The object of the research is the period of induction of accelerated oxidation of biotechnologically transesterified fatty systems that do not contain trans isomers of fatty acids. The paper defines the rational ratio of fatty raw materials in mixtures for biotechnological transesterification. The results obtained make it possible to develop biotechnologically transesterified three-component fat systems (palm stearin, coconut and sunflower, or soybean, or corn, or sesame oil) to obtain substitutes for milk fat. The proposed calculation of melting points of transesterified fat systems of a wide range of ratios of raw components allows us to justify such rational ratios of components that allow obtaining finished products with a melting point of 33.0...33.5 °C. It is effective to use the products of the developed composition in view of the technological requirements of consumers for their oxidizing capacity. The data obtained in the work are explained by the fatty acid and antioxidant composition of low-melting components of fat systems in a different range of their ratios, which determines different technological properties, in particular, the melting point and stability to oxidation of finished products. A feature of the obtained results is the competitiveness of the obtained fat systems, which are characterized by the absence of atherogenic components and the presence of biologically valuable polyunsaturated fatty acids in the composition. The results of the research make it possible to minimize the cost of raw components while preserving the nutritional value and technological characteristics. An applied aspect of using the scientific result is the possibility of expanding the range of milk fat substitutes with high nutritional value

Keywords: biotechnological transesterification, fat systems, fat peroxide value, oxidation induction period

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DEVELOPMENT OF BIOTECHNOLOGICALLY TRANSESTERIFIED THREE-COMPONENT FAT SYSTEMS STABLE TO OXIDATION

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1. Introduction

Given the limited resources of natural solid fats used in various branches of the food, cosmetic, and pharmaceutical industries, fats that have undergone chemical or physical modification are widely used [1, 2]. Until recently, hydrogenation was the main method of fat modification, which allows you to obtain products with high hardness and suffi-

cient stability to the oxidation process due to the content of a large number of trans isomers in them. Studies on the metabolism of industrial trans isomers of fatty acids in the human body allowed us to draw a conclusion about their atherogenic nature [3]. Unlike hydrogenation, transesterification, in particular biotechnological (using enzyme preparations as catalysts), does not affect the degree of saturation and does not cause isomerization of double bonds in fatty acids. Therefore, transesterification does not lead to the formation of trans isomers of fatty acids, which are dangerous for health. In addition, biotechnological transesterification makes it possible to obtain oxidation-stable products, including by preserving the content of antioxidants in raw components [4]. Unlike biotechnological, chemical transesterification does not allow preserving natural antioxidants of oils, the amount of which decreases several times in the process [5].

Requirements for the quality of transesterified fats vary and depend on the industry and conditions of their use. When creating transesterified fats, the following aspects must be taken into account [6, 7]:

– melting point;

– fatty acid composition (control of the amount of polyunsaturated fatty acids);

– formation of a β-crystalline form of the product during technological operations (in the case of solid fat production);

– the amount of trans isomers (no more than 2 % of the fat content in the product);

– resistance to oxidation.

Biotechnological transesterification makes it possible to obtain a fairly wide range of products when using a limited set of available raw materials. Various technological properties of finished products are achieved by varying the composition and ratio of raw ingredients of the fat mixture for transesterification [8].

The oxidative stability of transesterified fat systems is one of the key aspects of their use in the food, cosmetic and pharmaceutical industries. Intra- and intermolecular transesterification of fatty acids can change the structure (isomerization process of fatty acids) and, accordingly, the properties of fats, which can affect their resistance to oxidation [9].

To ensure the oxidative stability of transesterified fat systems, research is being conducted in the following areas [2, 9, 10]:

– selection of optimal transesterification methods,

– use of antioxidants during or after transesterification,

– effect of storage conditions (under the influence of heat, light and oxygen) on the oxidative stability of transesterified fatty products,

– study of the interaction of transesterified fats with other components of fat-containing products,

– testing stability to oxidative deterioration of products in real conditions of storage and transportation.

Therefore, research aimed at predicting the oxidative stability of biotechnologically transesterified fat systems allows us to reveal the dependence of storage duration on the type and ratio of raw ingredients, to rationalize a number of production processes. Thus, scientific research on the identification of patterns of influence of the type and ratio of raw components on the oxidative stability of transesterified fat systems is relevant. The results of such research are necessary for production in order to identify promising raw materials for transesterified fats, as well as to expand the range of finished products with a given stability to oxidative deterioration.

