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FRACTIONATION OF OIL OF A NEW LINE OF SUNFLOWER SEEDS

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**Introduction. Formulation of the problem**

Today the Ukrainian oil and fat industry has but limited choice of domestic natural fatty raw materials available. These are liquid oils of the linoleic and oleic group (sunflower and rapeseed) and solid or semi-solid animal fats (pork, beef, lamb) [1]. Still, the demand for solid plastic fats with certain desired properties

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Abstract. The main methods of obtaining fractionated oils and fats have been analysed. They involve three essentially different processes of fractionation of acylglycerols: dry fractionation, aqueous fractionation with a detergent, and solvent fractionation. Considerable attention has been paid to determining the conditions for fractionation of sunflower oil modified in its fatty acid composition. It has been emphasised that using stearic sunflower oil free from trans fatty acids as a source of fats is a topical task. The practical importance of complex research on fractional crystallisation of stearic sunflower oil has been substantiated. The experiments have allowed establishing the fatty acid and triacylglycerol composition of the oil of the new line of sunflower seeds of the saturated type X114B (stearic type). The structure of its acylglycerols has been mathematically determined. Data have been obtained that besides the increased stearic acid content (9.1% of the total fatty acids), the oil under study also contains a significant amount of the disaturated-monounsaturated fraction of acylglycerols (6.16%). The method of fractionating sunflower oil of the stearic type, which has been scientifically substantiated, involves one-stage fractional crystallisation from the melt. The conditions of fractional crystallisation have been experimentally established: the crystallisation temperature range (+6 – +9°C), the crystallisation time (38 days), and the cooling rate ($\approx 0.0051^\circ\text{C/s}$). The target fraction of sunflower oil of the stearic type has been obtained. It differs from the original oil in its fatty acid and acylglycerol composition. The yield of this oil fraction was 24.57%. It has been found that the fatty acid composition of this fraction has a content of palmitic acid increased by 0.9% and that of stearic acid higher by 3.3%, while its linoleic acid content decreased to 41.9%. The total amount of saturated fatty acids in the target fraction sample is 19.8% of all fatty acids. It has been found that the proportion of disaturated-monounsaturated acylglycerols in the target fraction increases by 3.27%. The resulting target fraction will be useful in flour and confectionery technologies as a substitute for fats containing trans fatty acids.

Key words: sunflower oil, crystallisation, fractionation, fractions, fatty acids, acylglycerols.

remains high and is solved by classical modification methods (hydrogenation, transesterification) or by using tropical oils and their fractionation products. However, the World Health Organization (FAO/WHO) has determined that the consumption of any amount of industrial trans fatty acids is harmful to health. In 2003, it was recommended to reduce the level of their consumption to 1% of the daily calorific intake

(2–3 g), and in 2009 year, to remove all industrial trans fats from food. Currently, there are the European Union's recommendations on limiting trans fatty acids in food: no more than 2% of the total content. A consequence is the limited use of hydrogenated oils. Besides, the World Health Organization (FAO/WHO) has determined that fats containing triglycerides of myristic, lauric, or palmitic acids increase the blood level of low-density lipoprotein cholesterol, while the triglycerides of stearic acid do not [2]. Sunflower oil contains a spectrum of fatty acids that make it unique as a healthy food. People's interest in healthy nutrition urges scientists to create new types of sunflower seeds, in particular, those with a modified fatty acid composition. Modified sunflowers can be a source of solid plastic fats free from trans fatty acids. The obtained target fractions of saturated sunflower oil not only can become competitive, but will also contribute to improving the nation's health.

Analysis of recent research and publications

In recent years, new lines of sunflower seeds have been developed. Their oil is significantly different in its composition from the classical oil, namely it contains an increased amount of saturated fatty acids, in particular palmitic or stearic [3-6]. In the future, if not today, processing of this oil by its modification (fractionation) can expand the range of high-quality solid plastic fats and reduce the need of the food industry, in particular, the fat-and-oil and confectionery industries, for special-purpose fats. Stearic acid-based fats can be a healthier alternative to the existing ones, especially to hydrogenated fats.

Fractionation of oils and fats is based on the differences in the solubility of the triacylglycerols that make up these products. These differences are directly related to a type of triacylglycerols in the fat system. The type of triacylglycerols is determined by its fatty acid composition and the distribution of fatty acids over individual positions in the triacylglycerol molecule. Triacylglycerols with different melting points are separated into fractions with different crystalline structures. More saturated triacylglycerols with high melting points are separated from the less saturated ones by filtration at certain temperatures [7].

Today, to obtain fractionated oils and fats, the three essentially different processes of fractionation of triacylglycerols are used [7-9]:

- dry fractionation – thermomechanical separation of a mixture of acylglycerols by crystallisation of the melt with subsequent separation of fractions by filtration in a vacuum;

- aqueous fractionation with a detergent – modified fractionation in the melt with isolation of fractions by separation or centrifugation using aqueous solutions of surfactants;

- solvent fractionation – separating a mixture of acylglycerols in the melt using a solvent (acetone, hexane, ethanol).

