Master Thesis

Emulsion properties of fatty acid esters in a biodiesel production process

Aleksandra Kazachenko

03/07/2023

Chair of Mining Engineering and Mineral Economics
Department Mineral Resources Engineering
Montanuniversitaet Leoben

A-8700 LEOBEN, Franz Josef Straße 18
Phone: +43 3842-402-2001
Fax: +43 3842-402-2002
bergbau@unileoben.ac.at

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.”

Abstract

This graduation research presents the description of producing biodiesel by transesterification reaction.

The characteristics of raw materials and reagents as well as as the qualitty of target and by products and their applications described. The fundamental chemistry laws and mechanism of transesterification reaction are presented, the main parameters affecting the process are described. Biodiesel separation and purification processes are studied.

In the scientific part the influence of the parameters on the formation and rate of the ether-water emulsion separation in a wet-washing process is studied. The optimal process conditions for ethyl esters of rapeseed oil are set as the mixing rate of 400-450 rpm and heating to the temperature of 40-45 °C.

The economic part provides an overview of the Russian and global biodiesel market. The life safety chapter considers accident prevention. The ecological part describes the impact of biodiesel production and usage on the environment.

The work consists of 82 pages, 24 figures, 5 tables and a reference list of 110 sources.

Zusammenfassung

Diese Abschlussarbeit präsentiert die Beschreibung der Herstellung von Biodiesel durch Umesterungsreaktion.

Die Eigenschaften von Rohstoffen und Reagenzien sowie die Qualität von Ziel- und Nebenprodukten und deren Anwendungen werden beschrieben. Die grundlegenden chemischen Gesetze und Mechanismen der Umesterungsreaktion werden vorgestellt, die wichtigsten Parameter, die den Prozess beeinflussen, werden beschrieben. Biodieseltrennungs- und -reinigungsprozesse werden untersucht.

Im wissenschaftlichen Teil wird der Einfluss der Parameter auf die Bildung und Geschwindigkeit der Ether-Wasser-Emulsionstrennung in einem Nasswaschprozess untersucht. Die optimalen Prozessbedingungen für Ethylester von Rapsöl werden als Mischgeschwindigkeit von 400-450 U / min und Erhitzen auf die Temperatur von 40-45 ° C eingestellt.

Der wirtschaftliche Teil gibt einen Überblick über den russischen und globalen Biodieselmarkt. Das Kapitel Lebenssicherheit befasst sich mit der Unfallverhütung. Der ökologische Teil beschreibt die Auswirkungen der Biodieselproduktion und -nutzung auf die Umwelt.

Das Werk besteht aus 82 Seiten, 24 Abbildungen, 7 Tabellen und einer Referenzliste mit 110 Quellen.

Table of Contents

1 Introduction

The main sources of energy nowadays are various fossil fuels: oil, coal, natural gas, etc. The demand for energy resources is steadily increasing along with population growth and the development of the automobile industry. At the same time the limited and non-renewable reserves of fossil fuels are decreasing every year. In addition, the reserves of combustible fossil fuels on the territory of the Russian Federation are now represented mainly by heavy oils, which have high viscosity and increased content of sulfur and other undesirable components, which reduces the yield of light products, complicates their extraction and noticeably increases the cost of fuels (Korshunov, Eremeeva and Drebenstedt, 2021).

Increasing demand for fuels, the need to develop new ways of obtaining light products from heavy oils and the limited resource base give rise to the need to search for alternative sources of fuels.

The scientific community has been working for decades on the idea of developing and introducing fuels from organic biomass, which would solve the issue of a limited resource base and allow the growing demand for vehicle fuels to be met. In addition, new fuels must meet current environmental requirements, have performance characteristics similar to conventional fuels for use in existing engine models, and be cost-effective to compete economically. One promising option to supplement or replace traditional diesel fuels in recent years has been the production of biodiesel, which has a wide range of advantages (Kondrasheva and Eremeeva, 2023).

Biodiesel is renewable, biodegradable, non-toxic, has a high flash point, better lubricating properties and is more environmentally friendly in comparison with conventional diesel fuel. Biodiesel has a high energy content like vegetable oils, while having higher volatility and lower viscosity, which is among the key characteristics of fuels used in diesel engines (Kondrasheva N. K., 2018a).

Biodiesel is a renewable, biodegradable liquid fuel produced from plant raw materials, animal fats and other reproducible organic resources. This type of fuel received its name due to the combination of such characteristics as its production

from biomass and the presence of performance indicators, the most consistent with the properties of traditional diesel produced from fossil fuels.

Biofuels are created as an alternative to fossil raw materials, which is due to a number of economic factors and the peculiarities of the resource base.

Over the years of research, many types of biofuels and methods have been developed, such as pyrolysis, the supercritical fluid method, and transesterification. Transesterification is the most commonly used method among all these methods, in which biodiesel and glycerol are obtained from oil (Kondrasheva and Eremeeva, 2023).

Biodiesel is more developed compared to other types of biodegradable fuels due to the possibility of using it in existing engine models. The development of biodiesel production is at the initial stage, so now this fuel is used rather in the form of an environmentally friendly additive to conventional diesel. Most often biodiesel is used in the form of an admixture to diesel fuel in the amount of up to 20% wt.%, such blends are labeled as "B0-B20". Pure biodiesel B100 is used less frequently.

Compared to petroleum diesel, biodiesel reduces carbon buildup, especially in older engine models, has lower greenhouse gas emissions, which is in line with the international environmental agenda and helps to combat the carbon footprint. Biodiesel is free of sulfur and other undesirable heterogeneous impurities that are harmful to equipment and the environment, but prolonged contact of fuel type B100 with rubber parts of engines is undesirable. Another advantage is the higher cetane number, which is a leading indicator for fuels used in engine systems operating on the principle of self-ignition of fuel at compression.

The object of the study in this paper is the production of biodiesel by transesterification reaction.

The subject of the study is the influence of various parameters on the yield of biodiesel in the process of transesterification of fatty acids with alcohols in the presence of an alkaline catalyst.

The aim of the study is to increase the yield of biodiesel in the transesterification reaction by selecting the optimal parameters of the wet cleaning process.

Research Objectives:

1. Analysis of existing raw materials for biofuel production
2. Study of options for the process of obtaining biodiesel by transesterification
3. Analysis of catalysts used in the transesterification process
4. Study of the main factors influencing the conduct of the reaction
5. Evaluation of modern methods of separation and purification of synthesis products
6. Study of the emulsion properties of fatty acid esters during water washing
7. Selection of optimal parameters of biodiesel purification

2 Biodiesel production basements

The fuel obtained from biomass through the conversion process is called biofuel. In turn, the term biomass refers to non-fossil biodegradable organic materials derived from plants, animals and microorganisms, gases and liquids released from their decomposition. It also includes by-products, residues and wastes from agriculture, forestry and related industries, as well as non-fossil and biodegradable organic fractions of industrial and municipal waste. Consequently, biofuel is any hydrocarbon fuel that is produced from living organic matter or once living material in a short period of time (days, weeks or even months). Biofuels can be seen as a way of providing energy security that replaces fossil fuels, the availability of which is limited, as well as an environmentally friendly fuel, since biomass is considered a carbon-neutral or greenhouse gas-neutral fuel.

Biofuels are fuels derived from biological and renewable sources such as vegetable oils, animal fats, as well as biomass and agricultural waste. It differs from traditional petroleum fuels in that its production and use has a lower environmental impact.

Biodiesel is a type of biofuel that is produced by the transesterification reaction of fats and oils. It has similar properties to diesel fuel and can be used in diesel engines without the need to change the engine design.

2.1 Feedstocks

Biodiesel opens wide prospects for the use of various types of organic raw materials in the production cycle. The selection of the type of feedstock depends on many factors, including the economic development of the country, climatic conditions and the geographical location of the country. It is important to keep in mind that the right choice of feedstock will reduce production costs.

In order to organize the available knowledge, the existing types of biodiesel were divided into several generations according to the type of organic matter from which it is synthesized:

The first generation includes biodiesel derived from food oil crops. Examples of the first generation raw materials are rapeseed, sunflower, palm oil and food

waste. This type of raw materials served as a promising option to replace petroleum diesel due to the renewability of the raw material base, ease of growing and wide availability. However, with the growth of biodiesel consumption there was a need to increase the area of arable land, and there was competition between biodiesel production and food oils. Food security issues have led to a search for other types of raw materials.

The second generation of raw materials were inedible oil crops, animal fats, whole plant tissues, agricultural residues and wood wastes. Examples of such raw materials are jatropha, maduca, salmon oil, tobacco seeds, jojoba oil, sea mango, waste cooking oils, beef fat, and pork tallow (Ambat, Srivastava and Sillanpää, 2018). Their advantages over first-generation raw materials are that cultivation of these types of plants requires less land, allows mixed crops to be grown, solves the problem of conflict with food production, and also allows recycling waste from other industries, which makes second-generation oils more environmentally friendly(Chimezie *et al.*, 2023). However, waste oils contain large amounts of free fatty acids, and the high concentrations of saturated fatty acids in animal fats make transesterification difficult. For vegetable oils with high fatty acid content, the introduction of raw material preparation steps is necessary, and the processing of animal fats requires preheating at 45°C. On the other hand, high concentrations of saturated fatty acids provide a more stable biodiesel with a high cetane number (Das, Ghatak and Mahanta, 2023).

Microorganisms and microbial oils are considered to be third-generation raw materials. The main examples of these raw materials are autotrophic and heterotrophic microalgae, yeasts, fungi, and bacteria for oil production (Cercado, Ballesteros and Capareda, 2018). Microalgae are promising as a new source of biodiesel, capable of producing four different types of biofuels: biohydrogen (through direct photoproduction), methane (through anaerobic digestion), crude bioleum (through thermochemical conversion) and biodiesel (from microalgal oil) (Athar and Zaidi, 2020). Microalgae are proposed to be used as a substitute for soil oil crops due to their higher oil productivity, lack of competition with the food industry and more environmentally friendly growth process (Maroušek *et al.*, 2023). Microalgae are capable of synthesizing and accumulating lipids in an amount of 30 to 70% of

their dry weight (Yaashikaa *et al.*, 2022a). However, the production of microalgae requires a large amount of natural light.

Another criterion for classifying raw materials for biodiesel production is the content of free fatty acids (FFA):

Excessive amounts of FFA can interfere with biodiesel production, for example through saponification reactions (Hájek *et al.*, 2020). Thus, raw materials can also be classified on the basis of their FFA content:

- Group 1: up to 1.5% FFA (soybean, rapeseed and palm oils);
- Group 2: FFA content less than 4% (vegetable oils, lard and poultry fat);
- Group 3: more than 20% FFA (animal fats and lubricants)(Gaurav *et al.*, 2019).

Feedstocks with FFA content less than 2.5 wt% are the most profitable source of biodiesel, since FFA content above this value usually requires pretreatment, which increases the production costs (Babadi *et al.*, 2022).

2.2 Biodiesel standarts

Biodiesel produced for use in engines as a mixture with petroleum diesel or in its pure form must have characteristics that meet established standards. The first normative documents defining the quality of biodiesel were created on the basis of already existing standards for diesel fuel.

In 2002, the American Society for Testing and Materials ASTM International adopted the first standard defining requirements for biodiesel ASTM D6751. A year later, the EN 14214 standard was approved in Europe. These documents are the basis for all existing specifications for biodiesel used in the world.

The approaches to the U.S. and EU biodiesel standards differ. In the U.S., ASTM D6751 establishes specifications for biodiesel, which will later be used as an additive to distillate diesel fuel. ASTM has published two automotive standards for biodiesel/diesel blends:

- ASTM D975, since 2008 it is possible to add up to 5% biodiesel;
- ASTM D7467 - Specification for biodiesel blends from B6 to B20.

The European standard EN 14214 is more narrowly focused and applies only to fatty acid methyl esters (FAME). Unlike ASTM D6751, B100 conforming to this standard can be used in a diesel engine without additives (if the engine is adapted to run on B100) or blended with diesel fuel to produce a blend in accordance with EN 590 or other applicable standards. A number of changes have been made to EN14214:2012, including an expansion of the scope of heating oil and updates for blends to B10. An additional set of climate classes based on monoglyceride content has also been established.

Biodiesel and diesel blends up to B7 are subject to EN 590. EN 16709, introduced in 2015, applies to B20 and B30 blends for use in vehicle fleets. The MEJK specified in EN 16709 must comply with EN 14214 and the diesel component with EN 590.