2. Literature review and problem statement

The study [11] analyzed the effect of enzymatic transesterification on the oxidative stability of single-component systems – cotton, palm, and soybean oils stored at different temperatures. Oxidation rates (peroxide and anisidine values) in transesterified oils have been shown to increase faster. In addition, transesterification reduces the content of tocopherols in the studied oils. But the issues related to the study of the oxidative stability of multicomponent transesterified fat systems remained unresolved. Such studies were carried out in [12], which investigated the effect of activation of the Lipozyme TL IM enzyme preparation for the biotechnological transesterification of fat systems based on mixtures of palm stearin, coconut and sunflower or soybean, or corn, or sesame oils by means of hydration with an aqueous solution of sodium bicarbonate with pH 7.4...7.7 (3 % by weight) on the oxidative stability of products. Oxidation rates of the product transesterified by the improved technology were compared to those of the raw material and the product produced by the traditional technology. It was determined that the improvement of biotechnology does not lead to an increase in the oxidation rates of products. But the oxidative stability of transesterified fats is lower than that of raw materials. It would be appropriate to study the influence of parameters of the transesterification process, which are varied in the work, on the oxidative stability of the finished product.

Physico-chemical parameters, including the oxidative stability of two-component fat mixtures transesterified by immobilized and native lipases (canola oil and palm stearin), were studied in [13]. In particular, it was shown that the oxidative stability of the obtained fat products was lower than that of the starting material, but higher when using the lipase enzyme preparation in immobilized form. The issue of determining the effect of the triacylglycerol composition and the content of polyunsaturated fatty acids in the developed products on oxidation rates during storage compared to the control remained unresolved.

This is the approach used in [14], where the oxidative stability of mixtures of beef stearin and rapeseed oil transesterified in different ratios was investigated. Immobilized lipases from Rhizomucor miehei (Lipozyme IM) and Candida antarctica (Novozym 435) were used as catalysts. During the study of the distribution of fatty acids of transesterified triacylglycerols according to sn-2 and sn-1,3 positions, it was found that it was close to random when using Novozym 435. When using Lipozyme IM, the composition of fatty acids in the sn-2 position remained practically unchanged compared to the original mixture. It was found that transesterified mixtures are less resistant to thermo-oxidative deterioration compared to non-esterified ones. When comparing the oxidative stability of transesterified products, a greater lability to oxidation of transesterified fat using Novozym 435 was revealed. An unresolved issue is the lack of data on determining the effect of the percentage content of the formed components (free fatty acids, mono- and diacylglycerols) on the index of oxidative stability.

The mentioned research questions [12, 14] were answered in a certain way in [15], where the oxidation stability of the bio-esterified mixture of goose fat and rapeseed oil in a certain ratio was investigated. A commercial preparation of immobilized lipase from Rhizomucor miehei (Lipozyme RM IM) was used as a catalyst. The initial mixture and transesterified products were separated into a fraction of pure triacylglycerols and a fraction containing free fatty

acids, mono- and diacylglycerols. It was determined that the main factors affecting the oxidative stability of the investigated native and transesterified fats were the concentration of tocopherols and the presence of free fatty acids, mono- and diacylglycerols. The structure of triacylglycerols was of secondary importance as a factor of oxidation stability of the fatty system. However, it must be taken into account that fats may contain other components (e. g. antioxidants, sterols, etc.), so it is important to consider their effect on oxidative stability. The issue of determining the effect of antioxidants on the oxidation parameters of transesterified fats remains unresolved.

As shown by the results of research [11–15], the process of transesterification, including enzymatic, has a negative effect on the content of antioxidants in the finished product and, accordingly, on its oxidative stability. Thus, there is not enough scientific data on the effect of the type, content, antioxidant composition and ratio of fatty raw materials of plant origin on the stability to oxidative deterioration of the products of biotechnological transesterification. Considering the results of the studies described in [16, 17], it is of interest to study the influence of natural antioxidants in the composition of raw materials on the oxidative stability of bio-esterified fat, which is not biodiesel, but a food product. Such studies would allow us to rationalize the production processes of bio-esterified fats, as well as to predict their expiration dates, as well as to promote attention to natural antioxidants that increase the oxidation stability of transesterified products. This should positively affect the shelf life and transportation of such products, as well as the expansion of their scope of application.

