UDC 665.1
DOI: 10.15587/1729-4061.2024.313095

# DETERMINATION OF RATIONAL PARAMETERS OF CHEMICAL TRANSESTERIFICATION TECHNOLOGY OF SUNFLOWER OIL

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*The object of the study is the process of chemical transesterification of sunflower oil.*

*Liquid vegetable oils are an important component in the products of chemical, cosmetic, paint, food and other industries. Among other oils, sunflower oil is of exceptional industrial importance.*

*Chemical transesterification technology is used to obtain oils, fats and their mixtures with specified properties required for various industries. An important task is to develop rational conditions for the oil transesterification process using a highly efficient and safe catalyst.*

*The process of chemical transesterification of refined deodorized frozen sunflower oil according to DSTU 4492 (CAS Number 8001-21-6) using potassium glyceroxide was studied. The original oil has the following parameters: peroxide value 0.2 ½ O mmol/kg, acid value 0.1 mg KOH/g, moisture mass fraction 0.03 %, crystallization temperature –18.38 °C.*

*The effect of transesterification parameters on the oil crystallization temperature was examined. The catalyst concentration in all experiments was 0.45 % by weight of the oil. The oil crystallization temperature was determined by differential scanning calorimetry. Rational parameters of oil transesterification were defined: temperature 110 °C, duration 1.5 hours. Under these conditions, there is a maximum increase in the oil crystallization temperature (up to –4.1 °C). The effectiveness of the rational oil transesterification parameters was confirmed by changes in the triglyceride composition by chromatography analysis.*

*The obtained rational conditions for the chemical transesterification of sunflower oil in the presence of the potassium glyceroxide catalyst can also be used in the processes of oil transesterification with other raw materials using this catalyst*

*Keywords: chemical transesterification of sunflower oil, potassium glyceroxide catalyst, oil crystallization temperature*

*Received date 09.07.2024*
*Accepted date 27.09.2024*
*Published date 30.10.2024*

***How to Cite:*** *Korchak, M., Shostia, A., Usenko, S., Floka, L., Hnitii, N., Morozova, L., Glavatchuk, V., Marushko, L., Nekrasov, S., Mylostyvyi, R. (2024). Determination of rational parameters of chemical transesterification technology of sunflower oil. Eastern-European Journal of Enterprise Technologies, 5 (6 (131)), 26–33. https://doi.org/10.15587/1729-4061.2024.313095*

## 1. Introduction

Transesterification technology helps to obtain oils, fats and products based on them with the required properties for various industrial purposes. As a result of the transesterification process, the physico-chemical parameters of fat change: triglyceride composition; melting point; crystallization rate and polymorphic form; hardness; content of solid triglycerides. The rearrangement of fatty acid residues in triglycerides causes changes in the melting and crystallization temperatures of the raw material. Thus, the melting temperature of soybean oil after transesterification increases by 12.5 °C, and that of palm kernel oil decreases by 1.4 °C. For oils and fats with significant changes in melting and crystallization temperatures, these indicators are used as an efficiency parameter for the conditions and catalyst of the transesterification process [1].

Transesterification is an alternative method of fat modification without forming trans-isomers of fatty acids, which are harmful to human health. For example, upon oil hydrogenation, the amount of trans-isomers of fatty acids can reach 50 % [2].

The transesterification process without catalysts can occur with a noticeable rate only at temperatures of 250 °C and above, but this leads to the breakdown of triglycerides. Catalysts lower the activation energy barrier and allow the process to be carried out at temperatures of (30–120) °C [3]. In chemical transesterification, alkaline catalysts are used: sodium, potassium and compounds of these metals (oxides, hydroxides, alkoxides, carbonates). Alkali metal alkoxides are widely used in industry, but these compounds are characterized by toxicity, explosion and fire hazards, and cause soil and water pollution [4]. Thus, the self-ignition temperature of sodium ethoxide is 50 °C [5].

