

Master Thesis

Modelling of three-component systems in biodiesel production technology

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Declaration of Authorship

„I declare in lieu of oath that this thesis is entirely my own work except where otherwise indicated. The presence of quoted or paraphrased material has been clearly signaled and all sources have been referred. The thesis has not been submitted for a degree at any other institution and has not been published yet.”

Preface, Dedication, Acknowledgement

I would like to express my special gratitude to my supervisor, Associate Professor Andrey Gerasimov, who helped me in the process of preparing my thesis.

Abstract

Scientific and technical achievements in the development of alternative energy sources contribute to the development of biofuel technologies and are aimed at researching methods for obtaining biofuels, optimizing these processes and introducing processes into the industry of the fuel and energy complex. For the production of biofuels, all new sources of raw materials of plant or animal origin, as well as industrial and domestic waste are involved. The main goal is to find optimal conditions for the production of biofuels that meet all standards and are not inferior in terms of their physical and chemical properties to fuels from non-renewable energy sources.

This final qualification work presents an analysis of existing technologies for the production of biodiesel fuel based on the use of various types of raw materials, catalyzed or non-catalyzed reactions, as well as the possibility of modeling the course of a chemical-technological process. The scientific section of the work presents the parameters of biodiesel synthesis, with a phase diagram of a three-component system being created.

Zusammenfassung

Wissenschaftliche und technische Errungenschaften bei der Entwicklung alternativer Energiequellen tragen zur Entwicklung von Biokraftstofftechnologien bei und zielen darauf ab, Methoden zur Gewinnung von Biokraftstoffen zu erforschen, diese Prozesse zu optimieren und Prozesse in die Industrie des Kraftstoff- und Energiekomplexes einzuführen. Bei der Herstellung von Biokraftstoffen werden alle neuen Rohstoffquellen pflanzlichen oder tierischen Ursprungs sowie Industrie- und Haushaltsabfälle einbezogen. Das Hauptziel besteht darin, optimale Bedingungen für die Produktion von Biokraftstoffen zu finden, die alle Standards erfüllen und hinsichtlich ihrer physikalischen und chemischen Eigenschaften Kraftstoffen aus nicht erneuerbaren Energiequellen nicht nachstehen.

Diese abschließende Qualifikationsarbeit stellt eine Analyse bestehender Technologien zur Herstellung von Biodieselskraftstoff dar, die auf der Verwendung verschiedener Arten von Rohstoffen, katalysierten oder nicht katalysierten Reaktionen sowie der Möglichkeit der Modellierung des Ablaufs eines chemisch-technologischen Prozesses basieren. Im wissenschaftlichen Teil der Arbeit werden die Parameter der Biodieselsynthese vorgestellt, wobei ein Phasendiagramm eines Dreikomponentensystems erstellt wird.

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1 Introduction

Involvement in the processing of new renewable sources of raw materials is primarily due to the need to find a replacement for energy resources, the number of which is rapidly decreasing (. The energy issue is currently one of the main problems faced by the world community. In this regard, obtaining biological fuel, as an environmentally friendly and alternative source of energy, has become one of the leading areas of scientific activity.

Biofuel is an energy resource obtained by processing biomass of different origin, the properties of which are close to traditional energy sources. The environmental side of biofuel production is also its main advantage, since the current environmental situation is deteriorating due to emissions of toxic and harmful substances into the atmosphere, as well as the formation of waste from various areas of industry. Even a partial use of this fuel will reduce the environmental load and become one of the solutions in achieving the goals of sustainable development.

The main widely studied type of biofuel is biodiesel, which is a non-toxic alternative energy source related to renewable energy resources (Muhammed Niyas M., Shaija, A. 2022). Biodiesel is widespread due to the currently studied way of its application as a diesel engine fuel without any changes or modifications. In contrast to diesel fuel obtained by processing petroleum raw materials, biodiesel has a number of positive aspects, by which it can be judged on its ecological and economic efficiency:

1) In the production of biodiesel can be used not only sources of raw materials of plant or animal origin, such as oil crops, but also various domestic, municipal, organic waste, as well as waste from the agricultural industry.

2) The absence of sulfur content in the production of biodiesel contributes to a complete reduction of sulfur dioxide emissions (SO_2) (Nayak S.K., et.al. .2020) At the same time carbon dioxide emissions into the atmosphere are reduced by 1.25 times, because when using biodiesel exactly the amount of carbon dioxide is returned into the atmosphere, which was absorbed by plants during growth. It is also worth noting the low content of carcinogenic benzene, which reduces the risk of cancer.

Compared to diesel fuel from traditional sources, the combustion of biodiesel occurs with a reduction of unburned hydrocarbons in the order of 90% (Sharma K., et.al. 2021).

3) In a comparative evaluation of technical and economic parameters it can be noted that the characteristics of biodiesel are similar in many respects, and in some points even superior to petroleum diesel fuel. For example, biodiesel has a higher cetane number, which increases the temperature of its ignitability. Also of no small importance is the high lubricating ability of biodiesel, which allows to increase the service life of diesel engines, since in the process of using this type of fuel in addition to combustion with energy release is lubrication of moving parts.

4) In addition to obtaining the main product, namely fatty acid methyl esters, the biodiesel production cycle also produces glycerol as a byproduct, which is widely used in the pharmaceutical and paint and varnish industries (Mendieta Lopez J., et. al. 2022).

However, in spite of a number of indicated advantages, today the technology of biodiesel production has a number of significant drawbacks, since research in this field is still continuing. The main problems are expanding the raw material base for the production of this fuel, improving its physical and chemical characteristics, in particular improving the calorific value and reducing the corrosive effect, research methods of biodiesel synthesis using different types of catalysts that can be completely and safely removed from the system (Putra, M.D., et.al.2018)

In order to improve the quality of biodiesel fuels, in addition to laboratory tests, the field of development of an optimal mathematical model describing the stages of biodiesel production under various conditions is relevant for today. Biodiesel is a complex multicomponent system, so mathematical modeling of the process will determine the thermodynamic parameters of the system, based on which will be selected the optimal parameters of fuel production, namely temperature and pressure of the process. Using the model of multicomponent systems will also allow to study and predict the change of the process, for example, when introducing new catalysts or changing raw materials (Souza M.F., Hirata G.F., Batista E.A.C.2020). Mathematical models work most effectively in biodiesel refining, especially when a large number of by-products are formed. Such models help to determine how to purify fuel in high yields of the target component and

isolate by-products for further marketing purposes. In particular, predictive modeling of the biodiesel process can be used as a determinant of the melting/crystallization behavior of fuel properties and kinematic viscosity for fats, oils and biodiesel fuel systems (Kant Bhatia S., et.al.. 2021)

Based on the above, the object of research of this scientific review are biodiesel fuel systems. The aim of the research is to study the influence of various parameters of biodiesel fuel system on yield and obtaining target components of biodiesel fuel based on modeling of two-phase systems. To achieve the goal, it seems necessary to solve the following tasks:

- analysis of existing modern methods of biodiesel production and ways to assess the characteristics of the resulting fuels;
- study of parameters used in the technology of biodiesel production, the effect of changes in these parameters on the general state of biodiesel systems;
- analysis of literature sources and identification of relevant data that can be used to model biodiesel fuel systems using UNIFAC group contribution parameters;
- development of a model of two-phase multicomponent biodiesel system, based on the parameters of biodiesel obtained during laboratory synthesis, allowing it to be further used to predict the behavior of the system when the properties of one of the components change.

2 Biodiesel classification

Biodiesel is a renewable fuel consisting of long-chain esters formed from fatty acids and methanol or ethanol, which can be obtained either by the transesterification reaction of vegetable oils and fats or by the esterification reaction of fatty acids contained in animal fats (Dhanya B.S., et.al. 2020).

Classification of biodiesel occurs according to the resource from which this type of fuel will be produced. The existing raw materials for production are divided into three main groups:

1. Production of biodiesel from first-generation feedstock.

This generation includes raw materials derived from agricultural crops, namely sunflower, rapeseed, corn, soybeans, from which later obtain oils, which become the starting material in the technology of biofuel production. Oil for biodiesel production of the first generation is also obtained from coconut. The first generation includes not only edible oils, but also oils of little use or not used in food. Edible oils are oils that are suitable as food ingredients due to their high nutrient content and the ability of the human body to absorb them easily. Non-food oils are those suitable only for industrial purposes due to their low nutritional value and hazardous content.

To date, the technology of biodiesel production uses the following types of edible oils, such as, sunflower, corn, palm, soybean, rapeseed, coconut, and rice bran oil. Non-food oils used as raw materials include cotton, castor, rubber, neem, and jatropha oils (Gutiérrez-López A.N., et.al. 2022).

The use of vegetable oils depends on the local availability of the oil source, e.g. rapeseed oil in Europe, palm oil in Southeast Asia, jatropha oil in India, coconut oil in the Philippines and soybean oil in Brazil and the USA (Gutiérrez-López A.N., et.al. 2022). Oil yield (in terms of kg/ha and % wt.) affects cost, since a high yield lowers the cost of production. Palm oil yield is about 5000 kg oil per hectare (20 wt%), followed by rapeseed oil (1000 kg/ha, 20 wt%) and sunflower oil (375 kg/ha, 37-50%). Among the non-food oils, jatropha oil (1590 kg/ha) gives the highest yield, followed by castor oil (1188 kg/ha).

Jatropha oil is considered the best raw material for biodiesel production because of its unpretentiousness to climatic conditions and minimal requirements for cultivation efforts. Different raw materials have different composition of fatty acids, which directly affects the properties of biodiesel.

As noted earlier, animal fats can be used as feedstock for biodiesel production. The attractiveness of involving animal fats as raw materials lies in their low cost, chemical inertness, zero corrosivity and high calorific value. The use of animal fat waste as a raw material for biodiesel production eliminates the need for its utilization and provides an affordable, economical, environmentally friendly biodiesel. Biodiesel based on animal fat has a higher cetane number (above 60) than biodiesel based on vegetable oil, due to the high content of saturated fatty

acids (Jiaqiang E., et.al. 2019). This leads to increased resistance to oxidation and reduction of NO emissions.

2. Production of biodiesel from second-generation feedstock.

This type of raw materials includes domestic waste, as well as waste from food and agricultural industries. A common example is waste vegetable oil used in cooking. The reuse of used oil is harmful to health and is mostly disposed of by landfilling. This type of waste is the most promising from an environmental point of view, as there will be a reduction of organic waste pollution in the environment. Waste oil is also an economical source of raw materials in the process of biodiesel production, as it is 2-3 times cheaper than vegetable oil (Badawy T., et.al. 2019).

3. Production of biodiesel from third-generation raw materials.

The feedstock in this case is produced from microalgae or heterotrophic microorganisms, and represents the least used source material for industrial production. This is primarily due to the high cost of biodiesel produced from microalgae, due to the costs of collecting the algal biomass and preparing it for processing, which includes many physical and chemical stages (Gozmen Sanli B., Özcanli M., Serin H.. 2020) Therefore, on an industrial scale, vegetable oils are the most preferred source of raw materials due to their low cost of production.

However, from the point of view of diesel engine performance the most suitable is the raw material of the third generation based on energy-ecoenergetic analysis (Odibi C., et.al. 2019). Also advantageous condition in the cultivation of algae is the absence of the need for fertile land and the possibility of growing them in wastewater. In this regard, the use of microalgae as a source material for biodiesel production is a promising area for the development and search for technologies that can significantly reduce the cost of production of this type of biomass and improve the economic aspect of biological fuel production.

3 Technology of biodiesel production

Vegetable oils are highly viscous, which makes them difficult to use directly in diesel engines. High viscosity leads to poor combustion, which affects the performance of the diesel engine. Conversion of oils into biodiesel today can be done in four ways, such as, pyrolysis, microemulsification, dilution and chemical

transesterification (Kant Bhatia S., et.al. 2021). Among the methods presented, transesterification of vegetable oils with alcohols is the most widely used, useful and preferred technique for reducing viscosity and density.

3.1 Pyrolysis

Pyrolysis (cracking) involves the thermal treatment of substances with the breaking of chemical bonds. Pyrolysis of vegetable oils and animal fats involves the cracking of the triglyceride structure into alkanes, alkenes and fatty acids. Pyrolysis system is the most economically available system of biodiesel product with lower hothouse gas emigrations

3.2 Dilution method

Biodiesel can be produced by mixing lacing petroleum diesel energy with ethanol or solvent. Mixing leads to lower viscosity and density of biodiesel (Debabrata Barik, Ganesan Vignesh. 2019). Blending ethanol in an amount of 4% of the total blend with diesel fuel increases braking torque, brake thermal efficiency, and braking power, while reducing specific fuel consumption. Since the ignition point of ethanol isn't as high as that of diesel energy, it leads to bettered energy combustion by grinding the incoming admixture.