In the Russian Federation the quality of biodiesel is regulated by GOST 33131-2014, which defines technical requirements for blends of biodiesel with petroleum diesel B6-B20 (the number denotes the volume content of biodiesel in the fuel). The standard is based on U.S. and EU regulations. The base biodiesel component used in the blends meets the requirements of ASTM D 6751-15a and the light or medium biodiesel component meets the requirements of ASTM D 975-156.

The main requirements for the quality of biodiesel blends B6-B20 in accordance with the current standard are shown in Table 1.

Table 1. Requirements for B6-B20 mixtures according to GOST 33131-2014

Property specification, units	Test method	Limits
Acid number, mg KOH/g	GOST 32327	0,3
Kinematic viscosity at 40 °C, mm /s^2	ASTM D 445-15	1,9-4,1
Flash point, °C, minimum	ASTM D 93-15	52
Cetane number, minimum	GOST 32508	40
Water and sediment content, % vol.	ASTM D 2709-96 (2011)e1	0,05
Oxidation stability, h, minimum	EN 15751:2014	6
Biodiesel content, % vol.	GOST 33077	6-20

2.3 Chemical basement

The method for producing biodiesel is based on a transesterification reaction in which fatty acids contained in vegetable oils or animal fats react with methanol or ethanol. The result is fatty acid esters, which form the basis of biodiesel, and the byproduct glycerin.

Figure 1 shows a diagram of the transesterification reaction (alcoholysis) of fats. Lipids of plant or animal origin are esters of glycerol and fatty acids, which are transesterified into methyl or ethyl esters of fatty acids and glycerol as a result of interaction with alcohol.

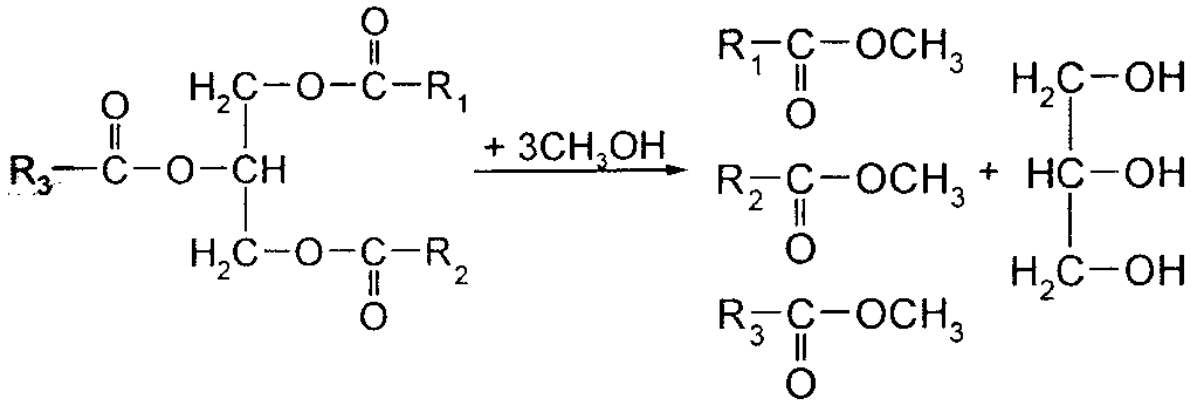


Figure 1. Reaction of transesterification (alcoholysis)

The chemical formula of biodiesel depends on the starting materials used. The general formula for esters of methanol or ethanol with fatty acids can be represented as R-O-CO-R', where R is a methyl or ethyl radical and R' represents unsaturated or saturated fatty acid residues, usually derived from plant or animal sources respectively.

The reaction can be carried out in the presence of an alkaline or acidic catalyst, as well as using enzymes. Each type of catalyst has its own characteristics. Alkaline catalysis is considered the most effective, but if the feedstock contains free fatty acids, a side reaction of saponification of fats - alkaline hydrolysis of free fatty acids to form their salts, also called soaps (Fig. 2) may occur.

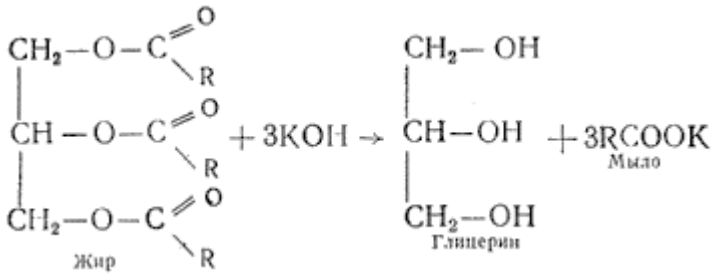


Figure 2. Saponification reaction of fats

The reaction of formation of salts of higher carboxylic acids is possible in the presence of water in the reaction mixture. The resulting soaps lead to the formation of stable emulsions, dramatically reducing the yield of the target product (Demirbas,

2008; Enweremadu and Mbarawa, 2009). Therefore, if the raw material contains a large amount of fatty acids, pretreatment of raw materials with sulfuric acid is used or acid catalysis is resorted to. In more detail the influence of catalysts on the process is considered in a separate chapter.

The reaction produces the target component, fatty acid esters, and the main byproduct, glycerol.

2.4 Catalysts

In general, three categories of catalysts are used to produce biodiesel: alkalis, acids, and enzymes (Nježić *et al.*, 2023).

Alkaline catalysts include sodium hydroxide (NaOH), sodium hydride, potassium hydroxide (KOH), potassium methoxide and others, while acidic catalysts can be phosphoric, organic sulfonic, sulfuric or hydrochloric acid. For biodiesel production, NaOH and KOH are most commonly used as catalysts. Alkaline and acid catalysts include homogeneous and heterogeneous catalysts. Because of the low cost of raw materials, sodium hydroxide and potassium hydroxide are commonly used as alkaline homogeneous catalysts, and alkali-catalyzed transesterification is most commonly used commercially (Zahan and Kano, 2018).

These materials are the most economical because the alkali-catalyzed transesterification process is carried out at low temperature and pressure, and the conversion rate is high without intermediate stages. However, alkaline homogeneous catalysts are highly hygroscopic and absorb water from the air during storage. They also form water when dissolved in an alcoholic reagent and lead to saponification side reactions that drastically reduce the yield of the reaction (Joshi, Gogate and Suresh Kumar, 2018). Therefore, they should be handled properly.

On the other hand, solid heterogeneous catalysts can be quickly separated from the product by filtration, which reduces the need for washing (Bet-Moushoul *et al.*, 2016). In addition, solid heterogeneous catalysts can catalyze transesterification and esterification reactions of feedstocks with high FFA content by omitting the preesterification step (Elgharbawy *et al.*, 2021). However, when a solid catalyst is used, the reaction proceeds at a slower rate because the reaction mixture is a three-

phase system, which inhibits the reaction for diffusion reasons (Rajkumari and Rokhum, 2020).

Enzymes are another type of catalyst. The main type of enzymes used are lipases derived from various sources: bacteria, plants, fungi and animals. Enzymatic catalysts have recently become more attractive because they avoid soap formation and the purification process is easy to perform. However, they are less frequently used commercially due to longer reaction times and higher costs. Compared to enzymatic catalysts, alkaline and acid catalysts are more commonly used in biodiesel production (Khan *et al.*, 2020).

2.5 Main factors affecting on biodiesel production

There are several factors, mentioned below, that strongly influence the transesterification reaction in biodiesel production.

Alcohol molar ratio. The yield of the ester largely depends on the molar ratio of alcohol to triglyceride. This is one of the most important factors because it affects the conversion, which ultimately determines the production cost and yield of biodiesel. Typically in the transesterification process, 3 moles of alcohol are required to produce 1 mole of triglycerides to 3 moles of fatty acid esters and 1 mole of glycerol for the reaction. The increased ratio of alcohol to oil also increases the purity and yield of the biodiesel. But it is at a certain alcohol concentration that the maximum fuel yield is achieved. In addition, the molar ratio depends on the type of catalyst used. According to the data presented, most of the alkali-catalyzed reaction requires about a 6:1 M ratio of methanol: oil for biodiesel production (yield > 98 wt%), and this ratio is sufficient to break the fatty acid-glycerol bonds (Ishak and Kamari, 2019). However, a large excess of ethanol increases the solubility of glycerol in the reaction mixture, which makes it difficult to release and impairs the distribution of the catalyst between the ether and glycerol layers (Manaf *et al.*, 2019).

Concentration of the catalyst. The amount of catalyst required for the reaction depends on the type of catalyst chosen and on the content of free fatty acids in the feedstock. A large amount of fatty acids in the raw material (more than 1.5-2%) requires additional consumption of an acid catalyst to prevent saponification reactions.

The highest yields of FAEE are observed when using 1-1.5 % potassium hydroxide from oil mass. However, an increase in the concentration of the catalyst above 1.3 % is not economically feasible, since it does not lead to a significant increase in the degree of transformation, but entails additional costs associated with the cost of the catalyst and work on removal of excess alkali from the reaction medium at the end of the reaction. In addition, an increase in the amount of potassium hydroxide causes the formation of an emulsion, which increases the viscosity of the mixture and promotes the dissolution of FAEE in the glycerol fraction, preventing the separation of reaction products and reducing the yield of the final product (Mathew *et al.*, 2021).

The reaction temperature also strongly influences the yield of esters and the reaction rate. High temperatures reduce the viscosity of the oils, which leads to a high reaction rate as well as a shorter reaction time. The range of optimal temperatures is from 50 °C to 60 °C and depends on the type of oils or fats to be treated (Paul and Adewale, 2018).

Reaction time is also an important parameter in biodiesel production. The optimal reaction time has a decisive influence on the completeness of the reaction and the product yield. If the reaction is not given enough time, some of the oil may remain unreacted and ultimately reduce the yield of the ester, and if the reaction time is longer than normal, it leads to side reactions, such as saponification. The duration of the reaction is selected for each type of feedstock and process individually (Tebas *et al.*, 2021).

Stirring. Stirring is mandatory for a reaction, and its speed plays an important role in the formation of the final product. Higher stirring speeds produce homogeneous systems, while slower stirring results in a lower phase contact surface and a lower product yield. The mixing speed must also be selected individually depending on the reactants, reactor type, design and volume.

2.6 Biodiesel separation and purification

Product-reaction mixture separation and biodiesel purification is an integral part of production, regardless of the type of process chosen for the synthesis. In most cases, in the production of biodiesel, the glycerine phase is first settled and

separated, the alcohol is distilled off by fractional distillation, and then the purification is started.

After alcohol separation, the ether phase is washed to remove free glycerol residue, soap and catalyst residue. Also a necessary step is drying of biodiesel, which allows removing excessive moisture, the presence of which in biodiesel is strictly regulated (Atadashi, Aroua and Aziz, 2011).

Various types of biodiesel purification are currently used, but dry and wet purification remain the most common.

Wet cleaning is a simple liquid-liquid extraction process in which unwanted components are transferred from the ether phase to the aqueous phase. Distilled water or water with the addition of mineral acids can be used for washing. Acidified water allows the neutralization of the remaining alkaline catalyst.

Water washing is the most common method of biodiesel purification, since this method does not require the use of complex technological equipment or expensive reagents. The obvious advantages are the high efficiency of wet cleaning in the removal of glycerol and methanol, as well as the removal of catalyst residues, especially when using acidified solutions (Chozhavendhan *et al.*, 2020). The disadvantage of this method is the need for subsequent drying of the product, since the presence of water in biodiesel is strictly regulated by standards. As a result of washing, large volumes of water are formed, which must be disposed of (Vávra, Hájek and Skopal, 2018).

The dry purification method can be used as an alternative to wet purification because this method does not require the use of large amounts of water. Dry purification of biodiesel is based on the use of adsorbents such as ion exchange resins, silicates, etc. (Catarino *et al.*, 2020)

The advantage of dry purification is that there is no risk of water ingress into the fuel, continuous operation is possible, total production time is reduced, and the volume of wastewater is drastically reduced. The disadvantages of ion-exchange resins include their inability to remove methanol, and dry purification requires the use of additional equipment, which increases operating costs compared to wet purification. The adsorbents used in the process can be regenerated or used ad

hoc, which also increases production costs (Sandouqa, Al-Shannag and Al-Hamamre, 2020).

Membrane separation is a more modern way of separating biofuels, which was originally used in water purification. The membrane can be organic or inorganic. Because of their chemical and thermal stability, the latter type, especially ceramic membranes, are more suitable for use with organic solvents. The ceramic membrane in combination with liquid-liquid extraction provides a continuous cross-separation of triglycerides from the fatty acid methyl esters mixture. Advantages are high sodium soap and alcohol separation potential, simple and flexible operation, low energy costs, easy operation and scalability. Disadvantages are the need for membrane cleaning, higher cost of biodiesel production, lower productivity due to possible contamination.