The paper [10] investigates dry fractionation of high-oleic-stearic oil in a heating block equipped with a stirrer, the speed of which was 30 rpm. The fractionation was carried out in the range of the heating temperatures from +15°C to +30°C, with different heating times and with the addition of crystallisation centres – 16.5% of stearic powder with a high melting point. The authors found that the addition of crystallisation centres, as well as the fractionation temperature, affected the composition of the final fraction, namely:

- the content of unsaturated acylglycerols was far lower (23.3%) without the use of crystallisation centres, but in parallel, the final yield of the solid fraction was higher (15.5%). The addition of crystallisation centres increased the proportion of unsaturated triacylglycerols in the final solid phase from 30% to 33%, but the proportion of the solid fraction decreased and amounted to 10–12%. Adding crystallisation centres did not change the total time of crystallisation;

- lower crystallisation temperatures led to an increase in the yield of the solid fraction from 9.4% at +19°C to 17.8% at +17.5°C. During fractionation at higher temperatures (+19°C), the liquid phase increased to 7.2%, and at lower temperatures (+17.5°C), it decreased to 6%. The solid phase with a high content of unsaturated acylglycerols (33.9%) was obtained at +19°C, while at +17.5°C, the content of these types of acylglycerols was only 23.8%. The temperature range in which crystallisation occurred was relatively narrow, and the rational fractionation temperature was +18.3°C.

However, at the last stage, to accelerate the filtration of the solid fraction at +5, the authors [10] used hexane as a solvent, which is not safe for human health.

In [11], it was studied how the fractionation temperature (+15°C, +18°C, and +21°C) affected refined, bleached, and deodorised mixtures of palm and sunflower oils (20:80 and 40:60). It was found that a lower fractionation temperature reduced the amount of monounsaturated acylglycerols and increased the amount of di- and polyunsaturated acylglycerols. Besides, a lower fractionation temperature produced a liquid fraction with a lower solid fat content and a lower cloud point than a higher temperature did. However, that study focused on a mixture of oils used for fractionation and contained no data on the characteristics of sunflower oil fractions.

In the paper [12], which continued the work [10], solid stearins of sunflower oil high in olein and stearin were obtained by solvent fractionation, with acetone used as the solvent. Solvent fractionation was carried out on a pilot mini-plant at temperatures from +15°C to +17°C and at the oil to solvent ratio ranging 1:2 to 1:4. The resulting stearins were filtered in a vacuum and washed with fresh acetone, which was followed by vacuum stripping to remove the solvent. Depending on the conditions of fractionation, the authors obtained

three types of solid stearins with 65%, 80%, and 95% of disaturated–monounsaturated acylglycerols. The authors of [12], as well as in [10], used a solvent hazardous to human health, acetone.

The authors of [13] investigated the fractionation of sunflower oil with a high content of olein and stearin using hexane and acetone as solvents. Fractionation with acetone was carried out at temperatures from +5°C to +10°C using different oil to solvent ratios. It was found that acetone was a more suitable solvent than hexane, since it made it possible to fractionate the oil at higher temperatures and at lower degrees of supercooling. Also, the paper considered combining dry fractionation and solvent fractionation to obtain individual stearins.

In [14], solvent fractionation of sunflower oil with an increased content of stearic and oleic acids was carried out in one stage. It was found that various stearic products could be obtained by adjusting the oil to solvent ratio and regulating the fractionation temperature. Stearins with the same melting profiles as in cocoa butter were obtained from sunflower oil with 17% and 20% stearic acid content. The use of these fractions as confectionery fats was discussed.

The studies described in the papers [12-14] concern solvent fractionation. Though the presence of a solvent increases the rate of fractionation, this process remains costlier and less environmentally friendly than dry fractionation is. Besides, the authors of these works did not carry out studies of sunflower oil with a stearic acid content lower than 17%.

Based on the above, it has been found that in the future, recently developed high-stearic oilseeds can certainly become a source of high-quality solid plastic fats that are healthier alternatives to the existing ones, especially to hydrogenated fats. Besides, studies of the conditions for dry fractionation of saturated sunflower oil are not sufficiently highlighted in the literature. Therefore, research in this direction is of practical importance.

The purpose of this work is to study the possibility and conditions of dry fractionation of sunflower seed oil of the saturated (stearic) type. For this purpose, it is necessary to achieve the following **objectives**:

- to determine experimentally the fatty acid and triacylglycerol composition and establish the structure of the acylglycerols of the stearic-type sunflower seed oil;
- to substantiate scientifically the fractionation method and suggest the conditions for fractional crystallisation of stearic sunflower oil;
- to determine experimentally the fatty acid and acylglycerol composition in the target fraction of stearic sunflower oil.

Research materials and methods

For the research, we used cold-pressed oil from sunflower seeds of the line X114B of the stearic type (from the work collection of the Yuryev Institute of

Plant Cultivation of the NAAS, samples from the years 2013–2018), and sunflower oil, which meets the requirements presented in DSTU 4492:2017.

The samples for determining the fatty acid composition of stearic sunflower oil and its fractions were prepared according to DSTU ISO 5509. The resulting solution of methyl esters of fatty acids was analysed according to DSTU ISO 5508 by gas-liquid chromatography on a Shimadzu chromatograph (Japan). The fatty acids were identified by comparing their retention time with that of the standards. The fatty acid content was calculated as a percentage of their total.

The triacylglycerol composition of stearic sunflower oil was determined according to ISO/TS 17383:2014 by capillary gas chromatography.