3.3 Microemulsification

Microemulsification is the process of mixing a colloidal solution of oil, alcohol and a surfactant. The droplet diameter in the microemulsion ranges from 1 to 150 nm. However, it has been found that the properties of microemulsions are very close to those of diesel fuel. Soot deposits have also been found on the injectors and exhaust valves of engines when using such fuel. Microemulsion can be made from biodiesel feedstock with ester and dispersant or from biodiesel feedstock, alcohol and alkyl nitrate (Debabrata Barik, Ganesan Vignesh. 2019) Alcohol is used to increase the volatility of the biodiesel while reducing the smokiness. Alkyl nitrate increases the cetane number of the fuel. Using microemulsified biodiesel will not cause any special problems, such as incomplete combustion, nozzle failure or fouling.

3.4 Transesterification method

The transesterification of normal glycerides with alcohols into fatty acid esters is an important reaction used in the production of detergents and soaps (Arachchige U.S.P.R., et.al. 2021). Almost all biodiesel is formed in a similar chemical process using the base-catalyzed transesterification method because it is the most economical method, requiring only low pressures and temperatures. The transesterification method is the reaction of triglycerides (fat/oil) with alcohol to form glycerol and esters. The reaction scheme is shown in Figure 1.

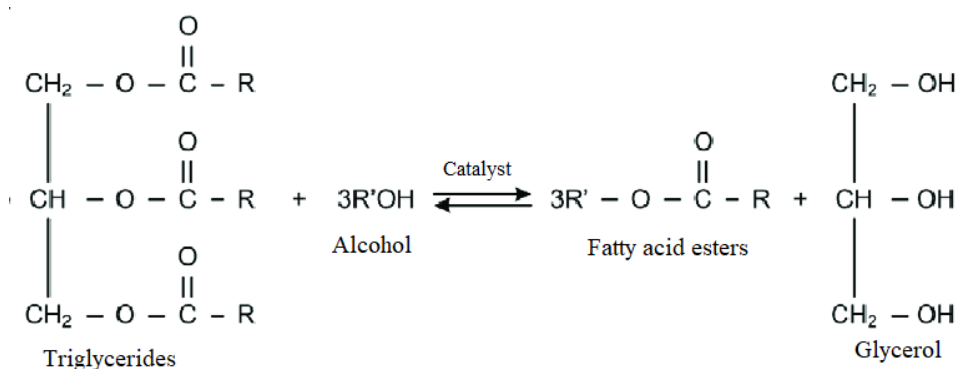


Figure 1: Transesterification reaction of biodiesel production

Process catalysts can act as heterogeneous, homogeneous and natural catalysts. Industrial technology is mainly based on the use of acid or alkaline catalysts represented by sulfuric acid or sodium (potassium) hydroxides, respectively. However, in addition to chemical catalysts, acceleration of the transesterification reaction can be carried out under the influence of enzymes, which are natural catalysts with environmentally safe conditions of their operation (Mansir, N., Teo, S.H., Rabi, I., Taufiq-Yap, Y.H. 2018).

In the case of an acid-catalyzed transesterification reaction, sulfuric or sulfonic acid is mainly used (Wang Y.-T., Fang Z., Zhang F 2019). The reaction mechanism consists of four stages. In the first step, the carbonyl group is protonated to form a carbocation in the second step, which is subjected to a nucleophilic attack (Fernando Trejo-Zárraga, 2018). Alcohol is attached to the intermediate in the third stage, and the ester is formed in the fourth stage by detachment of glycerol and catalyst regeneration. The carbocation formed in stage II is highly reactive, so water should be avoided during the reaction, since

this molecule can act as a nucleophile and form carboxylic acids, which is a side reaction. The mechanism of the acid transesterification reaction is shown schematically in Figure 2.

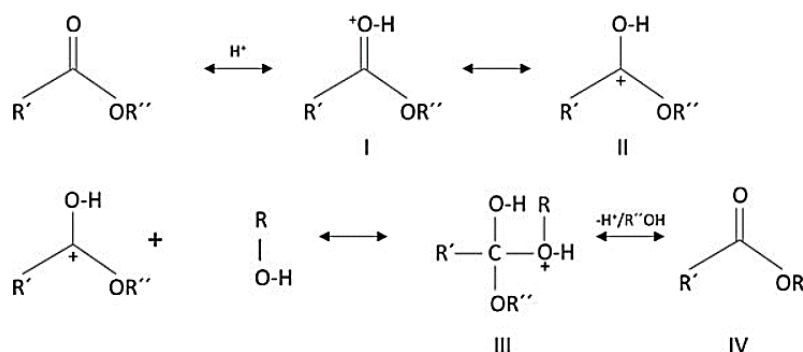


Figure 2: Acid transesterification reaction mechanism

When alkaline catalysts similar as hydroxides, alkoxides, sodium and potassium carbonates are used, the transesterification response also proceeds in four stages. When alkali is used, the first step is the conformation of an alkoxide, which is a strong nucleophile that attacks the electrophilic carbon in the carbonyl group of the triglyceride (Fernando Trejo-Zárraga, 2018). This attack transforms the carbonyl into a tetrahedral intermediate, as shown in the alternate step. The tetrahedral carbon is also separated from the intermediate in the third step to form an alkyl ether. In the last step, deprotonation of the catalyst regenerates the alkali, while a proton is attached to the diglyceride anion, as shown in Figure 3. The catalyst can reply with another alcohol patch, and the medium is repeated until the catalyst reacts with the alcohol patch again to form glycerol and alkyl ethers (Zabala, S., et.al.).

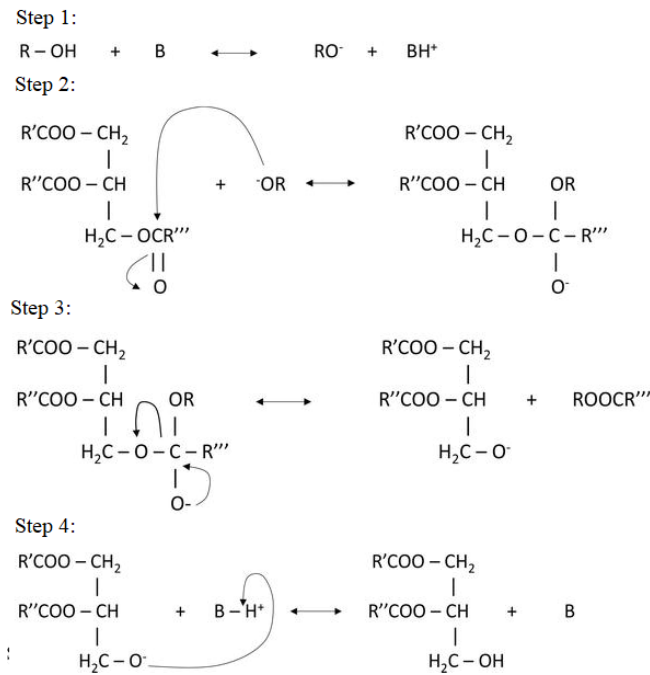


Figure 3:Alkaline transesterification reaction mechanism

The use of homogeneous catalysts has a number of disadvantages, such as the difficulty of removing catalysts from the system and the inability to reuse these types of catalysts. The use of heterogeneous catalysts is proposed in the scientific literature as one of the options for solving the problem. Unlike homogeneous catalysts, heterogeneous catalysts have a number of advantages:

1. reusability;
2. the relatively low cost of the catalyst when it is regenerated and reintroduced into the systems;
3. no need to remove the catalyst from the product;
4. catalyst selectivity, i.e. the catalyst accelerates only the direct transesterification reaction, while the catalyst residues do not contribute to the decomposition of esters, and thus have low sensitivity to the presence of free fatty acids;
5. simple technology in separating the catalyst from the glycerol;

The rate of the transesterification reaction in the case of a heterogeneous catalyst is lower than in the case of a homogeneous one, but because of their reusability and relatively simple separation scheme, heterogeneous catalysis becomes more cost-effective (Supamathanon N., et.al. 2021). As heterogeneous catalysts,

carbonates of alkali and alkaline earth metals (Touqeer T., et. al. 2020), metal oxides of various groups, such as zinc oxide ZnO are used.

Among these types of catalysts calcium oxide found the most wide application, which provides high yield of about 96-98% methyl esters of fatty acids. In comparison with potassium hydroxide CaO also has high basicity, relatively low price, which makes it easy to handle. Heterogeneous base CaO catalysts deposited on a modified geopolymer have been developed, characterized as inexpensive catalysts for biodiesel production by transesterification. The catalyst is prepared by microwave irradiation followed by calcination in air at 600 °C.

In addition to oxides of alkali and alkaline earth metals, oxides of transition metals such as zinc, zirconium, and titanium are proposed in the scientific literature as catalysts. For example, a heterogeneous nickel-doped ZnO nanocatalyst was developed, which is more stable than the traditional ones and can be used up to 5 cycles in the transesterification reaction (Putra, M.D., et.al. 2018).

A promising replacement for homogeneous catalysts are catalysts with nano-additives, which provide higher combustion of biodiesel in the engine, as well as reducing the amount of nitrogen oxide emissions NO_x due to excessive embedded O₂ (Xia C., et.al. 2021),

Currently, many scientific studies are also aimed at obtaining so-called "green" catalysts, such as immobilized enzymes (matrix) and heterogeneous catalysts derived from biomass (Mansir, N., Teo, S.H., Rabi, I., Taufiq-Yap, Y.H.2018).

The main disadvantages of heterogeneous catalysts are low chemical stability and high price. In this regard, the development of heterogeneous catalysts derived from biomass is currently under consideration. In contrast to standard heterogeneous catalysts, modified biomass catalysts are non-toxic, have high catalytic activity and stability under acidic and alkaline conditions and can withstand high water content. Biomass is mainly composed of C, O and N as well as various metal ions such as Na⁺, K⁺, Ca²⁺ and Mg²⁺. When biomass is burned to make heterogeneous catalysts, the C and O content is reduced, leaving various alkaline oxides (e.g. CaO, K₂O, MgO) as major components of the ash. These alkaline oxides have catalytic activity and can be used as catalysts for biodiesel production. Organic wastes of animal origin are rich in CaCO₃ and are converted

into CaO, the main catalyst for biodiesel production. Preparation of biocatalysts is simple, inexpensive and environmentally friendly; this differs from the preparation of chemical catalysts, which require multi-step reactions and chemical reagents (Touqeer T., et. al. 2020). CaO forms a methoxide anion, which acts as a nucleophile and attacks the electrophilic carbonyl carbon of triglycerides to form biodiesel. The catalysts obtained by incomplete carbonization of biomass consist of small sheets of polycyclic aromatic carbon with phenolic and carbonyl groups. These solid catalysts are stable and have numerous active centers containing SO_3H groups formed by sulfation of carboxyl groups.

In addition to conducting the process of biofuel production on homogeneous or heterogeneous catalysts, the scientific community is considering the introduction of polymeric materials in the production of catalysts for biofuels. Four possible options for using polymeric materials in biodiesel production have been considered, namely obtaining: polymeric biodiesel, polymeric catalysts, cold flow improvement additives, and stabilized exposure materials. The obtained catalysts proved to be effective as they can be used for a long time (up to the 10th cycle) and also have the property of non-toxicity. In addition to catalysis, the polymers have proven effective in improving the flowability of biodiesel.

4 Alternative ways of biodiesel production

One of the alternative and most promising is the method of obtaining biodiesel by transesterification reaction under supercritical conditions, which are conditions under which the liquid and gas phases cease to show any differences above a certain point, called critical. In this case the supercritical liquid has a number of properties inherent to liquids, such as high density and polarity, low viscosity, and increased dielectric permittivity (Aboelazayem O., Gadalla M., Saha B. 2018).

Because of the dependence of the density change on the variation of thermodynamic parameters of the system, the density values undergo changes even at small fluctuations of temperature or pressure near the critical point. This property makes it possible to increase the rate of the transesterification reaction, thereby carrying out the process in a short period of time without the use of catalysts while maintaining a high yield of the target product. It has been proved

that the transesterification reaction using supercritical methanol increases the production of biodiesel without the need for a catalyst.

Another modern method of producing biofuel is the transesterification reaction under the influence of ultrasound. The advantages of using ultrasonic waves are:

1. increase in the rate of reactions through the use of ultrasonic vibrations;
2. improving the quality of the final products;
3. allows the process to be carried out at a low flow rate of initial reagents.

The mechanism of the ultrasonic transesterification process is the creation of hydrodynamic perturbation by ultrasound due to pulsating bubbles in the initial two-phase mixture of vegetable oil and alcohol, which in turn leads to activation of molecules and intensification of the synthesis process.

An alternative method for obtaining biodiesel is also a reesterification reaction using a catalyst under the influence of microwave radiation (Silitonga A.S., et.al. 2020). The use of microwave radiation makes it possible to increase the reaction rate and temperature in a minimum time interval. To date, a mathematical model for the process of obtaining biodiesel fuel system by transesterification under the influence of microwave radiation has been developed. Transesterification by microwave radiation is an effective method of biodiesel production, as the physical and chemical properties of the product obtained meet ASTM D6751 and EN 14214 standards.