2.7 Process flowsheet

In this section we consider the basic scheme of biodiesel production from rapeseed oil and ethyl alcohol in the presence of an alkaline catalyst.

The production scheme includes the following blocks:

1. Reactor unit;
2. Alcohol separation unit;
3. Separation and purification unit.

The schematic diagram of the biodiesel production unit is shown in Figure 3 (Zhang *et al.*, 2003).

Technological scheme of a continuous process catalyzed by alkali using primary oil (Fig. 2). The reaction was performed at a molar ratio of methanol to oil of 6:1, 1% sodium hydroxide (in terms of oil), 60°C and 400 kPa.

Fresh methanol, recycled methanol, and anhydrous potassium hydroxide were mixed before injection into the R-101 reactor by a P101 pump. The vegetable oil was heated in the E-101 heat exchanger before being fed into the R-101. After the reactor, the flow was directed to a T-201 methanol distillation.

In T-201 there was distillation of alcohol by vacuum distillation at temperature up to 150 °C, the obtained pure distillate was returned to the recirculation for mixing with

pure methanol. The lower flow was directed to the washing column T-301 after cooling in the heat exchanger E-201 to 60°C.

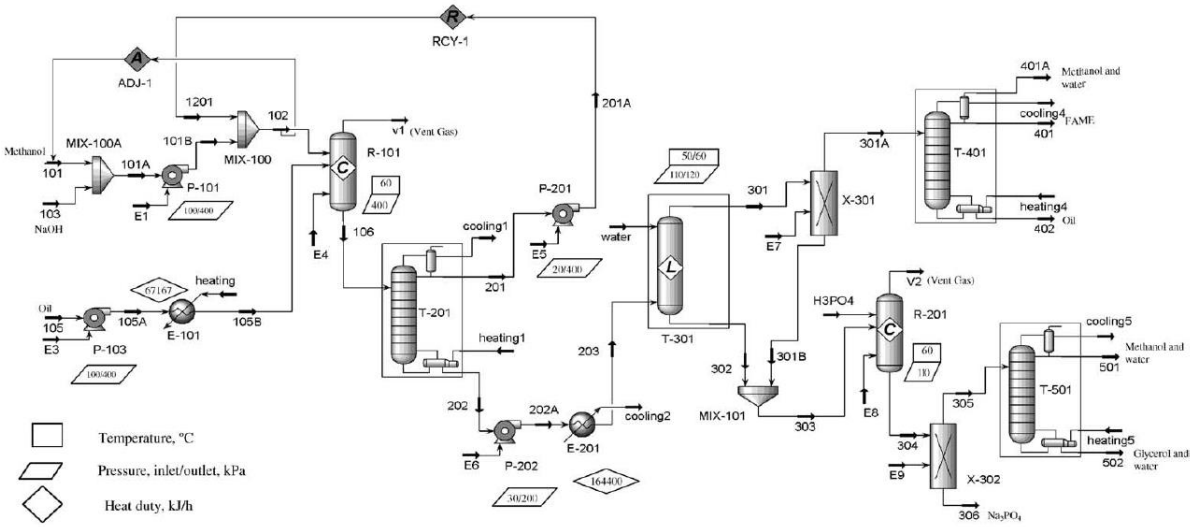


Figure 3. Schematic diagram of biodiesel production

The washing block is designed to separate MEJK from glycerol and residual alcohol and catalyst. The mixture in column T-301 was washed with water and separated into 2 phases. The FAME in the flow was separated from glycerol, methanol and catalyst by adding water (25°C). From the bottom of the column glycerol with water, methanol and catalyst residue was diverted.

A T-401 vacuum distillation column was used to produce a final biodiesel product meeting ASTM specifications (more than 99.6% purity). Water and methanol were removed as off-gases. The target product, FAME (99.65% purity) was obtained as a liquid distillate. The unreacted oil was diverted from the bottom of T-401 and after cooling was pumped to the rector for repeated transesterification.

The glycerol phase was purified from alkali in the R-201 neutralization reactor by addition of pure phosphoric acid. The resulting K_3PO_4 was removed in an X-302 gravity separator. The resulting potassium phosphate can be used as a valuable byproduct (e.g., fertilizer).

To obtain a glycerol byproduct of higher quality (approx. 92%), the stream was sent to T-501 for further removal of water and methanol by distillation.

3 Scientific research

3.1 Feedstocks

One of the main advantages of this alternative fuel is its potential to have a low carbon footprint (Devarajan *et al.*, 2022). Different countries have different primary biodiesel feedstocks depending on climate, environment, and major agricultural products (Elango *et al.*, 2019). For example, for rapeseed in Canada (Elgharbawy *et al.*, 2021), soybeans in the United States of America (USA) (Etim, Musonge and Eloka-Eboka, 2022), palm oil in Malaysia (Fadhil, Al-Tikrity and Ibraheem, 2019) And jatropha curcas in Nigeria (Falowo and Betiku, 2022) accounts for most of the biodiesel production, while European countries mainly use rapeseed and corn oils (Ganesan and Masimalai, 2020). In terms of global production, Indonesia and the United States were among the world's two largest producers of biodiesel, with 7.9 and 6.5 billion liters produced in 2019, respectively. The United States is expected to produce more than 1 billion gallons of biodiesel by 2025. After the approval of the Energy Policy Act of 2005, which provided tax incentives for certain energy sources, biodiesel production in the United States began to grow (Hadhoum *et al.*, 2022). It is estimated that by 2030, biodiesel could replace up to 7% of the world's total fossil fuels (Sales *et al.*, 2022; Zulqarnain *et al.*, 2021).

The initial production of biodiesel derived from agricultural products such as peanuts, soybeans and rapeseed has an impact on food production and the environment due to large amounts of arable land. In this first generation of biodiesel, all crude oil was derived from edible agricultural products such as soybeans, palm oil, and peanuts due to their ease of handling and great availability (Kumar *et al.*, 2020; Kumar, Singhal and Sharma, 2022; Noriega and Narváez, 2020). Meanwhile, second-generation biodiesel was produced using cellulosic substrates such as short-rotation trees, grassland plants, and waste products. Attempts to reallocate land to different types of crops to avoid competition with food resources remained relevant until the use of microalgae as a source of oil. Microalgae-based biodiesel can also be used to treat wastewater and to remove carbon dioxide from the air (Abo *et al.*, 2019). In addition, algae can be grown on any available surface, such as land, lakes, and oceans, and produce more triglycerides as a feedstock for

biodiesel production. The disadvantage of algae is that they are obligate phototrophs, indicating that they need light to survive.

The availability of oil sources is a critical factor in determining the economic viability of biodiesel production, as it accounts for approximately 80% of the total cost of biodiesel (Kumar *et al.*, 2020; Noriega and Narváez, 2020). Throughout the decade, various attempts have been made to find a source of inexpensive feedstock. Compared to standard fuels, oil from algae, vegetable oils, and animal fats has been demonstrated to be a source of biodiesel synthesis due to improved combustion, volatility, and viscosity characteristics. The amount of FFA and contaminants in biodiesel also affects the production technology used and the amount of fuel produced. Similarly, lipid residues such as waste vegetable oil and inedible beef fat have recently attracted much attention from the biodiesel industry. However, the discovery of new additional options that do not compete with food production is critical (Silviana *et al.*, 2022b).

Raw material costs make up the largest component of total production costs, and of these, the cost of feedstock for soybean oil is the largest factor, accounting for 80% of the total cost of production itself. These values are consistent with the results of other cost analyses of biodiesel production (Al-Saadi, Eze and Harvey, 2022). The significant contribution of feedstock costs to the cost of biodiesel underscores the potential value of low-cost alternatives to first-pressure vegetable oils in increasing the economic efficiency of biodiesel. Given this, it is more economical to produce biodiesel from crops selected for their high productivity and low cost requirements, or from low-cost feedstocks such as waste vegetable oil (Hadiyanto *et al.*, 2020) which is considered the most promising feedstock for biodiesel, despite its disadvantages, such as high FFA and water content. This study further confirms previous reports showing that the price of biodiesel is only compatible with fossil diesel when subsidy and tax exemption policies are implemented (Aghbashlo, Tabatabaei and Hosseinpour, 2018).

More than 95% of the feedstock used to make biodiesel comes from edible oils, the mass consumption of which leads to higher food prices. Competition with food makes edible oil not an ideal feedstock for biodiesel production because of the inevitable food shortage. The main advantage of edible oils is that the resulting

biodiesel typically has properties suitable for use as a replacement for diesel fuel, but they may not be sustainable sources (García-Martín *et al.*, 2018).

As a result, inedible oils or second-generation feedstocks become more attractive for biodiesel production and are guaranteed to be environmentally friendly feedstocks for biodiesel. Inedible oil plants can be grown on inedible land, and oils tend to be relatively cheap, affordable, and produce similar fuel yields and quality (Rocha-Meneses *et al.*, 2023).

Non-food oil resources have good potential to replace edible oil-based biodiesels in the near future. Microalgae offer a number of advantages that make them a potential feedstock for biodiesel production, such as fast growth rates, high yields, high oil content, no need for farmland or fresh water, and contribute to reducing greenhouse gas emissions. However, a major problem for industrial applications of biodiesel from algae is the high cost of the extraction process to extract the oil before turning it into biodiesel.

3.2 Biodiesel Production and Factors Affecting the Process

There are four standard primary methods by which feedstocks can be processed for use as a fuel substitute in diesel engines: 1) direct use of blended oils; 2) microemulsion of oils; 3) thermal cracking (pyrolysis) of oils; and 4) transesterification. All of these methods reduce the oil's viscosity, increase its resistance to oxidation, and increase its volatility to make it suitable for use as biodiesel (Mathew *et al.*, 2021). Currently, esterification is the most common method of producing biodiesel, while other approaches only produce a compound with lower triglyceride content (Maheshwari *et al.*, 2022). This paper considers the production of biodiesel by transesterification as the most common method of production.

Due to its effective viscosity reduction, transesterification is the most favorable method for biodiesel production (Liu *et al.*, 2021). Through transesterification, petroleum feedstocks and alcohols are catalyzed to form biodiesel (fatty acid alkyl esters) as the final product, along with the formation of glycerol as a byproduct (Nabgan *et al.*, 2022). After the separation process of both the byproduct and the final product, the excess alcohol is recovered and recirculated back to the first stage of the transesterification process. Transesterification uses alcohol, whereas hydrolysis uses water. Consequently, transesterification is also called alcoholism.

Methanol, ethanol, propanol, butanol, and amyl alcohol are the common alcohols used in this process (Manaf *et al.*, 2019). In the first stage of transesterification, triglycerides are converted to diglycerides, which are subsequently converted to monoglycerides followed by conversion of monoglycerides to glycerol (Kayode and Hart, 2019). At each step, three alkyl ester molecules are formed for each glycerol molecule. In general, this is an environmentally friendly process capable of processing a variety of petroleum feedstocks at moderate temperatures. Specific process parameters affecting the transesterification reaction are temperature, time, pressure, alcohol to oil ratio, concentration, catalyst type, stirring intensity and starting oil. The transesterification reaction can proceed with or without any catalyst, using primary or secondary single-atom aliphatic alcohols (Utami *et al.*, 2022).

There are several factors, mentioned below, that strongly influence the transesterification reaction in biodiesel production.

Alcohol molar ratio.

The ratio of alcohol to raw material is an important technological parameter influencing the equilibrium in the reaction system and the yield of the final product. The selection of the optimal ratio depends, among other things, on the type of alcohol selected for the process. When using ethanol instead of methanol, a higher alcohol:feedstock molar ratio is required to achieve optimum salinity. Some reports suggest that the optimum ratio for ethanol should be 9: 1. Using ethanol derived from sugarcane or soybeans would result in biofuel production entirely from renewable sources. This ratio was established after several experiments and was found to result in an incomplete reaction when the ethanol molar ratio is less than 6:1, and the 15:1 ratio causes problems in separating byproducts (Pooja *et al.*, 2021). For oil samples with high SFAs (free fatty acids), the alkaline catalyst is not conducive to the reaction, in which case an acid catalyst can be used to catalyze the reaction, but the alcohol concentration must be higher than when using an alkaline catalyst (Sahar *et al.*, 2018).

Catalyst concentration.

Different types of catalysts (alkali, acid, or enzyme) are known to be used in transesterification reactions, and the concentrations of each catalyst, i.e., their optimal value, must be carefully determined by titration to achieve the desired yield.

It has been reported that alkali catalyzes reactions at a higher rate than acid [32] (Sajjad *et al.*, 2022). Using an excessive amount of catalyst leads to increased soap formation, which ultimately reduces the final biodiesel yield.