To determine the structure of acylglycerols of stearic-type sunflower oil and its fractions, we used the method described in [15]: the molar percentage of triacylglycerols present in sunflower oil of the stearic type and its fractions was calculated by the formulae (1–3), where *A*, *B*, and *C* were the molar percentage of fatty acids *A*, *B*, and *C*. The molar percentage of triacylglycerols (%) only containing one fatty acid *A* is:

$$AAA = \frac{A^3}{10000}, \quad (1)$$

that containing two fatty acids *A* and *B* is:

$$AAB = \frac{3 \cdot A^2 \cdot B}{10000}, \quad (2)$$

that containing three different fatty acids *A*, *B*, and *C* is:

$$ABC = \frac{6 \cdot A \cdot B \cdot C}{10000}. \quad (3)$$

The temperature of stearic-type sunflower oil in the Zhukov device was studied as follows. The oil was poured into the Zhukov device by $\frac{3}{4}$ of its volume. The device was closed with a stopper so that the mercury-containing tube of the thermometer was approximately in the middle of the vessel. The device was placed in a cooling bath (ice as the cooling agent) at a constant temperature lower than the expected chilling point of the oil. The oil was stirred by shaking of the device periodically. Then the device was tilted, and in this position, the fluidity of the oil was observed. The experiment was continued by observing the decrease in the temperature, until the moment when a pronounced peak was visible on the horizontal part of the solidification curve. During the experiment, the temperature of the sunflower oil was measured every 60 seconds.

To carry out fractional crystallisation, a weighed portion of sunflower oil (20–25 g) was preheated in a 25–50 ml beaker to +30 – +35°C to eliminate any previous structure, and then cooled in a refrigerating chamber with the temperature automatically maintained at the values required by the experiment (+6 – +9°C). The cooling rate was 0.005–0.0067°C/s. The sample was held for a time interval required for crystals of solid fractions to form. The fractionation

temperature was monitored with a thermometer (Fig. 1). The experiment was carried out without stirring. Next, the solid part was separated. The samples of stearic sunflower oil fractions obtained (the target and the liquid ones), were used for subsequent analysis. To confirm the reliability of the result, three individual portions of oil were checked each time. The completion of fractional crystallisation is usually controlled either visually or by analysing the fractions obtained isolated at specified time intervals. The course and the completion of the fraction crystallisation of stearic sunflower oil were controlled by determining the fatty acid composition of the samples of the oil fractions obtained. At each stage of the crystallisation process, the fatty acid composition of the oil was monitored in the most important periods, namely before the start of crystallisation, upon reaching the predetermined crystallisation temperature, and while keeping a sample at this crystallisation temperature until this parameter of the liquid fraction stopped changing. The crystallisation process was considered completed if the last two measurements of the fatty acid composition of the liquid fraction gave the same values.



Fig. 1. Fractionation of stearic sunflower oil

The experiments were planned and the data processed by means of mathematical methods using the Microsoft Office Excel 2003 (USA) software package. The studies were carried out in triplicate. When determining the fatty acid composition of oil lipids, the relative error did not exceed 0.5% for the given degree of probability $P=95\%$.

Results of the research and their discussion

The experiments have allowed establishing the fatty acid composition of lipids and the triacylglycerol composition of stearic oil from sunflower seeds of the X114B line. Fig. 2 shows the data obtained on the fatty acid composition of the classic sunflower oil in comparison with the stearic-type oil from sunflower

seeds of the X114B line. It has been found that the stearic-type sunflower oil has an increased stearic acid content, which is 9.1% of all fatty acids (while in classic sunflower oil, the maximum content of this acid is only 3.8%), and besides, it has a slightly reduced linoleic acid content, which is 45.2% (while for classic sunflower oil, it ranges 48.3 to 74.0%). The total content of saturated fatty acids (palmitic and stearic) is 15.6%. The triacylglycerol composition of stearic sunflower oil is represented by 94.8% of triglycerides, 3.1% of diglycerides, and 1.6% of monoglycerides. The results obtained are consistent with other scientists' research on new lines of sunflower seeds with an increased content of saturated fatty acids, published in [16] and presented in Table 1.

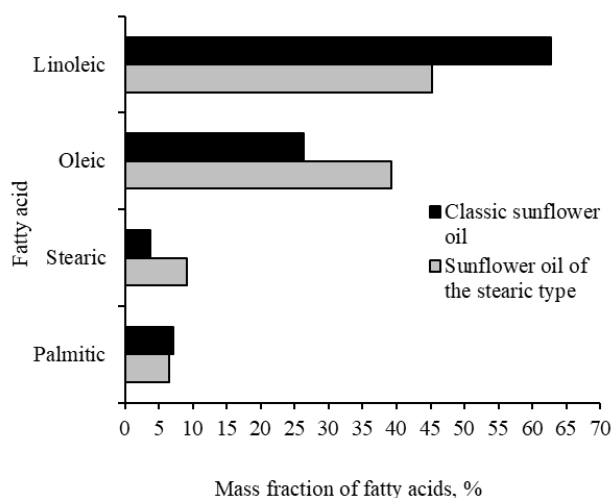


Fig. 2. Fatty acid composition of sunflower oil lipids

It should be noted that the structure of the acylglycerols of oils is an important characteristic of the raw material since the composition of acylglycerols is directly related to its physical characteristics and technological properties. Table 1 gives the acylglycerol composition of sunflower stearic oil calculated by the formulae (1–3), namely the content of acylglycerol groups of the types S_3 , S_2U , SU_2 , U_3 (S and U are, respectively, saturated and unsaturated acids).

According to the research results (Table 1), it has been found that in the stearic sunflower oil, there is a significant content of the disaturated–monounsaturated fraction of acylglycerols (type S_2U), which is 6.16%. The results coincide with those obtained from studying the structure of acylglycerols of the new line of stearic-type sunflower oil X114B by enzymatic hydrolysis [16], where the content of the disaturated–monounsaturated fraction of acylglycerols was 6.65% (these are the fractions that form the basis of special-purpose fats). This makes it possible to assume that fractionation of stearic-type sunflower oil allows obtaining fats that with an increased melting point and the corresponding composition of acylglycerols [16].

