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Mathematical model of the process of converting waste oils into diesel biofuel

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Abstract. The growing demand for renewable energy sources encourages the development of technologies for the production of biodiesel from waste, but the high content of free fatty acids in raw materials complicates transesterification, reduces fuel yield, and increases the need for purification. The purpose of the study was to develop and validate a mathematical model of the process of transesterification of used oils into diesel biofuels to optimise technological parameters. The rationalised model described in detail the patterns of triglyceride transformation in the presence of alcohol and a catalyst. It allowed tracking changes in the concentrations of reaction intermediates, in particular, diglycerides, monoglycerides, biodiesel, and glycerol, which is critical for predicting the effectiveness of the process. Stable values of the speed of the transesterification process are indicated using the Arrhenius equation, which helped to estimate the effect of temperature and the ratio of reactants on the overall kinetics of the reaction. As part of the study, numerical modelling and correlation of the model were carried out by systematising the results with the data obtained during the research and obtained from the results of the analysis of literature sources. Catalytic and non-catalytic variants of the process were analysed, which determined the most effective reaction conditions. The simulation results confirmed that an increase in temperature values to 60°C leads to an increase in the yield of diesel biofuels, so excessive heating above the boiling point of methanol causes its evaporation, which leads to a decrease in the efficiency of the process and the loss of raw materials. Optimal technological parameters that ensure the maximum yield of biodiesel with minimal material and energy costs were determined. The proposed mathematical model can be used in industrial settings to optimise the biofuel production process, helping to increase the efficiency of recycling

Keywords: kinetic model; free fatty acids; parameter optimisation; temperature regime; biofuel yield; energy efficiency

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Introduction

The crisis in the field of energy resources has affected almost all world countries, and it has not spared Ukraine, the high cost of mineral diesel fuel, usually due to the pricing policy for oils, fats, and reagents, which can account for up to 75% of the main production costs. Moreover, the use of alternative sources of raw materials, such as animal fats (beef fat, pork fat), used vegetable oils and waste from food and processing enterprises, in particular fat residues, is a promising approach to reducing production costs and environmental burden. These wastes are often disposed of by incineration, which is accompanied by additional economic and environmental costs. Attracting these resources to biodiesel production is an effective means of increasing the level of economic efficiency and minimising the negative impact on the environment (Aghbashlo *et al.*, 2021).

The problem of processing used oils into diesel biofuels is relevant from the standpoint of energy sustainability and reducing environmental pollution. Numerous studies have been carried out on various aspects of this process, in particular, the study of chemical reactions, optimisation of technological parameters, and the use of mathematical models for modelling and predicting processing results. Transesterification is the main method of converting fats and oils into biodiesel. Mathematical models have been developed to optimise the process and predict the yield of biodiesel depending on the oil quality and reaction conditions. A.S. Elgharbawy *et al.* (2021) and S. Vickram *et al.* (2023) presented models that include thermodynamic aspects of the reaction and the mechanism of interaction between oil molecules and methanol in the presence of various catalysts. The researchers noted that for waste oils that may have a high acid content, it is necessary consider account the altered kinetic parameters of the reaction. This model allows significantly increasing the efficiency of the process, reducing the cost of raw materials.

Studying the effect of temperature and catalyst selection on the efficiency of the transesterification process is an important part of developing optimal conditions for waste oil processing. H. Hosseinzadeh-Bandbafha *et al.* (2022) investigated the effect of different temperature regimes on the reaction rate using different alkaline and acid catalysts. They concluded that raising the temperature to optimal values (60-70°C) significantly improves the yield of biodiesel, but higher temperatures can lead to the development of by-products, which negatively affects the quality of biofuels. In addition, the use of non-standard catalysts, such as calcium salts, can reduce the cost of production and improve the selectivity of the reaction.

The cost-effectiveness of producing biodiesel from waste oils depends not only on the yield of biofuels, but also on the cost of energy and raw materials. M.U.H. Suzihaque *et al.* (2023) and K. Tucki *et al.* (2020) investigated the energy efficiency of various technological processes for processing oils into biofuels. They built a mathematical model that considers the energy costs of heating the oil, the cost of the catalyst and other components, and the energy value of the resulting biofuels. They note that the cost of producing biodiesel from waste oils may be significantly lower than from primary oils, but to achieve maximum economic effect, it is important to optimise energy costs and the choice of processing technology.

To improve the quality of diesel biofuels, it is important to consider hydrogenation processes that reduce the percentage of unsaturated bonds, which increases the resistance of biofuels to oxidation and ensures stable operation of engines. P. Maheshwari *et al.* (2022) proposed a mathematical model for the waste oil hydrogenation process based on the use of platinum and nickel-based catalysts. The researchers proved that the optimal conditions for the hydrogenation process include a temperature of 150-200°C and a pressure of 3-5 MPa, which allows achieving high oil conversion and reduce the level of unpleasant odours in the product.

Innovative approaches to waste oil processing include the use of bioengineering to improve the transesterification process. G.M. Mathew *et al*. (2021) considered the possibility of using microorganisms for the biological transformation of oils, which can help to reduce the need for chemical reagents and increase the efficiency of the process. In particular, it has been shown that some bacterial strains can speed up the esterification process by reducing temperature and reaction time, which, in turn, reduces energy costs and improves the environmental friendliness of the technology. This opens up new prospects for the sustainable development of bioenergy and reducing the impact of production on the environment.

A separate important part of the study is to consider the kinetics of the process of producing biodiesel from waste oils, since knowledge of the kinetic characteristics allows fine-tuning the process and improving its efficiency. H. Esmaeili (2022) developed kinetic equations for the transesterification process using waste oils, in particular, under conditions of high acidic oil values. The researcher noted that with a high content of free fatty acids in oil, it is important to use a multi-stage model, where the first stage includes acid neutralisation, and the second – direct transesterification.