The free fatty acid and water content affects the reaction to a greater extent because of the FFA and water content. For alkali-catalyzed alcohololysis, the oil samples used must have a FFA value less than unity, and all materials must be dehydrated (Nawaz *et al.*, 2023). In the case of higher FFA content (more than 1%), more base catalyst will be needed to neutralize the FFA. Water also inhibits the reaction by foaming and soap formation, resulting in increased viscosity. This soap wastes the available catalyst and reduces its efficiency, while foams and gels make it difficult to separate the glycerol. A study of the effect of FFA and water content on the alcoholysis of beef fat with methanol showed that the FFA and water content should be kept below 0.5% and 0.06% by weight of raw material, respectively, for the best conversion (Kumar, Singhal and Sharma, 2022).

The reaction temperature influences the reaction rate and the degree of conversion of the starting substances. Increasing the temperature has a positive effect on the speed of the process. However, it has also been found that if the temperature is increased beyond the desired range, it reduces the biodiesel yield due to saponification of triglycerides accelerated by the high temperature. To prevent alcohol evaporation, the temperature should generally be kept below the boiling point of the alcohol. The optimal temperature range is from 50 °C to 60 °C and depends on the type of oils or fats to be treated. In some cases, such as with supercritical methanol, a temperature of 350°C has been found to be optimal for the reaction (Paul and Adewale, 2018).

Biodiesel is inferior to petroleum diesel in viscosity, which reduces the geographical distribution and volume of biodiesel use in Russia due to the presence of climatic zones that require the use of Arctic brands of diesel with particularly low viscosities to prevent fuel solidification in engines at subzero temperatures. The quality of diesel engine operation at low temperatures depends on the ratio of bio-organic to petroleum diesel. Conventional diesel fuel and B5 blend in cold weather do not have significant differences in operation. It is possible to fight the crystallization of compounds in the fuel mixture by using additives that reduce the pour point (Kondrasheva N. K., 2017).

Another peculiarity of biodiesel is a limited shelf life. It is not recommended to store pure biodiesel for more than 2 weeks. However, following from this fact the need to develop small- and medium-tonnage regional fuel production for local needs will contribute to the redistribution of economic income between the regions of the country and provide additional jobs in the regions (Akram *et al.*, 2022).

Unfortunately, global consumption of biodiesel has been limited by two critical factors: the cost of production and overlap with food consumption (Rezania *et al.*, 2019). The cost of the catalyst, excess energy, catalyst removal, and biodiesel purification process accounts for 15-30% of total operating costs, with the remaining 70-85% coming from the cost of feedstock (Feng *et al.*, 2022). The high cost of biodiesel also hinders its commercialization. In countries with developed economies biodiesel is 1.5-3 times more expensive than fossil diesel fuel. Biodiesel production is expected to increase in the next few years because of its potential benefits for energy supply, farm expansion, economics, and pollution reduction (Julio *et al.*, 2022).

The main disadvantages associated with first-generation raw materials are food insecurity, water scarcity, soil degradation, deforestation and loss of biodiversity.

Biodiesel degrades with storage time, but it can be stored longer if used properly. The most influential factors affecting biodiesel storage include microbial contamination, storage material, feedstock types, and the nature of storage conditions such as exposure to light, oxygen, and temperature.

A common microbial contamination is the growth of certain bacteria and fungi in biodiesel tanks. The growth probably occurs at the fuel-water interface at the bottom of the tank. Therefore, the storage tank must always be clean and dry to prevent microbial contamination. In addition, an oxidative stability like biocides (commonly added to gasoline-diesel fuel) prevents microbial growth. The biodiesel storage tank or container should not be made of copper, lead, tin, zinc or aluminum, as these metals accelerate decomposition. The use of tin or aluminum injection molding for biodiesel storage has been shown to reduce the oxidative stability of biodiesel for a week (Isah *et al.*, 2022). Instead, a container made of steel, fluorinated polyethylene, fluorinated polypropylene, Teflon, or fiberglass is preferred. In fact, the presence of metals (acting as a catalyst) in biodiesel will cause

the metal-mediated initiation reaction to accelerate the formation of free radicals, resulting in a deterioration in the oxidative stability of the biodiesel. In addition to microbial attack and storage material, another cause of the latter is oxidation products, including various acids or polymers, which can cause deposits in the fuel system and lead to clogged filters and fuel system malfunctions (Saputra Nursal *et al.*, 2021).

Biodiesel containing large amounts of unsaturated methyl ester has a much higher decomposition rate. The report indicates that coconut biodiesel with a high concentration of saturated methyl ester may be more stable in long-term storage (Abomohra *et al.*, 2020; Baweja, Trehan and Kumar, 2021).

The nature of storage conditions is another factor leading to oxidative damage. Exposure to light, temperature, and oxygen (air) greatly affects the properties of fuel samples during long-term storage. Direct exposure to both air and sunlight greatly affected storage conditions because the release of free radicals from the ultraviolet radiation of sunlight and oxygen in the air rapidly accelerates the oxidation reaction and accelerates the decomposition of fuel during prolonged storage (Kumar, Singh and Srivastava, 2022).

To maintain stability, biodiesel should be stored in closed containers or stored after adding an antioxidant. As far as we know, many biodiesel producers store their biodiesel under pure nitrogen to prevent oxygen from entering the fuel.

Alcohols that can be used in the transesterification process include methanol, ethanol, propanol, etc. Among these alcohols, methanol and ethanol are the most commonly used. Methanol in particular is used because of its lower cost and physical and chemical advantages. Methanol can react quickly with triglycerides, and the alkaline catalyst is easily dissolved in it. However, because of its low boiling point, there is a great risk of explosion associated with methanol vapor, which is colorless and odorless. Both methanol and methoxide are extremely hazardous materials that should be handled with care. Care should be taken to ensure that humans are not exposed to these chemicals during biodiesel production. Raising biodiesel yields using less toxic alcohols is still a pressing issue (Etim, Musonge and Eloka-Eboka, 2022).

The price of biodiesel can vary greatly depending on the process used to produce it and the type of feedstock used in the process. Biodiesel costs about 1.5 times more than diesel fuel, depending on the source of the raw oils. 70-95% of the total cost of producing biodiesel comes from the cost of the feedstock (Li, 2022). For this reason, many biodiesel plants do not produce biodiesel throughout the year due to the lack of cheaper raw materials for economical biodiesel production. The high cost of biodiesel compared to petroleum-based diesel is a major obstacle to its widespread commercialization.

Biodiesel production costs range from $0.51/L and $0.98/L when using homogeneous and supercritical processes, respectively, for a waste vegetable oil-based biodiesel plant. The highest costs for supercritical production processes are associated with high energy costs for the process. Production of biodiesel using enzymes and biological catalysts tends to be more expensive than alkaline and acid catalysts because of the higher cost of enzyme catalysts (Velvizhi *et al.*, 2023).

Biodiesel treatment represents the last stage of biodiesel production and is one of the most environmentally expensive due to the generation of wastewater containing catalyst, glycerin, fatty acids, excess alcohol and emulsified water among other compounds. Such effluent must be treated before it is discharged into the environment. The biodiesel flushing and cleaning process should be efficient and generate as little waste to the environment as possible (Mohadesi *et al.*, 2019). Dry cleaning is a possible solution since no water is used in the process, in addition to being an economical process.

3.3 Separation and purification

The biodiesel purification process begins with gravitational precipitation of the glycerol phase followed by separation into ether and glycerol. In the process of transesterification the reaction-product mixture is separated into ether and glycerin phases. Due to the different densities of the ether and glycerol phases it is possible to perform separation by gravitational precipitation. However, this process requires a long time and can be difficult, especially when ethyl alcohol is used in the production scheme, as the emulsion formed during the reaction is more stable, and with excessive alcohol the solution may remain homogeneous and not separate by sedimentation. To reduce the time of the technological operation and to improve the

quality of separation of the mixture at this stage, the centrifugation process is used (Fayyazi *et al.*, 2021).

However, the degree of purification achieved by settling, centrifugation and decantation of biodiesel is not sufficient for the relevant standards, so the purification from glycerol continues in the following stages. The content of glycerol in the produced biofuel should not exceed 0.02% by mass of the finished product (Stojković *et al.*, 2014).

The separation and purification operations traditionally begin with the precipitation and separation of the glycerol phase. Further purification of the two phases is performed separately.

The peculiarity of biodiesel synthesis with alkaline homogeneous catalysis is the use of excess alcohol. According to the reaction equation, the molar ratio of alcohol:oil should be 3:1, but the esterification reaction is a reversible process. The introduction of excess alcohol into the reaction mixture is necessary to shift the equilibrium towards the products. After completion of reaction it is necessary to separate alcohol from reaction products, which is caused by technical and economic considerations. The alcohol is separated by fractional distillation, after which it can be reused in production. Alcohol recycling increases the economic sustainability of production (Rodriguez and Martinello, 2021). In addition, alcohol removal is necessary because the residual alcohol content in biodiesel should not exceed 0.2% according to ASTM standard.

Separation is more difficult in the case of ethanol rather than methanol because the resulting emulsion is very strong (Verma, Sharma and Dwivedi, 2016).

Increased alcohol content in the final product leads to increased wear of seals in the engine, corrosion of metal parts, reduces the ignition temperature and flash point. This creates additional difficulties during storage and transportation of the product. Alcohol reduces the quality of biodiesel fuel, degrading performance characteristics such as fuel viscosity and density.

Negative effects of excess alcohol in biodiesel include wear of natural rubber seals and gaskets when biodiesel is used in an engine. This would lower the ignition temperature of the final product, increasing storage, transportation and disposal problems. It would also reduce the viscosity and density of biodiesel and cause

corrosion of aluminum and zinc parts (Atadashi *et al.*, 2011). It has been tested that the flash point of biodiesel can drop from 170°C to less than 40°C, with only 1% residual methanol remaining in the resulting biodiesel (Suthar, Dwivedi and Joshipura, 2019). The alcohol concentration is a very important parameter that has a significant influence on the reaction yield and product quality. It is necessary to extract methanol efficiently, as it affects the unit cost of biodiesel production.

After alcohol separation, the ether phase is washed to remove free glycerol residue, soap and catalyst residue. Also a necessary step is drying of biodiesel, which allows removing excessive moisture, the presence of which in biodiesel is strictly regulated (Atadashi, Aroua and Aziz, 2011).

Various types of biodiesel purification are currently used, but dry and wet purification remain the most common.

Wet purification is the most primitive process, acidification with mineral acids allows the remaining alkaline catalyst to be neutralized. Cleaning at elevated temperatures improves the quality of the extraction. Stojković's studies compared purified castor oil ethyl esters by washing with water at different temperatures and pH. The best result was achieved at temperatures of 30 and 70 °C at pH 2 and 7, respectively (Stojković *et al.*, 2014).

The dry purification method can be used as an alternative to wet purification because this method does not require the use of large amounts of water. Dry purification of biodiesel is based on the use of adsorbents such as ion exchange resins, silicates, etc. (Catarino *et al.*, 2020)

Untreated biodiesel was treated with 4 wt% silicate adsorbent at 30°C after stirring for 60 min, the adsorbent was collected by filtration. However, a higher biodiesel yield was achieved by washing with water (96%) than by the process because some of the biodiesel remained in the column after purification. In this decalcification process, the protons of the resin functional groups are replaced by calcium ions of calcium soaps, glyceroxide, methoxide and hydroxide, which are believed to constitute the leached catalyst. Thus, removal of leached calcium occurs by adsorption into the cation-exchange resin (Catarino *et al.*, 2020). The advantages of dry purification are that there is no risk of water ingress into the fuel, but additional equipment is required, which increases the operating costs compared to wet

purification. The adsorbents used in the process can be regenerated or used ad hoc, which also increases production costs (Sandouqa, Al-Shannag and Al-Hamamre, 2020).

Membrane separation on a ceramic membrane combined with liquid-liquid extraction provides continuous cross-separation of triglycerides from a mixture of fatty acid methyl esters. The average pore size of the oil emulsion was determined to be 44 μm with lower and upper limits of 12 μm and 400 μm, respectively. Tubular ceramic membrane and ultrafiltration membrane represent these two membranes are more efficient and environmentally friendly in the purification process compared to other membranes (Sokač *et al.*, 2020). Advantages are the high potential of separation of sodium soap and alcohols, simplicity and flexibility in operation, low energy costs, ease of control and scaling, disadvantages are the need to clean the membrane, increasing the cost of biodiesel production, reduced productivity due to possible contamination.

The main factor limiting the use of biomass is the development of technologies for its separation, purification and transformation into biochemicals and biofuels. Inefficient separation and purification of biodiesel causes serious problems with diesel engines, such as clogging of filters, corking of injectors, increased amount of carbon deposits, excessive engine wear, seizure of oil rings, engine knocking, and thickening and gelling of lubricating oil (Saputra Nursal *et al.*, 2021).