Table 1 – Composition of acylglycerols of sunflower oil the of stearic type (according to [15])

S ₃	%	SU ₂	%	S ₂ U	%	U ₃	%
PPP	0.027463	OOP+OPO	2.996448	PPO+POP	0.49686	OLL+LOL	24.02615
StStSt	0.075357	OOS _t +OS _t O	4.195027	PPL+PLP	0.57291	OOL+OLO	20.83684
PPSt+PS _t P	0.115343	LLP+LPL	3.983928	StStL+StLSt	1.122904	LLL	9.234541
StStP+StPSt	0.16148	LLSt+LStL	5.577499	StStO+StOS _t	0.973846	OOO	6.023629
		POL+PLO+OPL	6.910176	PS _t O+POS _t +StPO	1.391208		
		StOL+StLO+OS _t L	9.674246	PS _t L+PLSt+StPL	1.604148		
Total	0.379642		33.33732		6.161875		60.12116
by [16]	0.25		36.37		6.65		56.73

P – palmitic acid (C16:0); St – stearic acid (C18:0); O – oleic acid (C18:1); L – linoleic acid (C18:2)

Dry crystal fractionation is typically used to separate hard stearic and soft oleic fractions in natural products containing both of these components in large quantities [1]. This process works without additives and makes it possible to obtain physiologically neutral products, since there is no contamination through additives. It has a high operational reliability, since there is no danger of explosion due to the use of solvents. Nor is there any load on water and air, since both remain completely free of additives. Considering the above, to obtain the target fraction of stearic-type sunflower oil, dry fractionation was used, which consisted in one-stage fractionation by crystallisation from the melt. It is an entirely physical process of fat modification, which is environmentally friendly since it involves using no catalysts and chemically active substances.

To establish the temperature range of stearic sunflower oil crystallisation, it has been studied, using a Zhukov device, how its temperature depends on the cooling time. Fig. 3 shows a pronounced peak observed on the solidification curve in the temperature range of +4 – +5°C. This peak indicates a release of the thermal effect of the phase transition of fat and corresponds to crystallisation of high-melting triacylglycerols. Thus, it can be assumed that the temperature of fractionation of stearic-type sunflower oil from the seeds of the X114B line is within the temperature range +4 – +5°C.

Besides, fractional crystallisation of the melt of sunflower stearic oil has allowed experimentally determining the temperature above which fractionation

stops being practical: at temperatures above +9°C, either there is no fractional distribution, or the resulting fractions have unsatisfactory physicochemical characteristics.

The efficiency of separating liquid and solid fractions is especially dependent on the cooling method, which determines the shape and size of the crystals. Rapid cooling leads to supersaturation, produces a lot of small crystals, and results in the formation of an amorphous, microcrystalline, soft residue with poor filtration properties. This shape will form mixed crystals. However, gradual cooling of the oversaturated oil results in the formation of stable β and β' macrocrystals, easily separable from the liquid fraction by filtration. So, high-quality crystallisation requires long and gradual cooling. It has been experimentally established that an increase in the cooling rate up to 0.0167°C/s leads to the formation of many small crystals, makes it impossible to carry out phase separation (filtration), and thus prevents the formation of the target fraction of stearic-type sunflower oil, which fractionation is aimed at. Based on the research by the scientists [6], it has been found that slow cooling in the nucleation period (at the rate 0.005–0.0067°C/s) leads to formation of more stable polymorphic forms. They have a higher melting point and higher mass fraction of solid triglycerols due to a decrease in the capture of the mother liquor during crystal formation, which is typical of dry fractionation.

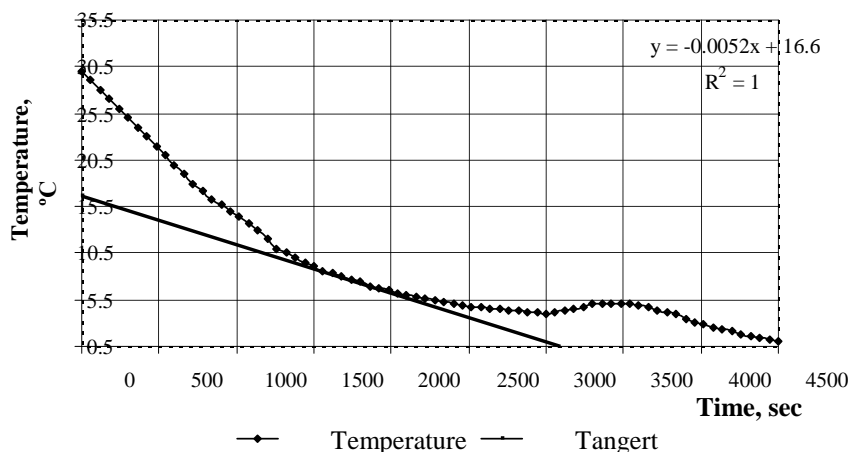


Fig. 3. Kinetic dependence of the temperature of stearic-type sunflower oil of the line X114B (°C) on the cooling time (s) in a Zhukov device

The cooling rate of stearic sunflower oil is clear from Fig. 4 that shows the temperature conditions of cooling the stearic-type sunflower oil to the crystallisation temperature. A tangent to the dependence (Fig. 4) is plotted, and its equations are given on the coordinate plane, where the coefficient at x in this equation is the value of the cooling rate of stearic sunflower oil, namely $\approx 0.0051^\circ\text{C/s}$. This is consistent with the data [6] about carrying out dry fractionation.

