The object of the study is the process of esterification of sunflower soapstock fatty acids with butanol.

Soapstock is a waste of the oil and fat industry, which is formed in the process of alkaline neutralization of oils. The processing of soapstock to obtain fatty acids is promising, since the disposal of waste is difficult and dangerous, and fatty acids are an industrially valuable product. Fatty acids obtained from soapstock are an available raw material for the production of fatty acid esters of low molecular weight alcohols, which are the basis of alternative biodiesel fuel.

The influence of the conditions of esterification of fatty acids from sunflower soapstock (CAS Number 61788-66-7) with butanol (CAS Number 71-36-3) in the presence of an alkylbenzenesulfonic acid catalyst on the acid value of the reaction mixture was studied. This indicator reflects an increase in the content of butyl esters.

The fatty acids used, obtained from soapstock by decomposition with sulfuric acid, meet the requirements of DSTU 4860 for first-grade fatty acids. The neutralization number of fatty acids is 186.0 mg KOH/g, the mass fraction of moisture and volatile substances is 1.7 %, the mass fraction of total fat is 97.5 %, the depth of cleavage is 67.1 % of oleic acid.

Rational conditions for the esterification process have been established, which correspond to the maximum reduction in the acid value of the reaction mixture: duration is 12 hours, catalyst concentration is 3.5 %. In this case, the acid value of the reaction mass was 4.05 mg KOH/g. The product yield was 91.5 %. Product parameters: mass fraction of esters – 92.7 %, mass fraction of total glycerol – 0.20 %, mass fraction of moisture 0.04 %, density at the temperature of 15 °C – 840 kg/m^3.

The results obtained make it possible to obtain a high-quality base for biodiesel fuel using soapstock fatty acids under rational conditions

Keywords: butyl esters of fatty acids, esterification of fatty acids, waste from the oil and fat industry

UDC 665.1
DOI: 10.15587/1729-4061.2025.326031

IDENTIFYING OF RATIONAL CONDITIONS FOR ETHERIFICATION OF SUNFLOWER SOAPSTOCK FATTY ACIDS

Gabriella Birta
Corresponding author
Doctor of Agricultural Sciences, Professor*
E-mail: natsytoys@gmail.com
Nadiya Levoshko*
Vladyslav Knysh
Department of Agro Resources
Institute of Water Problems and Land Reclamation of the National Academy of Agrarian Sciences of Ukraine
Vasylkivska str., 37, Kyiv, Ukraine, 03022
Svitlana Usenko
Doctor of Agricultural Sciences, Senior Researcher
Department of Animal Productivity Biology named after academician O. V. Kvasnytskyi**
Anatolii Shostia
Doctor of Agricultural Sciences, Senior Researcher
Department of Production Technology Livestock Products**
Tetiana Ovsiannikova
PhD, Associate Professor***
Tetiana Falalieieva
PhD, Associate Professor***
Larysa Marushko
Doctor of Pedagogical Sciences, Associate Professor
Department of Organic and Pharmaceutical Chemistry
Lesya Ukrainka Volyn National University
Voli ave., 13, Lutsk, Ukraine, 43025
Yevhen Semenko
PhD
Department of Logistics of Units
National Academy of the National Guard of Ukraine
Zakhysnykiv Ukrainy sq., 3, Kharkiv, Ukraine, 61001
Sergii Zygin
Department of Design Automation
Kharkiv National University of Radio Electronics
Nauky ave., 14, Kharkiv, Ukraine, 61166
*Department of Commodity Science, Biotechnology, Expertise and Customs
Poltava University of Economics and Trade
Ivana Banka str., 3, Poltava, Ukraine, 36003
**Poltava State Agrarian University
Skovorody str., 1/3, Poltava, Ukraine, 36003
***Department of Organic Synthesis and Pharmaceutical Technologies
National Technical University "Kharkiv Polytechnic Institute"
Kyrpychova str., 2, Kharkiv, Ukraine, 61002

Received 09.01.2025
Received in revised form 13.03.2025
Accepted date 25.03.2025
Published date 30.04.2025

How to Cite: *Birta, G., Levoshko, N., Knysh, V., Usenko, S., Shostia, A., Ovsiannikova, T., Falalieieva, T., Marushko, L., Semenko, Y., Zygin, S. (2025). Identifying of rational conditions for etherification of sunflower soapstock fatty acids. Eastern-European Journal of Enterprise Technologies, 2 (6 (134)), 6–13. https://doi.org/10.15587/1729-4061.2025.326031*

1. Introduction

The combustion of fossil fuels contributes significantly to greenhouse gas emissions, which have a negative impact on the atmosphere. One of the tools for reducing greenhouse gas emissions and harmful substances is the use of alternative energy sources, which include liquid biofuels for motor engines [1].