3. The aim and objectives of the study

The aim of the study is to determine the influence of the characteristics of fat components of plant origin on the induction period of oxidation of biotechnological transesterification products. This will make it possible to predict the shelf life of transesterified fat systems. The obtained data will also be useful for justifying the use of a wide range of low-melting vegetable oils as raw materials for obtaining oxidation-stable transesterified fat systems.

To achieve the aim, the following objectives should be accomplished:

– to determine the dependence of the melting point of transesterified fats on the content of low-melting oil in the mixtures;

– to determine the oxidative stability of biotechnologically transesterified fat systems;

– to analyze the economic feasibility of using the proposed raw components in the biotechnology of transesterification of fat systems.

4. Materials and methods

4. 1. Object and hypothesis

The object of the study is such technological characteristics of enzymatically transesterified three-component fat systems as the melting temperature and induction period of accelerated oxidation. The main hypothesis of the study is the dependence of the oxidation induction period of transesterified fatty systems on the fatty acid and antioxidant composition of raw materials.

The study assumes that the oxidation induction period of transesterified three-component fat systems under recommended storage conditions is directly proportional to their oxidation induction period under accelerated conditions. The recommended storage conditions should be considered storage in closed darkened rooms in the temperature range from 0 °C to +20 °C [18]. Accelerated oxidation conditions are oxidation at a temperature of +90±2 °C with free access of oxygen.

The following simplification is adopted in the study:

– generally available raw materials for enzymatic transesterification have similar physicochemical parameters, in particular, the content of moisture and volatile substances, the mass fraction of phosphorus-containing substances, acid, peroxide and anisidine values, as the raw materials that were studied. This simplification should prove obtaining a certain repeatability of the dependences determined during the study of the influence of the component composition of fat mixtures on the induction period of oxidation of transesterified fat systems.

4. 2. Materials used in the experiment

The following materials were used during the studies:

– refined, bleached and deodorized palm stearin (produced in Malaysia), according to CAS 91079-14-0;

– refined, bleached and deodorized coconut oil (produced in Malaysia), according to CAS 8001-31-8;

– refined, bleached and deodorized sunflower oil (produced in Ukraine), according to CAS 8001-21-6;

– refined, bleached and deodorized soybean oil (produced in Ukraine), according to CAS 8001-22-7;

– refined, bleached and deodorized corn oil (produced in Ukraine), according to CAS 8001-30-7;

– refined, bleached and deodorized sesame oil (produced in Ukraine), according to CAS 8008-74-0;

– Lipozyme TL IM immobilized enzyme preparation, which is Thermomyces lanuginosus lipase immobilized on silica gel (manufactured by Novozymes A/S, Denmark);

– Akomix milk fat substitute (produced by the AAK concern, Sweden) [18];

– natural melted butter (produced by the CE Mahdalynivskyi butter factory, Ukraine) [19].

4. 3. Method of biotechnological transesterification of fat systems

The transesterification process using Lipozyme TL IM was carried out under vacuum at a temperature of 70±1 °C (stirring – 500 rpm). The content of the enzyme preparation in the reaction mixture was 10 % by weight of the fat system according to [12]. The Lipozyme TL IM enzyme preparation was pre-moistened with an aqueous solution of sodium bicarbonate with a pH in the range of 7.4...7.7 and then aged for 15 minutes for activation. At specified time intervals, samples were taken from the reaction fat mixture for the analysis of physico-chemical parameters.

The pH of an aqueous solution of sodium bicarbonate for moistening the enzyme preparation was determined by the potentiometric method.

4. 4. Method of determining the physicochemical parameters of fatty raw materials and transesterified fats

The melting point of fat raw materials, fat reaction mixture and transesterified fats was determined according to DSTU EN ISO 6321.

The peroxide value of fat raw materials, fat reaction mixture and transesterified fats was determined by the titrimetric method according to DSTU ISO 3960.

4. 5. Method of accelerated oxidation and determination of the induction period of oxidation of transesterified fats

Accelerated oxidation of samples of transesterified fats was carried out at a temperature of 90±1 °C for 20 hours. During accelerated oxidation, primary oxidation products (peroxides and hydroperoxides) accumulated in triacylglycerols, which was identified by determining the peroxide value.

The induction period of oxidation of the samples was determined graphically, using the curve of the change in the peroxide value during the oxidation of the samples, which characterizes the accumulation of primary oxidation products (peroxides and hydroperoxides) in them. The shelf life of samples of transesterified fats is directly proportional to the value of the oxidation induction period.