An important aspect of the research is also the issue of environmental safety of the waste oil processing process. M.K. Pasha *et al*. (2021) considered possible negative environmental consequences of the use of waste oils in bioenergy technologies, in particular, the development of toxic by-products in the production of diesel biofuels. The researchers stressed the need to develop environmentally friendly technologies and implement effective systems for cleaning raw materials and waste from biofuel production.

More and more attention is being paid to combining conventional waste oil processing with renewable energy sources to reduce the cost of energy support for biodiesel production. C.T. Pinheiro *et al*. (2021) described the use of solar and wind energy to provide thermal power processes in biodiesel production, which can significantly reduce CO_2 emissions and improve the economic efficiency of the process. They presented a mathematical model for integrating these energy sources into the overall technological process, which reduces energy costs and increases the purity of the final product.

The search for effective catalysts is an important area of research in waste oil processing. M.S. Gad *et al*. (2023) investigated the effect of inorganic catalysts such as metal oxides (calcium oxide, magnesium oxide) on the transesterification process. They have proven that these catalysts provide high efficiency at low temperatures and are cost-effective, making the process more affordable for industrial use. In addition, a mathematical model was constructed to optimise the catalyst concentration and temperature regime to achieve maximum biofuel yield.

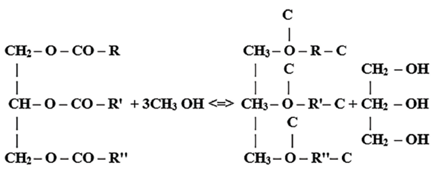
The purpose of the study was to develop and verify a mathematical model for the re-esterification of waste oils into diesel biofuels to optimise technological parameters, increase product yield, and minimise energy and material costs.

Materials and Methods

This study used waste vegetable oils and animal fats (beef fat, pork fat) as the main raw materials for the synthesis of diesel biofuels. During the process of transformation of vegetable oils or animal fats with alcohol (ethanol, methanol, bioethanol, etc.), they were modified into the corresponding esters of fatty acids, which are commonly called diesel biofuels.

For the rapid flow of the above-mentioned process, various types of catalytic systems are used, the most common of which are potassium hydroxide (KOH) or sodium hydroxide (NaOH). Such catalysts destroyed the molecular bonds in triglycerides, which allowed them to react with alcohol, the product of this transformation was esters, which are a component of diesel biofuels. Various catalysts, acid catalysts, biocatalysts (enzymes), heterogeneous catalysts, and nanomaterial-based catalysts were used to perform the transesterification reaction, each of these catalysts has its own advantages and disadvantages, and the choice depended on the type of raw material, reaction conditions, and final product requirements.

Diesel biofuels were obtained by performing an esterification or transesterification reaction. As a result of the transformation, fatty acid esters (FAE) and glycerol (crude glycerol) were formed. The reaction in this case occurred according to the scheme shown in Figure 1:



Vegetable oil Alcohol Catalyst Diesel biofuel Glycerol

Figure 1. *Scheme of the transesterification reaction*

Source: compiled by the author

The beginning of the re-esterification process was quite fast, but after 5-7 minutes the pace gradually decreased. The main amount of triglycerides was converted to diglycerides, producing FAEs (diesel biofuels), so this process was slower. Diglycerides were transformed into monoglycerides during the reaction, and those – into the corresponding esters, until the glycerol was completely precipitated. 1,520 minutes after the start, the reaction slowed down again, but did not stop completely. After 2 hours of the process at the appropriate temperature, which did not exceed 60°C, transesterification stopped, which was confirmed by stopping the phase separation.

The transesterification reaction was reversible and could proceed in two directions at different rates, which varied depending on a fixed value of the conversion rate b_n. To study changes in the reaction rate, a system of differential equations describing the process of waste oil synthesis was compiled:

$$d[Tr]/dt = b_1[Tr] + b_2[Di][BE], \quad (1)$$

$$d[Di]/dt = b_3[Di][A] + b_4[Mo][BE] + + b_1[Tr][A] - b_2[Di][BE], \quad (2)$$

$$d[Mo]/dt = b_5[Gl][BE] + b_6[Gl][BE] + + b_3[Di][A] - b_4 [Mo][BE], \quad (3)$$

$$d[Gl]/dt = b_5[Mo][A] - b_6[Gl][BE], \quad (4)$$

$$d[BE]/dt = b_1[Tr][A] - b_2[Di][BE] + + b_3[Di][A] - b_4[Mo][BE] + b_5[Mo][A] - b_6[Gl][BE], \quad (5)$$

$$d[A]/dt = -b_1[Tr][A] - b_2[Di][BE] + + b_3[Di][A] - b_4[Mo][BE] + b_5[Mo][A] - b_6[Gl][BE], \quad (6)$$

$$d[A]/dt = d[BE]/dt, \quad (7)$$

where: [Tr] – triglycerides, [Di] – diglycerides, [Mo] – monoglycerides, [Gl] – glycerol, [A] – Alcohol, [BE] – bioethyl ether, b_1, b_2, b_3, b_4, b_5, b_6 – fixed values of the conversion process speed. To obtain a simplified solution of the system of equations, numerical methods using Microsoft Excel were used. Fixed values of the conversion process rate were obtained from the study by C.T. Pinheiro *et al.* (2021) and are presented in Table 1.