The addition of 20 % biodiesel reduces the smoke of exhaust gases compared to petroleum fuel from 15 to 8 %. In addition, it reduces the integrated specific emissions of nitrogen oxides from 5.948 to 5.786 g/(kW·h); carbon monoxide from 2.782 to 2.007 g/(kW·h); unburned hydrocarbons from 1.006 to 0.792 g/(kW·h). The introduction of biodiesel based on fatty acid esters of low molecular weight alcohols in the amount of (2–35) % into hydrocarbon fuel does not require engine rebuilding. The advantage of biodiesel is also a higher cetane number (for pure biodiesel not less than 51, for mineral diesel fuel 42–45). Biodiesel has an ignition temperature of over 150 °C, which makes it safe to use [2].

The main method of synthesizing fatty acid esters is the reaction of interaction of fatty carboxylic acids (or oils, fats) and the corresponding low molecular weight alcohol in the presence of a catalyst. The process occurs according to the mechanism of transesterification – nucleophilic substitution with the formation of esters and water (or glycerol). The processing of oil refining waste to obtain fatty acids for the synthesis of esters is promising. Thus, a large-tonnage waste of oil refining is soapstock, which is formed at the alkaline neutralization stage. The amount of soapstock formed when obtaining 1 ton of refined oil is (10–20) % of the oil mass. The fat content in soapstock can reach 70 %. The fat components of soapstock are susceptible to oxidation and pose a fire hazard, so the disposal of this waste is a difficult issue [3].

The esterification of fatty acids is usually carried out using methanol or ethanol as reagents – acceptors of fatty acid acyls. In methanol esterification, the transformation occurs when mixing two mutually insoluble phases of oil and methanol. In the case of butanolysis, the oil is well soluble in alcohol and diffusion is not the limiting stage of the process. Thus, methanolysis of soybean oil in the presence of a methoxide catalyst occurs almost 15 times slower than butanolysis. The longer butanol chain improves the properties of the final biodiesel and its mixing with conventional diesel. But butanol is less studied in this direction [4].

Homogeneous or heterogeneous, alkaline or acidic catalysts can be used in the reaction. The use of alkaline catalysts is more common. But these catalysts lead to saponification of the resulting esters, which causes an increase in catalyst consumption, and also complicates the separation of the reaction products. Homogeneous acid catalysts are an alternative for the transesterification of raw materials with a high content of free fatty acids, including when obtaining esters from fatty acids of soapstocks. The use of acid catalysts is more effective than basic ones if the raw materials contain more than 1 % free fatty acids. As homogeneous acid catalysts, sulfuric, sulfonic acids, alkylbenzenesulfonic acids, etc. are used. In this case, the saponification reaction does not occur. However, a high temperature (above 100 °C), a high molar ratio of alcohol/oil (about 6:1 alcohol/oil) and a longer reaction time (3–48 h) are required compared to alkaline catalysts [5].

In addition to biodiesel, butyl esters are used for the synthesis of higher fatty alcohols. Butyl oleate is widely used in cosmetology, pharmaceuticals, light industry, and in the production of building materials [6].

Thus, fatty acid esters are a valuable product that is used as biodiesel, as well as for other industrial purposes. An important direction of research is the use of waste from the oil and fat industry as a source of raw materials for the synthesis of biodiesel. Considering a number of advantages of butanol as a reagent, there are promising studies on the rational conditions for the use of this alcohol in order to obtain esters from the fatty acids of the refining waste.

2. Literature review and problem statement

The main direction of research is the production of methyl esters of fatty acids as a basis for biodiesel. But the use of butanol as a reagent for the production of esters is of increasing interest. Therefore, there are a number of studies on the production of butyl esters of fatty acids from various fatty raw materials using catalysts of various natures.

The work [7] is devoted to the production of butyl esters from sunflower oil. Butanolysis was carried out using potassium butoxide. A high molar yield of butyl esters was achieved – (93–96) %. Samples after removal of butanol under vacuum with subsequent washing with water and drying are characterized by a butyl ester content of (94–95) %. The disadvantage of the work is the lack of data on the influence of catalyst concentration and other process conditions on the quality and yield of the product. The reason for this could be the complexity of the process equipment and the duration of the experimental butanolysis processes.

The transesterification of sunflower oil with butanol and ethanol on alkoxide-containing dried potassium hydroxide solutions was investigated [6]. A diesel engine operating on mixtures based on butyl esters of fatty acids with a biocomponent content of up to 80% was tested. Better energy characteristics of butyl esters were observed compared to ethyl esters. A gradual decrease in harmful emissions was shown with an increase in the volume fraction of both ethyl and butyl esters. In particular, a decrease in NO_x emissions by (17–18) % was recorded with the highest content of the biodiesel fraction. The disadvantage of the study is the lack of results on the influence of ethanolysis and butanolysis conditions on the efficiency of the process and the quality indicators of the esters. This can be explained by the fact that the primary task was to compare the test results of the obtained ethyl and butyl esters, while establishing rational process conditions requires a long research time.