The procedure of extraction and purification of FAEE can be carried out in two ways. The first one is the extraction of FAEE by vacuum distillation at a pressure of 100÷130 Pa and temperature 170÷220 °C without preliminary preparation, the second one is the classical method: sequential extraction, washing and drying of the product. The peculiarity of FAEE production and use of ethyl alcohol as transesterifying agent are difficulties of phase separation and separation of reaction products due to high solubility of FAEE in ethanol, which increases in the presence of low-molecular fatty acids playing a role of solubilizers in this case (Hájek *et al.*, 2020). In addition, FAEE have an extremely high ability to form emulsions in case of contact with water, therefore during washing water must be added slowly, and the mixture itself must be stirred with utmost care.

The chosen purification method influences some physicochemical properties of the obtained biofuel, in particular its resistance to oxidation. The FAEE content in the

samples obtained after vacuum distillation can reach 99÷100%, but the oxidation resistance determined by the Rancimat-method (Läubli and Bruttel, 1986) according to EN 14112, was only 1 h instead of the required 6 h. At the same time, FAEE purified by the traditional method met the standard requirements for resistance to oxidation, but their purity did not exceed 97 %. It is connected with the fact that during vacuum distillation natural antioxidants (tocopherols) which provide necessary oxidation stability of esters remain in the cube residue and are almost completely absent in the final product (Läubli and Bruttel, 1986). Therefore, immediately after obtaining the FAEE purified by vacuum distillation, some amount of antioxidants should be added to them beforehand to prevent premature oxidation.

The wet washing process requires large amounts of water to remove the remaining catalyst and clean the biodiesel, resulting in a significant amount of wastewater that must be handled effectively (Fayyazi *et al.*, 2021; Šalić *et al.*, 2020; Sokač *et al.*, 2020). This additional step in the biodiesel synthesis process increases the overall cost of production, making it uncompetitive compared to petroleum-based diesel production (Kumar *et al.*, 2020; Noriega and Narváez, 2020).

3.4 Future prospects of biodiesel production

The promising biofuel market is in the early stages of development, but its popularity is growing worldwide. The development of biofuels for large-scale commercialization is limited by technological and environmental challenges. However, lower production costs and subsequent market introduction has been presented as a key success factor (Bashir *et al.*, 2022). Bio-ethical socio-economic implications, food security, land use (habitat loss, less availability of land for food production, deforestation), regional sustainability (pressure on water supplies), biomass pretreatment and production technology are major sources of problems in biodiesel production and development. They exist in either the technical or political aspects of biodiesel development. Moreover, local problems and technical risks in development must be identified through modeling, economic analysis, and sensitivity analysis in each region because they depend on geography (Hosseinzadeh-Bandbafha *et al.*, 2022). In addition to reducing the effects of climate change, improving energy security, rural development and the transition to a low-carbon economy all contribute significantly to the development of biofuel production.

However, it must be emphasized that there is an urgent need to reduce commodity prices and improve the quality of biofuels, which combine non-terrestrial raw materials with traditional energy crops (Babadi *et al.*, 2022). Replacing conventional homogeneous (base) catalysts with heterogeneous catalysts, calcium-based catalysts, and dry-washing biodiesel purification are processes that contribute to the sustainability of biodiesel production (Selemani and Kombe, 2022).

It is critical to consider the importance of food safety and sustainability by developing biodiesel from unused non-food resources for a more sustainable future by reusing biowaste such as WTO and algae oil (Yaashikaa *et al.*, 2022b). This could offset concerns about potential greenhouse gas emissions from indirect land use changes associated with the production of biofuels from food raw materials that have not been identified. Biodiesel can reduce emissions of nitrogen oxides, CO, CO_2, polycyclic aromatic hydrocarbons (PAHs) and nitrated (Kondrasheva N. K., 2018b).

Germany produces more than half of the world's biodiesel and sells it at a lower price than petroleum diesel. Other countries, such as Brazil, the United States, Australia, Italy, Malaysia, and Austria, already use biodiesel. For example, Malaysia uses a blended fuel (5% palm oil and 95% conventional diesel) (Elgarahy *et al.*, 2023). Because of the high demand for energy due to the rapid growth of the world's population, biodiesel can be seen as one of the promising and environmentally friendly alternatives to liquid fossil fuels. The introduction of alternative fuels such as hydrogen, ethanol, and biodiesel will reduce the dependence of most countries on imported fuel sources. Thus, this trend is expected to positively impact current energy supplies to potentially switch from petroleum products (such as gasoline and diesel) to biodiesel in most countries that are striving to meet their sustainability and carbon emissions targets.

There is growing interest of industry and society in decarbonization through the use of biofuels, especially from non-food resources. It is important to determine public opinion, awareness and knowledge about biofuels in order to gain consumer approval in this regard. Decarbonization faces significant geopolitical challenges because it directly affects the current allocation of resources among countries. Significant technological advances and political agreements are needed to stimulate biofuels and agricultural technologies as well as research and development innovation and to move industry to the next level to minimize greenhouse gas

emissions while enhancing economic growth. Growing reliance on biofuels also requires continued support for research and development and policies to improve agricultural productivity, especially in developing countries (Pydimalla *et al.*, 2023).

A new approach in the field of raw materials is genetically modified plants to improve biomass characteristics, increase the yield of vegetable oil (lipid content) and even create new bioenergy crops needed for biodiesel production (Mathew *et al.*, 2021). The first genetically modified oil plants were corn and canola. This method of sustainable biodiesel production is one of the most promising because these genetically modified crops (GM crops) do not compete with food crops, while being able to produce a higher yield of vegetable oils (Jafarihaghighi *et al.*, 2022).

Pretreatment of acidic raw materials.

Many pretreatment methods have been proposed to reduce the high content of free fatty acids in oils, including steam distillation, alcohol extraction, and esterification by acid catalysis (Atadashi *et al.*, 2012). Acid catalyzed esterification makes the best use of the free fatty acids in the oil and turns it into biodiesel (Elgharbawy *et al.*, 2021). A common pretreatment is the esterification of FFA with methanol in the presence of acidic catalysts (usually sulfuric acid). The catalysts can be homogeneous acid catalysts or solid acid catalysts. Compared to the former, solid acid catalysts offer some advantages for eliminating separation, corrosion, toxicity, and environmental concerns, but reaction rates are lower (Jisieike *et al.*, 2023).

As described earlier, the free fatty acids will be converted into biodiesel by direct acid esterification, and the water must be removed. If the acidity of the oils or fats is very high, pretreatment by one-step esterification may result in an ineffective reduction of the FFA due to the high water content produced during the reaction. In this case, a mixture of alcohol and sulfuric acid can be added to the oils or fats three times (three-step pre-esterification). The time required for this process is about 2 h, and the water must be removed with a separating funnel before adding the mixture to the oils or fats for a second esterification (Adama, Aluyor and K, 2021) . Furthermore, some researchers reduce the percentage of FFA by using acidic ion exchange resins in a compacted bed. Strong commercial acidic ion exchange resins can be used to esterify FFA in waste cooking oils, but loss of catalytic activity can be a problem (Elgharbawy *et al.*, 2021). An alternative approach to reducing FFA is to use iodine as a catalyst to convert free fatty acids into biodiesel. The obvious

advantage of this approach is that the catalyst (iodine) can be recycled after the esterification reaction. Under optimal conditions (i.e., amount of iodine: 1.3 wt.% oils; reaction temperature: 80°C; ratio of methanol to oils: 1.75:1; reaction time: 3 h) the SLC content can be reduced to <2% (Atadashi *et al.*, 2012).

Another new pretreatment method is to add glycerol to the acidic feedstock and heat it to a high temperature of about 200 °C, usually using a catalyst such as zinc chloride. The glycerol reacts with the FFA to form monoglycerides and diglycerides. Then the FFA level becomes low, and biodiesel can be produced using the traditional alkali-catalyzed transesterification method.

The advantage of this approach is that no alcohol is required during pretreatment, and the water resulting from the reaction can be immediately evaporated and removed from the mixture. However, the disadvantages of this method are its high temperature requirements and relatively low reaction rate (Selemani and Kombe, 2022).

To reduce the cost, some researchers have developed new biocatalysts in recent years. An example is the so-called whole-cell biocatalysts, which are immobilized in biomass carrier particles. The advantage is that no purification is required to use these biocatalysts (Rocha-Meneses *et al.*, 2023).

Despite the development of various modern methods of biodiesel purification, wet purification in combination with drying remains the main method used. In order to optimize this process it is necessary to select optimal parameters, which reduces the cleaning time and the amount of waste produced. In this respect the use of acid washing improves the quality of the cleaning process. Membrane technology is considered one of the promising solutions to the issue, but still requires additional research and finding ways to reduce the cost of the process for industrial implementation. (Silviana *et al.*, 2022a)

4 Research part

4.1 Biodiesel production by transesterification reaction

Diesel biofuel, which is a mixture of complex monoesters of higher fatty acids obtained by transesterification of vegetable oils and animal fats, is one of the most

common alternative fuels that meet the basic requirements for energy carriers - environmental purity, availability of renewable raw material sources and safety in operation (Jeyaseelan *et al.*, 2023).

Existing technologies usually use methyl alcohol as a transesterifying agent, which is a flammable, toxic liquid of the third hazard class, having a negative effect mainly on the human nervous and vascular system when it enters the body through the respiratory tract or skin. Safe ethyl alcohol or its mixtures with other low molecular weight alcohols can serve as an alternative to methanol for biodiesel production. Thus, in. (Xu *et al.*, 2022) shows that ethyl esters of higher fatty acids have characteristics similar to diesel fuel, and their use as fuel or additives to its various types helps reduce the content of nitrogen oxides and toxic polyaromatic hydrocarbons in exhaust gases. The low volatility of the resulting biofuel samples makes it possible to reduce the elasticity of blended fuel vapors and thus increase its explosive safety (Coniglio *et al.*, 2013).

The fat or oil must be in a dry (anhydrous) state, pure and have neutral pH, in other words the free fatty acid content must be lower than 1.5 wt% (Ayu *et al.*, 2019). The starting product is heated to about 80°C, after anhydrous methanol (99.7 wt.%) is added in excess order. At a stoichiometric ratio of alcohol to oil, the yield of FAEE usually does not exceed 60-65 %. In this case most part of the catalyst stays in glycerin phase. With increasing amount of ethanol the catalyst is evenly distributed between both phases and the yield of esters gradually increased, reaching a maximum at ratios from 5:1 to 9:1. The ethanol/oil mixture at a ratio of 6:1 was chosen as optimal because further increasing the alcohol content worsens the separation of the reaction products and the upper ether fraction is partially enriched with glycerol, which reduces the yield of esters [101].

Reaction mixture containing 0.1-0.5 wt.% sodium hydroxide or potassium hydroxide in dissolved form. Once the addition of alcohol is complete, the mixture is stirred for several minutes and left to stand. Immediately the glycerol begins to precipitate.

The top layer consists of ethyl ethers, unreacted alcohol and alkali, residual glycerol and a small amount of soap. All these impurities are removed from the esters by repeated washing with small amounts of warm water. This technique makes it possible to obtain ethyl esters directly from fat without a corresponding intermediate operation, secondly, the reaction temperature is low, and thirdly, it does not require

apparatus made of special corrosion-resistant material (Karacan and Karacan, 2015).

To set up and refine the methodology of the experiment, initially the synthesis of ethyl ester of oleic acid was carried out, then the synthesis of biodiesel from rapeseed oil and ethyl alcohol was made.

The reactions were performed on an AutoMATE | Linear, Automated Parallel Synthesis Platform, H.E.L Group laboratory unit (Fig. 4), which is a platform with four parallel reactors, temperature control, and equipped with a magnet agitator and reflux condenser.

Figure 4. AutoMATE | Linear, Automated Parallel Synthesis Platform, H.E.L Group

The biodiesel plant (Fig. 5) consisted of a reactor with heating, a stirrer, a temperature sensor, a trap, and a reflux condenser.

The esterification reaction of oleic acid with ethanol was carried out in the presence of a sulfuric acid as a catalyst. The molar ratio acid:alcohol was 3:1. Sulfuric acid was added in a volume of 0.5% wt. The reaction was carried out under heating to 85°C and stirring. Excess water was removed from the system as azeotropic mixture of water and benzene (boiling point = 69.4 °C).

Figure 5. Installation for biodiesel production

Biodiesel was produced in the reaction of transetherification of lipids of rapeseed oil on an alkaline catalyst. A rectified ethyl alcohol (not less than 96.2 vol.% ethanol) was used as a transesterifying agent.