5 Research methodology

5.1 Methods for the transesterification reaction

Rapeseed oil (GOST 31759-2012) was used as an initial reagent in the ethanol transesterification reaction with a purity of ≥ 99 wt.%. The fatty acid composition of the oil presented in Table 3 was determined according to GOST 30418-96.

The HEL Auto-MATE Reactor System, an automatic chemical process control system, was used to conduct the transesterification reaction, allowing for an almost completely isolated system. Figure 12 shows an image of the HEL Auto-MATE Reactor System.

Name of fatty acid	Chemical formula	Content, % wt.
Palmitic acid	$C_{16}H_{32}O_2$	9,0
Stearic acid	$C_{18}H_{36}O_2$	5,2
Linoleic acid	$C_{18}H_{32}O_2$	63,3
Oleic acid	$C_{18}H_{34}O_2$	21,2
Erucic acid	$C_{22}H_{42}O_2$	1,3

Table 1: Fatty acid composition of rapeseed oil

In the cells of the apparatus were placed reaction vessels of 150 ml connected to a reflux condenser and connected to a system of thermocouples, providing continuous control over the temperature regime of the process. The necessary mass of rapeseed oil (~9.6 g) and alkaline catalyst (~0.5 wt.%) was placed in these vessels, and the mass of alcohol (~23.53 g) in the necessary proportions for reaction was tapped into an additional vessel. The reaction vessel with the oil and catalyst sample was placed in a heating cell and the reaction mixture was heated to 70° C with stirring. Stirring was performed using a propeller stirrer with a speed of 200 rpm. Once the set temperature was reached, ethyl alcohol was added to the reaction mixture and the synthesis countdown was started. To obtain fatty acid esters in different yields the synthesis time was varied from 1 to 5 minutes.

After that, the resulting mixture was filtered from the phospholipids and traces of insoluble substances obtained during the reaction. In this synthesis variant, there is no phase separation due to excessive alcohol and side reactions, i.e., the mixture is homogeneous.



Figure 4: Automatic chemical process control system HEL Auto-MATE Reactor System

Concentration of the target product, i.e. ethyl esters of fatty acids, was determined on a gas chromatograph "Chromatec Crystal 5000.2" with a HP FFAP capillary column $50\text{ m} \times 0,32\text{ mm} \times 0,5\text{ }\mu\text{m}$ with helium as a carrier gas. The concentration was calculated using the internal standard method by formula 1. A sample of $40\text{ }\mu\text{l}$ of the substance was dissolved in 1 mL of ethyl alcohol, used as solvent, then $60\text{ }\mu\text{l}$ of dodecane, used as internal standard, was added.

$$C_{et} = \frac{S_{et}}{S_{is}} \cdot C_{is} \quad (1)$$

where C_{et} и C_{is} - are the concentrations of the ether and internal standard, respectively;

$\frac{S_{et}}{S_{is}}$ - the ratio of the peak area of the ether to the peak area of the internal standard.

5.2 Methodology for constructing a theoretical model of the three-component diagram using the UNIFAC group contribution model

Various equilibrium systems exist to describe biodiesel production and purification processes. However, the most relevant system is the equilibrium in the liquid-liquid system between the products of the transesterification reaction. For multicomponent systems, knowledge of phase equilibrium is a prerequisite for the design of process equipment and separation devices in operating plants on an industrial scale. Because of the presence of polar compounds in the system under study, these systems are very complex (Ferreira, M.C., et.al.. 2018). Therefore, classical equations of state are not capable of interpreting and predicting the behavior of these systems. Local composition models are the most common models for studying the phase behavior of systems containing biodiesel. Given the time and cost of each experiment, a reliable thermodynamic model is needed to accurately predict system behavior. It should be noted that most thermodynamic models have parameters that are clearly independent of the system properties and must be selected with some experimental data and optimization methods. Consequently, models with fewer parameters or predictive models without fitting parameters, but with average higher errors, are an alternative. A number of authors (Asoodeh, A., Eslami, F., Sadrameli, S.M. 2021, Souza M.F., Hirata G.F., Batista E.A.C 2020) have shown that the NRTL and UNIQUAC models

successfully correlate experimental liquid-liquid data in biodiesel ternary systems. And the UNIFAC model is the most successful for predicting the group contribution.

In this part of the paper, experimental and calculated phase liquid-liquid equilibrium data were compared for ternary mixtures consisting of ethyl esters of fatty acids-glycerol-ethanol and triglycerides-glycerol-ethanol, using the UNIFAC (functional group activity factor) group contribution method, which can predict molecular interactions through structural group interactions. Thus, UNIFAC is an option when available models for calculating activity coefficient in liquid-liquid equilibrium are limited in use to the temperature and components in which the experimental data were measured and cannot be extrapolated to other mixtures at a different temperature (Ferreira, M.C., et.al.. 2018) Thus, the calculation of the activity coefficient using the UNIFAC model was based on equation (2)

$$\ln \gamma_i = \ln \frac{\varphi_i}{x_i} + \frac{Z}{2} q_i \ln \frac{\theta_i}{\varphi_i} + l_i - \frac{\varphi_i}{x_i} \sum_{j=1}^m x_j l_j + \sum_k \vartheta_{ki} Q_k (\ln \Gamma_k - \ln \Gamma_k^{(i)}) \quad (2)$$

where Γ_k и $\Gamma_k^{(i)}$ - is the residual activity coefficient of group k in the mixture and comparison solution containing only molecules of type i, respectively. When comparing the formulas for calculating the UNIFAC and UNIQUAC models we can replace that the main difference is the residual part determined by the energy parameters between the groups (Noriega, M.A., Narváez, P.C. 2019). This parameter is calculated as follows (3):

$$\ln \Gamma_k = 1 - \ln \left(\sum_m \theta_m \psi_{mk} \right) - \sum_m \left(\frac{\theta_m \psi_{mk}}{\sum_n \theta_n \psi_{nm}} \right) \quad (3)$$

where θ_m - is the fraction of the area of group m, which is calculated as follows (4):

$$\theta_m = \frac{X_m Q_{mk}}{\sum_l X_l Q_l}; X_m = \frac{\sum_j \vartheta_m^j x_j}{\sum_j \sum_n \vartheta_n^j x_j} \quad (4)$$

where X_m - is the mole fraction of group m in the mixture; ϑ_k^i - number of groups k in molecule i, R_k and Q_k - molecular volume and surface area of subgroups (these values are presented in Magnussen et al.), ψ_{mk} - group interaction parameters, determined by formula (5):

$$\psi_{mk} = \exp\left(-\frac{a_{mn}}{T}\right) \quad (5)$$

where T is temperature, ° C, and a_{mn} - is the group interaction coefficient determined experimentally for each pair of interacting groups. The values of this coefficient are given in the literature (Mendieta Lopez J., et. al., Noriega, M.A., Narváez, P.C..2019)

After calculating the activity coefficient, the next step is to calculate the mole fractions of the components that are in the upper and lower phases at the establishment of equilibrium in the system. The calculation is made based on the equality of chemical potentials at phase equilibrium (6)-(7):

$$f_i^E = f_i^R \quad (6)$$

$$(\gamma_i x_i)^E = (\gamma_i x_i)^R \quad (7)$$

where the upper indices E and R are the phases of the extract and raffinate, respectively.

In accordance with equations (6) and (7) at equilibrium of phases, the equality between the ratio of activity coefficients of refined and extract phases and the ratio of mole fractions of extract and refined phases will represent a constant called the distribution coefficient k_i (8):

$$k_i = \frac{x_i^E}{x_i^R} = \frac{\gamma_i^R}{\gamma_i^E} \quad (8)$$

The material balance of the system based on the composition of the two-phase system is presented in equations (9)-(10):

$$F = E + R \quad (9)$$

$$Fz_i = Ex_i^E + Rx_i^R \quad (10)$$

where F, E and R are the number of moles of feedstock, biodiesel phase and glycerol phase, respectively, z_i -mole fraction of component i in the feed. Using equations (9)-(10) and definition β as a ratio of the extracted phase to the feed (E/F), the mole fraction of component i in the glycerol-rich phase will be expressed as follows (11):

$$x_i^R = \frac{z_i}{1 + \beta(k_i - 1)} \quad (11)$$

And in the biodiesel-rich phase the mole fraction of the component will be equal to (12):

$$x_i^E = x_i^R \times k_i \quad (12)$$

The working equation for determining the phase condition after summing the mole fractions of the components of the refined phase will be as follows (13):

$$\sum_i \frac{z_i(1 - k_i)}{1 + \beta(k_i - 1)} = 0 \quad (13)$$

Thus, to carry out the calculation we set the initial data: the composition of phases x_i^E, x_i^R and phase separation β . Then, the activity coefficients of each of the equilibrium phases were determined in accordance with the applied UNIFAC model (Mendieta Lopez J., et. al. 2022) and the distribution coefficient k_i based on the composition of the phases. Then a new value of phase equilibrium was determined after solving equation (13). After determining β , substituting the new value into equation (13) to find the new phase composition, we proceed to solve equations (12) and (13) to find x_i^E and x_i^R . In case the results do not converge to those given at the beginning of the calculation algorithm, we recalculate the activity and distribution coefficients until the necessary convergence is achieved.

5.3 Methods for constructing an experimental model of the phase diagram of a three-component system

Construction of the experimental phase equilibrium model for three-component mixtures was carried out by gradually removing the volatile component of the system and fixing the composition of the phases at the point of separation.

After synthesis and chromatographic analysis the obtained biodiesel mixture was placed in a heat-resistant beaker and the initial mass of the mixture was recorded by weighing on an analytical scale Mettler Toledo 204 with an accuracy of 0.0001 g. Then in a preheated to 60° C cell HEL Auto-MATE Reactor System the beaker was placed and the gradual evaporation of ethyl alcohol was started. Evaporation was carried out until the solution became cloudy or the alcohol completely evaporated. When the solution became turbid, the beaker was removed from the cell and quickly weighed to determine the composition of the interface and the transition of the system from heterogeneous to homogeneous state. Then the

beaker was placed back in the cell and evaporation of alcohol was continued until a constant mass of the solution, indicating that the component was completely removed from the solution. The mass difference between the initial and final solution was the mass of alcohol removed from the system, which was used in calculations to find the concentration of ethyl alcohol in the initial experimental mixture.

For the starting point, the alcohol concentration % wt. was determined from equation (14):

$$w'_{EtOH} = \frac{m_{EtOH}}{m_{before}} \cdot 100 \quad (14)$$

where m_{EtOH} - mass of evaporated alcohol, g, m_{before} - mass of the solution before evaporation, g.

At the point of separation, the alcohol concentration was calculated as follows (15):

$$w''_{EtOH} = \frac{m_{EtOH} - (m_{before} - m_{separation})}{m_{separation}} \cdot 100 \quad (24)$$

where $m_{separation}$ - mass of the solution at the point of formation of the two phases, g.

The obtained composition of the phases at the interface was plotted on a three-component diagram presented in Microsoft Excel and a liquid-liquid equilibrium curve was plotted based on the experimental data. The residual part was represented as a pseudo-component, since the exact composition of this phase cannot be determined.

6 Theoretical and experimental studies

The physical essence of the transesterification process is the reaction of glycerides present in the oil with alcohol (methanol or ethanol) using an alkaline catalyst (KOH, NaOH) to form esters and glycerol as a byproduct (Figure 5). The catalyst is prepared by adding potassium hydroxide (KOH) to alcohol (ethanol) and stirring thoroughly until completely dissolved. The final goal of the catalyst preparation step is to produce the ethoxide ion ($-OCH_2CH_3$), which attacks triglyceride molecules and creates ethyl esters. In the catalyst preparation step,

the OH⁻ ions separate the hydrogen ion to form water (H₂O). Water increases soap formation in the presence of free fatty acids, which ultimately reduces the biodiesel production process performance. It is important to treat oils with low free fatty acid content (<2% by weight of oil) to avoid soap formation as a result of the saponification reaction.

The transesterification reaction proceeds until the system reaches a state of equilibrium. The use of a catalyst accelerates the rate of the direct reaction. The composition and amount of the esters and glycerol formed largely depend on the composition of the feedstock and the ratio of the reagents, namely feedstock:alcohol.