In the work [8], the transesterification of soybean and castor oil with methanol and butanol using heterogeneous basic catalysts for biodiesel production was investigated. CaO, MgO and ZnO, including those supported on γ-Al_2O_3, were considered as catalysts. During the transesterification of castor oil with butanol, the MgO/γ-Al_2O_3 and ZnO/γ-Al_2O_3 catalysts showed yields of butyl esters of 97 % and 85 %, respectively. However, the effect of catalyst concentrations and process conditions on the completeness of butanolysis and methanolysis was not shown. The reason for this may be the high material and time costs for such studies.

The process of butanolysis of rapeseed oil was investigated using eggshells with a size of (0.315–0.1) mm as a heterogeneous catalyst, with a CaO content of 89.01 % [9]. The shell was previously calcined at 850 °C for 4 h. The optimal process conditions were determined: molar ratio of 1-butanol to oil 11.3:1, catalyst amount 7.41 %, reaction duration 11.81 hours at 110 °C. Under the specified conditions, the yield of the obtained esters reaches 98.78 %. The disadvantage of the work is the long energy-consuming preparation of the catalyst, the need for a significant amount of catalyst to achieve high process efficiency, the lack of data on the influence of process conditions on product quality indicators. The objective reason for this is the study of the principle possibil-

ity of using this catalyst, as well as significant material and time costs to establish the dependence of product quality on process conditions.

In the work [10], rational conditions for obtaining butyl esters from mahua oil using acidic and basic catalysts were investigated. The molar ratio of butanol to mahua oil 6:1, 2 % concentrated sulfuric acid were identified as optimal conditions. At the same time, the content of free fatty acids in the product was 1.1 % (in the initial raw material this indicator was 19.8 %). In the second stage, the molar ratio of butanol to oil 6:1, 1.5 % potassium hydroxide, process temperature 80 °C, duration 90 min. and stirring speed 500 rpm. were determined as optimal conditions with a butyl ester yield of 94.8 %. The work obtained important data on the production of butyl esters, but the disadvantage is the study of different rational conditions and different response functions for acidic and basic catalysts. After all, it is known that acid catalysts require a higher temperature and duration of the process than alkaline ones. But a significant advantage of acid catalysts is the possibility of using them in the processing of waste oils, oil and fat waste with a high content of free fatty acids. Also, a disadvantage is the high cost of the mahua oil used – 9 USD/kg. For example, the cost of sunflower oil – 1.7 USD/kg. The objective reason is the prevalence of this oil in India, where the study was conducted, as well as significant time and material costs for considering all process parameters for both catalysts.

Enzyme catalysts are also used to obtain butyl esters. The synthesis of butyl esters of fatty acids from sunflower oil with 1-butanol using homogeneous lipase Rhizomucor miehei [11] was studied. The process was carried out in a continuous installation consisting of a cascade of a stirred tank reactor and a continuous centrifugal contact separator. The yield of butyl esters was obtained up to 93 % with a process duration of 8 hours. However, there is no data on the influence of the main process conditions (catalyst concentration, duration) on the completeness of the process and on the parameters of the reaction mixture. The reason for this may be the fundamental verification of the operation of this installation for obtaining butyl esters and the significant duration of the research.

The use of residual fatty acids obtained in the process of palm oil refining for the production of butyl esters was investigated [12]. Immobilized lipases (Novozym 435 and Lipozyme RM IM) were used as catalysts. The maximum conversion (above 90 %) was achieved with a biocatalyst amount of up to 2.0 % and a stoichiometric excess of *n*-butanol of up to 10 %. The disadvantage is the lack of data on the influence of the process duration on the parameters of the reaction mixture, in particular, the acid value, which reflects a decrease in the content of free fatty acids in the mass. The reason for this could be the reduced stability of enzyme catalysts compared to chemical ones.

In the work [13], the enzymatic synthesis of fatty acid esters from macauba acid oil (Acrocomia aculeata) using fermented dry babassu cake (Orbygnia oleifera) with lipase activity from Rhizomucor miehei was considered. The reactions were carried out under the influence of ultrasonic irradiation using different alcohols. Higher yields of the ester were obtained using butanol. The content of butyl esters of about 80 % was achieved after 70 hours with a molar ratio of alcohol:oil of 5.47:1, at 40 °C. Therefore, a biocatalyst made from agricultural waste was used. But the disadvantage is the low content of butyl esters, the duration of the process. The reason for this may be the low temperature stability of the catalyst and the impossibility of increasing the temperature to increase the efficiency of the process.