Alternative, safer transesterification catalysts are alkali metal glyceroxides, being true process catalysts. These compounds do not form explosive or fire-hazardous dust, have high storage stability, and are effective even at increased oxidation rates of the initial fatty raw materials [1]. This property is important because metal alkoxides and enzymatic catalysts require a high degree of oil release from spoilage products. Oxidation products significantly reduce the activity of other alkaline catalysts [6]. The production of such catalysts does not require complex equipment, expensive reagents and is possible directly at an enterprise, which is an advantage over other chemical and enzymatic transesterification catalysts. The cost of potassium glyceroxide is $ 5/kg [3].

One of the most common vegetable oils is sunflower oil. Sunflower is the third largest oilseed crop in terms of production in the world, with a total share of 10 %. Transesterification of high-melting fat and sunflower oil mixtures helps to obtain high-quality plastic fats for various purposes.

Transesterification of oil-fat mixtures allows obtaining a wide range of triglycerides with different melting points. This is important for fatty products, especially to ensure the appropriate plastic properties of margarines and shortenings. Transesterification of mixtures of fully hydrogenated oils with vegetable oils produces a predominantly crystalline β'-form, providing a creamy taste in margarines and shortenings.

Transesterified fats are more stable. For example, the disadvantage of products based on unmodified palm oil is a gradual increase in hardness during storage (from 250 to 300 $g/cm^2$ in 60 days). In transesterified palm oil, the hardness does not exceed 220 $g/cm^2$ after 60 days of storage [2]. Transesterified mixtures of palm and sunflower oils have a lower hardness (365 $g/cm^2$) than non-transesterified ones (444 $g/cm^2$). This is important for shortenings used in bakery products.

Transesterification of sunflower oil and an acylating agent (usually methyl or ethyl alcohol) in the presence of a catalyst produces biodiesel fuel. Using such fuel reduces the emission of hydrocarbons and solids by 50 %, carbon oxides by (40–50) %, nitrogen oxides by (5–10) %, soot by 60 % [7].

Thus, individual transesterified sunflower oil is not used in industry, but it is an important raw material for many fat products. It is appropriate to study the patterns and rational conditions of oil transesterification in the presence of a promising and safe catalyst – potassium glyceroxide. Using individual sunflower oil will help to more clearly determine the dependence of oil properties on transesterification conditions and quickly define the most effective process conditions. This will allow more effective use of this catalyst in the transesterification technology of oil-fat mixtures to obtain high-quality plastic fats.

## 2. Literature review and problem statement

Sunflower oil is one of the most industrially important oils. At the same time, sunflower oil transesterified in individual form is not applied for industrial purposes, but is widely used as a raw material for producing transesterified oil-fat mixtures with the necessary physico-chemical properties. For example, sunflower oil is an important component in cocoa butter equivalents, which are obtained by transesterification of oil-fat mixtures [8]. In the production of cocoa butter equivalents, sunflower stearin obtained by fractionating the corresponding type of sunflower oil is also used [9]. However, the influence of transesterification process parameters on the physico-chemical properties of the product, in particular, the melting and crystallization characteristics, is not shown.

In [10], the crystallization process of transesterified mixtures of palm stearin with vegetable oils was studied. After transesterification, the solids content in the mixtures was (4–55) % between 45 and 0 °C, indicating that the transesterified mixtures had a wider plasticity range compared to physical mixtures – (18–60) % between 45 and 0 °C. The transesterified mixtures had a higher number of β′ crystals, which is desirable for manufacturing fatty products. However, it is not shown how the transesterification parameters affect the melting and crystallization characteristics of the investigated mixtures.

The work [11] confirmed that unlike physical mixtures, transesterified mixtures of palm stearin and vegetable oils had a larger number of β′ crystals (β′/β=6/4–7/3). The transesterified mixtures had small spherical or short acicular crystals, uniformly and densely distributed in the crystal network. The resulting fat is promising for use in products that require rapid freezing. But the influence of transesterification conditions on the crystallization characteristics of the product is not shown, and there are no data on rational transesterification parameters.