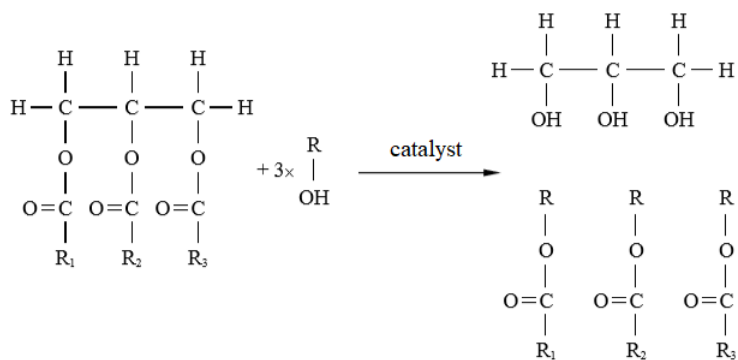


Figure 5: Scheme of triglycerides transesterification reaction with formation of esters and glycerol

In many literary sources the data when the system after transesterification reaction is a two-phase mixture with a clear boundary of separation, allowing by decantation to separate top phase from bottom phase, thus to separate top phase rich with target product from bottom phase rich with by-products (Habaki H., Hayashi T., Egashira R. 2018) are specified. In practice, during the reaction of transesterification of rapeseed oil with ethanol, it was found that with a significant excess of ethanol taken in such amounts to increase the conversion of esters and decrease the time of reaction, the resulting mixture is a liquid without separation boundary, which indicates that the system is in a homogeneous state. The reason is increased solubility of glycerol obtained in the reaction with significant introduction of excess ethanol into the system (Filho J.C.G., et.al. 2021). In this connection, a variant of phase equilibrium modeling of the system obtained directly after biodiesel synthesis was proposed in order to evaluate the behavior of the

system during separation of one of the components, followed by a choice of purification options for both the target and by-product products.

The first step in the study of the phase equilibrium of the experimental system was to build a theoretical model of the three-component system, assuming that the system consists of pure substances (Ferreira, M.C., et.al. 2018). The group distribution of the molecules represented in the system according to UNIFAC was used for the construction (Povarov V.G. Efimov I.I, 2023). The data are presented in Table 4. As shown in the table, oil is considered as a separate triglyceride component with a molecular weight of 903 g/mol, and fatty acid ethyl esters as a pseudomolecule with an average molecular weight of 301 g/mol, despite the fact that these substances are mixtures of fatty acids and esters with different chains. Complex systems are presented as integral molecules (pseudomolecules) to simplify the UNIFAC algorithm calculations. Thus, to introduce the biodiesel component into the UNIFAC model, an integral molecule with the structure $(CH_3)_2(CH_2)_m(CH=CH)_n(CH)_p(OH)_pCH_2COO$. Parameters m, n and p denote the number of CH₂ groups, CH=CH and CHOH in the ester and can be no integer numbers calculated. These parameters accurately reflect statistically the amounts of each of the groups included in the formulas (Noriega, M.A., Narváez, P.C..2019) The mixture of fatty acids in this case is proposed to be represented as a pseudomolecule with the general formula: $(CH_3)_h(CH_2)_k(CH=CH)_1(CH)_m(OH)_n(COOH)_p$

	CH ₃	CH ₂	CH	CH=CH	CH ₂ COO	OH
Triglyceride	3,00	39,82	1,00	4,70	3,00	0,00
Fatty acid esters	2,00	12,88	0,00	1,48	1,00	0,00
Glycerin	0,00	3,00	0,00	0,00	0,00	3,00
Ethanol	1,00	1,00	0,00	0,00	0,00	1,00

Table 2: Group assignments for calculating the UNIFAC model

The data in Table 2 are needed to correct the group interaction coefficient a_{mn} determined by Equation 5, as well as in the direct calculation of activity coefficients in the UNIFAC model.

Figures 6 and 7 show phase diagrams of three-component systems: fatty acid esters-glycerol-ethanol and triglycerides-glycerol-fatty acid esters. The molar composition of the mixture was calculated from the equations for calculating the

UNIFAC activity coefficient model. The calculation data are given in Tables 3 and 4.

F AE, % wt.	99,65	0,01	97,81	0,02	96,05	0,06	94,37	0,11
Ethanol, % wt.	0,35	99,99	0,41	92,40	0,47	85,33	0,53	78,74
Glycerin, % wt.	0,00	0,00	1,78	7,57	3,48	14,61	5,10	21,15

F AE, % wt.	92,75	0,21	91,20	0,36	89,71	0,57	88,28	0,87
Ethanol, % wt.	0,59	72,58	0,66	66,83	0,72	61,45	0,78	56,42
Glycerin, % wt.	6,66	27,21	8,14	32,81	9,57	37,97	10,94	42,71

Table 3:Phase composition of the system fatty acid esters - ethanol-glycerol

F AE, % wt.	9,19	4,43	9,94	19,56	15,20	28,14	20,30
Ethanol, % wt.	22,20	91,46	85,82	24,30	80,39	26,62	75,06
Triglyceride, % wt.	68,61	4,11	4,24	56,14	4,41	45,23	4,64

F AE, % wt.	35,02	25,39	40,24	30,74	43,69	37,19	44,56
Ethanol, % wt.	29,25	69,63	32,34	63,75	36,23	56,07	42,41
Triglyceride, % wt.	35,72	4,97	27,43	5,51	20,09	6,74	13,03

Table 4: Phase composition of the system fatty acid esters - triglyceride - ethanol

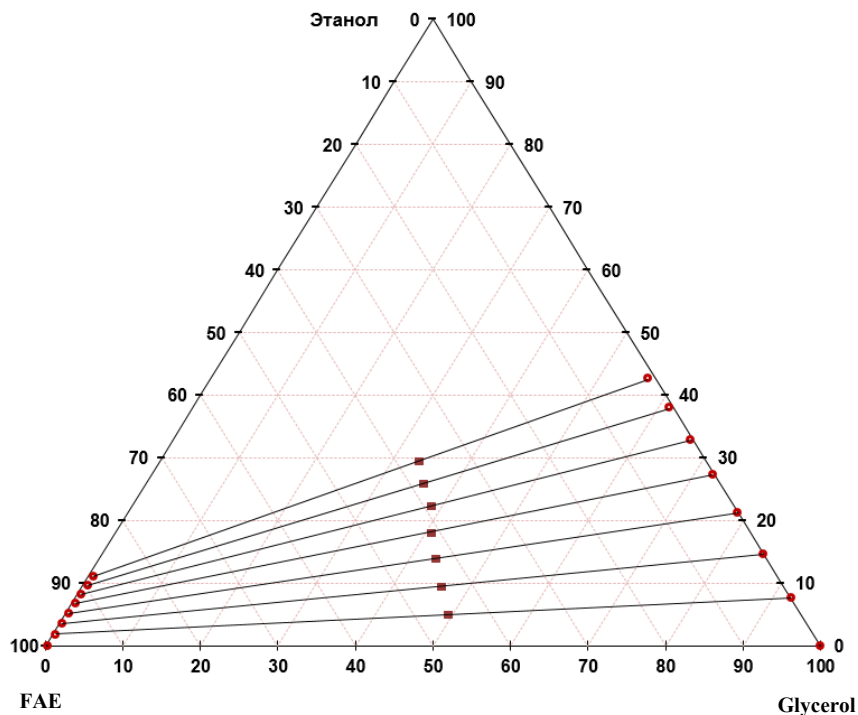


Figure 6:Diagram of liquid-liquid equilibrium with bonding lines of ternary system FAE + ethyl alcohol + glycerol (mass fraction) calculated according to UNIFAC model algorithm

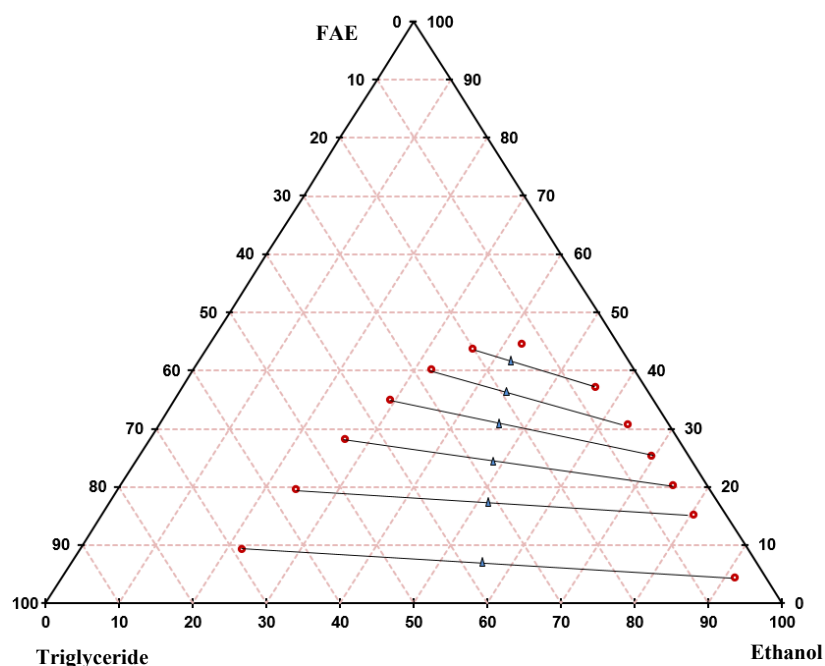


Figure 7: Diagram of liquid-liquid equilibrium with bonding lines of ternary system ELC + ethyl alcohol + triglyceride (mass fraction) calculated by UNIFAC model algorithm

When comparing the calculated phase equilibrium data obtained for the systems with the experimentally obtained data presented in the sources (Noriega, M.A., Narváez, P.C. 2019, Mendieta Lopez J., et. al. 2022), it was found that our model correlates with the liquid-liquid equilibrium diagrams in the framework. Thus, based on the presented diagrams, it is possible to draw conclusions about the behavior of the system, knowing the concentration of the components in the mixture. However, in constructing the liquid-liquid equilibrium of these systems, the influence of other components present as byproducts was not taken into account.

The next step was to carry out the transesterification reaction of rapeseed oil with ethanol according to the method 5.1. to obtain the experimental mixtures. In order to obtain different yield of fatty acids esters the synthesis time was varied from 1 to 5 minutes. Experimental data were recorded in the synthesis log, which is shown in Table 5. In this case the phase compositions at which the separation was observed and the point of phase separation was recorded are highlighted by color. The number of experiments was determined based on the need to add points of this or that composition on the phase equilibrium curve.

The chromatographic analysis was the calculation of the peak area of fatty acid esters in the experimentally obtained mixture followed by the calculation of their

total concentration. The chromatographic information was analyzed using Chromatec Analytic software. The concentration of fatty acid esters in the initial mixture was calculated using equation (1). A calibration multiplier f_i was introduced into the equation taking into account the influence of impurities contained in the standard. The calibration multiplier for this series of experiments was 1.35.

Figure 8 shows chromatograms of the initial biodiesel mixtures, in which the peaks of fatty acid esters are marked. Peak 1 is a peak of the standard sample - dodecane, so it is not shown in the figures. The remaining peaks correspond to the ethyl esters of palmitic, linoleic, oleic, stearic, and erucic acids, respectively.

The erucic acid peak is not observed in all diagrams, which is due to the low concentration of this acid in the initial oil and makes it difficult to detect using gas chromatography. All peaks in this case correspond to the composition of the initial oil given in Table 1.

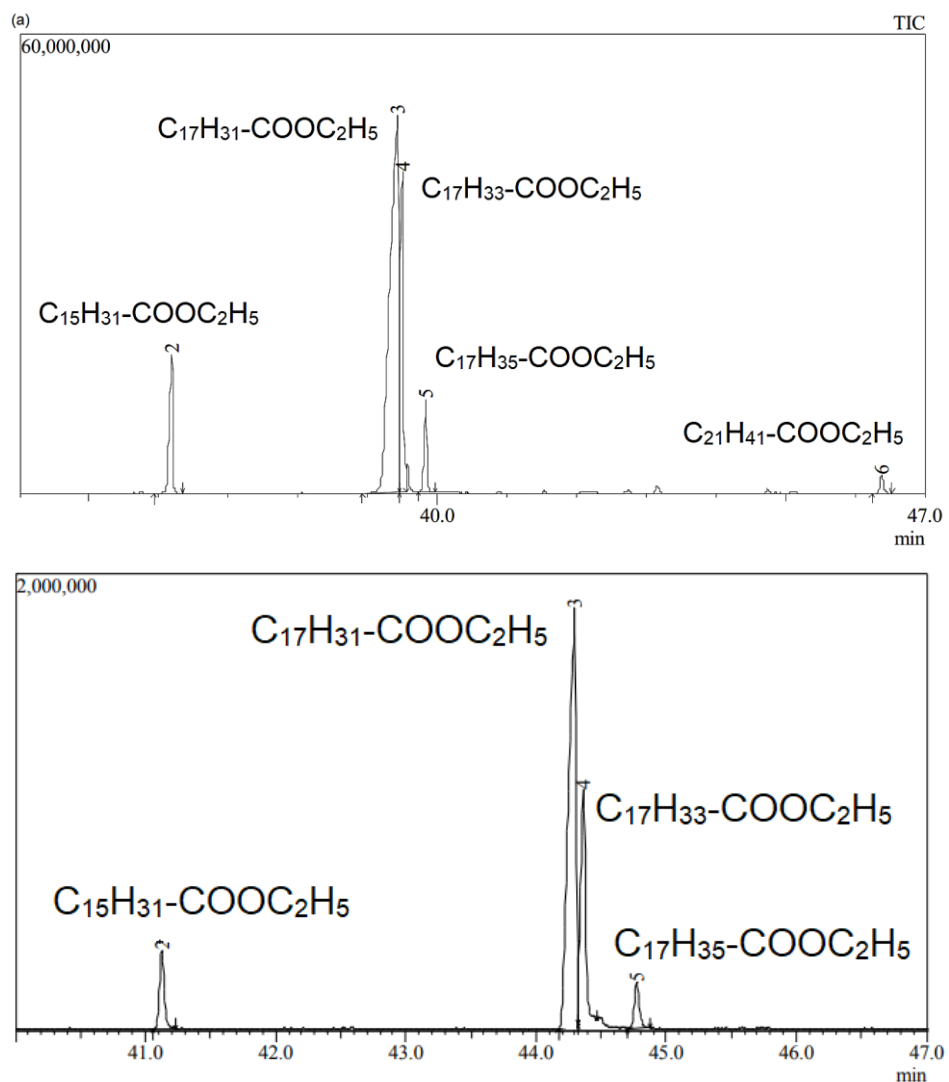


Figure 8: Chromatograms of the initial solution after the synthesis: a) with erucic acid peak; b) without erucic acid peak.