The topical direction is the study of fat-containing waste for the production of butyl esters. A method of using fat waste generated at a tannery for the production of methyl and butyl esters has been proposed [4]. The corresponding animal fat esters were obtained. The yield was 99.2 % for methyl esters and 98.9 % for butyl esters. The produced butyl esters were characterized by better cetane number, heat of combustion and calorific value, density, dynamic viscosity, kinematic viscosity and flash point. For example, the kinematic viscosity for butyl esters was 3.6 mm^2/s, and for methyl esters – 4.1 mm^2/s. The calorific value of biodiesel with the addition of butyl esters was 39.2 MJ/kg, and for methyl esters – 38.4 MJ/kg. Thus, the possibility of producing high-quality esters from fat-containing waste has been demonstrated, but there is no data on the influence of process conditions on the quality indicators of the resulting product. This requires samples of raw materials with identical quality indicators, which is difficult to ensure when using production waste.

Animal wastewater sludge was studied as a raw material for obtaining butyl esters of fatty acids [14]. The studied wastewater contained 84.3 % lipids. The sediment was esterified with butanol, catalyzed by 4-dodecylbenzenesulfonic acid. The optimized conditions determined the molar ratio of 1-butanol:total number of fatty acid chains to be 1.66:1, the catalyst concentration was 10 % at 105 °C for 3 hours. The yield of butyl esters of fatty acids was 95 %. The disadvantage is the high concentration of the catalyst. The objective reason for this may be the desire to minimize the duration of the process.

A relevant direction is the use of waste from the oil and fat industry for the production of fatty acid esters. Thus, in the work [3], rational conditions for the decomposition of sunflower soapstock with sulfuric acid to obtain fatty acids were determined: temperature (90–95) °C, duration 40 min. Under these conditions, the yield of fatty acids is 79.0 %, the neutralization number is 180.0 mg KOH/g. The obtained fatty acids can be used as raw materials for the production of esters. The work investigated only the production of fatty acids, but further studies on their use for the esterification reaction are advisable.

Thus, butyl esters are obtained from oils, fats and oil and fat raw materials with different contents of free fatty acids using catalysts of different nature. Butyl esters have a number of advantages from the point of view of application as biodiesel fuel. A particularly relevant direction is the production of butyl esters using production waste, in particular, from soapstock fatty acids. But there is not enough data on the rational conditions for obtaining esters from such raw materials. Therefore, the unresolved issue remains the establishment of the influence of technological conditions of the process of esterification of soapstock fatty acids on the physicochemical parameters of the product, in particular, the acid value, which reflects the efficiency of the process.

3. The aim and objectives of the study

The aim of the study is to determine the influence of technological conditions for esterification of sunflower soapstock fatty acids with butanol on the acid value of the reaction mixture. This will allow effective use of soapstock fatty acids

to obtain butyl esters, which are the basis of biodiesel, and to predict the acid value of the product depending on the process conditions (duration and catalyst concentration).

To achieve the set aim, the following objectives were solved:

– to determine the conditions for fatty acids esterification with butanol (duration, catalyst concentration), which correspond to the minimum acid value of the reaction mixture;

– to investigate the quality indicators of the obtained product.

4. Materials and methods

4. 1. The object and hypothesis of the study

The object of the study is the process of esterification of sunflower soapstock fatty acids with butanol. The main hypothesis of the study is that increasing the process duration and catalyst concentration increase the efficiency of the process by reducing the acid value of the reaction mixture. The assumption is made that with increasing the process duration, a larger amount of water is removed from the reaction mixture, and the efficiency of the process increases. A simplification is made – during the study, fatty acids with standard parameters were used, and the possibility of using acids of lower quality was not taken into account. Standard research methods were used in the work.

4. 2. Researched materials and equipment used in the experiment

The following materials and equipment were used in the study:

– fatty acids from sunflower soapstock (CAS Number 61788-66-7);

– p.a.-grade butanol-1 (CAS Number 71-36-3);

– linear alkylbenzenesulfonic acid, class A (CAS Number 27176-87-0).

4. 3. Methods for determining organoleptic and physicochemical parameters of initial fatty acids

The parameters of the initial fatty acids sample were determined using the methods given in [3].

4. 4. Methods for conducting the esterification process

The required amount of fatty acids, butanol and catalyst (alkylbenzenesulfonic acid) were placed in a two-necked round-bottom flask, to which a Dean Stark nozzle and a condenser cooled by running water were attached. The condenser was used to return the evaporated butanol to the flask. The flask was placed in a flask heater, and a thermometer was placed in the flask. The process was carried out at the boiling point of the flask contents (122±2) °C. The molar ratio of butanol:fatty acids in all experiments was 6:1. The duration of the process and the concentration of the catalyst were used in each corresponding experiment according to the experimental plan. After the end of the process, samples were taken from the flask to determine the acid value.

4. 5. Methods for determining the quality parameters of the resulting product

The parameters of the obtained product were determined according to standard methods intended for the analysis of fatty acid esters:

– mass fraction of esters – according to EN 14103 (gas chromatography method);

– mass fraction of total glycerol – according to EN 14105;

– mass fraction of moisture – according to EN ISO 12937;

– density at the temperature of 15 °C – according to EN ISO 3675.