The most stable crystal structures are known to form when slowly grown from the melt. Therefore, fractionation is usually a long process. In this process, it is important to detect the moment when crystallisation is completed, since during long-term fractionation of the studied oil, not only dinaturated but also monounsaturated acylglycerols are released. This leads to a decreased yield of the liquid fraction, a lower melting point of the high-melting fraction, and complications in the filtration process [1,13].

In this study, to control the course of fractionation, a chemical method was chosen as more accurate. It consists in determining the fatty acid composition of

the liquid fraction of stearic sunflower oil. This is different from the work [17], where the same purpose is achieved by determining the changes in a physical parameter of oil, namely in the the refraction angle of the liquid fraction of sunflower oil. Fig. 5 presents the kinetic dependences of the change in the content of saturated fatty acids in the liquid fraction of stearic-type sunflower oil on the time of crystallisation.

On analysing the graphical dependences (Fig. 5), it has been found that an increase in the crystallization time led to a gradual decrease in the content of saturated fatty acids in the liquid fractions of stearic-type sunflower oil. After the completion of crystallisation, the content of palmitic acid in the liquid fraction of the oil was 5.5%, which was 1% less than in the original stearic sunflower oil. The stearic acid content was reduced to 8.5%, and the total amount of saturated fatty acids was up to 14.0%. So, the results of the studies confirm that the fatty acid composition of the liquid fraction of stearic sunflower oil can be used to control the course of the fractionation process. The data obtained coincide with the results of work [16].

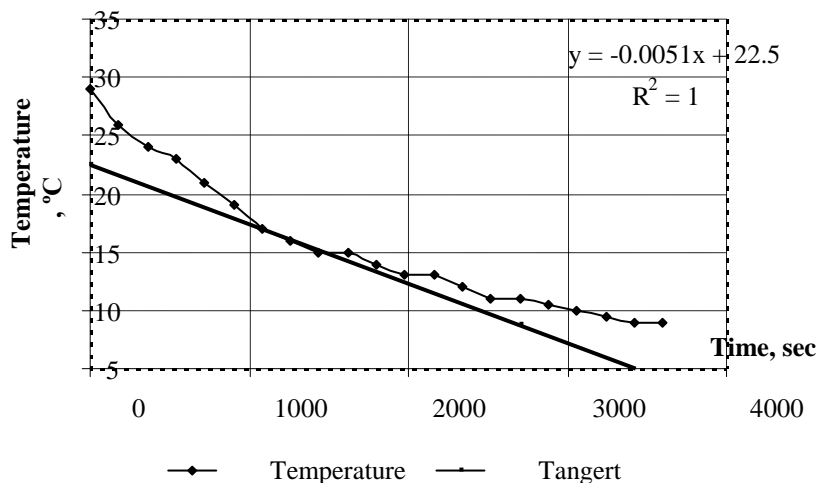


Fig. 4. Conditions of cooling sunflower oil of the stearic type to the crystallisation temperature $+9^\circ\text{C}$

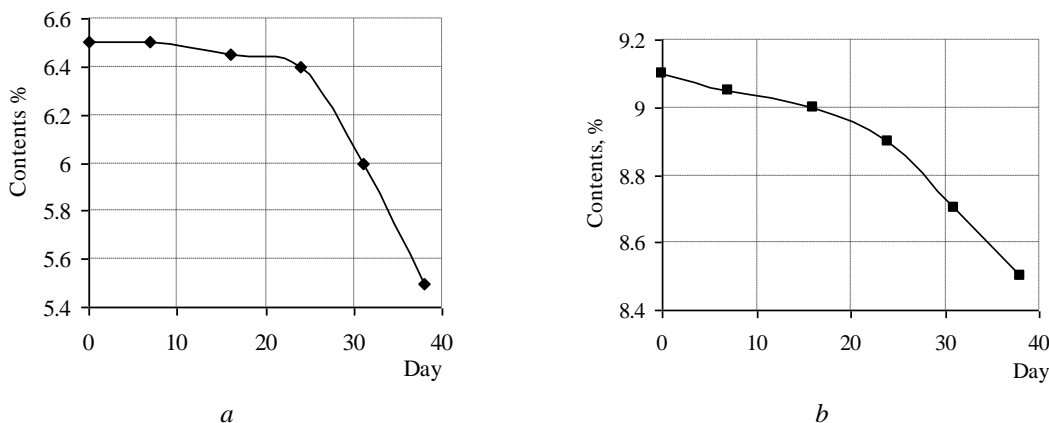


Fig. 5. Kinetic dependences of the content of saturated fatty acids in the liquid fraction of stearic-type sunflower oil upon the crystallisation time: a – palmitic, b – stearic

Experimentally, by the method of crystallisation from the melt (Fig. 1), the target fraction of sunflower oil of the stearic type was obtained, its yield being 24.57% (Fig. 6), and the yield of the liquid fraction, respectively, 75.43%.

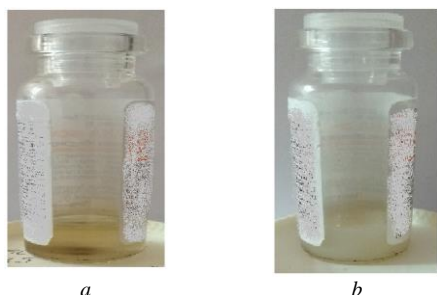


Fig. 6. Target fraction of stearic sunflower oil:
a – at +20°C, b – at +6°C

In the target fraction of stearic-type sunflower oil obtained by crystallization from the melt (Fig. 1), the fatty acid composition of lipids and the composition of acylglycerols have been experimentally determined and analysed. The data obtained are given in Tables 2, 3. The fatty acid composition of lipids of the target fraction of stearic sunflower oil (Table 2) is represented by such saturated fatty acids as palmitic and stearic (7.4% and 12.4% respectively) and by unsaturated fatty acids: oleic (38.3%) and linoleic (41.9%). This composition differs from that of the initial oil (Fig. 2) in the content of palmitic and stearic acids (increased by 0.9% and by 3.3% respectively) and in the linoleic acid content that decreases to 41.9%. The total amount of saturated fatty acids in the sample of the target fraction is bigger by 4.2% and makes up 19.8% of the total fatty acids.