After chromatographic analysis and definition of concentrations of ethyl ethers of fatty acids according to the formula (1), experimental construction of the phase diagram was carried out according to the technique 5.3. For this purpose, an experimental mixture was weighed, phase state (homogeneous) was fixed and placed in a preheated cell of reactor system with gradual evaporation of ethyl alcohol. Figure 9 shows the reaction vessels placed in the heating cells.

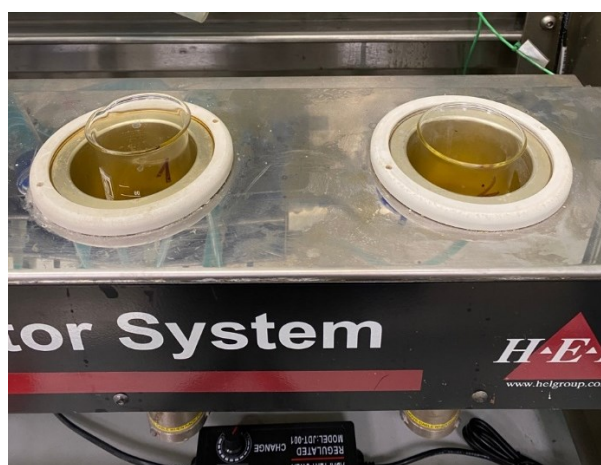


Figure 9: Process of ethyl alcohol evaporation

The process of evaporation is carried out to the point of visual determination of solution turbidity. The mixture was re-weighed and the mass data was entered into a table. The data were then used to calculate the component composition at the starting point, at the point of separation, and at the end point. The calculation was made on the basis of determining the final mass of completely evaporated alcohol and the amount of alcohol required to remove to form a heterogeneous mixture. The mass of completely evaporated alcohol was determined from the difference in mass of the initial mixture and the mixture, which after evaporation had a constant mass.

Figure 10 shows a heterogeneous mixture with no ethyl alcohol in the system. It was observed that decreasing the alcohol concentration in the mixture contributed to a clearer separation of the upper and lower phases.

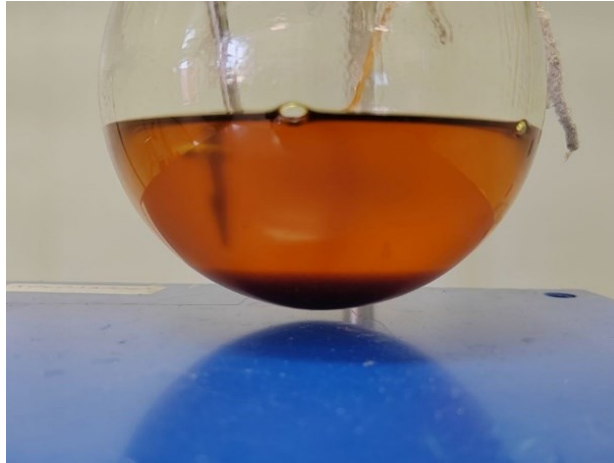


Figure 10: Heterogeneous mixture consisting predominantly of an upper phase rich in fatty acid ethyl esters and a lower (glycerol) phase

№	Date	Reaction time, min	Mass of reagents, g.		Mass of the mixture in the process of evaporation, g.				Concentration of components at the starting point, % wt.			Concentration of components at the separation point, % wt.			Concentration of components after alcohol removal, % wt.		
			m _{КОН}	m _{гp.м.}	m _{исх}	m _{разд}	m _{кон}	m _{ЕТОН}	EJC	Alcohol	Chief	EJC	Alcohol	Chief	EJC	Alcohol	Chief
1	16.02.23	3.00	0,12	9,18	23,79	9,05	8,21	15,58	22,0	65,5	12,5	62,4	13,8	23,8	60,7	0,0	39,3
2		4.00	0,12	9,23	26,64	-	7,63	19,01	13,3	71,4	15,3	-	-	-	46,5	0,0	53,5
3	20.02.23	1.00	0,12	9,18	26,08	10,40	8,82	17,26	26,1	66,2	7,7	65,5	15,2	19,4	77,2	0,0	22,8
4		2.00	0,13	9,55	25,97	10,33	8,80	17,17	30,4	66,1	3,5	76,3	14,8	8,9	89,6	0,0	10,4
5	01.03.23	1.00	0,12	9,21	27,66	10,26	9,47	18,19	23,4	65,8	10,8	63,1	7,7	29,2	68,4	0,0	83,1
6		2.00	0,12	9,53	26,78	-	8,46	17,94	15,4	67,0	17,6	-	-	-	46,7	0,0	53,3
7		3.00	0,12	9,27	28,34	-	8,49	19,84	14,9	70,0	15,0	-	-	-	49,8	0,0	50,2
8		4.00	0,12	9,20	26,87	-	8,36	18,52	15,3	68,9	15,8	-	-	-	49,2	0,0	50,8
9	09.03.23	1.00	0,13	9,17	27,56	-	8,61	18,96	5,3	68,8	25,9	-	-	-	16,9	0,0	83,1
10		2.00	0,12	9,62	27,57	-	9,01	18,56	4,4	67,3	28,2	-	-	-	13,6	0,0	86,4
11		3.00	0,12	9,12	28,65	-	9,16	19,48	16,6	68,0	15,4	-	-	-	51,7	0,0	48,3
12	16.03.23	4.50	0,12	9,19	27,64	9,62	7,90	19,73	20,9	71,4	7,7	60,1	17,9	22,1	73,1	0,0	26,9
13		5.00	0,12	9,27	26,68	-	9,01	17,67	14,8	66,2	18,9	-	-	-	44,0	0,0	56,0
14	20.03.23	4.20	0,12	9,19	27,24	10,32	9,06	18,18	25,4	66,7	7,8	67,2	12,2	20,6	76,5	0,0	23,5
15		5.00	0,12	9,26	27,65	10,86	8,91	18,73	19,9	67,8	12,3	50,7	17,9	31,4	61,7	0,0	38,3

Table 5: Experimental data for phase equilibrium of biodiesel-ethyl alcohol-glycerin system

Thus, using mixtures different in the content of ethyl esters of fatty acids, the phase diagram of liquid-liquid equilibrium of the experimental biodiesel mixture was constructed. In contrast to standard methods of construction, this method involves the removal of one component from the system while maintaining the content of other components, because after the synthesis the mixture is not a pure product, but a complex system, which also provides for the presence of an alkaline catalyst that is not removed. In this regard, biodiesel, as in the phase composition calculations using the UNIFAC model, was treated as a pseudomolecule, which was a pure component, since the concentration of fatty acid ethyl esters is fairly accurately known through chromatographic analysis. The ethyl alcohol was also considered a pure component. The byproducts of the reaction, including glycerol and the catalyst, were treated as a residue, taken as a single molecule in general.

The result of this series of experiments was the construction of liquid-liquid equilibrium of biodiesel system synthesized from rapeseed oil and ethanol. Figure 11 shows the diagram of liquid-liquid equilibrium of the experimental biodiesel (ELC) - ethanol - residue system. Data on concentrations were taken from Table 5.

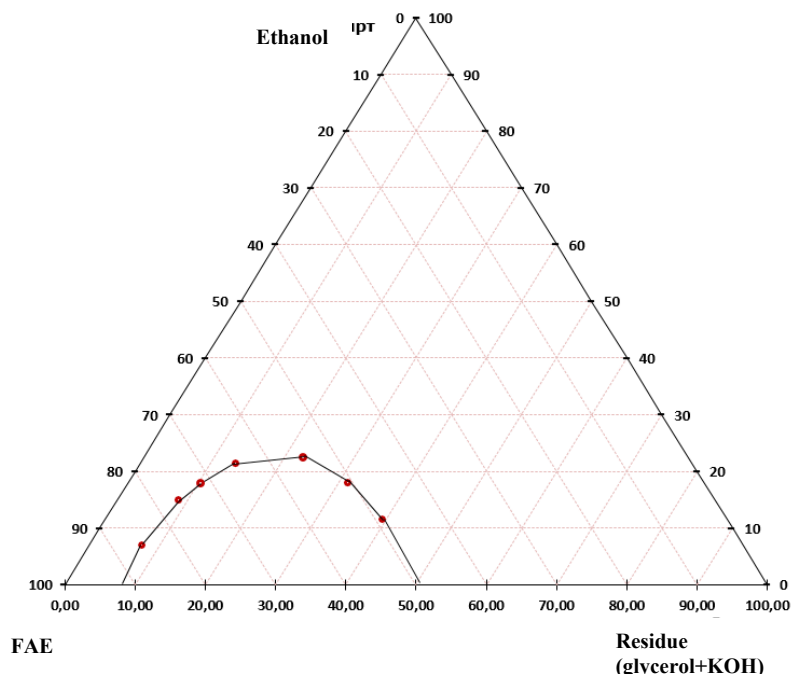


Figure 11: Experimental liquid-liquid equilibrium diagram of the biodiesel (FAE) - ethanol - residue system

After constructing the phase diagram, the obtained biodiesel was compounded with diesel fuel in the ratio of 5% biodiesel to 95% diesel and tested according to

international standards and compared with the properties of petroleum diesel. The results are presented in Table 6.

Physical property	Oil Diesel	Mixture of biodiesel and diesel fuel
Density, kg/m ³ (ISO 12185:1996)	829,4	834,6
Viscosity, cSt (GOST 33-2016)	2,621	2,723
Flash point, ° C (GOST 305-2013)	63	63
Cloud point, ° C (GOST 5066-2018)	-7	-7
Filterability limit temperature, ° C	-20	-14
Sulfur content, ppm (GOST 32139-2013)	6,0	5,8
Water content, mg/kg	34	56

Table 6: Physical properties of biodiesel produced from rapeseed oil

6.1 Analysis of the results of the study

Figure 6 shows the binodal for the system glycerol + ethyl alcohol + FAE calculated by the UNIFAC model algorithm, where the phase distribution of the system components can be observed.

Fatty acid ethyl esters and glycerol are completely soluble in ethanol, while biodiesel and glycerol do not mix well with each other. At this time, fatty acid ethyl esters are more soluble in the glycerol-rich phase than glycerol in the fatty acid ethyl esters phase.

The results obtained are in agreement with the data of (Shiozawa, S., et.al. 2020) and (Nunes, J.C. et.al. 2019, Pereira E., Meirelles A.J.A., Maximo G.J. 2020), which carried out the construction of liquid-liquid equilibrium for the ternary systems ethyl esters of fatty acids + glycerol + ethyl alcohol at different temperatures. These studies showed the same relationship between the miscibility of the system components and temperature. As can be seen, the ends of the binding lines corresponding to the high glycerol phase and the high fatty acid ethyl ester phase agree well with the binodal curves. The slopes of the binding lines show that the solubility of ethyl alcohol in the phase with high ethyl ester content is lower than in the phase with high glycerol content.

Figure 15 shows the binodal for the triglyceride + ethyl alcohol + FAE system. It can be seen that the miscibility between rapeseed oil and ethyl alcohol is very low. At the same time, the presence of ethyl esters of fatty acids in the system leads to an increase in their mutual solubility. Thus, rapeseed oil and ethyl alcohol are mixed in any ratio when the content of fatty acid ethyl esters in the ternary system is more than 45 wt.%. The end points of the binding lines corresponding to the high ethyl alcohol

phase and the high oil phase agree well with the binodal curves. The slopes of the binding lines show that more ethyl esters will transfer to the oil phase after phase separation due to the greater similarity of the polarities of ethyl esters and rapeseed oil.

The experimentally obtained phase diagram shown in Figure 19, however, does not agree with the liquid-liquid equilibrium obtained by solving the UNIFAC model equations (Esipovich, A.L., et.al.. 2018) Rapeseed oil and ethanol are insoluble in each other, but as the ratio of fatty acid esters increases, the ternary system of oil-ethyl fatty acid esters-ethanol can form a homogeneous phase. Generally, the biphasic region extends to higher concentrations of ethyl esters at lower temperatures.