Table 1. *Value of the transesterification reaction rate at 60°C for waste oils*

Fixed values of the conversion process speed	b_1	b_2	b_3	b_4	b_5	b_6
Indicator, $(\text{Mol\% min})^{-1}$	0.045	0.10	0.212	1.223	0.241	0.0065

Source: C.T. Pinheiro *et al.* (2021)

Under the appropriate temperature regime, the process of diesel biofuel formation occurred only if all components of the reacting mixture were energetically self-sufficient. According to C.T. Pinheiro *et al.* (2021), such energy was defined as activation energy, and the molecules were activated independently. According to the equation, fixed values of the conversion process speed *b* and activation energy E_a were associated with the corresponding dependencies:

$$b = A \cdot e^{-Ea/RT}, \quad (8)$$

where, E_a – activation energy value, A – frequency factor, R – universal gas constant (8.31 J/Mol·K), T – absolute temperature, K.

Therefore, under a fixed temperature regime, the conversion rate was determined by the activation energy level E_a. With an increase in E_a, the number of molecules that had sufficient energy levels for activation decreased, which, in turn, contributed to a decrease in the reaction rate, and vice versa. Accordingly, when E_a at zero, the reaction was instantaneous, since the molecules had enough energy to quickly initiate the process. Indicator E_a characterised the specifics of the interaction of substances and was determined experimentally on the basis of dependence $b = f(T)$. By writing equation (8) in logarithmic form (9) and defining the constants at two temperatures (10), the value E_a was obtained:

$$ln\frac{b_1}{b_2} = \frac{(T_2 - T_1)}{RT_2 \cdot T_1} E_a; \quad (9)$$

$$E_a = \frac{RT_1T_2\, ln\left(\frac{b_{T_2}}{b_{T_1}}\right)}{T_2 - T_1}. \quad (10)$$

Table 2 shows the results of calculations of the activation energy for reactions, the constants of which are indicated in Table 1.

Table 2. *Activation energy characteristics for potassium hydroxide (KOH)*

Activation energy	E_1	E_2	E_3	E_4	E_5	E_6
Indicator, $(Mol \cdot K)^{-1}$	14,145	9,852	19,710	13,939	7,021	8,988

Source: C.T.Pinheiro *et al*. (2021)

The initial system of differential equations (1-7) can be represented as the following system of discrete equations:

$$(Tr^{P+1} - Tr^P)/\Delta t = b_1Tr^PA^P + b_2Di^PBi^P, \quad (11)$$

$$(Di^{P+1} - Di^P)/\Delta t = b_1Tr^PA^P - b_2Di^PBi^P - - b_3Di^PA^P + b_4Mo^PBi^P, \quad (12)$$

$$(Mo^{P+1} - Mo^P)/\Delta t = b_3Di^PA^P - b_4Mo^PBE^P - - b_3Mo^PA^P + b_6Gl^PBi^P, \quad (13)$$

$$(Gl^{P+1} - Gl^P)/\Delta t = b_5Mo^PA^P + k_6Gl^PBi^P, (14)$$

$$(Bi^{P+1} - Bi^P)/\Delta t = b_1Tr^PA^P - b_2Di^PBi^P + b_3Di^PA^P - b_4Mo^PBi^P + b_5Mo^PA^P - b_6Gl^PBi^P, (15)$$

$$(A^{P+1} - A^P)/\Delta t = - b_1Tr^PA^P + b_2Di^PBi^P - - b_3Di^PA^P + b_4Mo^PBi^P - b_5Mo^PA^P + b_6Gl^PBi^P, \quad (16)$$

where P – size-independent interval, Bi – bioethanol concentration, Mol, Δt – time step, h. The current time point t was calculated using the following equation:

$$t = p \cdot \Delta t. \quad (17)$$

Equations of the system (11-16) can be rewritten as:

$$Tr^{P+1} = (1 - b_1\Delta tA^P)Tr^P + b_2\Delta tDi^PBE^P, \quad (18)$$

$$Di^{P+1} = (1 - b_2\Delta tBE^P - b_3\Delta tA^P)Di^P + + b_1\Delta tTr^PA^P + b_4\Delta tMo^PBE^P, \quad (19)$$

$$Mo^{P+1} = (1 - b_4\Delta tBE^P - b_3\Delta tA^P)Mo^P + + b_1\Delta tDi^PA^P + b_6\Delta tGlL^PBE^P, \quad (20)$$

$$Gl^{P+1} = (1 - b_6\Delta tBE^P)Gl^P + b_5\Delta tMo^PA^P, \quad (21)$$

$$BE^{P+1} = (1 - b_2\Delta tDi^P - b_4\Delta tMo^P - b_6\Delta tGl^P)BE^P + + (b_1\Delta tTr^P + b_3\Delta tDi^P + b_5\Delta tGl^P)A^P, \quad (22)$$

$$A^{P+1} = (1 - b_1\Delta tTr^P - b_3\Delta tDi^P - b_5\Delta tGl^P)A^P + + (b_2\Delta tDi^P + b_4\Delta tMo^P + b_6\Delta tGl^P)BE^P, \quad (23)$$

The solution of this system of discrete equations is possible if the coefficients of the equations are not greater than one.

Results and Discussion

For calculations based on the results of experimental studies, the initial concentration of the reacting mixture was chosen in a molar ratio of 9:1. The calculation results obtained in Microsoft Excel presented in Table 3 indicate that the reaction occurs with acceleration in the first 0.69 hours, after which the rate of diesel biofuel formation decreases.