4. 6. Method of determining the economic feasibility of using raw materials in the biotechnology of transesterification of fat systems

The economic effect (E_e) represents a reduction in the cost of production, provided that the use of raw components in production is compared with commercial analogs and is calculated by the formula (1):

$$E_e = \sum_{i=1}^{n} P_i \cdot C_i - \sum_{j=1}^{m} P_j \cdot C_j, \quad (1)$$

where P_i, P_j are the cost of raw components in the composition of the commercial analog and the proposed transesterified fats, respectively, \$/kg; C_i, C_j are the content of raw components in the composition of the commercial analog and the proposed transesterified fats, respectively, kg/t.

4. 7. Research planning and results processing

Three-factor and one-factor experiments were used in studies on the biotechnological transesterification of three-component fat systems with a given oxidation stability. Each experiment was repeated three times. Statistical models of the dependence of the melting point of transesterified fats on the composition and ratio of the components of fat mixtures were calculated using the approximation of experimental data by constructing a trend surface. The dynamics of changes in the peroxide value of lipids of biotechnologically transesterified fats with different low-melting components were used to determine the induction periods of oxidation of transesterified fats of different composition. Processing of the obtained data and construction of graphical dependencies were performed using Stat Soft Statistica v 6.0 (USA) and Microsoft Excel (USA) packages.

5. Results of studies of biotechnological transesterification of three-component fat systems with a given oxidation stability

5. 1. Determination of the dependence of the melting point of transesterified fats on the content of low-melting oil in the mixtures

A study of the rational ratio of components of fat mixtures with various low-melting components for biotechnological transesterification was carried out in order to obtain thermostable systems with a melting point of 30...34 °C (similar to that of milk fat):

– palm stearin, coconut and sunflower oils;
– palm stearin, coconut and soybean oils;
– palm stearin, coconut and corn oils;
– palm stearin, coconut and sesame oils.

The experiments were conducted according to the composition-property plan. The content of components of fat mixtures is taken as factors:

– $c_{p.st.}$ – palm stearin content;
– $c_{cn.o.}$ – coconut oil content;
– $c_{sf.o.}$ – sunflower oil content;
– $c_{sb.o.}$ – soybean oil content;
– $c_{c.o.}$ – corn oil content;
– $c_{ses.o.}$ – sesame oil content;

the response function is the melting point ($MT_{f.p.}$) of transesterified fatty products.

The content of components of fat mixtures was varied in the range of 0...100 % with a step of 25 %. The obtained melting point values of transesterified fatty products were in the range of –18.7...47.4 °C. The surfaces of the obtained dependencies are shown in Fig. 1–4.

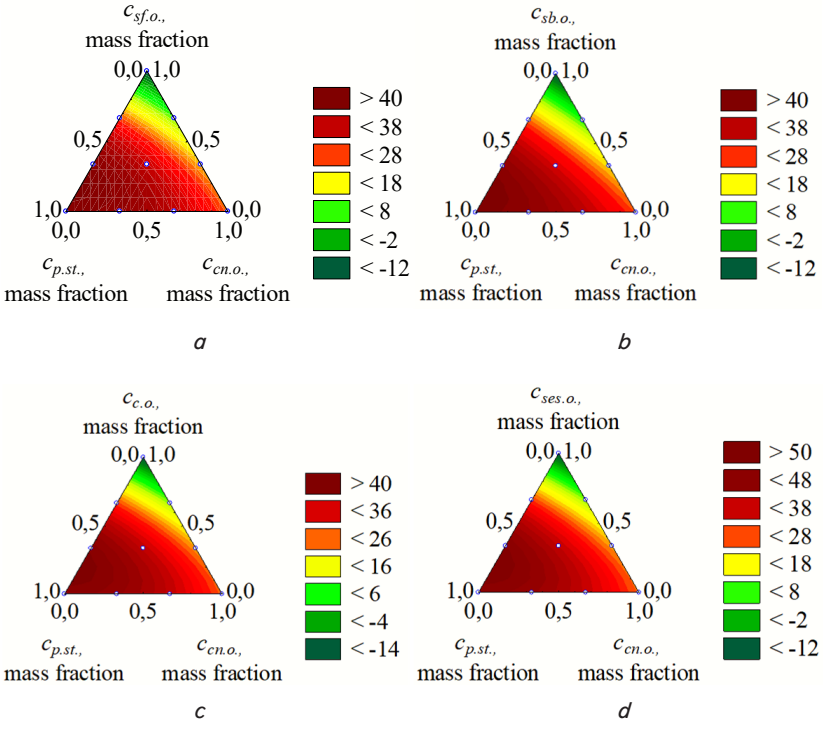

Fig. 1. Dependence of the melting point of transesterified fats on the type of low-melting oil, composition and ratio of components of fat mixtures: *a* – palm stearin, coconut and sunflower oils; *b* – palm stearin, coconut and soybean oils; *c* – palm stearin, coconut and corn oils; *d* – palm stearin, coconut and sesame oils