Table 2 – Fatty acid composition of lipids in the target fraction of sunflower oil of the stearic type

Essential fatty acids	Mass fraction of fatty acids, % of the total fatty acids
C _{16:0}	7.4
C _{18:0}	12.4
C _{18:1}	38.3
C _{18:2}	41.9
ΣC ₁₆ and C ₁₈	19.8

Table 3 – Composition of acylglycerols in the target fraction of sunflower oil of the stearic type

S ₃	%	SU ₂	%	S ₂ U	%	U ₃	%
PPP	0.040522	OOP+OPO	3.256496	PPO+POP	0.629192	OLL+LOL	20.17196
StStSt	0.190662	OOST+OSStO	5.456831	PPL+PLP	0.688333	OOL+OLO	18.43881
PPSt+PStP	0.203707	LLP+LPL	3.897454	StStL+StLSt	1.932763	LLL	7.356006
StStP+StPSt	0.341347	LLSt+LStL	6.530869	StStO+StOSSt	1.766702	OOO	5.618189
		POL+PLO+OPL	7.125179	PStO+POST+StPO	2.108645		
		SOL+StLO+OSStL	11.93949	PStL+PLSt+StPL	2.306846		
Total:	0.776239		38.20632		9.432482		51.58496

The composition of acylglycerols of the target fraction of stearic-type sunflower oil is represented by monoacid, dicacid, and triacid triacylglycerols, which contain both saturated and unsaturated fatty acids, as well as by trisaturated (type S₃) and triunsaturated (type U₃), monosaturated–diunsaturated (type SU₂) and the target disaturated–monounsaturated fraction of acylglycerols (type S₂U). The results of calculating the composition of acylglycerols of the target fraction, according to the formulae (1–3) of the method described in [16] (Table 3), confirm the tendency for a 3.27% increase in the target disaturated–monounsaturated fraction of acylglycerols. The target fraction of stearic sunflower oil also contains more acylglycerols of the S₃ and SU₂ types (by ≈0.38% and ≈4.87% respectively). Besides, the target fraction of sunflower stearic oil has a slightly lower content of acylglycerols of the U₃ type: 51.58% versus 60.12% of the initial oil (Table 1).

Systematisation and analysis of the research data on sunflower oil with an increased content of glycerides of saturated fatty acids (stearic sunflower oil) reveals the specific feature of this oil, namely its ability to form a solid fraction at low temperatures. So, it can be stated that fractionating this oil by crystallisation from the melt makes it possible to obtain fractions, liquid and target. They differ in their contents of saturated fatty acids and the corresponding composition of acylglycerols, which is different from that of the initial oil. Besides, they have different melting and crystallisation temperatures. However, further research is necessary. New methods of intensifying the fractionation process should be searched for in order to accelerate fractional crystallisation of sunflower oil, establish rational parameters of this process, and study melting and crystallisation of the target oil fraction. It should also be studied how the latter can be used in food technologies, since processing stearic-type sunflower oil by fractionation can expand the range of high-quality solid plastic fats.

Conclusions

1. The experiments have allowed establishing the fatty acid and acylglycerol composition of oil from the new line of sunflower seeds of the stearic type X114B. It has been found that sunflower oil of the stearic type contains a greater amount of stearic acid (9.1%), and a reduced content of linoleic acid (45.2%). The total content of saturated fatty acids (palmitic and stearic) is 15.6%. The acylglycerol composition of sunflower oil of the stearic type is characterised by a significant content (6.16%) of the disaturated–monounsaturated fraction of acylglycerols (type S₂U), and the contents of acylglycerols of the S₃, SU₂, and U₃ types are, respectively, 0.38%, 33.34%, and 60.12%. The triacylglycerol composition of stearic sunflower oil is represented by 94.8% of triglycerides, 3.1% of diglycerides, and 1.6% of monoglycerides.

2. The method of obtaining the target oil fraction has been scientifically substantiated. It consists in one-stage fractional crystallisation from the melt. It is an environmentally friendly method of modifying stearic-type sunflower oil, which involves using no catalysts or chemically active substances. The following conditions for fractional crystallisation of stearic sunflower oil have been suggested: the fractionation temperature range +6 – +9°C, the cooling rate 0.0051°C/s, and the crystallisation time 38 days.

3. In the target fraction of sunflower oil of the stearic type, the fatty acid and acylglycerol composition has been experimentally determined. It has been found that in comparison with the initial stearic-type sunflower oil, the target fraction of sunflower oil of the stearic type obtained by one-stage fractional crystallisation from the melt contains a greater amount of stearic and palmitic acids (12.4% and 7.4%) and a smaller amount of linoleic acid (41.9%). The total content of saturated fatty acids (palmitic and stearic) in the target fraction of stearic sunflower oil is 19.8%. The acylglycerol composition of the target fraction of sunflower oil of the stearic type is characterised by an increased content (up to 9.43%) of the disaturated–monounsaturated fraction of acylglycerols (type S₂U). The contents of acylglycerols of the S₃, SU₂, and U₃ types are, respectively, 0.78%, 38.21%, and 51.58%.