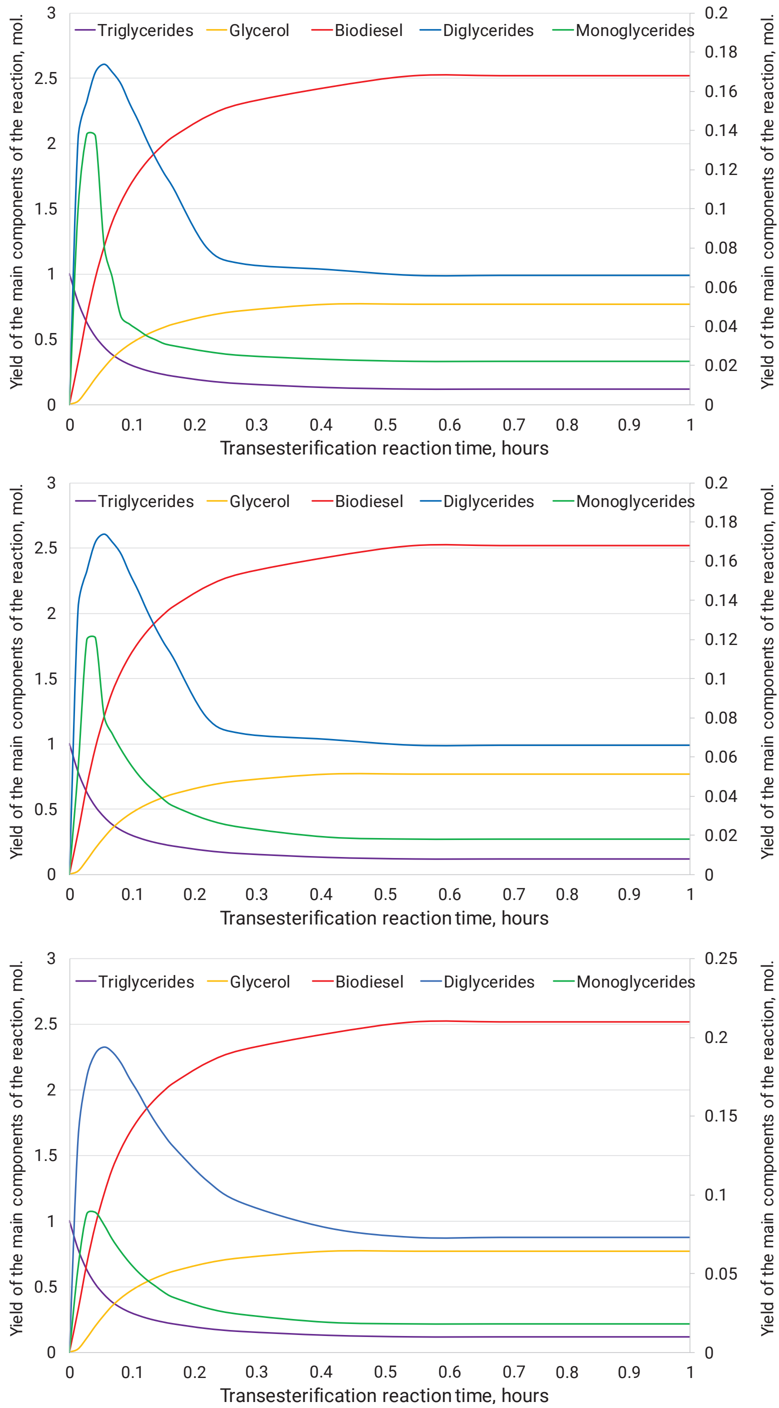
Table 3. *Time dynamics of the concentration of reaction components at a temperature of 65°C*

Reaction time, h	Components of the reaction mixture				
	Tr	Di	Mo	Gl	BE
0	1	0	0	0	0
0.014	0.784	0.136	0.054	0.025	0.321
0.028	0.629	0.175	0.088	0.108	0.675
0.042	0.519	0.19	0.089	0.201	0.972
0.056	0.44	0.194	0.081	0.284	1.209
0.069	0.383	0.191	0.072	0.354	1.397
0.083	0.34	0.184	0.064	0.413	1.549
0.097	0.307	0.174	0.057	0.462	1.673
0.111	0.282	0.165	0.051	0.503	1.775
0.125	0.261	0.155	0.046	0.538	1.861
0.139	0.244	0.146	0.042	0.568	1.934
0.153	0.23	0.138	0.038	0.594	1.997
0.167	0.218	0.131	0.035	0.617	2.051
0.222	0.182	0.109	0.028	0.681	2.208
0.278	0.16	0.095	0.024	0.721	2.306
0.417	0.131	0.079	0.019	0.771	2.431
0.556	0.119	0.073	0.018	0.771	2.52
0.694	0.119	0.073	0.018	0.771	2.52
0.833	0.119	0.073	0.018	0.771	2.52
1.0	0.119	0.073	0.018	0.771	2.52

Note: Tr – triglycerides, Di – diglycerides, Mo – monoglycerides, Gl – glycerol, BE – bioethyl ether
Source: developed by the author

The graphical dependencies shown in Figure 2 show the effect of temperature on the yield of bioethyl ether (diesel biofuel). Based on the results of modelling, it was found that an increase in temperature above 60°C does not cause a significant increase in the yield of biodiesel.