Approximate dependences of the melting point ($MT_{f.p.}$) of transesterified fat products on the content of the components of fat mixtures ($c_{p.st.}$, $c_{cn.o.}$, $c_{sf.o.}$, $c_{sb.o.}$, $c_{c.o.}$, $c_{ses.o.}$) are presented using equations (2)–(5).

– for the fatty system: palm stearin, coconut and sunflower oils:

$$MT_{f.p.}(c_{p.st.}, c_{cn.o.}, c_{sf.o.})=46.3971\cdot c_{p.st.}+ +25.24\cdot c_{cn.o.}-13.5314\cdot c_{sf.o.}+23.0786\cdot c_{p.st.}\cdot c_{cn.o.}+ +90.9643\cdot c_{p.st.}\cdot c_{sf.o.}+40.2429\cdot c_{cn.o.}\cdot c_{sf.o.}; \quad (2)$$

– for the fatty system: palm stearin, coconut and soybean oils:

$$MT_{f.p.}(c_{p.st.}, c_{cn.o.}, c_{sb.o.})=46.52\cdot c_{p.st.}+ +25.6486\cdot c_{cn.o.}-12.9229\cdot c_{sb.o.}+ +20.8929\cdot c_{p.st.}\cdot c_{cn.o.}+78.8786\cdot c_{p.st.}\cdot c_{sb.o.}+ +27.5143\cdot c_{cn.o.}\cdot c_{sb.o.}; \quad (3)$$

– for the fatty system: palm stearin, coconut and corn oils:

$$MT_{f.p.}(c_{p.st.}, c_{cn.o.}, c_{c.o.})=46.4657\cdot c_{p.st.}+25.1657\cdot c_{cn.o.}- -15.12\cdot c_{c.o.}+23.0786\cdot c_{p.st.}\cdot c_{cn.o.}+96.6214\cdot c_{p.st.}\cdot c_{c.o.}+ +48.4714\cdot c_{cn.o.}\cdot c_{c.o.}; \quad (4)$$

– for the fatty system: palm stearin, coconut and sesame oils:

$$MT_{f.p.}(c_{p.st.}, c_{cn.o.}, c_{ses.o.})=46.3714\cdot c_{p.st.}+ +25.3714\cdot c_{cn.o.}-13.9286\, c_{ses.o.}+22.8214\cdot c_{p.st.}\cdot c_{cn.o.}+ +98.4214\cdot c_{p.st.}\cdot c_{ses.o.}+47.5714\cdot c_{cn.o.}\cdot c_{ses.o.}. \quad (5)$$

The significance check of the coefficients of the equation of the approximate dependences (2)–(5) of the melting point of transesterified fats on the composition and ratio of components of fat mixtures was determined using the least squares method. The adequacy of the obtained regression equations (2)–(5) was checked by the coefficients of determination R^2, which are equal to 0.957, 0.946, 0.971, and 0.961, respectively. The obtained values of the coefficients of determination for dependencies (2)–(5) indicate a high influence of variations in the composition and ratio of components of fat mixtures on variations in the melting point of transesterified fats. The significance of the equation of approximation dependencies (2)–(5) is determined by calculating the Fisher test (F), based on the assumption (null hypothesis) that the equation is statistically insignificant. The calculated Fisher test values were:

– for the approximation dependence (2): F (3, 6)=16.281;

– for the approximation dependence (3): F (3, 6)=18.563;

– for the approximation dependence (4): F (3, 6)=15.192;

– for the approximation dependence (5): F (3, 6)=18.648.

The calculated values of Fisher's test are greater than its critical table value F_{table} (3, 6)=4.46 at the significance level p=0.05. This result allows us to reject the null hypothesis and with a probability of 95 % accept the values of the coefficients of determination:

– R^2=0.957 for dependence (2);

– R^2=0.946 for dependence (3);

– R^2=0.971 for dependence (4);

– R^2=0.961 for dependence (5).