It has been proven experimentally that about 50.5 wt.% ethyl ester is needed to achieve a homogeneous phase at 60 °C. Since the fatty acid ethyl ester content at the end of transesterification is usually quite high, this makes the system homogeneous. The presence of excess ethanol can reduce the mutual solubility of glycerol and esters to a certain extent, and the formation of two phases can contribute to the separation of glycerol from the biodiesel mass. For the liquid-liquid phase equilibrium of this system, the traditional UNIFAC thermodynamic model proves inadequate for modeling the liquid-liquid equilibrium boundary at various temperatures, since the system contains impurities that contribute to influence the establishment of equilibrium in the system.

Experimental results show that the two-phase zone is much narrower and lower compared to the theoretical phase diagram and captures only a small insolubility zone of esters and glycerol. The data indicate that a significant excess of ethyl alcohol, as well as the presence of extraneous components in the mixture, prevents the system from transitioning from the homogeneous state to the heterogeneous state for the most part.

Further study of the influence of impurities on the behavior of the system and the establishment of equilibrium in it plays an important role, since these data will allow to supplement the state diagram of the system and to adjust the equations for calculating the component composition in accordance with the UNIFAC model, that is, will allow to modify it.

7 Economic part

According to statistics given by the international energy agency IEA (IEA Report (2021)), in 2022 the global demand for biofuels was expected to increase by 6% compared to 2021. In 2021, the global biofuel market was valued at nearly 110 billion U.S. dollars, which was about 9% less than the previous year. However, despite the decline in 2021 due to the effects of the Covid-19 pandemic, the biofuels market is expected to grow. Meanwhile, the cumulative compound annual growth rate (CAGR) according to is estimated at 3.6% from 2022 to 2032. Figure 12 shows the volume of the biofuel market in the world.

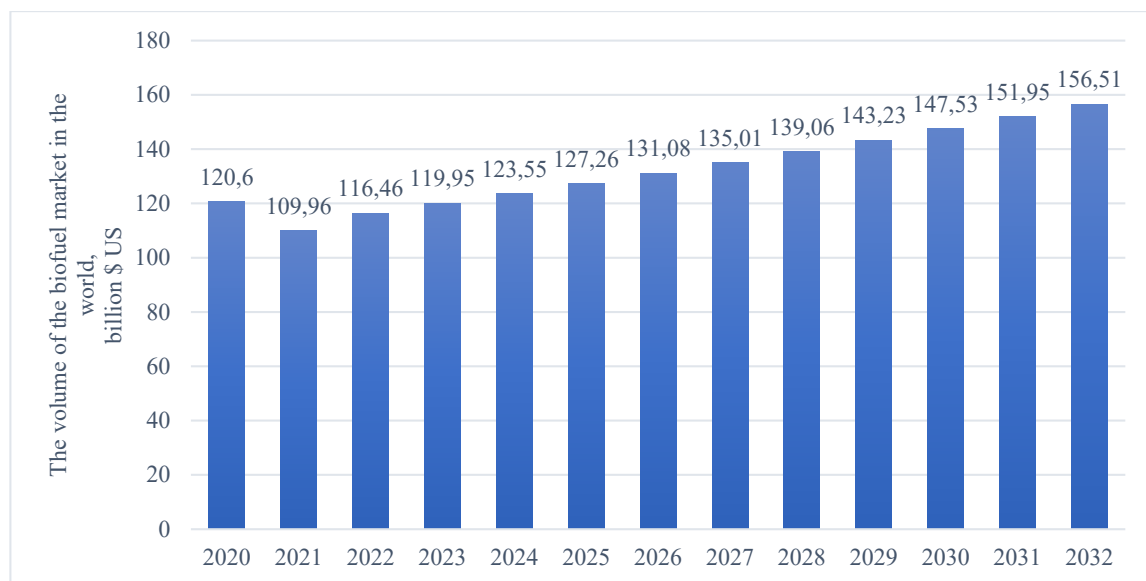


Figure 12: Global Biofuel Market Volume

According to analytical data, the highest growth of the biofuel market in the period from 2021 to 2030 will be observed in the Middle East and Africa, which will amount to 9.6%. At the same time, Europe is expected to have the lowest average annual growth rate within four percent compared to other regions. Figure 13 shows the average annual growth rate of biofuels in the world by region.

The current policy of the European Union in the field of biofuel production and consumption is aimed at developing second-generation biofuels, that is, fuels that can be obtained from biomass of non-food origin, as well as overcoming market barriers and improving logistics systems. At the same time, the production of biofuels must be organized so as not to cause significant damage to the environment, not to create competition with the production of food and not to endanger biodiversity. The

organization of this production is concluded in three main European research projects (Sustainable Development Goals Report (European Commission)), such as:

1. Bioethanol for Sustainable Transport project to study the replacement of gasoline and diesel fuel use with bioethanol through the mass introduction of vehicles and distribution stations running exclusively on bioethanol fuel in 10 cities and/or regions.
2. Project "Biogas as vehicle fuel" (Biogasmax), aimed at investigating the technical reliability, economic efficiency, environmental and social advantages of biogas fuel compared to petroleum fuel, as well as large-scale demonstrations and expansion of the biogas fleet.
3. The project "Demonstration of second-generation vegetable oil fuel in engines with improved characteristics" (2ndVegOil), aimed at preparing a set of actions to prepare the soil for its large-scale use for second-generation vegetable oils, including straw, perennial grasses, cake and jatropha in modified engines, including hybrid engines.

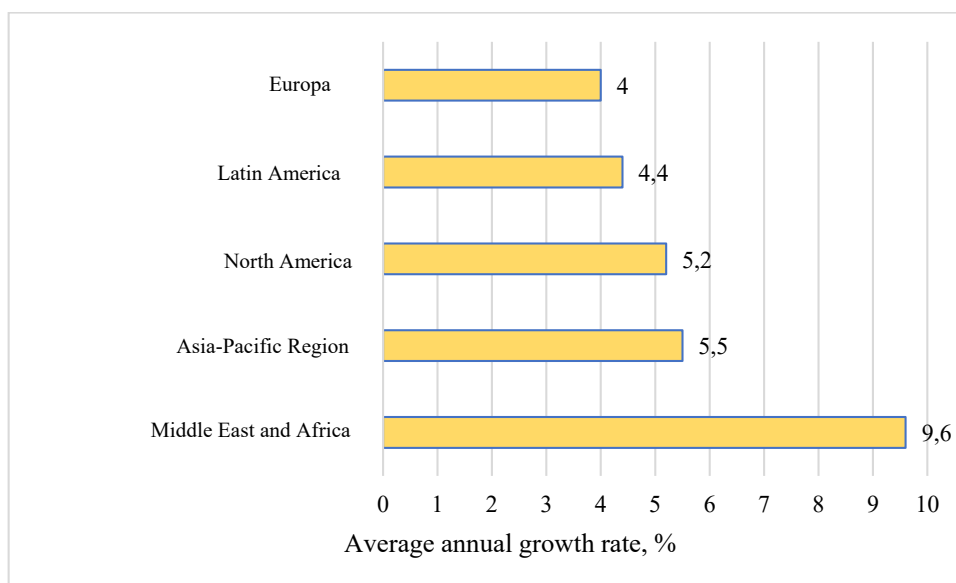


Figure 13: Average annual growth rate of biofuels in the world by region

The development of fuel quality standards for each type of fuel, which are being developed by the European Normalization Committee, is also important for market development.

Biofuels are sold as an alternative to petroleum-based motor fuels produced from petroleum feedstocks. The most common representatives of renewable fuels are ethanol and biodiesel produced by distillation or processing of raw materials such as grain crops, vegetable oils and cooking fats.

Biodiesel is a renewable energy source used as fuel in diesel engines, obtained from plant and animal extracts by transesterifying them with alcohols. Although biodiesel is currently widespread in many industries, the predominant sector with a high percentage of biodiesel use is the automotive and truck industry. This is primarily due to the fact that biodiesel is a completely environmentally friendly substitute for petroleum diesel fuel, as it is well compatible with the diesel engine, which does not require any functional or technical changes. Figure 14 shows the total production of biodiesel worldwide from 2010 to 2027. It is expected that the biodiesel market could reach \$144.8 billion by 2028 with an average annual growth rate of 4.21% from 2023 to 2028.

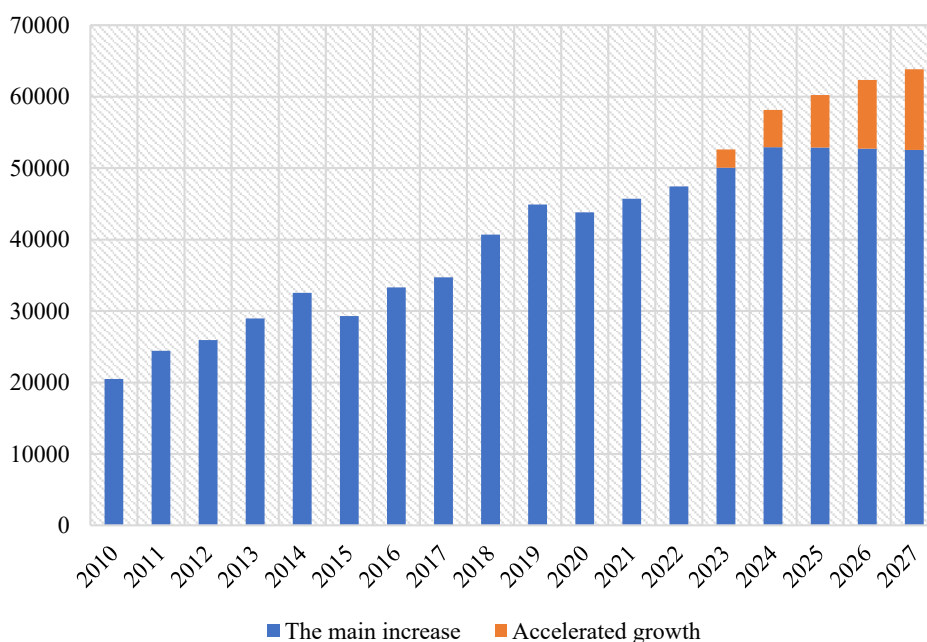


Figure 14: Total Biodiesel Production in the World, 2010-2027.

Growing demand and increasing consumption of biodiesel will be the main factors driving the growth of the global biodiesel market. However, trends in fuel consumption and political changes in emerging economies play a significant role in changing the biodiesel market. Traditionally, the U.S., Brazil, Indonesia, China, and Thailand have been the largest consumers of biodiesel, primarily due to environmental policies aimed at reducing greenhouse gas emissions (IEA Report (2021)). Figure 15 shows a chart of biofuel demand by fuel type and region for the period from 2021 to 2022.

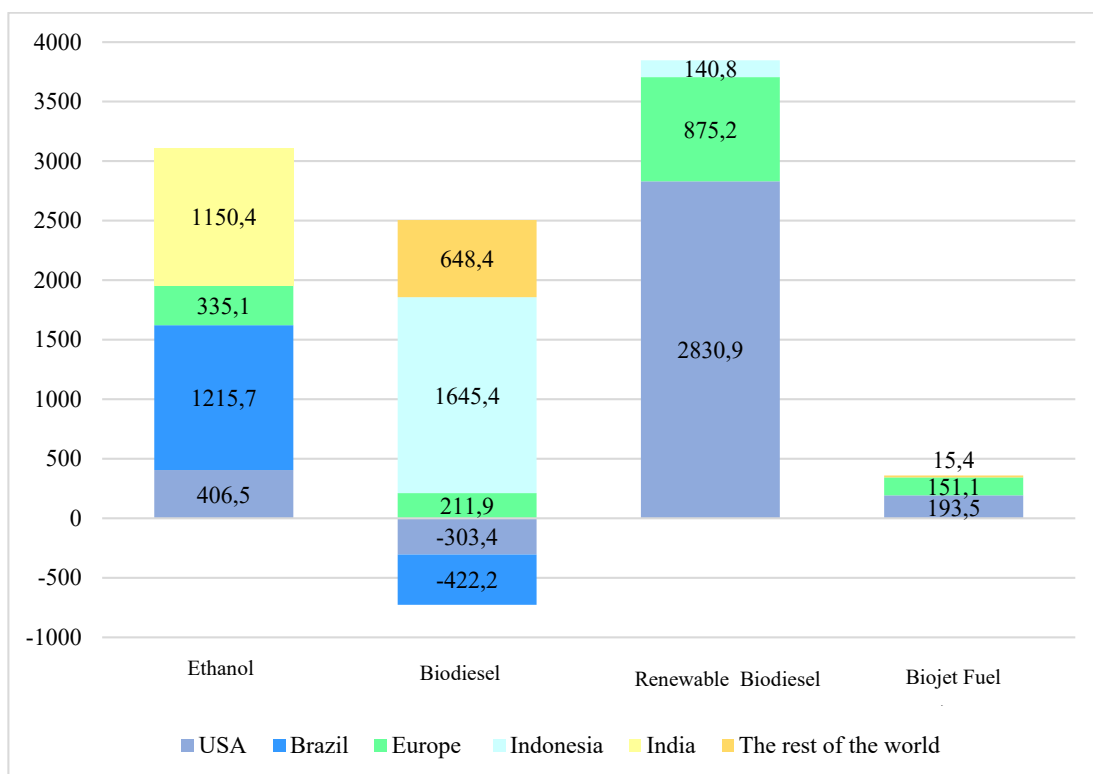


Figure 15: Demand for biofuels by fuel type and region, 2021-2022.