In [12], palm stearin and sunflower oil (PS:SO) mixtures obtained by mixing 40 to 80 % palm stearin in 10 % increments were studied. The mixtures were transesterified in the presence of enzymatic catalysts Pseudomonas sp. and Rhizomucor miehei (Lipozyme 1M 60). Pseudomonas lipase caused a greater sliding melting point decrease (33 %) in the PS:SO (40:60) mixture than R. miehei (13 %). Pseudomonas lipase induced greater randomization of fatty acids, particularly palmitic acid, in palm stearin with unsaturated sunflower oil fatty acids than R. miehei lipase. Such mixtures are promising for use in margarine products. The disadvantage of the work is the lack of data on the influence of transesterification process parameters on the physico-chemical indicators of mixtures, in particular, the crystallization or melting temperature.

Enzymatic (Lipozyme TL IM catalyst) and chemical transesterification (sodium methoxide catalyst) of ternary mixtures of hydrogenated soybean, rapeseed and sunflower oils as raw materials for vanaspati was studied. In all mixtures, the melting point and solids content decreased upon transesterification, without significant differences for both methods [13]. The disadvantage is the use of an explosive, fire-hazardous chemical catalyst. There is also no data on rational transesterification conditions for both methods.

The work [14] investigated the production of shortening by chemical transesterification of sunflower oil and pork fat mixtures. Mixing and transesterification of the fat:sunflower oil mixture in a (90:10) % ratio allowed extending the melting range from –40 to 60 °C. Transesterification improved the physical properties of fat, while mixing did not lead to significant changes. But it was not found which transesterification parameters are most effective.

The work [15] shows that preliminary transesterification of sunflower oil with a high content of oleic and stearic acids increased the efficiency of further fractionation at lower process temperatures (8 °C). Fractionation produced stearins with a high content of saturated fatty acids with a higher yield than using oil without preliminary transesterification (28.3 % vs. 18.7 %). The disadvantage of the work is the lack of data on rational oil transesterification conditions.

Enzymatic transesterification processes require less stringent reaction conditions and produce less waste than chemical ones. Such catalysts provide more opportunities for transesterification selectivity. However, such catalysts need to be purchased, and enzymatic catalysts cost more than chemical ones. Promising transesterification catalysts are glyceroxides of alkali metals, in particular, potassium glyceroxide, having several advantages over other catalysts. Such a catalyst can be produced at an enterprise. The work [16] found that using potassium glyceroxide, the triglyceride composition of palm olein is closer to statistically equilibrium than using sodium methoxide. The effectiveness of potassium glyceroxide was confirmed even at high peroxide values of raw materials (12.7 ½ O mmol/kg) [1]. The palm olein melting temperature also changed by more than 12.0 °C, corresponding to a significant change in the triglyceride composition. So, the expediency of using potassium glyceroxide in transesterification processes was experimentally confirmed, but rational conditions for using this catalyst were not shown. At the same time, only one raw material was used – palm olein.

Thus, the processes of sunflower oil transesterification with other raw materials are widely used in manufacturing fat products for various purposes. However, there is insufficient data on the dependence of the melting and crystallization characteristics of transesterified products on transesterification parameters, as well as on rational transesterification conditions. Common catalysts need to be purchased and have a number of drawbacks. Research on rational transesterification conditions in the presence of an alternative chemical catalyst potassium glyceroxide, having several advantages over other catalysts, is relevant. For this purpose, it is advisable to use sunflower oil as an important component of oil-fat mixtures and investigate the effect of the potassium glyceroxide catalyst on the crystallization temperature, being one of the most important indicators for oils and fats.

## 3. The aim and objectives of the study

The aim of the study is to determine rational parameters of the chemical transesterification of sunflower oil using an effective and safe potassium glyceroxide catalyst. This will help to predict the properties of transesterified sunflower oil depending on the process conditions, as well as apply rational conditions in industrial transesterification processes of oil and fat raw materials using the potassium glyceroxide catalyst.

To achieve the aim, the following objectives were accomplished:

– to determine the dependence of the crystallization temperature of transesterified sunflower oil on the transesterification process parameters and determine the parameter values that cause maximum changes in the crystallization temperature of transesterified oil;

– to study the triglyceride composition of the original sunflower oil and transesterified under rational conditions.