As essential, and the equations of approximation dependencies (2)–(5) as significant.

Based on the obtained results of the experiments, rational ratios of the components of fat mixtures are substantiated, at which the melting point of transesterified fat products is the specified 30...34 °C. The proposed composition of fat systems is given in Table 1.

Table 1

Composition of fat systems for obtaining biotechnologically transesterified fat systems with a melting point of 30...34 °C

Components of fat systems	Composition 1	Composition 2	Composition 3	Composition 4
Palm stearin, mass fraction	0.32	0.35	0.30	0.22
Coconut oil, mass fraction	0.25	0.25	0.25	0.45
Sunflower oil, mass fraction	0.43	–	–	–
Soybean oil, mass fraction	–	0.40	–	–
Corn oil, mass fraction	–	–	0.45	–
Sesame oil, mass fraction	–	–	–	0.33

The melting points of the obtained biotechnologically transesterified fat systems of composition 1–4 (Table 1) were experimentally determined, which amounted to 33.0, 33.5, 33.5, 33.5 °C, respectively. The melting points, determined by the approximate dependences, were 33.1, 33.6, 33.6, 33.5 °C, respectively.

5. 2. Determination of the oxidative stability of biotechnologically transesterified fat systems

The dynamics of accelerated oxidation of biotechnologically transesterified fat products, the composition of which is shown in Table 1, were studied. As comparison products, the Akomix milk fat substitute (Sweden), which is a refined mixture of vegetable oils and hydrogenated vegetable fat [18], and natural melted butter (Ukraine) were considered [19]. The results of the studies are shown in Fig. 2.

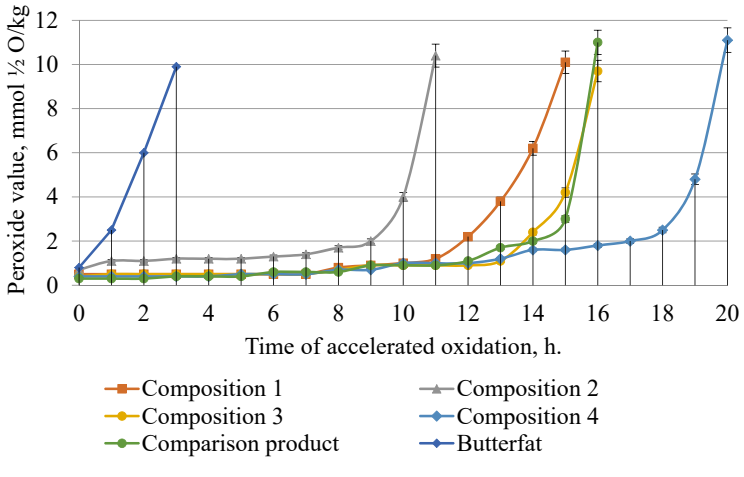

Fig. 2. Dynamics of changes in the peroxide value of lipids of biotechnologically transesterified fats with various low-melting components (Table 1) and comparison products

Based on the results obtained, it is possible to state an increase in the induction period of accelerated oxidation in transesterified fat systems depending on the low-melting component in the series:

– soybean oil (9.5 hours);
– sunflower oil (13 hours);
– corn oil (14.3 hours);
– sesame oil (18.3 hours).

The induction period of accelerated oxidation of comparison products: milk fat substitute – 14.7 hours and milk fat – 1.0 hours.

5. 3. Analysis of the economic feasibility of using raw materials in the biotechnology of transesterification of fat systems

The results of the analysis of the economic feasibility of using the proposed raw components in the biotechnology of transesterification of fat systems are given in Tables 2, 3.