4. It has been found that sunflower oil of the stearic type can form a solid fraction at low temperatures. Fractionating this oil by crystallisation from the melt makes it possible to obtain fractions, liquid and target. They differ in their contents of saturated fatty acids and the corresponding composition of acylglycerols, which is different from that of the initial oil.

References:

- Hladkyi FF, Kunitsya KV, Litvinenko OA, Kolomatska VP. Doslidzhennia skladu atsylhlitseryniv olii nasinnia soniashnyku nasychenoho typu. Visnyk NTU «KhPI». 2012;63(969):33-38.
- Tom S. Fats and Fatty Acids in Human Nutrition. Report of an Expert Consultation. Food and Nutrition Paper 91. Rome: Food and Agricultural Organisation of the United Nations, 2011.
- Salas JJ, Martínez-Force E, Harwood JL, Venegas-Calderón M, Aznar-Moreno JA, Moreno-Pérez AJ, et al. Biochemistry of high stearic sunflower, a new source of saturated fats. J. Progress in Lipid Research. 2014 Jul;55:30-42. DOI: <http://doi.org/10.1016/j.plipres.2014.05.001>
- Pleite R, Martínez-Force E, Garcés R. Increase of the stearic acid content in high-oleic sunflower (*Helianthus annuus*) seeds. J. Agric. Food Chem. 2006 Nov 14;54(25):9383-88. DOI: <https://doi.org/10.1021/jf061654f>
- Kirichenko VV, Kolomackaya VP. Selekcija podsolnechnika na povishenie adaptivnogo potentsiala i kachestva masla. Maslo-zhirovii kompleks. 2010 Dec;4:24-28.
- Fernández-Moya V, Martínez-Force E, Garcés R. Oils from improved high stearic acid sunflower seeds. J. Agric. Food Chem. 2005 May 18;53(13):5326-5330. DOI: <https://doi.org/10.1021/jf0503412>
- O'Braien R. Zhiri i masla. Proizvodstvo. Sostav i svoistva. Primenenie. 2th ed. Sankt-Peterburg: Professiya; 2007.
- Hladkyi FF, Tymchenko VK, Demydov IM, Nekrasov PO, Piven OM, Fediakina ZP. Tekhnolohiia modyfikovanykh zhyriv. Kharkiv: NTU «KhPI»; 2012.
- Kuznetsova LM, Papchenko VYu, Demydov IM. Fraktsiiuvannia tropichnykh olii. Kyiv: Ahrarna nauka; 2015.
- Bootello MA, Garcés R, Martínez-Force E, Salas JJ. Dry fractionation and crystallization kinetics of high-oleic high-stearic sunflower oil. J. Am. Oil Chem. Soc. 2011 October;88(10):1511-1519. DOI: <https://doi.org/10.1007/s11746-011-1827-7>
- Mamat H, Aini IN, Said M, Jamaludin R. Physicochemical characteristics of palm oil and sunflower oil blends fractionated at different temperatures. J. Food Chemistry. 2005;91(4):731-736. DOI: <https://doi.org/10.1016/j.foodchem.2004.06.045>
- Bootello MA, Martínez-Force E, Hartel RW, Garcés R. Evaluation of high oleic-high stearic sunflower hard stearins for cocoa butter equivalent formulation. J. Food Chemistry. 2012 March;134(3):1409-1417. DOI: <https://doi.org/10.1016/j.foodchem.2012.03.040>
- Bootello MA, Garcés R, Martínez-Force E, Salas JJ. Effect of solvents on the fractionation of high oleic-high stearic sunflower oil. J. Food Chemistry. 2015 Apr 1;172(1):710-717. DOI: <https://doi.org/10.1016/j.foodchem.2014.09.136>
- Salas JJ, Bootello MA, Force EM, Garcés R. Production of stearate-rich butters by solvent fractionation of high stearic-high oleic sunflower oil. J. Food Chemistry. 2011 Jan 15;124(2):450-458. DOI: <https://doi.org/10.1016/j.foodchem.2010.06.053>
- Kim GY. Engineering the crystallization behavior of triacylglycerols using high behenic acid stabilizers. Guelph: University of Guelph; 2017.
- Kunitsya KV, Litvinenko OA, Hladkyi FF. Struktura atsylhlitseryniv olii novykh linii nasinnia soniashnyku nasychenoho typu. Skhidno-levropeiskyi zhurnal peredovykh tekhnolohii. 2013;2/6(62):7-10.
- Kunitsya KV, Litvinenko OA, Hladkyi FF. Ratsionalni umovy fraktsiinoi krystalizatsii soniashnykovoi olii palmitynovoho typu z rozchynu. Skhidno-levropeiskyi zhurnal peredovykh tekhnolohii. 2014;1/6(67):8-12.