## 4. Materials and methods

### 4. 1. The object and hypothesis of the study

The object of the study is the process of chemical transesterification of sunflower oil. The main hypothesis of the study is that the transesterification parameters affect the process efficiency, which can be estimated by changes in the oil crystallization temperature. The study assumes that a change in the crystallization temperature corresponds to a change in the triglyceride composition of the oil. The study makes a simplification that the indicators of oxidative and hydrolytic deterioration of the original oil (peroxide and acid values) within the standard values do not affect the results of the work. The work uses standard research methods.

### 4. 2. Examined materials and equipment used in the experiment

The following materials and equipment were used in the work:

– refined deodorized frozen sunflower oil according to DSTU 4492 (CAS Number 8001-21-6);

– DSC differential scanning calorimeter, model Q20 (USA);

– Hewlett Packard HP-6890 gas chromatograph.

### 4. 3. Method of determining the physico-chemical parameters of sunflower oil

The characteristics of the original and transesterified sunflower oil are determined by the following standard methods for oils and fats:

– mass fraction of moisture and volatile matter – according to ISO 662:2016;

– acid value – according to ISO 660:2020;

– peroxide value – according to ISO 3960:2017;

– triglyceride composition – according to ISO/TS 17383:2014 (gas chromatography).

To determine the oil crystallization temperature, a modern operational and reliable method of oil and fat research is applied – differential scanning calorimetry (DSC) according to ISO 11357-1:2023. The essence of the method is that the device records the dependence of the difference in heat flows (between a cell with a sample and an empty one) on time. During the processes in the sample related to the release or absorption of heat (in particular, phase transitions), deviations from a monotonous change in the signal's time dependence (anomalies) occur. In the TA Universal Analysis software environment, the temperature parameters of the anomalies characterizing the oil crystallization temperature were measured automatically.

**4. 4. Method of sunflower oil transesterification**

Experimental transesterification processes were carried out under the methodology given in [1]. The temperature and duration of the process in each experiment were set according to the experimental design. The catalyst concentration in all experiments was 0.45 % by weight of the oil. The catalyst concentration was chosen from previous studies, which involved experimental transesterification of sunflower oil at a temperature of 110 °C with a duration of 1 hour. At different catalyst concentrations, the following oil crystallization temperatures were obtained: for 0.3 % catalyst –10.4 °C; for 0.35 % catalyst –8.3 °C; for 0.4 % catalyst –7.5 °C; for 0.45 % catalyst –6.2 °C; for 0.5 % catalyst –6.0 °C. Therefore, with an increase in the catalyst concentration above 0.45 %, there is almost no increase in the oil crystallization temperature, so the 0.45 % catalyst concentration was chosen for research.

**4. 5. Research planning and results processing**

The work uses a second-order full factorial experiment. Processing of the obtained results and construction of the response surface were performed in the StatSoftStatistica v6.0 (USA) package environment in accordance with [1]. The choice of levels and intervals of factor variation was based on previous studies [1, 16]. Each experiment was performed twice. During calculations, the following tabs of the "General Regression Models" module were used: Parameter Estimates (equation coefficients, standard error, 95 % confidence interval); "Observed, Predicted, and Residual Values" (calculation of response function values); "ANOVA" (analysis of variance).

## 5. Results of developing rational transesterification parameters of sunflower oil in the presence of potassium glyceroxide

**5. 1. Determining the dependence of the crystallization temperature of transesterified sunflower oil on transesterification parameters**

The quality indicators of the original refined deodorized frozen sunflower oil were studied. The defined parameters of the experimental sample and standard parameter values by DSTU 4492 are given in Table 1.

Table 1

Physico-chemical parameters of the original sunflower oil

| Parameter | Characteristic | Norm according to DSTU 4492 |
|---|---|---|
| Mass fraction of moisture and volatile matter, % | 0.03 | 0.10 |
| Acid value, mg KOH/g | 0.1 | 0.5 |
| Peroxide value, ½ O mmol/kg | 0.2 | 10.0 |

The crystallization temperature of the original sunflower oil by the DSC method was –18.38 °C. Therefore, the experimental sample of oil meets the DSTU 4492 requirements.