As can be seen in the United States as well as in Brazil, demand for biodiesel has been quite low over the period. The decline in demand in Brazil is primarily due to price and market changes in the biodiesel market. Brazil's National Petroleum Agency lowered its greenhouse gas emissions targets for the transportation sector by 50% in 2020 due to fuel supply problems caused by the effects of the COVID-19 pandemic, and also reduced the mandate for blending biodiesel with petroleum diesel from 13% in 2021 to 10% due to rising biodiesel pricing and costs. In Brazil, however, the biodiesel market is expected to stabilize and the overall consumption of ethanol and biodiesel is expected to increase further due to the desire to reduce oil imports and increase the use of local resources.

The decline in demand for biodiesel in the U.S. is due to a decline in support for the sector. This is primarily due to the fact that the main investment is in renewable diesel due to attractive policies. Renewable diesel, unlike biodiesel, is made from renewable raw materials, such as waste from the food and fisheries industries. Renewable diesel has the same chemical composition as fossil diesel and is therefore fully compatible with existing diesel engines. Biodiesel has a different chemical composition than fossil diesel, so blending is limited. The U.S. government has also launched a sustainable aviation fuel program, which aims to create 11 billion liters of green aviation fuel by 2030.

However, growth in ethanol and biodiesel production has remained steady thanks to demand in Latin America and Asia. In Asia, India's efforts to reach 20 percent blended ethanol by 2025 are supporting global ethanol demand growth, while Indonesia's plan to introduce B30, that is blending 30 percent biodiesel with petroleum fuels, planned for 2022, is driving biodiesel production expansion. The increase in biodiesel production in Indonesia is also linked to the national policy that provides significant financial support to biodiesel producers, which covers the gap between biodiesel and diesel prices.

In the European Union, total consumption of diesel fuel and gasoline declined during the period. At the same time the overall demand for biodiesel was also reduced due to the decline in the use of petroleum energy resources, as well as due to disruptions in the supply of palm oil, which is one of the main sources of raw materials for the production of biodiesel. At the same time the production of biodiesel from vegetable sources of raw materials will gradually decline, while the production of biodiesel from waste oils will gradually increase. According to analytical data (IEA Report (2021)) the European Union will reduce the share of global production by about 4%, but will also remain the largest producer of biodiesel in the world. Figure 16 shows a chart showing the overall picture of global biodiesel production and consumption by region for 2022.

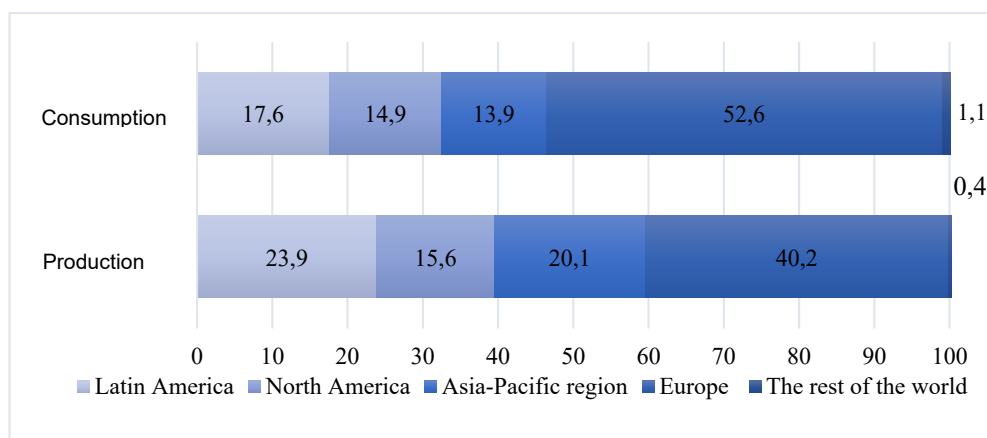


Figure 16: Global biodiesel production and consumption by region, 2022.

7.1 Overview of the Russian biodiesel market

Today, the main sector of consumption in the global energy market is occupied by fossil fuel sources. However, due to the implementation of support programs for the introduction of renewable resources as energy sources in foreign countries, the

market of renewable energy sources in global consumption is gradually growing. Figure 17 shows a diagram of global energy consumption by fuel.

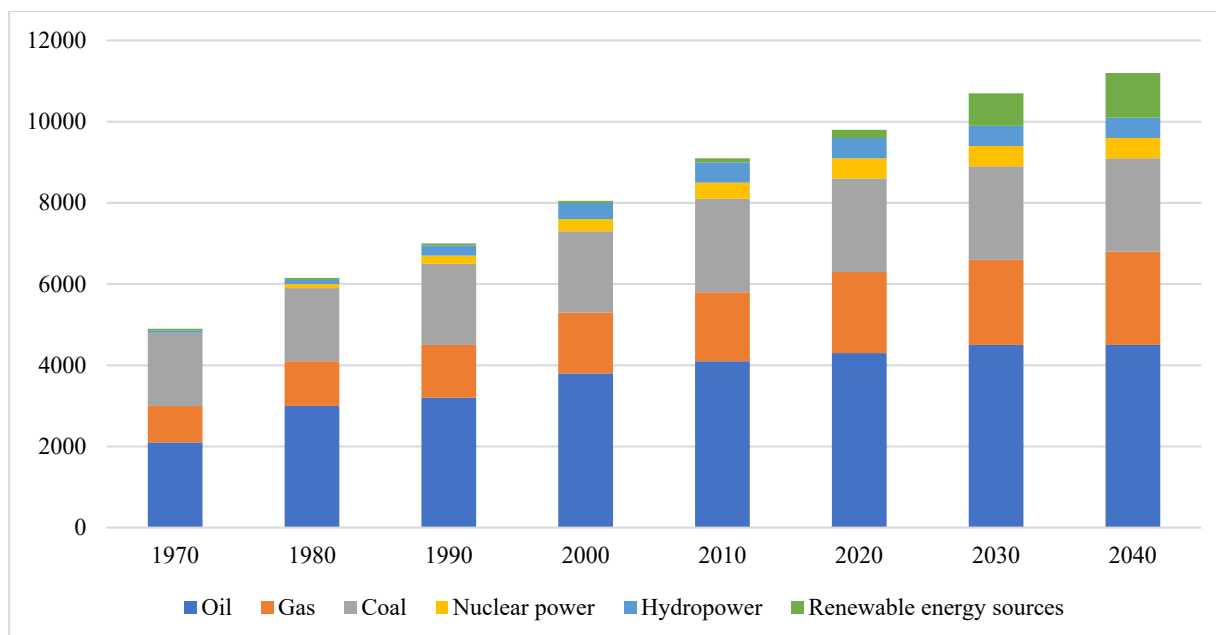


Figure 17: Change in World Primary Energy Consumption by Fuel, bln tonnes

In the Russian Federation, the main part of the energy consumption sector is occupied by fossil fuels, since the reserves of oil, gas and coal are quite large. For this reason, the development of the biofuel industry market is slow. The volume of the biodiesel market in 2021 was estimated at 2 615.9 tons (Kostuk L.V. 2011). At the same time, the share of liquid biofuels (bioethanol and biodiesel), according to analysts' calculations, is 0.3% of the total energy market.

The high price of oil has also not been an impetus for the development of the biofuel industry due to its low investment appeal. In addition, Russia lacks a legislative framework for biofuel production, including biodiesel production. It is necessary to introduce additional state support to attract both domestic and foreign investors to the sector. As measures of support tax privileges and credits, as well as reduction of customs duties on imports and exports of raw materials and products are considered. It is also necessary additional state support in the field of research projects not only for the production, but also for approbation of finished products in various regions of Russia, as at the moment there is no technology of biodiesel production, tested in various conditions, including the conditions of the Far North.

However, according to analytical data, the Russian Federation has sufficient resources to create a single cycle of biodiesel production and implementation. First of

all, a large amount of agricultural land allows the cultivation of oil crops necessary for biodiesel production. The most attractive raw material is rape, as it is quite undemanding to external conditions and has a fairly low value of acidity. Because of low capital investments, as well as lack of support for agricultural producers, rapeseed processing is not carried out on a proper level, which affects the low quality of raw materials for biodiesel production, which meets the current domestic standards, but exceeds the international standard DIN 51605 and makes this raw material unsuitable for export. The main measure to increase the cultivated area of rapeseed is proposed to reduce the economic pressure in the production and consumption of rapeseed as an oilseed crop, for example, the abolition of the export duty of 20%.

Stricter environmental requirements for petroleum diesel fuel, requiring a reduction in the concentration of sulfur, worsens the lubricating properties of the fuel. As a solution to this problem it is proposed to use biodiesel, which when mixed with diesel fuel will increase its lubricating ability due to the high concentration of fatty acid esters. The use of biodiesel in this case will avoid the use of expensive additives. To this end, the first steps were taken to introduce biodiesel at the legislative level, namely the introduction of the state standard GOST 52368-2005, which allows the presence of fatty acid methyl esters in diesel fuel up to 5% by volume. However, additional measures of state support for the use of this type of fuel, such as partial or complete abolition of excise duties, are necessary.

7.2 Calculation of economic effect when using a mixture of biodiesel and diesel fuel in a modified diesel engine

Economic efficiency from the use of a mixture of biodiesel with diesel fuel in the ratio of 5% biodiesel and 95% diesel fuel is determined on the basis of determining the costs of technical modernization of the diesel engine of the tractor unit (implementation of dual-fuel feeding system) with a subsequent comparison of the costs when the engine runs on 100% oil diesel fuel.

As input data we used the current values of the coefficients, tariff rates of tractor driver, the current cost of diesel and biodiesel fuel.

The efficiency from the use of new types of motor fuels for the diesel engine can be expressed by the formula (25):

$$\vartheta = \Pi_{\text{дт}} \frac{T_2}{T_1} \cdot \frac{P_1 + E_H}{P_2 + E_H} + \frac{(И_1 - И_2) - E_H \cdot (K_2 - K_1)}{P_2 + E_H} - \Pi_{\text{см}} \quad (25)$$

where $\Pi_{\text{дт}}$, $\Pi_{\text{см}}$ - reduced costs when using standard diesel fuel and a mixture of biodiesel and diesel fuel, respectively, rubles; T_1 , T_2 - annual loads of the tractor, hours; P_1 , P_2 - shares of deductions from the carrying value of the tractor, rubles; $И_1$, $И_2$ - costs of tractor operation, rubles; K_1 , K_2 - associated capital investments, rubles.

When new fuels are used, the associated capital investments K_1 are absent, K_2 represent the costs of constructive modernization of the engine to run on a mixture of fuels, and the parameters P_1 and P_2 are generally not determinative. Equation 26 provides a formula for calculating cost-effectiveness:

$$\vartheta = \frac{(И_1 - И_2) - E_H \cdot K_2}{P_2 + E_H} \quad (26)$$

Share of deductions from the book value of the tractor:

$$P_2 = \frac{1}{C_c} \quad (27)$$

where C_c - service life of the tractor before overhaul, years.

$$C_c = \frac{T_H}{T_\Gamma} \quad (28)$$

where T_H - operating time of the tractor before the overhaul, hours; T_Γ - annual operating time of the tractor, hours. According to the literature data T_H is 6000 hours, and $T_\Gamma = 1200$ hours.

$$C_c = \frac{6000}{1200} = 5 \text{ years}$$

$$P_2 = \frac{1}{5} = 0,2$$

The annual operating costs are determined by the dependence:

$$И = C_{\text{от}} + C + A \quad (29)$$

where $C_{\text{от}}$ - remuneration of the tractor driver, rubles; C - costs of fuel and lubricants, rubles; A - depreciation charges, rubles.

The remuneration of the tractor driver is determined by the following equation:

$$C_{\text{от}} = C_q \cdot K_1 \cdot K_2 \cdot K_3 \cdot K_4 \cdot K_5 \cdot T_{\Gamma H} \quad (30)$$

where C_4 is the tariff rate, which is 85.69 rubles/hour; K_1 is the coefficient that takes into account the grade increment; K_2 is the coefficient that takes into account the salary increment; K_3 is the coefficient that takes into account deductions for insurance premiums; K_4 is the coefficient for extra payments for products; K_5 is the coefficient that takes into account vacation pay.

For tractor drivers, according to the legislation, there is an additional payment for the planned output of 25-50%. We take this coefficient (K_4) to be 1.3. There is also an additional payment for quality work on time at the rate of 8% and extra payment for driving class (2nd class) at the rate of 10%.