A mixture of ethanol (210 ml) and oleic acid (200 ml) with a molar ratio of 6:1 and a 1.0% wt. catalyst (potassium hydroxide alcohol solution) by raw material and benzene (to remove water from the reaction system as an azeotrope) was placed in the reactor and slowly heated to 80°C. The synthesis time was 4 hours. At the end of the synthesis the reaction mixture was cooled to room temperature (Fig. 6).

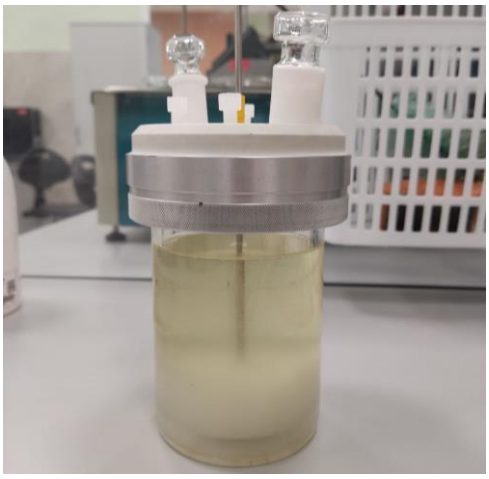


Figure 6. Reaction mixture after the end of synthesis

4.2 Separation and purification

The mixture of substances from the reactor was poured into a separating funnel (Fig. 7). After stratification of the model solution, two phases were formed. The upper phase was a mixture of ethyl ester of oleic acid (OAEE) and the residue of unreacted oleic acid. The lower phase contained the catalyst (H_2SO_4) and the benzene residue.

Figure 7. Separation of the reaction mixture into two phases

Reaction of transesterification of rapeseed oil was carried out twice. First time the conversion of esters was less than 50% due to insufficient purity of alcohol. The mixture after reaction remained homogeneous. Second reaction was carried out observing all conditions and using sufficiently pure components. Two phases were formed after settling: the upper one consisting of FAEE and potassium salts (soap) and the lower one containing glycerol, excess ethanol, rape oil residue, unreacted potassium hydroxide, soaps formed and products of incomplete transesterification (mono- and diglycerides). The obtained FAEE were purified by distillation of residual ethanol and benzene. For this purpose, the reaction mixture was heated to 90-100 °C and heated to constant mass. After that the residual oleic acid was removed by crystallization. The mixture was poured into a conical flask and cooled to -10 °C, after turbidity of the solution the acid was separated from the ether by vacuum filtration.

4.3 Methods of analysis

Fourier-IR spectroscopy (Fourier-IRS) is a well-known and proven analytical technique for identifying unknown chemicals by absorbing infrared light from a

chemical substance. The spectrum - the set of bands formed by absorption - is unique to each substance or group of atoms. The absorption intensity is directly proportional to the quantitative content of the characteristic groups of atoms and allows quantification of the component content in a mixture (Tarasevich B.N., 2012).

A Nicolet 6700 FTIR spectrometer was used to analyze the obtained ethyloleate (Fig. 8).

The Nicolet 6700 FT-IR spectrometer allows the acquisition of infrared spectra in the mid-, far- and near-infrared regions. It allows qualitative and quantitative analysis of the chemical composition of substances, characterization of the structure of molecular compounds. Spectral range: 25000 - 20 cm^{-1} ; resolution up to 0,09 cm^{-1}; scanning speed up to 75 scans/sec. The instrument is most effective in the analysis of organic substances.

Figure 8. Nicolet 6700 FT-IR spectrometer

X-ray fluorescence analysis is based on the absorption and subsequent emission of X-rays by samples. Atoms of each element emit their (characteristic) radiation, which has a wavelength and energy strictly defined for the element.

By recording the spectrum, the qualitative elemental composition of the sample is determined. The quantitative content of an element in the sample is determined by the intensity of radiation of different wavelengths or energies.

The samples were analyzed for potassium content using an energy dispersive X-ray fluorescence spectrometer Shimadzu EDX-7000P (Fig. 9). The spectrometer is capable of non-destructive analysis of solid and liquid samples. It provides qualitative and quantitative determination of elements from Na to U by measuring the energy and intensity of the secondary fluorescence radiation.

Figure 9. Shimadzu EDX-7000P energy dispersive X-ray fluorescence spectrometer

Consideration of globules of the emulsion formed during wet washing of FAEE was carried out using a stereoscopic microscope "LOMO" MSP-2 (Fig. 10). The emulsion was viewed and photographed through the light. The range of the microscope magnification varies from x21 to x135 magnification.

Figure 10. LOMO stereoscopic microscope MSP-2.

4.4 Formation and destruction of emulsions

Vigorous mixing of two immiscible liquids can form emulsions. In the absence of emulsifiers, the resulting emulsions will eventually separate under the action of gravity.

Gravity settling is one of the simplest and most economical methods of separating multicomponent systems. However, the sedimentation of particles can take from several hours to several weeks. In order to organize a production process it is

necessary to intensify a separation step. It is possible to use demulsifiers to intensify separation. It is effective way, but it requires extra capital expenditures. A simpler way to intensify the process is to heat the mixture to accelerate coagulation and precipitation of globules.

The macroemulsion properties of fatty acid esters were studied first with a model solution and then with FAEE. A mixture of oleic acid ethyl ester (with oleic acid admixture of 15%) and water was used as a model solution with a volume ratio of components of 1:1.

The samples were thermostatted, followed by stirring for 3-4 minutes, which resulted in the formation of an unstable emulsion (Fig. 11). Then, the height of the water layer h_1, the emulsion phase and water h_2 and the total height of the mixture h_3, as well as the time of stratification of the emulsion layer were measured. Measurements were carried out in the temperature range from 30 to 50 °C within 5°C increments at mixing speeds from 250 to 500 rpm in increments of 50 rpm. According to the data obtained, the thickness of the emulsion and ester layers were determined.

Evaluation of the stability of emulsions was carried out visually, by the degree of release of one of the components of the emulsion.

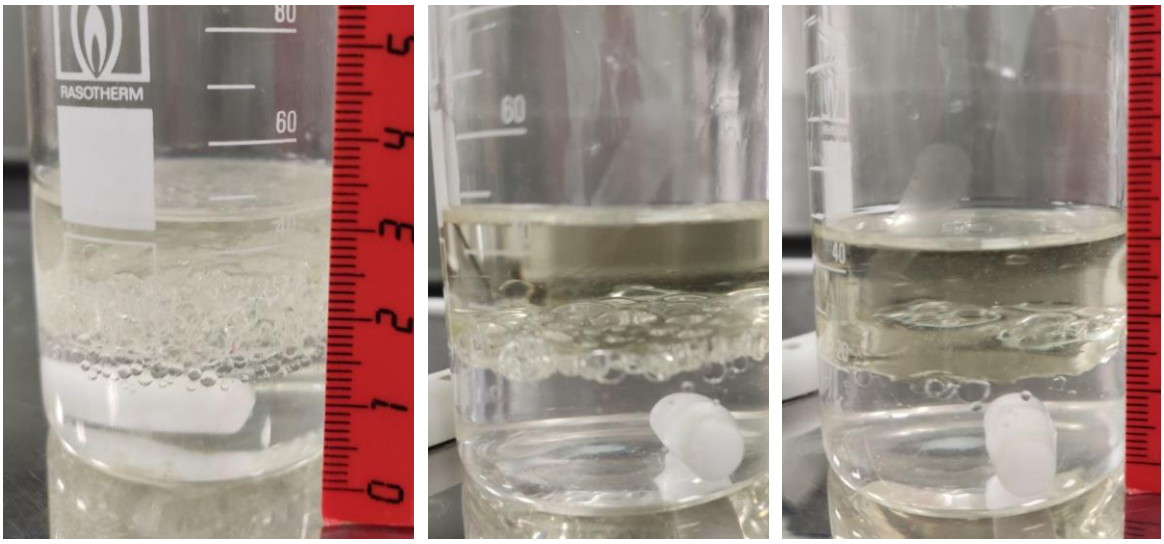


Figure 11. Emulsion formation and destruction

The second series of experiments consisted of three experiments and were performed using ethyl ethers of rapeseed oil (FAEE), the glycerol phase, and the

undivided low-FAEE distillate. The volume ratio of the components in the FAEE:water washing step was 1:1.

The sedimentation rate of particles in laminar settling mode is described by Stokes equation:

$$v = \frac{d^2 g \Delta\rho}{18\mu},$$

where d - diameter of the deposited particle,m

$\Delta\rho$ - density difference of the dispersed phase and the dispersion medium, kg/m^3

g - gravity acceleration, m/s^2

μ - dynamic viscosity of the medium, Pa-s.

The particle deposition rate can be defined as the ratio of the average distance traveled by each particle to the time in which the particle reached the phase. In practice, it is difficult to obtain values of the diameter of the deposited particles and to estimate the particle deposition rate, but it can be observed that the mixing rate will be pre-proportional to the ratio of the height of the emulsion layer to the stratification time $v \sim h_{em} / \tau_s$. An increase in the stirring speed will lead to a decrease in the size of the emulsion droplets, i.e., the stirring speed is inversely proportional to the diameter of the emulsion globules $d \sim 1/S$. Then the time of stratification of components can be conventionally represented as follows: $\tau_s \sim k \cdot h_{em} \cdot S^2$, where k is the proportionality factor. From the obtained ratio we can conclude that the graph of the emulsion stratification time dependence on the stirring speed will be a quadratic function.

4.5 Results and Discussion

4.5.1 OAEE and FAEE obtained

The synthesis of the model solution was the esterification of oleic acid with ethyl alcohol in the presence of sulfuric acid (Fig. 12). The reaction was carried out using an excess of alcohol to shift the equilibrium toward the product, OAEE.

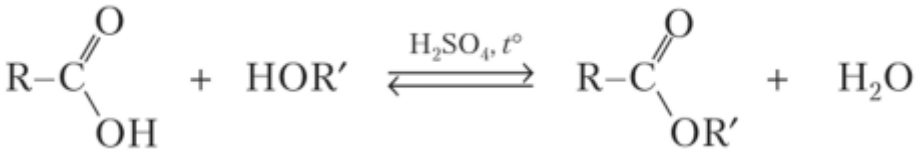


Figure 12. The esterification reaction

The purity of the ester was checked with an IR spectrometer. Figure 13 shows successively the spectra: ethyloleate before purification from oleic acid, ethyloleate after purification from acid impurity. The spectrum of oleic acid is presented for a comparison. As can be seen in the first spectrum, the two characteristic peaks 1737 and 1709, responsible for ethyloleate and oleic acid, are approximately equal, indicating a high proportion of acid admixture in the ethyloleate (approx. 50%). After crystallization of the acid, the 1709 peak decreased noticeably, hence the main amount of oleic acid was removed from the ether.