The influence of sunflower oil transesterification parameters on the degree of conversion and efficiency of the transesterification process was determined. Changes in the melting and crystallization temperatures of oils and fats reflect the efficiency of redistribution of fatty acid residues in triglyceride molecules [6]. So, the crystallization temperature of sunflower oil was chosen as the response function ($y$). The following factors of variation – transesterification process parameters (at four levels) were studied:

– $x_1$ – transesterification temperature, °C (from 70 to 130 °C);

– $x_2$ – transesterification duration, hours (from 0.5 to 2 hours).

Analysis of experimental data was carried out using the StatSoftStatistica v6.0 package (USA).

The study applied a response function in the form of a second-degree polynomial:

$$y=b_0+b_1 \cdot x_1+b_2 \cdot x_2+b_{11} \cdot x_1^2+b_{22} \cdot x_2^2, \quad (1)$$

where $y$ – crystallization temperature of transesterified sunflower oil, °C; $b_0$ – free term of the regression equation; $x_1$ – transesterification temperature, °C; $x_2$ – transesterification duration, hours; $b_1$, $b_2$, $b_{11}$, $b_{22}$ – coefficients of each polynomial element.

Table 2 shows the planning matrix, experimental ($y_e$) and calculated ($y_c$) values of the crystallization temperature of transesterified sunflower oil samples.

To test the significance of the regression dependence coefficients (1), a Pareto chart was constructed, shown in Fig. 1.

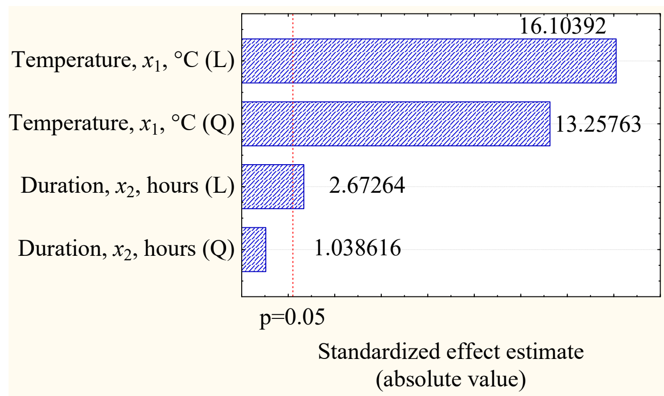


Fig. 1. Pareto chart for testing the significance of regression equation coefficients (L – linear effect, Q – quadratic effect)

The given Pareto chart (Fig. 1) represents standardized coefficients sorted by absolute values. Analysis of the data in Fig. 1 indicates that the quadratic transesterification duration is insignificant, since the point column of this effect does not cross the vertical line, representing a 95 % confidence probability. Therefore, this regression term was excluded from the resulting model.

The regression dependence of the crystallization temperature of transesterified sunflower oil on the temperature and duration of transesterification in the presence of potassium glyceroxide in natural variables, after removing the insignificant term, has the following form:

$$y=-56.980+0.827 \cdot x_1+2.778 \cdot x_2-0.003 \cdot x_1^2. \quad (2)$$

The adequacy of the developed model was confirmed by the analysis of variance method, the results of which are presented in Table 3.