The results of experimental studies of the degree of conversion of waste oils to diesel biofuels in dynamics, compared with theoretical calculations of the mathematical model, showed that with a probability of 0.95, the obtained values lie within the confidence interval. Calculating the equations of the discrete system (18)-(23) proves the possibility of increasing the yield of bioethyl ether from 86.7 to 87.4% and increasing the temperature of the transesterification process from 55°C to 60°C (Fig. 2a, 2b). An important technological indicator is the time to establish equilibrium during the reaction process (0.33-0.56 hours), which will be one of the main parameters that will determine the design characteristics of the reactor for the synthesis of diesel biofuels. It should be noted that the temperature increase to 70°C (Fig. 2b) reduces the ester yield to (85%). After determining the optimal process conditions, the most rational parameters are selected, which will serve as the basis for designing the appropriate equipment.



a b c

Figure 2. *Influence of temperature on the productivity of the diesel biofuel production process using bioethanol*

Note: a) reaction temperature – 55°C, b) reaction temperature – 60°C, c) reaction temperature – 65°C
Source: developed by the author

Molar balance equations are solved using the Mathlab application package:

1. Change in Tr (triglyceride) concentration (Fig. 3, 4).

For the purpose of a more detailed study of changes in the concentration of Tr and BE (bioethyl ether), changes in the alcohol concentration were ignored, and the reaction time was limited to 2 hours:

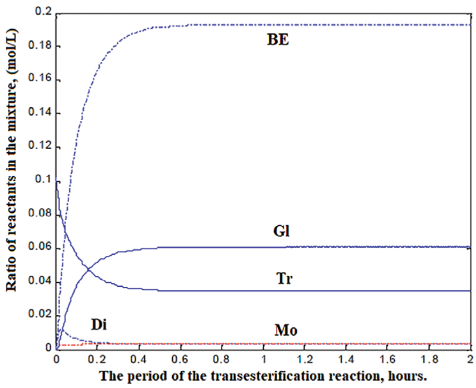


Figure 3. *Effect of triglyceride concentration on the yield of reaction components: V = 66.42%, [Tr] = 0.034, [BE] = 0.1922, [Tr] · 2 = 0.411*

Note: V – bioethyl ester yield, Tr – triglycerides, Di – diglycerides, Mo – monoglycerides, Gl – glycerol, BE – bioethyl ester

Source: developed by the author

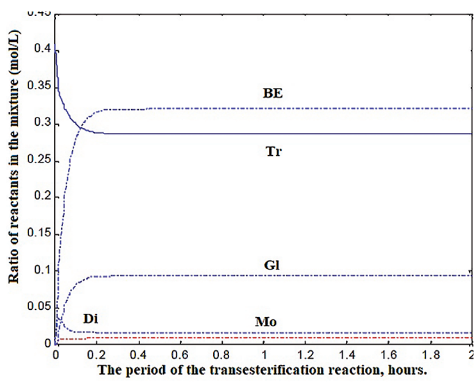


Figure 4. *Effect of triglyceride concentration on the yield of reaction components: V = 29.7%, [Tr] = 0.278, [BE] = 0.298*

Note: V – bioethyl ester yield, Tr – triglycerides, Di – diglycerides, Mo – monoglycerides, Gl – glycerol, BE – bioethyl ester

Source: developed by the author

As can be seen from the graphs in Figures 3, 4, the conversion of triglycerides increases at low concentrations, and at higher ones.

2. Changes in bioethanol concentration, [B]: [B]/2 = 1.3891 (Fig. 5, 6).

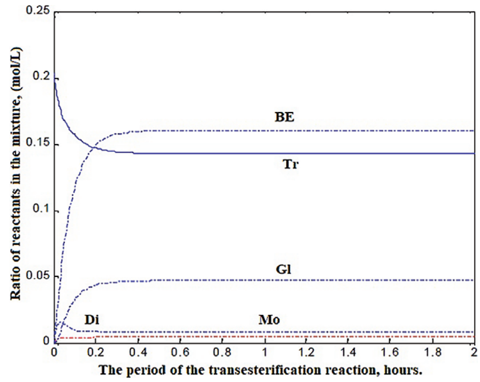


Figure 5. *Effect of bioethanol concentration on the yield of reaction components: V = 28.93%, [Tr] = 0.1437, [BE] = 0.1606, [B] · 2 = 5.662*

Note: V – bioethyl ester yield, Tr – triglycerides, Di – diglycerides, Mo – monoglycerides, Gl – glycerol, BE – bioethyl ether

Source: developed by the author

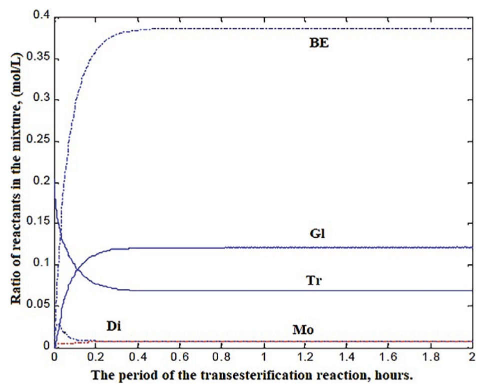


Figure 6. *Effect of bioethanol concentration on the yield of reaction components: V = 65.53%, [Tr] = 0.06755, [BE] = 0.3862*

Note: V – bioethyl ester yield, Tr – triglycerides, Di – diglycerides, Mo – monoglycerides, Gl – glycerol, BE – bioethyl ester

Source: developed by the author

After analysing the results of graphical dependencies (Fig. 5 and 6), it can be argued that the ester yield changes in proportion to the bioethanol concentration, with an increase in the amount it increases, and with its decrease it decreases.