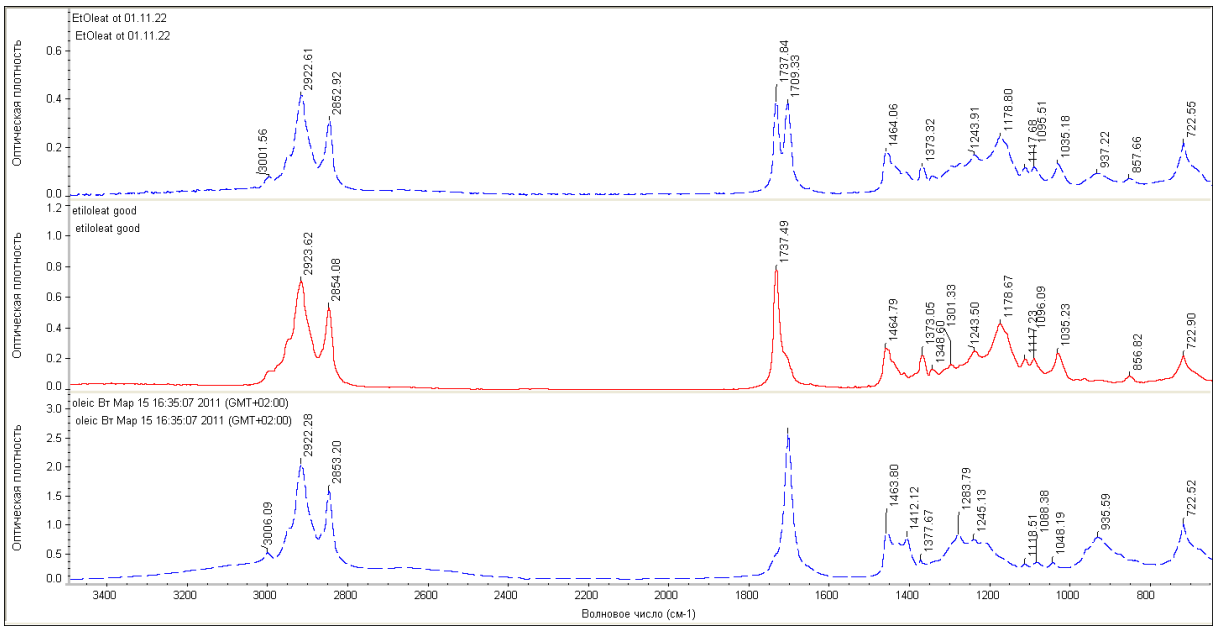


Figure 13. IR spectra (top to bottom): mixture of ethyloleate and oleic acid, purified ethyloleate and oleic acid, respectively

The process of obtaining biodiesel from rapeseed oil consisted in the reaction of transetherification of triglycerine esters contained in vegetable oil by the action of excessive amount of alcohol in the presence of an alkaline catalyst (Fig. 14):

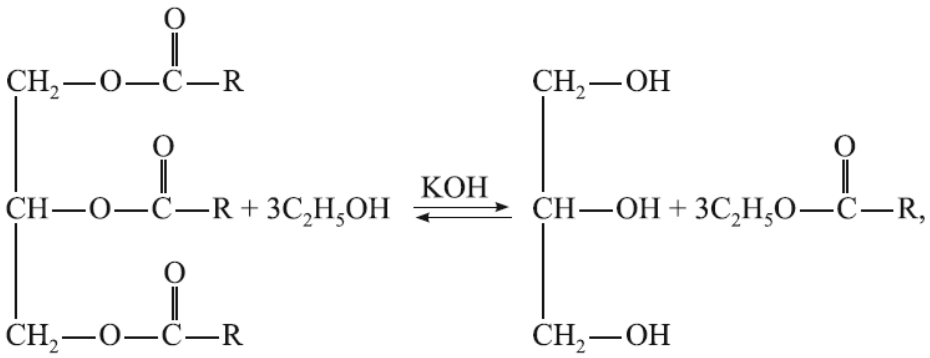


Figure 14. Alkaline transesterification of fatty acids with ethyl alcohol.

R - hydrocarbon radicals C_{14} - C_{24}

In the first synthesis, technical alcohol with 93% vol. of ethanol was used. This resulted in a low yield of the target product, which left the mixture homogeneous after the reaction was completed. The mixture obtained consisted of FAEE, glycerol - a valuable by-product, ethanol, residues of unreacted catalyst, salts of carboxylic acids, mono- and diglycerides, also containing some phospholipids, phosphatides, carotenes, tocopherols, sulfur compounds and other impurities included in the initial vegetable oils (Ganesan and Masimalai, 2020).

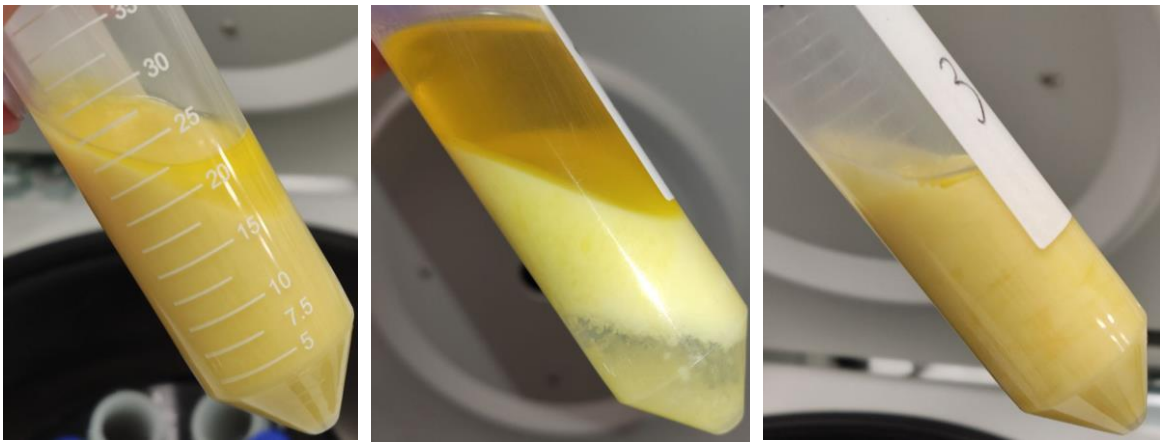
For the second synthesis, rectified ethyl alcohol with an ethanol content of at least 96.2 vol.% was used. The resulting mixture was separated into an ether phase (FAEE, saponification products due to the presence of potassium and a small amount of free fatty acids) and a glycerol phase with mono- and diglycerides, residues of non-reacted rapeseed oil.

4.5.2 Separation and purofocation of FAEE

The first step in the purification of esters is the vacuum distillation of the residual alcohol. After this mixture is separated into upper and lower phases.

Water washing of the samples (homogeneous phase, FAEE top and Glycerol bottom) resulted in the formation of persistent emulsions. Centrifugation at a speed of 5000 rpm for 5 min was used for separation. This only slightly increased the degree of separation (Fig. 16). X-ray fluorescence analysis of the samples showed that they contained potassium, the percentage of potassium is shown in Figure 16. The presence of potassium led to saponification and emulsification reactions of the solution.

The obtained emulsions were examined on an LOMO MSP-2 stereomicroscope. The images are presented in Appendix 1. The results of separation of emulsions on the centrifuge are duplicated by images from the microscope. The largest emulsion is the ether phase emulsion, which is subjected to separation better than others. Next is the emulsion of the homogeneous mixture with water. The most finely dispersed is the emulsion of the glycerol phase, which did not undergo stratification during centrifugation.



a - homogeneous mixture (5.68%K)	b - ether phase (0.45%K)	c - glycerol phase (1.36%K)

Figure 15. Separation of ether-water emulsion after centrifugation

For further studies, the esters of fatty acids of rapeseed oil were subjected to potassium purification. The ether phase was purified from alkali residues by carbonation - carbon monoxide CO_2 was passed through the solution, resulting in the formation of potassium carbonates and hydrocarbonates that were subsequently removed by water washing. The final content of potassium in FAEE after purification was 0.005 wt%.

4.6 Influence of heating and stirring on OAEE-water emulsion

The effect of heating rate and stirring speed on the formation and separation time of macroemulsion in a mixture of oleic acid ethyl ester (with an admixture of oleic acid 15%) and water with a volume ratio of 1:1 was studied.

The data obtained in the laboratory study and calculations of the emulsion layer height h_{em} and ester layer height h_{et} (ethyloleate) are shown in Table 2.

Table 2. Effect of heating and stirring on the formation of ether-water macroemulsion

W, rpm	h_1 , cm	h_2 , cm	h_3 , cm	Delamination time, min	h_{em} , cm	h_{et} , cm
temperature 30°C						
250	1,1	1,9	3,1	53	0,8	1,2
300	1	2,7	3,1	64	1,7	0,4
350	0,9	2,9	3,1	71	2	0,2
400	0,7	2,9	3,1	74	2,2	0,2
450	0,6	2,9	3,1	79	2,3	0,2
500	0,5	3	3,1	85	2,5	0,1
temperature 35°C						
250	0,8	1,8	3,1	38	1	1,3
300	1	2,4	3,1	41	1,4	0,7
350	1	2,8	3,1	55	1,8	0,3
400	0,9	2,8	3,1	59	1,9	0,3
450	0,7	3	3,1	67	2,3	0,1
500	0,6	3	3,1	70	2,4	0,1
temperature 40°C						
250	1,1	2,1	2,9	16	1	0,8
300	1	2,3	2,9	22	1,3	0,6
350	0,9	2,4	2,9	25	1,5	0,5
400	0,7	2,4	2,9	29	1,7	0,5
450	0,6	2,7	2,9	32	2,1	0,2
500	0,5	2,7	2,9	32	2,2	0,2
temperature 45° C						
250	0,6	1,9	2,9	13	1,3	1
300	1,1	2,2	2,9	19	1,1	0,7
350	1,1	2,3	2,9	24	1,2	0,6
400	1	2,4	2,9	24	1,4	0,5
450	0,9	2,5	2,9	26	1,6	0,4
500	0,6	2,7	2,9	31	2,1	0,2
temperature 50° C						
250	1,2	2	2,9	16	0,8	0,9
300	1,1	2,1	2,9	16	1	0,8
350	1,1	2,3	2,9	17	1,2	0,6
400	1	2,5	2,9	22	1,5	0,4
450	0,9	2,6	2,9	26	1,7	0,3
500	0,7	2,6	2,9	27	1,9	0,3

After processing the experimental data, the following regularities were established: the dependence of the height and time of stratification of the emulsion layer on the stirring speed for temperatures in the range of 30-50 °C.

Figure 16 shows a graph of isotherms for ether-water system. The data obtained suggest that increasing the stirring speed of the mixture promotes emulsion formation, while heating reduces the intensity of formation of emulsion systems. To

avoid the formation of emulsions it is necessary to increase the reaction temperature and reduce the stirring speed.

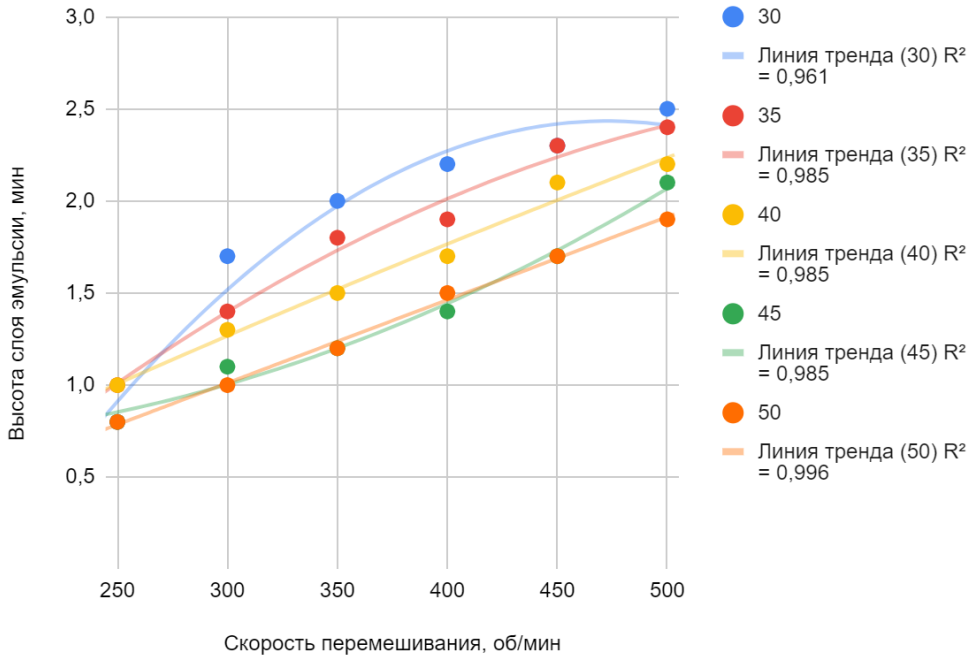


Figure 16: Emulsion isotherms in the coordinates stirring speed, rpm - height of the emulsion layer, cm.

Figure 17 shows the effect of heating and stirring speed on the delamination time of the emulsion. It can be seen that heating contributes to the destruction of the emulsion, but with increasing temperature the effect of heating decreases, and heating the mixture above 40-45 ° C can be considered inappropriate. With increasing temperature the effect of stirring speed on the time of stratification of the emulsion decreases. Thus, selection of the optimal temperature minimizes the effect of stirring speed on the formation of emulsions.

Combining the conclusions based on the two graphs described above suggests that by selecting the optimal temperature regime it is possible to form an emulsion layer to increase the reaction surface by sufficiently intensive mixing, since heating will contribute to the subsequent stratification of the formed emulsion.