4. 6. Research planning and processing of results

The full factorial experiment of the second order was applied. Mathematical processing of the results was performed in the software package StatSoftStatistica v6.0 (USA), where the "General Regression Models" module was used. According to this module, the coefficients of the regression equation, standard error, estimated values of the response function were calculated, and variance analysis was performed. In each experiment, two repetitions were performed.

5. Results of establishing the rational conditions for esterification of sunflower soapstock fatty acids with butanol

5. 1. Determination of butanolysis conditions that correspond to the minimum acid value of the reaction mixture

The fatty acids used in the study were obtained from sunflower soapstock by decomposition with sulfuric acid, according to the method given in [3]. The parameters of the experimental fatty acids in comparison with the standard parameters (according to DSTU 4860) are presented in the Table 1.

Table 1

Organoleptic and physicochemical parameters of fatty acids

Name of parameter	Characteristics	
	Test sample	Standards according to DSTU 4860 (for fatty acids of the first grade)
Color at the temperature of 20 °C	Brown	Brown
Odor	Specific for fatty acids	Specific for fatty acids
Mass fraction of moisture and volatile substances, %	1.7	not more than 2.0
Mass fraction of total fat, %	97.5	not less than 97.0
Depth of cleavage, % oleic acid	67.1	not less than 55.0
Presence of mineral acids	None	Not allowed

Therefore, the experimental sample of fatty acids meets the requirements of DSTU 4860 for first-grade fatty acids.

The influence of the duration of the process of esterification of fatty acids with butanol and the concentration of the catalyst (alkylbenzenesulfonic acid) on the acid value of the reaction mixture (response function), which corresponds to the completeness of the reaction, was established. The influence of the following variation factors on the response function (at four levels) was investigated:

– x_1 – esterification process duration (from 2 to 17 hours);

– x_2 – catalyst concentration (from 0.5 to 5.0 %).

The obtained research results were processed in the StatSoftStatistica v6.0 package (USA). To describe the obtained dependence, the second-degree polynomial was used:

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

where y – acid value of the reaction mixture, mg KOH/g; b_0 – free term of the equation; x_1 – esterification process duration, hours; x_2 – catalyst concentration, %; b_1, b_2, b_{11}, b_{22} – coefficients of the corresponding elements of the polynomial.

The experimental research planning matrix, experimental (y_e) and calculated (y_c) values of the acid value are presented in the Table 2.

Table 2

Research design matrix and response function value (acid value of the reaction mixture)

Experiment No.	Variation factors				Acid value of reaction mixture y_e, mg KOH/g (experimental value)	Acid value of reaction mixture y_c, mg KOH/g (calculated value)
	Process duration, x_1		Catalyst concentration, x_2			
	Coded level	hours	Coded level	%		
1	–1	2	–1	0.5	10.75	10.20
2	–1	2	–0.5	2	8.67	8.43
3	–1	2	+0.5	3.5	7.12	7.49
4	–1	2	+1	5	6.97	7.40
5	–0.5	7	–1	0.5	8.11	8.17
6	–0.5	7	–0.5	2	6.75	6.40
7	–0.5	7	+0.5	3.5	5.54	5.46
8	–0.5	7	+1	5	5.03	5.37
9	+0.5	12	–1	0.5	6.78	6.77
10	+0.5	12	–0.5	2	4.56	4.99
11	+0.5	12	+0.5	3.5	4.05	4.06
12	+0.5	12	+1	5	4.06	3.96
13	+1	17	–1	0.5	5.51	5.98
14	+1	17	–0.5	2	3.95	4.21
15	+1	17	+0.5	3.5	3.67	3.27
16	+1	17	+1	5	3.51	3.18

The regression equation reflecting the dependence of the acid value of the reaction mixture on the process duration and catalyst concentration, in natural variables, has the form:

$$y = 11.964 - 0.518 \cdot x_1 - 1.648 \cdot x_2 + 0.012 \cdot x_1^2 + 0.186 \cdot x_2^2. \quad (2)$$

The significance of the coefficients of the regression equation was assessed on the basis of variance analysis using Fisher's private F-test. The private F-test is based on a comparison of the increase in factor variance due to the influence of the additionally included factor with the residual variance per one degree of freedom for the regression model as a whole. The actual value of the F-test was compared with the tabular one at the 5 % or 1 % level of significance and the number of degrees of freedom: n and $n–m–1$ (m is the number of equation terms (without a free term), n is the number of experiments). The 5 % level of significance was used in the work. If $F_{fact.} > F_{tab.}$ (n, $n–m–1$), then the additional inclusion of the factor x_i in the model is statistically justified and the pure regression coefficient b_i at the factor x_i is statistically significant. If $F_{fact.} < F_{tab.}$ (n, $n–m–1$), then the additional inclusion of the factor x_i in the model does not significantly increase the proportion of explained variation of the characteristic y, therefore, it is inappropriate to include it in the model. The regression coefficient in this case is statistically insignificant. Using Fisher's private F-test, the significance of all regression coefficients was checked under the assumption that each corresponding factor x_i was introduced into the regression equation last.