ФРАКЦІОНУВАННЯ ОЛІЇ НАСІННЯ СОНЯШНИКУ НОВОЇ ЛІНІЇ

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Анотація. Проведено аналіз основних методів одержання фракційованих олій та жирів, в яких застосовано три істотно різних процеси фракціонування ацилгліцеролів – сухе фракціонування, водне фракціонування з детергентом та фракціонування з розчинником. Значну увагу приділено питанню визначення умов фракціонування олій соняшникової зі змінним жирнокислотним складом. Підкреслено актуальність використання олій соняшникової стеаринового типу як джерела жирів, що не містять транс-ізомери жирних кислот. Обґрунтовано доцільність комплексних досліджень з фракційної кристалізації олій соняшникової стеаринового типу. Експериментально встановлено жирнокислотний та триацилгліцеринний склад олій нової лінії насіння соняшнику насиченого типу Х114В (стеариновий тип). Математично визначено структуру її ацилгліцеролів. Отримано дані щодо наявності в досліджуваній олії окрім підвищеного вмісту стеаринової кислоти, а саме 9,1% від суми жирних кислот, ще й значного вмісту дінасічено-мононенасиченої фракції ацилгліцеролів у кількості 6,16%. Науково обґрунтовано метод проведення фракціонування олій соняшникової стеаринового типу – одностадійна фракційна кристалізація з розплаву. Експериментально встановлено умови фракційної кристалізації - інтервал температур кристалізації (+6...+9°C), час кристалізації (38 діб) та швидкість охолодження ($\approx 0,0051^\circ\text{C}/\text{c}$). Одержано цільову фракцію олій соняшникової стеаринового типу, що відрізняється від вихідної олії жиронислотним та ацилгліцерольним складом, вихід цієї фракції олій склав 24,57%. Встановлено, що жирнокислотний склад характеризується збільшенням вмісту пальмітинової кислоти на 0,9% та стеаринової – на 3,3% у поєднанні із зниженням вмісту лінолевої кислоти до 41,9%. Сумарна кількість насичених жирних кислот у зразку цільової фракції становить 19,8% до суми жирних кислот. З'ясовано, що дінасічено-мононенасичена частка ацилгліцеролів у цільовій фракції збільшується на 3,27%. Отримана цільова фракція буде корисною для використання в технологіях борошняних та кондитерських виробів замість жирів, що містять транс-ізомери жирних кислот.

Ключові слова: олія соняшникова, кристалізація, фракціонування, фракції, жирні кислоти, ацилгліцероли

Список літератури:

1. Дослідження складу ацилгліцеринів олій насіння соняшнику насиченого типу / Гладкий Ф.Ф. та ін. // Вісник НТУ «ХП». 2012. № 63. С. 33-38.
2. Tom S. Fats and fatty acids in human nutrition – report of an expert consultation. Food and Nutrition Paper 91 // Food and Agriculture Organization of the United Nations. Geneva. 2010. P. 55.
3. Biochemistry of high stearic sunflower, a new source of saturated fats / Salas J.J. et al // J. Progress in Lipid Research. 2014. Vol. 55. P. 30-42. DOI: <http://doi.org/10.1016/j.plipres.2014.05.001>
4. Pleite R., Martínez Force E., Garcés R. Increase of the stearic acid content in high-oleic sunflower (*Helianthus annuus*) seeds // J. Agric. Food. Chem. 2006. Vol. 54, Issue 25. P. 9383-9388. DOI: <https://doi.org/10.1021/jf061654f>
5. Кириченко В.В., Коломацкая В.П. Селекция подсолнечника на повышение адаптивного потенциала и качества масла // Масло-жировой комплекс. 2010. № 4. С. 24-28.
6. Fernández-Moya V., Martínez-Force E., Garcés R. Oils from improved high stearic acid sunflower seeds. J. Agric. Food. Chem. 2005. Vol. 53, Issue. 13. P. 5326-5330. DOI: <https://doi.org/10.1021/jf0503412>
7. О'Брайен Р. Жиры и масла. Производство, состав и свойства, применение. СПб.: Профессия, 2007. 752 с.
8. Технологія модифікованих жирів: підручник / Гладкий Ф.Ф., Тимченко В.К., Демидов І.М. та ін. Харків: НТУ «ХП», 2012. 210 с.
9. Кузнецова Л.М., Папченко В.Ю., Демидов І.М. Фракціонування тропічних олій: наукове видання. К.: Аграр. Наука, 2015. 48 с.
10. Dry fractionation and crystallization kinetics of high-oleic high-stearic sunflower oil / Bootello M.A. et al // J. Am. Oil. Chem. Soc. 2011. Vol. 88, Issue 10. P. 1511-1519. DOI: <https://doi.org/10.1007/s11746-011-1827-7>
11. Physicochemical characteristics of palm oil and sunflower oil blends fractionated at different temperatures / Hasmadi M. et al // J. Food Chemistry. 2005. Vol. 91, Issue. 4. P. 731-736. DOI: <https://doi.org/10.1016/j.foodchem.2004.06.045>
12. Evaluation of high oleic-high stearic sunflower hard stearins for cocoa butter equivalent formulation / Bootello M.A. et al // J. Food Chemistry. 2012. Vol. 134, Issue. 3. P. 1409-1417. DOI: <https://doi.org/10.1016/j.foodchem.2012.03.040>
13. Effect of solvents on the fractionation of high oleic-high stearic sunflower oil / Bootello M.A. et al // J. Food Chemistry. 2015. Vol. 172, Issue. 1. P. 710-717. DOI: <https://doi.org/10.1016/j.foodchem.2014.09.136>
14. Production of stearate-rich butters by solvent fractionation of high stearic-high oleic sunflower oil / Salas J.J. et al // J. Food Chemistry. 2011. Vol. 124, Issue. 2. P. 450-458. DOI: <https://doi.org/10.1016/j.foodchem.2010.06.053>
15. Kim G. Y. Engineering the crystallization behavior of triacylglycerols using high behenic acid stabilizers. Ontario, Canada, 2017. 95 p.
16. Структура ацилгліцеринів олій нових ліній насіння соняшнику насиченого типу / Куниця К.В. та ін. // Східно-Європейський журнал передових технологій. 2013. № 2/6 (62). С. 7-10.
17. Рациональні умови фракційної кристалізації соняшникової олій пальмітинового типу з розчину / Куниця К.В. та ін. // Східно-Європейський журнал передових технологій. 2014. № 1/6 (67). С. 8-12.