Table 2

Cost of transesterified fats based on the proposed raw components

Transesterified fats	Name of raw components	Cost, $/kg	Content in the product, kg/t	Product cost, $/ton
Composition 1	Palm stearin	75	320	70,560
	Coconut oil	114	250	
	Sunflower oil	42	430	
Composition 2	Palm stearin	75	350	87,550
	Coconut oil	114	250	
	Soybean oil	82	400	
Composition 3	Palm stearin	75	300	90,150
	Coconut oil	114	250	
	Corn oil	87	450	
Composition 4	Palm stearin	75	220	176,400
	Coconut oil	114	450	
	Sesame oil	320	330	

Table 3

Cost of comparison products

Comparison products	Name of raw components	Cost, $/kg	Content in the product, kg/t	Product cost, $/ton
Akomix milk fat substitute	Hydrogenated soybean oil	395	170	138,000
	Palm oil	75	600	
	Coconut oil	114	230	
Natural melted butter	Milk fat	385	1,000	385,000

The calculations given in Table 2, 3 prove the economic feasibility of the production of transesterified fats using the selected raw components compared to the Akomix milk fat substitute and natural melted butter. The ratio of the cost of the developed transesterified fats:

– with a soybean oil content of 40 % – almost 1.6 times lower compared to the Akomix milk fat substitute and 4.4 times lower compared to natural melted butter;

– with a sunflower oil content of 43 % – 2 times lower compared to the Akomix milk fat substitute and 5.5 times lower compared to natural melted butter;

– with a corn oil content of 45 % – 1.5 times lower compared to the Akomix milk fat substitute and 4.3 times lower compared to natural melted butter;

– with a sesame oil content of 33 % – 1.2 times higher compared to the Akomix milk fat substitute and 2.2 times lower compared to natural melted butter.

6. Discussion of the results of the analysis of the development of biotechnologically transesterified three-component fat systems stable to oxidative deterioration

The rational ratio of fatty raw materials (palm stearin, coconut and sunflower, or soybean, or corn, or sesame oil) with various low-melting components in mixtures for biotechnological transesterification in order to obtain analogs of milk fat was determined. The obtained research results, namely graphical (Fig. 1, *a–d*) and approximation dependences (2) (5), allow predicting the melting point of transesterified fat products depending on the type of low-melting oil, the composition and ratio of the components of fat mixtures. Thus, the obtained approximation dependences (2)–(5) can be useful for the development of biomodified fat systems for various technological purposes (milk fat substitutes, cocoa butter equivalents, cooking fats, etc.) that differ in melting point.

Using approximation dependencies (2)–(5), the ratio of the components of fat mixtures (Table 1) is substantiated, whose melting point after enzymatic transesterification is in the given range of 33.0...33.5 °C. Thus, using reasonable ratios of the specified fat components, it is proposed to obtain biomodified fat products with a given melting point, which will differ in certain technological characteristics, in particular, oxidative stability. The developed products are proposed to be used as substitutes for milk fat, free from trans isomers of fatty acids, enriched with polyunsaturated fatty acids.

The dynamics of accelerated oxidation of the developed compositions of biotechnologically transesterified fat systems (Table 1), as well as comparison products (Fig. 2), were determined. It is worth noting that the selected comparison products differ in composition from the developed transesterified fats. Akomix milk fat substitute contains trans isomers of fatty acids and, accordingly, does not contain polyunsaturated fatty acids. Natural melted butter differs in composition from the developed product in the following parameters:

– significantly lower content of polyunsaturated fatty acids (linoleic compared to compositions 1, 3, 4 and α-linolenic compared to composition 2);

– low content of lauric fatty acid;

– high content of low molecular fatty acids (butyric, caproic, caprylic, capric).

The induction periods of accelerated oxidation of the developed biomodified fats differ from those of the Akomix milk fat substitute as follows:

– in biomodified fat with a soybean oil content of 40 % – 1.5 times lower;

– in biomodified fat with a sunflower oil content of 43 % – 1.1 times lower;

– in biomodified fat with a corn oil content of 45 % – almost no difference;

– in biomodified fat with a sesame oil content of 33 % – 1.2 times higher.

It is worth noting that the induction periods of accelerated oxidation of the developed biomodified fats exceed those of milk fat:

– in biomodified fat with a soybean oil content of 40 % – 9.5 times;

– in biomodified fat with a sunflower oil content of 43 % – 13 times;

– in biomodified fat with a corn oil content of 45 % – 14.3 times;

– in biomodified fat with a sesame oil content of 33 % – 18.3 times.