Table 2

Planning matrix and values of sunflower oil crystallization temperature

| No. of experiment | Factors of variation | | | | Oil crystallization temperature $y_e$, °C (experimental value) | Oil crystallization temperature $y_c$, °C (calculated value) |
|---|---|---|---|---|---|---|
| | Transesterification temperature, $x_1$ | | Transesterification duration, $x_2$ | | | |
| | Coded level | °C | Coded level | hours | | |
| 1 | –1 | 70 | –1 | 0.5 | –15.0 | –14.4 |
| 2 | –1 | 70 | –0.5 | 1 | –13.7 | –13.4 |
| 3 | –1 | 70 | +0.5 | 1.5 | –12.5 | –12.4 |
| 4 | –1 | 70 | +1 | 2 | –11.2 | –11.8 |
| 5 | –0.5 | 90 | –1 | 0.5 | –8.2 | –8.7 |
| 6 | –0.5 | 90 | –0.5 | 1 | –7.5 | –7.7 |
| 7 | –0.5 | 90 | +0.5 | 1.5 | –6.4 | –6.8 |
| 8 | –0.5 | 90 | +1 | 2 | –6.4 | –6.1 |
| 9 | +0.5 | 110 | –1 | 0.5 | –5.8 | –5.7 |
| 10 | +0.5 | 110 | –0.5 | 1 | –4.9 | –4.7 |
| 11 | +0.5 | 110 | +0.5 | 1.5 | –4.1 | –3.8 |
| 12 | +0.5 | 110 | +1 | 2 | –3.5 | –3.2 |
| 13 | +1 | 130 | –1 | 0.5 | –5.4 | –5.5 |
| 14 | +1 | 130 | –0.5 | 1 | –4.0 | –4.4 |
| 15 | +1 | 130 | +0.5 | 1.5 | –3.7 | –3.6 |
| 16 | +1 | 130 | +1 | 2 | –3.0 | –2.9 |

Table 3

Analysis of variance results

| Factor | Sum of squares, SS | Degree of freedom, df | Mean square, MS | F-value | Significance level, p-value |
|---|---|---|---|---|---|
| Free term of the equation | 84.45801 | 1 | 84.45801 | 504.3980 | 0.000000 |
| Transesterification temperature, °C (L) | 43.42406 | 1 | 43.42406 | 259.3361 | 0.000000 |
| Transesterification temperature, °C (Q) | 29.43062 | 1 | 29.43062 | 175.7648 | 0.000000 |
| Transesterification duration, hours (L) | 1.19605 | 1 | 1.19605 | 7.1430 | 0.021691 |
| Transesterification duration, hours (Q) | 0.18063 | 1 | 0.18063 | 1.0787 | 0.321275 |
| Error | 1.84188 | 11 | 0.16744 | – | – |
| Coefficient of determination $R^2$=0.992. Adjusted coefficient of determination $R^2_{adj}=0.989$ | | | | | |

By analyzing the critical points of the regression equation (2) in the StatSoftStatistica v6.0 (USA) environment, rational parameters of sunflower oil chemical transesterification were determined: temperature 110 °C and duration 1.5 hours. Under these conditions, the crystallization temperature of sunflower oil is –4.1 °C. The corresponding graphic dependence of the crystallization temperature of sunflower oil on the transesterification parameters in the presence of potassium glyceroxide (response surface) is shown in Fig. 2.

As shown in Fig. 2, the largest response function values are observed under the conditions of transesterification temperature above 100 °C and duration of more than 1 hour.

As the values of the variation factors increase, the growth of the response function values gradually slows down. So, after a temperature increase of more than 110 °C and with a duration of more than 1.5 hours, there is no significant increase in the crystallization temperature of transesterified oil.

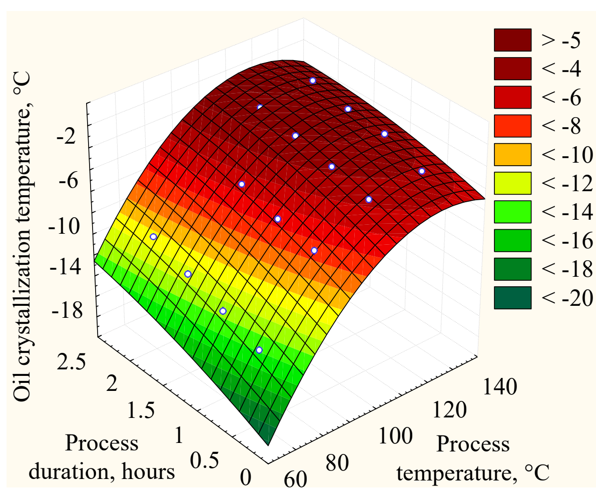


Fig. 2. Dependence of the crystallization temperature of transesterified sunflower oil on the temperature and duration of chemical transesterification