3. Effect of catalyst concentrations [K]. [K]/2 = 4.025 (Fig. 7, 8).

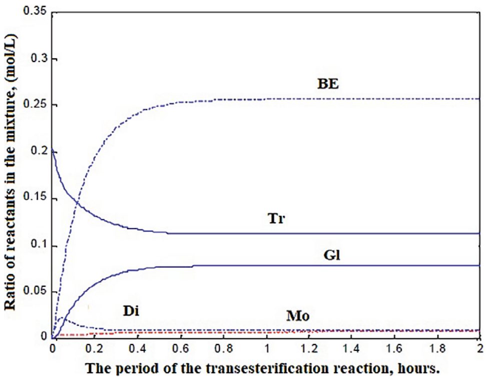


Figure 7. *Effect of the catalyst concentration on the yield of reaction components: V = 45.52%, [Tr] = 0.1114, [BE] = 0.2562, [K] · 2 = 15.9*

Note: V – bioethyl ester yield, Tr – triglycerides, Di – diglycerides, Mo – monoglycerides, Gl – glycerol, BE – bioethyl ester

Source: developed by the author

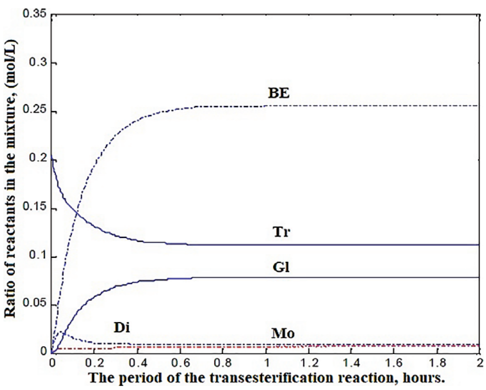


Figure 8. *Effect of the catalyst concentration on the yield of reaction components: V = 44.92%, [Tr] = 0.111, [BE] = 0.256*

Note: V – bioethyl ester yield, Tr – triglycerides, Di – diglycerides, Mo – monoglycerides, Gl – glycerol, BE – bioethyl ester

Source: developed by the author

The reaction rate remains unchanged when the catalyst concentration changes. Although it is possible to use a higher concentration in some cases, it should be remembered that an excessive increase in it can negatively affect the yield of diesel biofuels. How the reaction course changes when the catalyst concentration decreases to 0.1% is shown in Figure 9 ([K]/10 = 0.805).

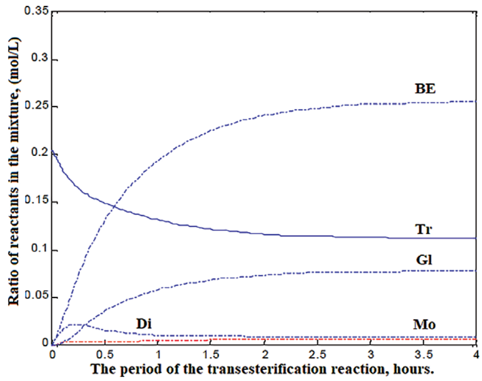


Figure 9. *Effect of the catalyst concentration on the yield of reaction components: V = 44.01%, [Tr] = 0.112, [BE] = 0.2445*

Note: V – bioethyl ester yield, Tr – triglycerides, Di – diglycerides, Mo – monoglycerides, Gl – glycerol, BE – bioethyl ester

Source: developed by the author

In order to improve the visualisation of changes in the concentrations of reaction components, Figure 10 does not show the concentration curves of bioethanol and catalyst.

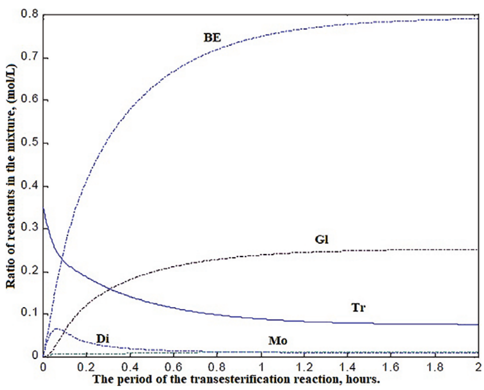


Figure 10. *Final concentrations of reaction components after transesterification*

Note: V – bioethyl ester yield, Tr – triglycerides, Di – diglycerides, Mo – monoglycerides, Gl – glycerol, BE – bioethyl ether

Source: developed by the author

Based on the results of computer modelling (Fig. 10), it was found that the rapid increase in the concentration of bioethyl ether is explained by its high conversion rate. However, triglycerides decompose more slowly than diglycerides, the conversion rate of which first increases and then decreases due to their subsequent conversion to monoglycerides and bioethyl ether. Reaching the equilibrium of the reaction is accompanied by an increase in the concentration of monoglycerides, the conversion rate of which is higher than that of diglycerides.

The results of the analysis of graphical dependencies indicate that a significant decrease in the level of reaction components leads to an increase in their residence time in the reactor. From the conducted studies, it follows that the reaction proceeds better at a reduced concentration of the catalyst and increased concentrations of triglycerides and methanol, but the concentration of the catalyst significantly affects the residence time of the mixture in the reactor. The conversion results are calculated:

$$V = (1 - 0.08/0.4) \cdot 100 = 79.2\%$$

The resulting value of converting oils to fuel is necessary for designing equipment with effective parameters. The results shown in Figure 2 show that an increase in temperature to 60°C contributes to an increase in the yield of methyl esters due to the acceleration of the transesterification reaction. However, a further increase in temperature above 60°C does not significantly improve the yield of biodiesel due to methanol evaporation and the possibility of adverse decomposition reactions. In particular, at 70°C, the product yield decreases slightly (up to 85%), which is consistent with the literature data (Cheliadyn *et al.*, 2020; Jayaraman *et al.*, 2022).

Based on the results of modelling, it was found that an increase in the ratio of alcohol to triglycerides from 3:1 to 6:1 provides an increase in ester yield by 8.5%. A further increase in this indicator to the level of 9:1 does not significantly increase the yield, which confirms the need to rationalise alcohol consumption. The results obtained are consistent with studies by Z. Khan *et al.* (2021), which determined the economically feasible 6:1 ratio.

The results shown in Figures 7 and 8 show that the optimal concentration of the catalyst ensures an efficient reaction, while its excessive concentration can lead to the formation of undesirable byproducts, such as soap. Reducing the catalyst concentration to one-tenth of the optimal one significantly slows down the reaction, which requires an increase in the residence time of the mixture in the reactor. This was confirmed by O. Konur (2021), which emphasise the need to optimise the catalyst concentration, considering economic and technological aspects.