The economic feasibility of using the proposed raw components in the biotechnology of transesterification of fat systems for the production of milk fat analogs with different oxidative stability was analyzed (Table 2). As a result, the prospects of using the selected oil raw material compared to the raw material of a similar commercial comparison product –-Akomix milk fat substitute (Table 3) were proved. It is worth noting that this comparison product has a lower nutritional value due to the lack of polyunsaturated fatty acids and contains such atherogenic components as trans isomers of fatty acids. In addition, the cost of transesterified fats of the developed composition is 2.2–5.5 times lower than that of natural melted butter, i.e. milk fat (Table 3). The lower cost of the developed biomodified fats compared to comparison products is due to the rather low cost of raw materials – palm stearin, coconut, sunflower, soybean and corn oils (Table 2). The only exception is sesame oil, which is quite expensive. But transesterified products containing sesame oil have an advantage among the proposed fat systems, which is high stability to oxidative deterioration due to the presence of specific antioxidants [20].

The results of the study differ from the results of [11] in that three-component rather than one-component transesterified fat systems were created and investigated. It is worth noting that the development is a continuation of research on determining the oxidative stability of finished modified fats developed by the improved technology described in [12]. Also, the development differs from [13, 14], which describes the oxidation resistance of fat mixtures biomodified by various forms of enzyme preparations, but in the context of its dependence on the form of the enzyme preparation, and not on the ratio of raw components. In addition, the development differs from [15], which describes the characteristics of the transesterified two-component fat system of constant composition, and not under the condition of a varied ratio of components for transesterification. From the work [16], which studies the effect of natural antioxidants on the oxidative stability of a non-food transesterified product – biodiesel, this development differs by studies of a food transesterified product – a substitute for milk fat. Thus, determining the mutual impact of the selected raw components on the oxidative deterioration of biomodified fats – substitutes for milk fat is interesting from both scientific and practical points of view. The results of the research (Fig. 1, *a–d* and approximation dependences (2)–(5)) allow us to effectively calculate the ratio of the selected oil raw materials for the substantiation of bioesterified fat systems with specified melting points. In addition, on the basis of dependencies (2)–(5), the composition of four fat systems with different low-melting components was calculated to obtain bioesterified substitutes for milk fat with known stability to oxidative deterioration.

The limitation of using the obtained results (Fig. 1, 2 and dependences (2)–(5)) is that certain types of oil raw materials were used in the experimental studies for biotechnological transesterification. Therefore, in the case of using other types of oil raw materials in this biotechnology, it is necessary to take into account its fatty acid and antioxidant composition to adjust the melting point and stability to oxidative deterioration of finished products.

The drawback of the study is the lack of crystallization thermograms of biotechnologically transesterified fat systems with a defined melting point of the calculated composition (Table 1). In addition, the study did not take into account the effect of individual antioxidants on the stability to oxidation of transesterified fat systems. The antioxidant capacity of oil raw materials was taken into account comprehensively depending on the type of oil and its characteristics according to regulatory documentation. Thus, it is possible to outline promising areas of work on the development of biotechnologically transesterified three-component fat systems stable to oxidative deterioration. This is primarily a study on the influence of the content of polyunsaturated fatty acids in the raw oil material, as well as native and artificially added antioxidants, on the induction period of accelerated oxidation of the bioesterified product.

7. Conclusions

1. The rational ratio of oil raw materials in three-component mixtures for biotechnological transesterification was determined, at which the melting point of transesterified products is 33.0–33.5 °C. For a fat mixture consisting of palm stearin, coconut and sunflower oils, the calculated ratio is 0.32: 0.25: 0.43, respectively. For a fat mixture consisting of palm stearin, coconut and soybean oils – 0.35: 0.25: 0.40, respectively. For a fat mixture consisting of palm stearin, coconut and corn oils – 0.30: 0.25: 0.45, respectively. For a fat mixture consisting of palm stearin, coconut and sesame oils – 0.22: 0.45: 0.33, respectively.

2. The dynamics of accelerated oxidation (90±2 °C) of biotechnologically transesterified fat systems was determined by the change in their peroxide value compared to milk fat substitute and natural melted butter. The induction periods of accelerated oxidation of transesterified products are longer than that of natural melted butter (1.0 h) and similar or shorter than that of the Akomix milk fat substitute (14.7 h).

3. The economic feasibility of using the proposed raw components in the biotechnology of transesterification of fat systems is analyzed. The cost of the developed transesterified fats is 2.2–5.5 times lower than that of natural melted butter and 1.5–2.0 times lower than that of the Akomix milk fat substitute. The only version of the composition of the transesterified product that is 1.2 times more expensive than the milk fat substitute is a sample containing sesame oil.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this study, including financial, personal, authorship, or any other, that could affect the study and its results presented in this paper.

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Data availability

The manuscript has no associated data.

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