The results of the analysis are shown in the Table 3. The characteristics are given for the following parameters: the free term of the equation; the terms of the equation relating to the duration of the process and the concentration of the catalyst, the first (L) and the second stage (Q).

According to the Table 3, in all cases the actual F-criterion is higher than the tabulated value (2.46). This indicates that all coefficients of the equation are significant. It is important to note that the Table 3 shows the original and adjusted coefficients of determination. Like the original coefficient of determination, the adjusted coefficient allows to assess the correspondence of the regression model to the original data, as well as to compare models with different numbers of independent variables. The value of the adjusted coefficient of determination varies in the range from 0 to 1, but is always slightly less than the original value. With a good fit of the model and the data, the original and adjusted coefficients of determination should be close in value and close to 1, which is demonstrated by the data in the Table 3.

By analyzing the critical points of equation (2) in the environment of the StatSoftStatistica v6.0 package (USA), the esterification conditions were determined, which correspond to the minimum of acid value: duration – 12 hours, catalyst concentration – 3.5 %. In this case, the acid value of the reaction mixture was 4.05 mg KOH/g. The product yield under these conditions was 91.5 %.

The graphical dependence of the acid value of reaction mixture on the duration of esterification and catalyst concentration was constructed (Fig. 1).

Table 3

Results of variance analysis

Parameter	Sum of squares, SS	Degrees of freedom, df	Mean square, MS	F-value	Significance level, p-value
Free term of the equation	137.9371	1	137.9371	828.4834	0.000000
Process duration, hours (L)	7.0297	1	7.0297	42.2222	0.000044
Process duration, hours (Q)	1.5438	1	1.5438	9.2725	0.011145
Catalyst concentration, % (L)	6.8665	1	6.8665	41.2416	0.000049
Catalyst concentration, % (Q)	2.8140	1	2.8140	16.9016	0.001726
Error	1.8314	11	0.1665	–	–
Coefficient of determination R^2=0.971. Adjusted coefficient of determination $R^2_{adj} = 0.961$					

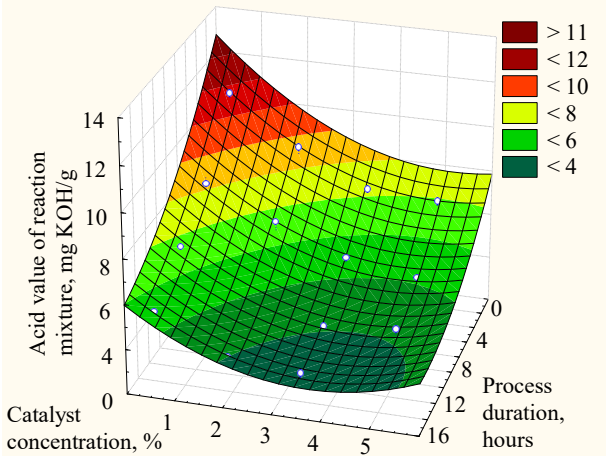

Fig. 1. Dependence of the acid value of reaction mixture on the duration of esterification and catalyst concentration

According to the Fig. 1, it is determined that with an increase in the duration and concentration of the catalyst, the acid value of the reaction mixture decreases. The duration of the process has a more significant effect on the decrease in the values of the response function. After increasing the duration of the process over 12 hours and the catalyst concentration over 3.5 %, the decrease in the acid value slows down significantly, and further increase in these factors is inexpedient. Therefore, the rational conditions for esterification of fatty acids with butanol are the following: duration – 12 hours, catalyst concentration – 3.5 %. In this case, the acid value of the reaction mixture was 4.05 mg KOH/g. The yield of the obtained product is 91.5 %.

5. 2. Study of quality parameters of the obtained product

As a result of the esterification reaction, the product was obtained, which consists of butyl esters of fatty acids, the remainder of alcohol and a small amount of fatty acids. The product was subjected to drying in the vacuum at the temperature of 95 °C for 1 hour in laboratory conditions. The qualitative parameters of the product obtained under rational conditions and dried were investigated (Table 4).

Table 4

Product quality parameters

Name of parameter	Characteristics
Mass fraction of esters, %	92.7
Mass fraction of total glycerol, %	0.20
Mass fraction of moisture, %	0.04
Density at the temperature of 15 °C, kg/m^3	840

In industry, the product obtained after transesterification of oils and fats (or esterification of acids) is sent to vacuum distillation to remove alcohol and separate esters. The distilled alcohol is used for subsequent esterification reactions.