**5. 2. Study of the triglyceride composition of the original and transesterified sunflower oil**

Changes in the melting and crystallization temperatures of various oils and fats indicate the completeness of transformations in the transesterification reaction [6]. But the most reliable method to confirm the effectiveness of the transesterification process is gas chromatography analysis, which helps to quantify the content of all available triglycerides in the original and transesterified oil. Table 4 shows the results of determining the triglyceride (TG) content in the original oil ($a_0$), transesterified under specified rational conditions ($a_1$) in the presence of potassium glyceroxide and transesterified under similar conditions in the presence of sodium methoxide ($a_2$). Differences in the content of the corresponding triglycerides in the original and transesterified oil with potassium glyceroxide ($\Delta a_{01}$), as well as in the original and transesterified oil with sodium methoxide ($\Delta a_{02}$) are given. The corresponding absolute measurement errors of each triglyceride content are presented (for the original oil $\Delta_0$, for transesterified oil with potassium glyceroxide $\Delta_1$, for transesterified oil with sodium methoxide $\Delta_2$). In Table 4, the following designations of fatty acid residues in triglycerides are applied: P – palmitic, O – oleic, L – linoleic, S – stearic.

Table 4

Results of studying the triglyceride composition of the original and transesterified sunflower oil

| TG | Mass fraction of triglycerides, % | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | POP | PLP | POS | POO | PLS | PLO | PLL | OOO+ +SLS | SLO | OOL | SLL | SOO | OLL | LLL | Total |
| No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | |
| $a_0$ | 0.37 | 1.29 | 0 | 0.62 | 2.31 | 6.97 | 10.9 | 1.47 | 12.87 | 4.94 | 7.91 | 6.03 | 22.16 | 22.16 | 100.00 |
| $a_1$ | 0.67 | 1.39 | 0.9 | 1.24 | 2.21 | 8.83 | 8.92 | 1.3 | 6.44 | 7.27 | 13.91 | 8.3 | 20.71 | 17.91 | 100.00 |
| $a_2$ | 0.54 | 1.18 | 0.56 | 1.13 | 2.20 | 7.55 | 9.63 | 1.25 | 9.70 | 6.53 | 11.36 | 7.52 | 20.56 | 20.35 | – |
| $\Delta a_{01}$ | –0.3 | –0.1 | –0.9 | –0.62 | 0.1 | –1.86 | 1.98 | 0.17 | 6.43 | –2.33 | –6.00 | –2.27 | 1.45 | 4.25 | – |
| $\Delta a_{02}$ | –0.17 | 0.11 | –0.56 | –0.51 | 0.11 | –0.58 | 1.27 | 0.22 | 3.17 | –1.59 | –3.45 | –1.49 | 1.6 | 1.81 | – |
| $\Delta_0$ | 0.04 | 0.15 | 0.00 | 0.07 | 0.25 | 0.56 | 0.87 | 0.16 | 1.03 | 0.54 | 0.79 | 0.48 | 1.11 | 1.43 | – |
| $\Delta_1$ | 0.07 | 0.13 | 0.1 | 0.14 | 0.24 | 0.71 | 0.70 | 0.14 | 0.51 | 0.58 | 1.07 | 0.66 | 1.03 | 1.01 | – |
| $\Delta_2$ | 0.06 | 0.14 | 0.06 | 0.12 | 0.24 | 0.75 | 0.77 | 0.14 | 0.77 | 0.52 | 0.91 | 0.75 | 1.03 | 0.10 | – |

As shown in Table 4, for potassium glyceroxide, 12 out of 14 triglycerides have a difference between the content in the original and transesterified oil being greater modulo than the absolute measurement error. Only for triglycerides No. 2 and No. 5, this difference is smaller than the measurement error. For sodium methoxide, this difference is smaller than the measurement error for the three triglycerides (No. 2, No. 5, and No. 6). So, the potassium glyceroxide catalyst showed efficiency comparable to the industrial catalyst. The obtained data correlate with the results in [16]. It was found that using potassium glyceroxide, the triglyceride composition of palm olein changes to a greater extent and becomes closer to statistically equilibrium than using sodium methoxide. Therefore, this catalyst is promising.