The results obtained are consistent with the conclusions of other researchers. For example, S. Ali *et al.* (2020) confirmed that at 60°C, the yield of biodiesel is maximum, and increasing the temperature to 70°C does not provide additional benefits. Similarly, the calculated activation energy values correspond to the range given by M. Athar & S. Zaidi (2020) and K.S. Eldiehy *et al.* (2022), which confirms the validity of the model.

Compared to research by P.B. Aurtherson *et al.* (2023), where alternative catalysts based on calcium and magnesium were used, the current model demonstrates higher efficiency when using classical alkaline catalysts at temperatures below 60°C. The main advantage of this study is the accuracy of predicting reaction kinetics and optimising parameters for industrial applications. The disadvantage is the need for additional purification of biodiesel from residual catalysts, which requires additional energy costs.

Compared to the approaches by Y. Devarajan *et al.* (2022), who used enzymatic catalysis, the current model has a significantly shorter reaction time and a higher yield of biofuels, but biocatalytic processes have environmental advantages due to the absence of residual chemical catalysts. This opens up prospects for further research on combined methods to improve the efficiency of biofuels. A.A. Babadi *et al.* (2022) pointed out the need to improve the processes of purification of biodiesel from impurities. Compared to these results, the current study demonstrates a higher level of purity of the final product by optimising the catalyst neutralisation process. M. Mushtruk *et al.* (2022) proved that the use of acid catalysis has a number of technological disadvantages, among which is the mandatory neutralisation of the acid before transesterification, which leads to the development of precipitates in the form of salt, which complicate the further purification of the final product. With this in mind, active scientific research is aimed at developing heterogeneous catalysts that can be easily separated from the reaction medium after the process is completed. Despite the commercial availability of some of them, the effectiveness of such catalysts and their resistance to contamination at moderate temperatures and atmospheric pressure remain open questions.

The use of such secondary raw materials for the synthesis of diesel biofuels is a promising technology that will help to improve the environmental situation and reduce dependence on expensive petroleum products. Biodiesel made from recycled materials has a number of key advantages:

- the use of secondary raw materials in biofuel production helps to reduce greenhouse gas emissions due to lower CO_2 levels in diesel biofuels compared to conventional diesel fuel (Mushtruk *et al.*, 2024). This helps to reduce the negative impact on the climate and reduces the ecological footprint.
- recycling of secondary raw materials, reduces the cost of biofuel production (Mushtruk *et al.*, 2022). In addition, it reduces the cost of disposing of such waste and minimises its negative impact on the environment.
- waste oil synthesis technology on biodiesel ensures efficient use of resources and reduces the burden on natural resources (Zulqarnain *et al.*, 2021). This corresponds to the principles of a circular economy, where waste is converted into useful raw materials for new production cycles.

Mathematical modelling is a powerful tool for engineering analysis, which reduces the time of experimental research and reduces material costs. It minimises the need for large experimental installations by optimising process parameters through numerical analysis and theoretical forecasting. In particular, such models allow establishing patterns between the physical and chemical properties of transformation of secondary raw materials, which is an important stage in the development and improvement of energy-efficient technologies for the production of biodiesel from waste oils and industrial waste.

According to P.J. Ahranjani *et al.* (2024), one of the important technological factors that makes it impossible to use waste oils for a direct transesterification reaction is the high content of free fatty acids (FFA), usually exceeding 2 mg KOH/g. This makes it impossible to directly apply alkaline catalysis in the transesterification reaction, since the alkaline catalyst (NaOH, KOH) is used to neutralise FFA, which leads to the formation of soap residues and by-products. The formation of water during the reaction further complicates the purification of the resulting biodiesel, reducing its yield and quality. Y. Zhao *et al.* (2021) proved that one of the most common methods of overcoming this problem is esterification, which is quite widely used in industrial production. In addition, R. Kukana & O.P. Jakhar (2022) investigated alternative approaches, such as enzymatic catalysis and the use of supercritical synthesis of various types of alcohols, which can potentially improve the efficiency of the process.

Studying the possibility of using two-stage systems that simultaneously produce electrical and thermal energy is an important area for optimising waste oil processing processes. K. Ganesan *et al.* (2021) demonstrated the effectiveness of such systems based on bioreactors, where waste oils were used as a source of raw materials. As a result of their research, a mathematical model of a two-stage process was developed, which reduces energy consumption and carbon dioxide emissions, and increases the efficiency of waste oil processing. Since biodiesel derived from waste oils can contain high levels of sulphur and oxygen-containing compounds, improving fuel purification processes is an important aspect. M.A. Hazrat *et al*. (2021) presented the latest method of elimination of sulphur and oxygen impurities of biodiesel using a combination of catalytic and physico-chemical processes, which can significantly reduce the level of sulphur and ensure compliance with international standards. The researchers created a mathematical model to describe the process, which allows optimising the cleaning parameters at all stages of production.

Considering the carbon balance in biodiesel production processes is crucial for assessing their sustainability. G.V. Subhash *et al*. (2022) developed a mathematical model that considers all stages of the biodiesel life cycle – from oil collection to fuel combustion in engines. The model includes not only CO_2 emissions, but also other pollutants, such as nitrogen and sulphur oxides, and allows comparing different technologies and raw materials for their environmental efficiency. The results showed that biodiesel made from waste oils has a significantly lower carbon footprint compared to conventional fuels.