The EN 14214 standard sets requirements for finished fatty acid methyl esters used for diesel engines. The mass fraction of esters must be at least 96.5 %, the mass fraction of total glycerol must not exceed 0.20 %, the mass fraction of moisture must not exceed 0.05 %, the density at the temperature of 15 °C must be (860–900) kg/m^3.

Thus, the product obtained under the developed rational conditions is a high-quality raw material for further distillation and obtaining purified butyl esters, which are used as biodiesel fuel.

6. Discussion of the results of establishing the rational conditions for esterification of sunflower soapstock fatty acids

The work investigated the effect of the conditions for esterification of fatty acids from sunflower soapstock with standard parameters (Table 1) with butanol in the presence of an alkylbenzenesulfonic acid catalyst on the acid value of the reaction mixture. The acid value of the mixture decreases as the reaction progresses and reflects the degree of conversion of the reactants. The following esterification conditions (variation factors) were investigated: process duration and catalyst concentration (Table 2). The full factorial experiment of the second order was used. The adequacy of the calculated mathematical model and the significance of the regression coefficients were confirmed by variance analysis (Table 3). According to the Table 3, for all parameters the actual *F*-criterion is higher than the tabulated value (2.46). This indicates that all coefficients of the equation are significant. The original and adjusted coefficients of determination are close in value and close to 1.

Based on the Fig. 1, it is determined that increasing the duration of the process causes a more significant decrease in the acid number of the reaction mass than increasing the concentration of the catalyst. During the course of the butanolysis reaction, water is released, which causes a shift in the reaction towards the formation of fatty acids and alcohol. Water is removed from the reaction mixture (using a Dean Stark nozzle), therefore, with an increase in the reaction time, more complete removal of water and more efficient conversion of reagents into esters occur. Based on the analysis of the critical points of the regression equation (2) in the StatSoft-Statistica v6.0 (USA) software package, rational conditions for esterification of fatty acids of sunflower soapstock were determined: process duration – 12 hours, catalyst concentration – 3.5 %. In this case, the acid value of the reaction mass was 4.05 mg KOH/g. Product yield – 91.5 %. The parameters of the obtained product: mass fraction of esters – 92.7 %, mass fraction of total glycerol – 0.20 %, mass fraction of moisture 0.04 %, density at the temperature of 15 °C – 840 kg/m^3 (Table 4). The mass fraction of esters in the obtained product is less than for distilled methyl esters according to EN 14214 (not less than 96.5 %). Thus, a high-quality product was obtained, which can be used for distillation and separation of butyl esters directly.

Existing scientific studies [4, 6–14] present data on the production of butyl esters of fatty acids from oils and various fat-containing raw materials, including industrial waste. For example, in [7], the production of butyl esters by butanolysis of sunflower oil with an alkaline catalyst was considered. The possibility of obtaining butyl esters from the sludge of animal wastewater containing a lipid component with an acidic catalyst [14] has been shown. Therefore, the same principle as in existing studies was used to obtain esters in this work. This work differs from other studies [4, 6–14] in that fatty acids obtained from the waste of alkaline neutralization of sunflower oil – soapstock – were used as raw materials. Soapstock is a high-tonnage waste, the disposal of which is a

problem. Therefore, this work solves the issue of establishing rational conditions for esterification of fatty acids from sunflower soapstock. The developed rational conditions allow obtaining butyl esters, which after final industrial processing can be used as biodiesel fuel.

The use of certain rational conditions for esterification is limited by the intervals of variation of factors, as well as the qualitative parameters of the initial fatty acids, since fatty acids with standard indicators were used for the work. The use of acids with non-standard parameters requires additional research.

The disadvantage of the work is the lack of research on the influence of esterification conditions on other quality parameters of the obtained product, except for the acid value. Also, important parameters are the content of moisture, glycerol, alcohol, etc.

Further research on the influence of other conditions (temperature, molar ratio of alcohol and fatty acids) on the efficiency of esterification is promising. Also important are studies on the influence of the conditions of extraction of fatty acids from soapstock on the yield and quality parameters of esters.

7. Conclusions

1. The rational conditions for esterification of sunflower soapstock fatty acids with butanol were determined: duration – 12 hours, catalyst concentration – 3.5 %. Under these conditions, the acid value of the reaction mixture was 4.05 mg KOH/g. The yield of the obtained product was 91.5 %.

2. The qualitative parameters of the obtained product were investigated: mass fraction of esters – 92.7 %, mass fraction of total glycerol – 0.20 %, mass fraction of moisture – 0.04 %, density at the temperature of 15 °C – 840 kg/m^3. Therefore, the obtained product has a high concentration of butyl esters and can be sent to vacuum distillation under production conditions to obtain esters, which are directly used as biodiesel fuel.

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.