## 6. Discussion of the results on developing rational parameters of chemical transesterification of sunflower oil

The paper examines the chemical transesterification technology of refined deodorized frozen sunflower oil when adding the potassium glyceroxide catalyst. A second-order full factorial experiment was used. Two factors of variation (temperature and duration of transesterification) at four levels were considered (Table 2). The significance of the regression dependence coefficients was checked by the Pareto chart (Fig. 1), in which the quadratic transesterification duration is insignificant. The analysis of variance of the developed model was conducted and its adequacy was confirmed (Table 3). The coefficient of determination and the adjusted coefficient of determination are close to 1. Analyzing the critical points of the regression equation (2) in the StatSoftStatistica v6.0 (USA) environment, rational parameters of chemical transesterification of sunflower oil were determined: temperature 110 °C and duration 1.5 hours. Under these conditions, the crystallization temperature of the oil increased from –18.38 °C (original oil) to –4.1 °C (transesterified oil). So, the crystallization temperature increased by 14.28 °C. According to the graphical dependence in Fig. 2, the highest values of the oil crystallization temperature are observed under the conditions of transesterification temperature above 100 °C and duration of more than 1 hour.

The result was confirmed by gas chromatography analysis (Table 4), indicating that the change in concentration as a result of transesterification beyond the absolute measurement error occurred for 12 out of the 14 available triglycerides (86 %).

Existing studies [1, 8–16] provide data on enzymatic and chemical processes of transesterification of oil-fat mixtures of various compositions. Changes in melting temperatures, solids content, crystallization nature of mixtures upon transesterification were investigated. In this work, unlike [1, 8–16], the effect of chemical transesterification parameters on the crystallization temperature of sunflower oil was determined. At the same time, the chemical catalyst potassium glyceroxide is used, which is safer and more affordable than other catalysts. The defined transesterification conditions in the presence of potassium glyceroxide will allow more effective use of this catalyst in industrial production processes of transesterified fats. The works [1, 16] confirmed the effectiveness of the potassium glyceroxide catalyst using changes in the melting temperature and chromatography analysis of changes in the triglyceride composition of palm olein. In contrast to these studies, this work determined rational parameters of the transesterification process using other raw materials (sunflower oil). The response parameter is the crystallization temperature of the oil, while the change in the triglyceride composition was confirmed by chromatography analysis.

The obtained data confirming changes in the triglyceride composition of the oil correlate with the results in [16]. Using potassium glyceroxide, the triglyceride composition of palm olein becomes closer to statistically equilibrium than using sodium methoxide.

The limitation of the obtained results is that rational transesterification conditions were determined for only one type of oil – refined deodorized frozen sunflower oil. For other oils and fats, as well as with other quality indicators, it may be necessary to adjust the transesterification parameters.

The shortcoming of the work is the lack of data on using oil or fat transesterified under the specified rational parameters, when adding the catalyst applied, in specific products. After all, oils and fats significantly affect the quality indicators, shelf life and technological properties of the final product.

A promising area of work is to study the transesterification processes of sunflower oil in mixtures with other oils and fats. Transesterification of oil and fat mixtures with different consistency characteristics provides fatty products with the required melting and crystallization temperature range.

## 7. Conclusions

1. The dependence of the crystallization temperature of transesterified sunflower oil on the transesterification process parameters was determined. The crystallization temperature of the original oil is –18.38 °C. The process temperature has a more significant influence on the response function values than duration. Rational transesterification parameters of sunflower oil when adding the potassium glyceroxide catalyst were determined: temperature 110 °C, duration 1.5 hours. Under these transesterification conditions, the crystallization temperature of the oil increased by 14.28 °C.

2. The triglyceride composition of the original sunflower oil and transesterified under the developed conditions was investigated by gas chromatography. Changes in concentrations due to transesterification in the presence of potassium glyceroxide beyond the calculated absolute measurement error occurred for 12 of the 14 triglycerides detected. Using sodium methoxide, this concentration change occurred for 11 out of the 14 triglycerides. This indicates the prospects of research and use of the potassium glyceroxide catalyst.

## Conflict of interest

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

## Financing

The study was conducted without financial support.

## Data availability

The manuscript has no associated data.

## Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the current work.

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