According to the Tax Code of the Russian Federation, the employer must pay monthly insurance contributions on payments accrued to employees, insurance contributions are transferred to the following state funds (Labor code of the Russian Federation dated 30.12.2001):

1. Pension Fund of the Russian Federation - 22% of the payroll;
2. Federal Compulsory Medical Insurance Fund - 5.1% of the payroll;
3. Mandatory Social Insurance Fund - 2.9% of payroll on insurance contributions for compulsory social insurance against temporary inability to work and in connection with maternity and insurance contributions for compulsory
4. Social insurance contributions for compulsory social insurance against accidents at work and occupational diseases - 0.3% of payroll 0.3% of the payroll.

Thus, the total amount of insurance premiums will be 30.3% of payroll.

$$C_{OT} = 85,69 \cdot 1,1 \cdot 1,08 \cdot 1,303 \cdot 1,3 \cdot 1,1 \cdot 1200 = 227618,9 \text{ rub.}$$

The annual fuel consumption of a tractor diesel engine is determined in accordance with statistical data according to the equation:

$$A_T = G_T \cdot C_T \cdot T_{\Gamma H} \quad (31)$$

where G_T - hourly fuel consumption, kg/hour; A_T - fuel cost, rubles/kg

The cost of 1 kg of diesel fuel is 45.7 rubles. The cost of a mixture of biodiesel and diesel fuel will be:

$$C_{CM} = a \cdot C_{BD} + b \cdot C_{DT} \quad (32)$$

where $C_{\text{ДТ}}$, $C_{\text{БД}}$ - the cost of 1 kg of diesel and biodiesel, respectively, rubles/kg; a, b - the share of the components of the mixture: biodiesel and diesel. The price of biodiesel was taken on the basis of the market price of biodiesel in Germany, since biodiesel is not sold wholesale in Russia. The price of biodiesel was 27 rubles. Thus, the cost of the mixture will be:

$$C_{\text{CM}} = 0,05 \cdot 27,0 + 0,95 \cdot 45,7 = 44,8 \text{ rub/kg} \quad (33)$$

$$A_{\text{ДТ}} = 12,1 \cdot 45,7 \cdot 1200 = 663564,0 \text{ rub.}$$

$$A_{\text{CM}} = 10,7 \cdot 44,8 \cdot 1200 = 575232,0 \text{ rub.}$$

The depreciation charge is determined according to the dependence:

$$A = \frac{(B + C_{\text{MOD}}) \cdot E_{\text{H}}}{100} \quad (34)$$

There are no costs for upgrades according to the literature. Depreciation charges are the same for biodiesel and diesel and are as follows:

$$A_1 = \frac{1098700 \cdot 14,7}{100} = 161508,9 \text{ rub}$$

The annual operating costs will be:

$$И_{\text{ДТ}} = 227618,9 + 663564,0 + 161508,9 = 1052691,8 \text{ rub.}$$

$$И_{\text{CM}} = 227618,9 + 575232,0 + 161508,9 = 964359,8 \text{ rub.}$$

The annual economic effect will be given that the cost of modernization is absent:

$$\mathfrak{E} = \frac{(1052691,8 - 96151,3)}{0,2 + 0,147} = 254559,08 \text{ rub}$$

Thus, the annual economic effect of the implementation of a mixture of biodiesel and diesel fuel will be **254559.08** rubles per tractor.

However, the calculation was based on the market price of biodiesel in Germany. Due to the fact that abroad established production technology and there is a market for biodiesel, the market price was half the cost of biodiesel. In order to achieve a positive economic effect, the price of biodiesel in Russia should be at or below the selling price of conventional diesel fuel.

8 Evaluation of environmental efficiency of biodiesel production

To date, many developed countries have established strict standards for the reduction of toxic exhaust emissions into the atmosphere. In addition to environmental standards, the energy crisis has also influenced the development and research of ways to introduce technologies for the production of fuels from renewable and environmentally friendly energy sources in order to use them in carburetor and diesel engines without additional technical modernization. In European countries, measures have recently been taken to introduce and widely disseminate biological diesel fuels - esters of fatty acids derived mainly from vegetable oils. In tropical countries such as Malaysia palm oil is used as a vegetable source of raw materials, while in European countries rapeseed oil is common, and for diesel engines rapeseed-methyl esters (biodiesel) are used. In Russia, rapeseed is the most promising raw material for biodiesel production, as due to natural and climatic conditions it provides a fairly high yield of this crop.

Environmental impact assessment includes an assessment of the impact on the individual components of ecosystems associated with emissions and wastes.

8.1 Impact on the atmosphere

The comparative characteristic of atmospheric air pollution at each stage of biodiesel production compared to the use of conventional diesel fuel is presented in Table 7.

Name of emissions	Content kg/ton of fuel				
	Diesel fuel	Biodiesel			
		Growing	Obtaining oil	Using	Total
Carbon dioxide	2730	286	470	2250	2940
Carbon monoxide	125	13	46	30	89
Hydrocarbons	55	5,7	10,5	7,3	23,5
Nitrogen dioxide	35	3,6	5,2	54	62,8
Soot	15	1,5	-	4,5	6
Sulfur dioxide	4	0,4	-	0,7	1,1
Benz(a)pyrene (g/t)	0,175	0,02	-	0,31	0,33

Table 7: Comparative characteristics of emissions into the atmospheric air when using diesel fuel and when producing and using biodiesel

In general, the CO₂ emissions when using biodiesel are higher than for conventional fuels. Nevertheless, it must be kept in mind that for biodiesel the CO₂ cycle is cyclic or closed. It is a renewable resource, and the amount of CO₂ that is released into the

environment is compensated for by appropriate utilization by rapeseed plants during photosynthesis (Wicker R.J., et.al. 2021).

Thus, the combustion of biodiesel emits exactly the same amount of carbon dioxide that was consumed from the atmosphere by the plant, which is the original raw material for oil production during its entire life cycle.

Emission of carbon monoxide, hydrocarbons, soot, sulfur dioxide into the atmospheric air is significantly lower when using biodiesel. This is due to two circumstances. Firstly, the percentage of carbon and sulfur in rapeseed oil is lower than in diesel fuel. Secondly, the high oxygen content in biodiesel (10-12% of the mass), allows a noticeable reduction in atmospheric emissions of these harmful compounds due to more efficient combustion.

Application of biodiesel causes increase in emissions of nitrogen oxides and benzopyrene in relation to conventional fuel. This negatively affects, first of all, the formation of acid precipitation and photochemical smog.

Biodiesel has good lubricating properties, which makes it possible to exclude amide-based anti-wear additives from the fuel composition, thus reducing the content of nitrogen oxides in exhaust gas. However, the effect of reducing the content of nitrogen oxides in exhaust gases depends on the amount of biocomponent in biodiesel (which should exceed 20% in this case) and the modernization of the fuel system of vehicles (Mathew G.M., Raina D., Narisetty V. et. al. 2021). Also, improving the lubricity of the fuel mixture extends the life of the vehicle, increasing the time interval until the next maintenance.

8.2 Impact on components of the aquatic environment

According to a study by scientists (Mathew G.M., Raina D., Narisetty V. et. al. 2021), biodiesel, when released into water bodies, does not cause significant harm to organisms living in the aquatic environment because of its high degree of biodegradability. Microorganisms are able to process this type of fuel almost completely (up to 99%) in 28 days, which makes it possible to achieve almost complete minimization of damage to aquatic components of the environment. At the same time, the use of biodiesel as an additive to petroleum diesel fuel also increases the rate of its decomposition in case it gets into water bodies.

However, the main source of raw materials in the biodiesel cycle in Russia is rape, which is quite demanding to the chemical and mineralogical composition of the sown soils. In this regard, in order to achieve a high degree of crop yield in the conditions of growing crops in the Russian Federation it is necessary to use high doses of both macrofertilizers such as nitrogen, phosphorus, potassium and microfertilizers containing zinc, molybdenum and manganese.

Over time, fertilizers, through acidified soil, enter groundwater, which then feeds other water bodies, thereby increasing their concentrations of pollutant chemical components. One such element is phosphorus, which helps stimulate eutrophication of water bodies, that is, a decrease in oxygen concentrations and a consequent increase in nutrients. One example of eutrophication is algae blooms in aquatic environments, which results in a decrease in consumptive water quality and disruption of biodiversity. There may also be a decrease in the recreational potential of water bodies.

8.3 Impacts on soil ecosystems

Rape, as one of the main sources of raw materials for biodiesel production, can be grown only on fertile and well-structured soils with a sufficiently high content of micro- and macroelements. In this case, one of the conditions for a high degree of yield is a low soil acidity close to neutral.

To achieve the necessary conditions, producers of this crop resort to the use of various fertilizers that improve the chemical and mineralogical composition of soils. In this regard, there is an increase in concentrations of such elements as nitrogen, zinc and manganese, which negatively affect the enzymatic and microbiological activity of soil ecosystems.

The negative impact on the soil also includes its compaction, as rape refers to crops of intensive type of cultivation. This technology requires repeated passes of a tractor unit in order to achieve the required degree of compaction, which is 1 g/cm^3 . Compaction of the soil, in turn, leads to the blockage of pores through which water and oxygen flow, thereby negatively affecting the functioning of soil systems.

9 Conclusion

Biodiesel is an alternative fuel source, which is a full or partial replacement of diesel fuel, as it can be used in diesel engines without any modifications. Biodiesel production is basically reduced to the traditional process of transesterification of fatty acids with alcohols in the presence of homogeneous catalysts. At the moment, this is the main industrial-introduction scheme for biodiesel production.

In comparison with diesel fuel produced by the oil variant, biodiesel has a number of significant advantages, such as a high octane number, excellent lubricating ability, obtaining significant products in the pharmaceutical industry. The possibility of using raw materials of plant origin, as well as various wastes, makes biodiesel more environmentally friendly compared to conventional fuels. In addition, the combustion of biodiesel produces fewer emissions of carbon dioxide and hydrocarbons, and there are no sulfur dioxide emissions at all.

However, despite the environmental friendliness of the biodiesel production technology, the process is hampered by a number of negative reasons. One of them is the complexity of obtaining pure biodiesel. Since this product is in a complex multicomponent mixture, the separation stage cannot be formalized by a simple technological operation only. It is necessary to carry out a complex of measures to obtain complex esters of fatty acids of a given purity. First of all, the difficulty is to separate the homogeneous catalyst from the mixture. It is also necessary to separate the biodiesel and the byproduct of the process - glycerol. In case of incomplete separation under the influence of the remaining catalyst, a reverse decomposition of esters may occur, producing acids, which are strong corrosive agents.

Another reason is also the low chemical stability of biodiesel, which has a shelf life of only 3 months. The efficiency of biodiesel also decreases in the cold time. In this regard, research and development is needed to create an optimal production scheme and improve the quality of biodiesel that meets all the requirements of world standards. Despite the fact that the directions for solving the above problems have already been outlined and are gradually bringing positive results, this area of research remains relevant and requires increased attention.

Based on the analysis of scientific sources, the following conclusions were made and the following solutions were proposed:

Replacement of homogeneous catalysts with heterogeneous catalysts capable of exhibiting their catalytic activity over several synthesis cycles. The options under consideration include oxides of alkali earth and transition metals.

The possibility of using nanocomposites and polymeric materials as one of the constituent elements of the catalyst. These materials significantly increase the catalytic activity.

Development of an additional method for the synthesis of fatty acid esters. A promising direction is to conduct the process under supercritical conditions, using one of the reagents as a fluid.

Modification of the biodiesel production scheme using microreactors as the main reaction apparatus.

Finding the optimal model to make a predictive model of the biodiesel production process in order to select the working scheme of biodiesel separation and purification.

The result of the scientific part of the master's thesis was a diagram of liquid-liquid equilibrium of biodiesel fuel system: biodiesel + ethanol + residue (mainly glycerol). This diagram is a model of system behavior after biodiesel synthesis. It was found that to carry out the separation process of biodiesel and residual fractions, the content of fatty acid ethyl esters in the system should reach 50.5 %. This concentration is the minimum for transition of the system from homogeneous to heterogeneous state. In this case, the compiled prognostic model according to UNIFAC differs from the experimentally obtained because the theoretical model was built based on the properties of pure components, while the experimental model describes the properties of the system obtained directly after the synthesis and represents in fact a multicomponent system. In this connection, the diagram is presented for the system of ethyl ethers, ethanol, and the residual phase presented as a pseudo-component. For the phase equilibrium of this system, the traditional UNIFAC thermodynamic model is inadequate for modeling the liquid-liquid equilibrium boundary at various temperatures, since the system contains impurities that contribute to influence the establishment of equilibrium in the system.

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13 List of Abbreviations

FAE	Fatty acid esters
UNIFAC	UNIQUAC Functional-group Activity Coefficients
UNIQUAC	Universal Quasi-Chemical equation
NRTL	The non-random two-liquid model
IEA	International energy agency