References

1. Babadi, A. A., Rahmati, S., Fakhlaei, R., Barati, B., Wang, S., Doherty, W., Ostrikov, K. (Ken). (2022). Emerging technologies for biodiesel production: Processes, challenges, and opportunities. Biomass and Bioenergy, 163, 106521. https://doi.org/10.1016/j.biombioe.2022.106521
2. Mahlia, T. M. I., Syazmi, Z. A. H. S., Mofijur, M., Abas, A. E. P., Bilad, M. R., Ong, H. C., Silitonga, A. S. (2020). Patent landscape review on biodiesel production: Technology updates. Renewable and Sustainable Energy Reviews, 118, 109526. https://doi.org/10.1016/j.rser.2019.109526
3. Sytnik, N., Kunitsia, E., Mazaeva, V., Kalyna, V., Chernukha, A., Vazhynskyi, S. et al. (2021). Rational conditions of fatty acids obtaining by soapstock treatment with sulfuric acid. Eastern-European Journal of Enterprise Technologies, 4 (6 (112)), 6–13. https://doi.org/10.15587/1729-4061.2021.236984
4. Kurczyński, D., Wcisło, G., Leśniak, A., Kozak, M., Łagowski, P. (2022). Production and Testing of Butyl and Methyl Esters as New Generation Biodiesels from Fatty Wastes of the Leather Industry. Energies, 15 (22), 8744. https://doi.org/10.3390/en15228744
5. Ali Ijaz Malik, M., Zeeshan, S., Khubaib, M., Ikram, A., Hussain, F., Yassin, H., Qazi, A. (2024). A review of major trends, opportunities, and technical challenges in biodiesel production from waste sources. Energy Conversion and Management: X, 23, 100675. https://doi.org/10.1016/j.ecmx.2024.100675
6. Konovalov, S., Patrylak, L., Zubenko, S., Okhrimenko, M., Yakovenko, A., Levterov, A., Avramenko, A. (2021). Bench Motor Testing of Blended Fuels on their Basis. Chemistry & Chemical Technology, 15 (1), 105–117. https://doi.org/10.23939/chcht15.01.105
7. Konovalov, S. V., Zubenko, S. O., Patrylak, L. K., Yakovenko, A. V. (2021). Fuel-grade sunflower oil butyl esters: synthesis, purification, oxidation stability. Catalysis and Petrochemistry, 32, 40–53. https://doi.org/10.15407/kataliz2021.32.040
8. Navas, M. B., Lick, I. D., Bolla, P. A., Casella, M. L., Ruggera, J. F. (2018). Transesterification of soybean and castor oil with methanol and butanol using heterogeneous basic catalysts to obtain biodiesel. Chemical Engineering Science, 187, 444–454. https://doi.org/10.1016/j.ces.2018.04.068
9. Gaide, I., Makareviciene, V., Sendzikiene, E., Gumbytė, M. (2023). Rapeseed Oil Transesterification Using 1-Butanol and Eggshell as a Catalyst. Catalysts, 13 (2), 302. https://doi.org/10.3390/catal13020302
10. Sathish Kumar, R., Krupa Vara Prasad, A. (2019). Environment friendly butyl ester biodiesel production from mahua oil: optimization and characterization. SN Applied Sciences, 1 (8). https://doi.org/10.1007/s42452-019-0913-6

11. Ilmi, M., Abduh, M. Y., Hommes, A., Winkelman, J. G. M., Hidayat, C., Heeres, H. J. (2018). Process Intensification of Enzymatic Fatty Acid Butyl Ester Synthesis Using a Continuous Centrifugal Contactor Separator. Industrial & Engineering Chemistry Research, 57 (2), 470–482. https://doi.org/10.1021/acs.iecr.7b03297
12. Sousa, R. R. de, Lázaro, C. da C., Gomes, C. B. de S. M. R., Silva, A. S. da, Fernandez-Lafuente, R., Ferreira-Leitão, V. S. (2023). Butyl-esters synthesis from palm fatty acid distillate catalyzed by immobilized lipases in solvent-free system – Optimization using a simplified method (SER). Process Biochemistry, 128, 158–166. https://doi.org/10.1016/j.procbio.2023.02.030
13. Todeschini, J. K. P., Aguieiras, E. C. G., Castro, A. M. de, Langone, M. A. P., Freire, D. M. G., Rodrigues, R. C. (2016). Synthesis of butyl esters via ultrasound-assisted transesterification of macaúba (Acrocomia aculeata) acid oil using a biomass-derived fermented solid as biocatalyst. Journal of Molecular Catalysis B: Enzymatic, 133, S213–S219. https://doi.org/10.1016/j.molcatb.2017.01.007
14. Wallis, C., Cerny, M., Lacroux, E., Mouloungui, Z. (2017). Recovery of slaughterhouse Animal Fatty Wastewater Sludge by conversion into Fatty Acid Butyl Esters by acid-catalyzed esterification. Waste Management, 60, 184–190. https://doi.org/10.1016/j.wasman.2016.07.003