Free fatty acids are a significant factor affecting the quality of biodiesel, as their high content can lead to the development of soap and reduce the yield of biofuels. R. Ganesan *et al*. (2021) studied the effect of the free fatty acid content in waste oils on the efficiency of transesterification and developed a mathematical model for their neutralisation before the esterification process. The researchers developed a strategy that includes multi-stage oil purification, which reduces the content of free fatty acids and increases the yield of biodiesel.

Development of rational technologies for improving the processing of waste oils N.H. Razak *et al*. (2021) considered bioengineered methods to improve the waste oil processing process, in particular, the use of genetically modified microorganisms to accelerate transesterification processes. Modelling of these processes has shown that the use of catalytic systems based on modified bacteria can significantly reduce energy costs and reaction time.

Based on the results of the literature analysis, it was established that an important focus of research in the field of waste oil processing for diesel biofuels is the use of mathematical modelling to optimise technological processes. Modelling allows not only to more accurately predicting the results of the reaction, but also to reduce energy costs, improve environmental indicators and economic efficiency of production.

Modelling in such areas as the use of catalysts, hydrogenation processes and biodiesel purification is particularly important. Models that consider carbon balance and environmental efficiency allow comparing different technologies and raw materials that contribute to the sustainable development of bioenergy. In addition, mathematical modelling is becoming an important tool for improving energy and economic efficiency, in particular, through the integration of cogeneration technologies, and when using bioengineered solutions.

A. Dahiya (2020) explored the possibility of integrating renewable energy sources into biodiesel production. In this study, such integration was not considered, but the proposed parameters allow minimising energy costs even in conventional production conditions. B. Chen *et al.* (2022) presented a model that considers the full carbon balance of biodiesel production. The current study focuses on the kinetic aspects of the process, but the results indicate a potential reduction in CO_2 emissions due to the efficient use of waste oils.

The study confirms the high level of efficiency of the developed mathematical model for transesterification of waste oils into biodiesel. Comparison of theoretical results obtained through numerical modelling with experimental data shows a strong correlation between forecasts and actual results. The key parameters that determine the efficiency of the process are the reaction temperature, the molar ratio of alcohol to triglycerides, and the concentration of the catalyst.

Conclusions

The mathematical model of the process of transesterification of used oils into biodiesel has demonstrated its effectiveness as a tool for optimising technological parameters. The use of Microsoft Excel and MathLab allowed predicting the dynamics of the process with high accuracy and adjusting the reaction conditions to increase the yield of the final product. Rational parameters of transesterification were established, which ensure the maximum yield of diesel biofuels (90%), a temperature of 60°C, an alcohol-to-triglyceride ratio of 6:1, and a catalyst concentration of 1.5%. This makes the process economically viable for industrial use. Based on the simulation results, it was found that the temperature regime is a key to the efficiency of the reaction. Raising the temperature to 65°C accelerates the conversion of triglycerides and increases the yield of biofuels. However, a further increase in temperature, especially above the boiling point of bioethanol (~65°C at atmospheric pressure), leads to alcohol loss, which reduces the efficiency of the reaction.

Graphical dependences of the yield of the main components of the reaction, including triglycerides, diglycerides, and methyl esters, allow visualising the effect of reagent and catalyst concentrations on the process. This contributes to more accurate forecasting of the final characteristics of biofuels and improved process management. The results obtained can be used for further optimisation of industrial production of biodiesel, improvement of technological modes, and development of more efficient mathematical models for estimating the parameters of the obtained diesel biofuel.

Among the promising areas of further research are the integration of renewable energy sources into the production of biofuels, the creation of environmentally friendly catalysts, and the improvement of methods for cleaning the final product. It is also important to implement combined approaches to catalytic activation, including the use of bioengineering and nanotechnology solutions to improve the efficiency and environmental friendliness of production processes.

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Conflict of Interest

None.

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Математична модель процесу перетворення відпрацьованих олій в дизельне біопаливо

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Анотація. Зростання попиту на відновлювані джерела енергії стимулює розвиток технологій виробництва біодизеля з відходів, однак високий вміст вільних жирних кислот у сировині ускладнює переестерифікацію, знижує вихід палива та підвищує потребу в очищенні. Метою дослідження була розробка та валідація математичної моделі процесу переестерифікації відпрацьованих олій у дизельне біопаливо для оптимізації технологічних параметрів. Раціоналізована модель детально описала закономірності трансформації тригліцеридів у присутності спирту та каталізатора. Вона дозволила відстежувати зміну концентрацій проміжних продуктів реакції, зокрема дигліцеридів, моногліцеридів, біодизеля та гліцерину, що є критично важливим для прогнозування ефективності процесу. Сталі значення швидкості процесу переестерифікації вказані через рівняння Арреніуса, що дозволили оцінити вплив температури та співвідношення реагентів на загальну кінетику реакції. У рамках дослідження проведено чисельне моделювання та кореляцію моделі шляхом систематизації результатів з даними, які були отримані під час проведення досліджень та отриманих за результатами аналізу літературних джерел. Було проаналізовано каталітичні та некаталітичні варіанти процесу, що дозволило визначити найефективніші умови проведення реакції. Результати моделювання підтвердили, що збільшення температурних показників до 60°C призводить до збільшення виходу дизельного біопалива, тому надмірне нагрівання понад температуру кипіння метанолу спричиняє його випаровування, що призводить до зниження ефективності процесу та втрати сировини. Визначено оптимальні технологічні параметри, які забезпечують максимальний вихід біодизеля при мінімальних матеріальних та енергетичних витратах. Запропонована математична модель може бути використана в промислових умовах для оптимізації процесу виробництва біопалива, сприяючи підвищенню ефективності переробки вторинної сировини

Ключові слова: кінетична модель; вільні жирні кислоти; оптимізація параметрів; температурний режим; вихід біопалива; енергетична ефективність