nuclear magnetic resonance (NMR), which allows setting the percentage content of solid triacylglycerols (TTG) in a sample of fat at a certain temperature. The NMR method makes it possible to assess the mass fraction of TTG with high accuracy and reproducibility of the received data. The results of the studies are in Fig. 3.

6. Discussion of the results of the study of the composition and properties of the products of ethanolysis of palm stearin

As a result of the performed research, the possibility of modification of fatty raw materials by fermentative ethanolysis was proved, and the products with the required physical-chemical indicators were obtained. This technology has significant advantages over the existing ones, because it eliminates the possibility of the formation of trans-isomers of fatty acids in the products of modification, and also provides their enriching with physiologically-active ingredients, namely, ethyl esters of fatty acids. Considering the need for healthcare improvement of the population of Ukraine, which is predetermined by relevant government programs, the task of organization of production of the specified fatty foods is extremely urgent.

The disadvantage of the results of the presented study is the possibility to obtain only limited range of specialty fats. A selected raw material, palm stearin, due to certain features of its composition, does not allow obtaining confectionery fats by the indicator of hardness.

The authors plan to continue studies on modification of other fatty raw materials, the use of which will allow obtaining high-quality confectionery fats with defined characteristics.

When analysing the received data, it should be noted that in comparison with the original product, palm stearin, the modified fatty products differ in a lower melting temperature and less content of hard triacylglycerols, and as a result, better plasticity.

As a result of the reaction, the fatty product contains incomplete AG and ethyl esters of fatty acids. Ethyl esters of fatty acids provide the same effect as the acids, but they have better organoleptic properties, better indicators of digestion and are better tolerated, especially during a prolonged use. Defining a component composition of the obtained products of the synthesis (MAG, DAG, TAG, ethyl esters of fatty acids) was carried out on the gas chromatograph CP-3800, the obtained results are in Fig. 4.

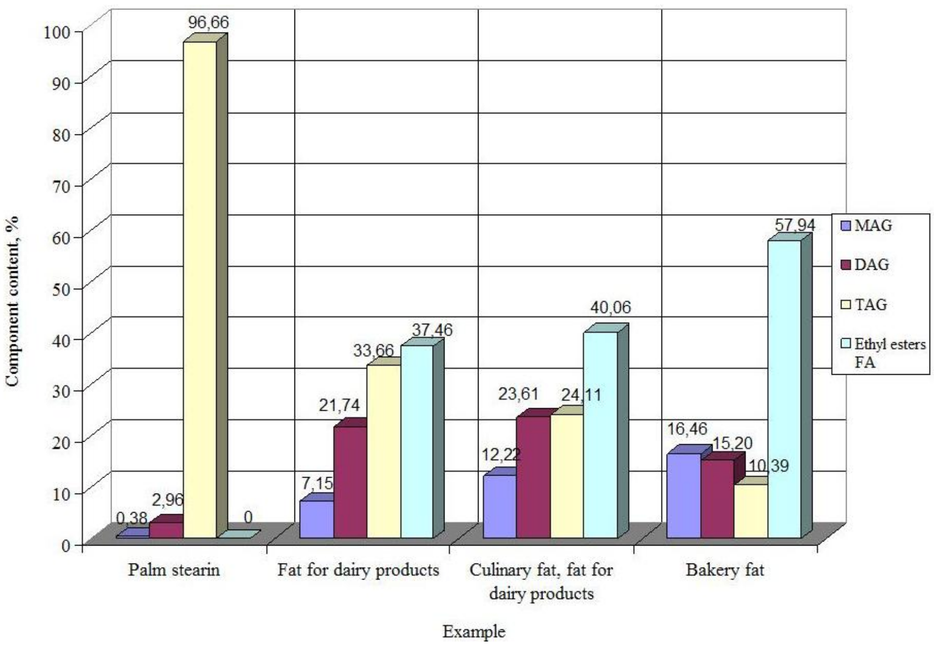

Fig. 4. Component composition of the obtained products of the synthesis

The use of a modified fatty raw material based on palm stearin allows obtaining a product free from trans-isomers of fatty acids. The resulting product and the food systems based on it are promising functional products in terms of weight regulation of a human body and are acceptable substitutes for traditional fats in everyday food.

It is important to note that in the process of such a modification for obtaining specialty fats, fully hydrated vegetable oil, salomas of brand M6, may serve as an alternative raw material. Due to the complete saturation of double bonds, this product does not contain trans-isomers and has altered physical and chemical characteristics. The use of such fat raw material also allows obtaining modified products of high quality and with predetermined characteristics.

7. Conclusions

1. New technology of modification of fats was developed, which allows obtaining, by alcoholysis of fatty raw material, a new type of specialty fats for use in the food industry (culinary, bakery and dairy products). The rational conditions of obtaining such fats were defined: the amount of enzyme Lipozyme TL IM – 12 % by mass of fatty acids; mole ratio of fatty acid: ethyl – 1:3; process temperature – 60 °C; duration of the process – depending on the required qualification.

2. It was established that the obtained fats meet the requirements of the regulation by the indicators of quality, which are set for the specialty fats, and which, additionally, are enriched with the physiologically-active ingredients – ethyl esters of fatty acids, which are better digested and reduce the resynthesis of fat in a human body.

3. The ways to use the obtained products of the synthesis were established in accordance with the normative documentation on this type of product, and are determined by physical and chemical indicators. The raw material for obtaining the confectionary fat, which was proposed, is a fully hydrogenated vegetable oil. Thus, by using the developed method, and choosing the necessary raw material while varying the conditions of the reaction, one can obtain a whole range of specialty fats.

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THE INFLUENCE OF MECHANOLYSIS ON THE ACTIVATON OF NANOCOMPLEXES OF HETEROPOLYSACCHARIDES AND PROTEINS OF PLANT BIOSYSTEMS IN DEVELOPING OF NANOTECHNOLOGIES

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Запропоновано та розроблено нанотехнологію білкових рослинних добавок у формі нанопорошков і нанопюре із гороху, яка заснована на процесах глибокої переробки сировини. В якості інновації використовували дрібнодисперсне подрібнення термообробленої сировини, яке супроводжується неферментативним біокаталізом-механолізом нанокомплексів біополімерів (гетерополісахардів і білків) в розчинну легкозасвоювану форму

Ключові слова: нанотехнологія, дрібнодисперсне подрібнення, механоліз, нанокомплекси, біополімери, гетерополісахариди

Предложена и разработана нанотехнология белковых добавок в форме нанопорошков и нанопюре из гороха, которая основана на глубокой переработки сырья. В качестве инновации использовали мелкодисперсное измельчение термообработанного сырья, которое сопровождается неферментативным биокатализом-механолизом нанокомплексов биополимеров (гетерополисахаридов и белков) в растворимую легкоусваиваемую форму

Ключевые слова: нанотехнология, мелкодисперсное измельчение, механолиз, нанокомплексы, биополимеры, гетерополисахариды

1. Introduction

It is known that vegetable raw materials, particularly fruits, vegetables are a source of biologically active substances for human body, such as vitamins, carotenoids, anthocyanins, chlorophyll, phenolic compounds, minerals and indigestible components, i. e. prebiotics such as heteropolysaccharides, protein, cellulose, pectin substances, etc. [1–4].

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