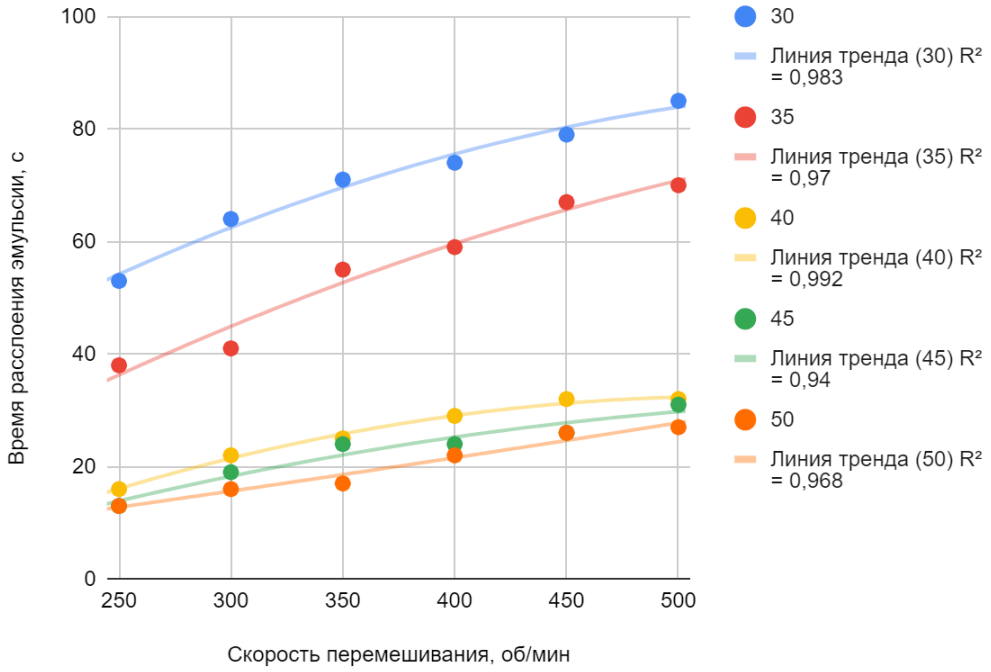


Figure 17: Emulsion isotherms in the coordinates stirring speed, rpm - time of stratification of the emulsion layer, s.

4.7 Influence of heating and stirring on FAEE-water emulsion

The ether phase was used to evaluate the effect of heating and stirring rate on emulsion formation and separation in the process of wet cleaning of biodiesel. Biodiesel was obtained by the reaction of esterification of rapeseed oil with ethyl alcohol in the presence of an alkaline homogeneous catalyst. The results of laboratory experiments are presented in Table 3.

Table 3. Effect of temperature and stirring on the formation of FAEE-water macroemulsion

W, rpm	h_1 , cm	h_2 , cm	h_3 , cm	Delamination time, min	h_{em} , cm	h_{et} , cm
temperature 30°C						
250	1,0	2,0	3,1	9	1,0	1,1
300	1,3	2,5	3,1	17	1,2	0,6
350	0,3	2,8	3,1	30	2,5	0,3
400	0,1	2,9	3,1	38	2,8	0,2
450	0,1	3,0	3,1	40	2,9	0,1
500	0,1	3,0	3,1	40	2,9	0,1
temperature 35°C						
250	1,6	2,2	3,1	9	0,6	0,9
300	1,0	2,5	3,1	14	1,5	0,6
350	0,1	2,7	3,1	28	2,6	0,4
400	0,1	3,0	3,1	30	2,9	0,1
450	0,1	3,0	3,1	30	2,9	0,1
500	0,1	3,1	3,1	31	3,0	0,0
temperature 40°C						

250	1,5	2,3	3,1	8	0,8	0,8
300	1,0	2,5	3,1	13	1,5	0,6
350	0,5	2,7	3,1	21	2,2	0,4
400	0,4	2,8	3,1	22	2,4	0,3
450	0,1	2,8	3,1	23	2,7	0,3
500	0,1	3,0	3,1	23	2,9	0,1
temperature 45° C						
250	0,9	1,7	3,1	6	0,8	1,4
300	1,0	1,7	3,1	6	0,7	1,4
350	0,5	2,6	3,1	16	2,1	0,5
400	0,3	2,7	3,1	18	2,4	0,4
450	0,1	2,9	3,1	21	2,8	0,2
500	0,1	3,0	3,1	23	2,9	0,1
temperature 50° C						
250	1,4	2,1	3,1	6	0,7	1,0
300	1,1	2,0	3,1	7	0,9	1,1
350	0,3	2,8	3,1	15	2,5	0,3
400	0,1	2,9	3,1	20	2,8	0,2
450	0,1	3,0	3,1	21	2,9	0,1
500	0,1	3,0	3,1	21	2,9	0,1

The synthesized FAEE have a number of impurities, which include glycerol, residual catalyst content, and saponification products due to the presence of fatty acids in the feedstock. The presence of impurities leads to easier emulsification in the wet cleaning process and increases the contact surface of the phases (Fig. 18). However, there is a significant increase of emulsion separation time in comparison with the model solution (Fig. 19).

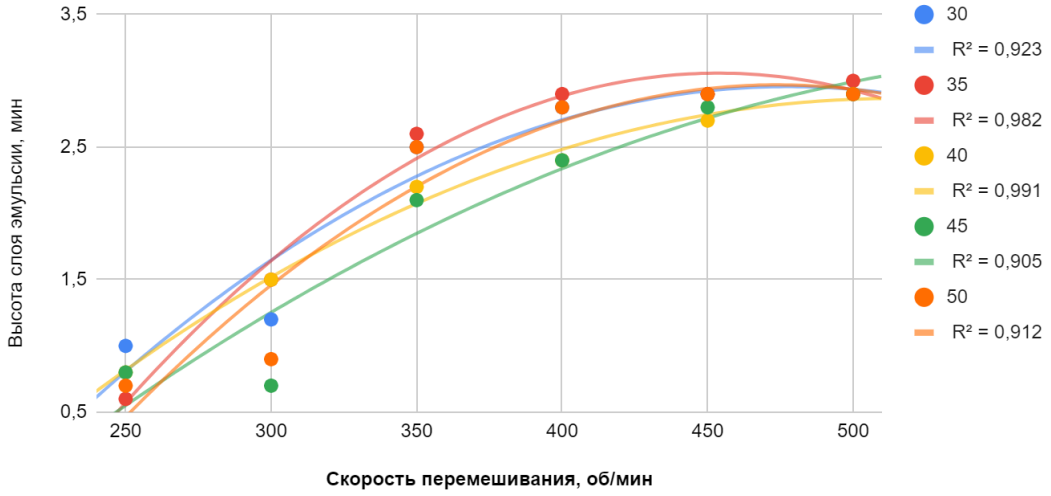


Figure 18. Isotherms of FAEE-water emulsion in the coordinates stirring speed, rpm - height of emulsion layer, cm.

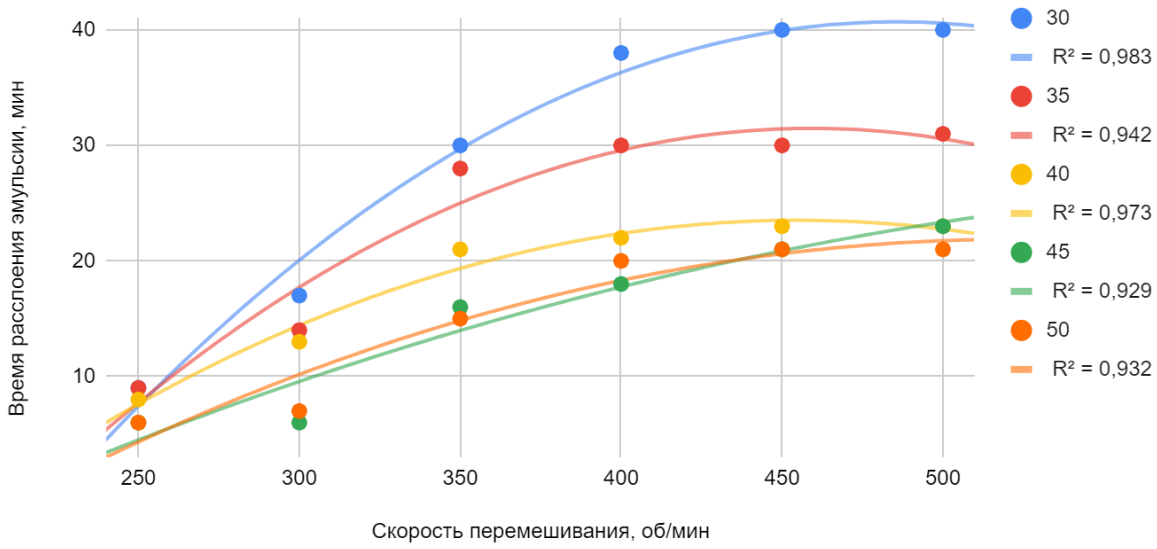


Figure 19. Emulsion isotherms in the coordinates stirring speed, rpm - time of stratification of the emulsion layer, s.

Analysis of the obtained FAEE-water isotherms showed that temperature has less active influence on emulsion formation compared to the model solution, the optimal is mixing in the speed range of 400-450 rpm, since a further increase in the mixing speed leads to the opposite effect, colliding emulsion globules and increasing their size, thereby reducing the contact surface of phases.

Also the temperature graph has less obvious dependence, which can be considered as a quadratic function or two linear segments with different angular coefficient. The data obtained during the experiments are not enough to form unambiguous conclusions.

The temperature has a significant influence on the emulsion separation rate. The graph tends to a quadratic function, so it is possible to select the optimal heating temperature, further increase of which will not lead to a significant decrease in the process time. For the speed range of 400-450 rpm, which provides the necessary contact area of the phases for extraction, it will be reasonable to heat the mixture to a temperature of 40-45 ° C.

5 Economic part

5.1 Analysis of the global biodiesel market

The growth of the global biodiesel market is driven by the need to find renewable energy sources that can subsequently replace fossil fuels. At the same time,

environmental requirements for fuels are increasing in order to limit emissions of nitrogen oxides and greenhouse gases into the atmosphere. A decrease in oil reserves leads to an increase in the cost of conventionally produced fuels, which in turn increases the profitability of producing biodiesel and other types of renewable energy.

According to the International Energy Association (IEA), biodiesel production has increased almost 2.5-fold, from 20.4 billion liters in 2010 to 47.4 billion in 2022 (Figure 20) (IEA, 2023).

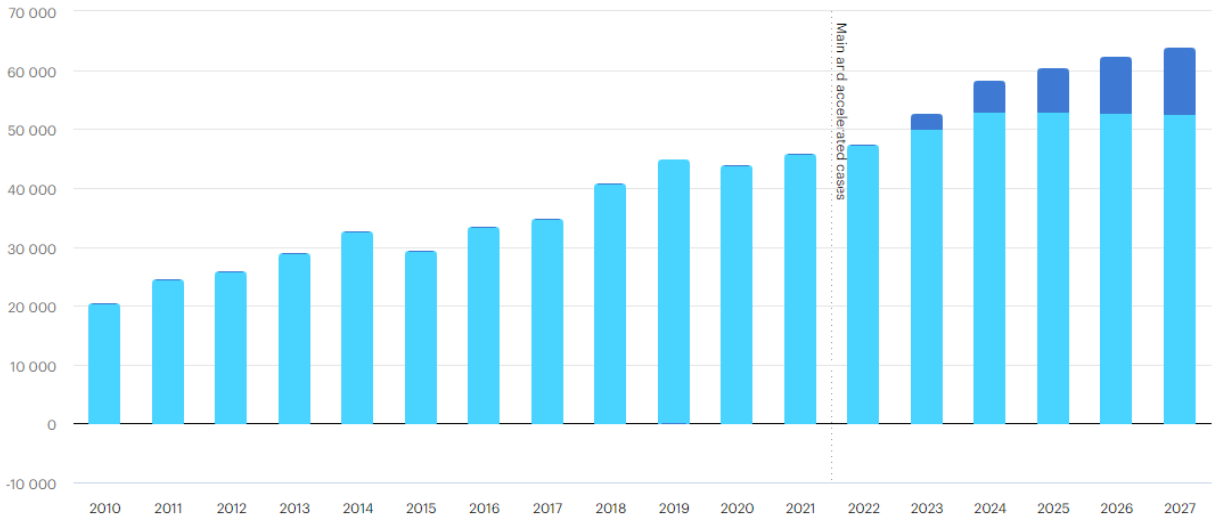


Figure 20. World biodiesel production in millions of liters in 2010-2027, including realistic and optimistic development projections for 2022-2023

Based on biodiesel production data from the IEA report, let's estimate the global rate of biodiesel production development. Table 4 shows the results of calculating the annual growth of biodiesel production from 2010 to 2027.

Based on the results of the calculations, a graph showing the annual growth rate of biodiesel production and fuel production growth as a percentage compared to 2010 was plotted (Fig. 21).

Despite fluctuations in production volumes, the trend of increasing production rates remains noticeable. In the past few years, the momentum has been reduced due to the pandemic, but compared to 2018, production has not only returned to previous volumes, but also increased by 16.5%.

Table 4. Assessment of the rate of world biodiesel production development

The Year	Production, mln l./year	Annual production growth, %	Growth compared to 2010, %
2010	20486		0
2011	24435	19,3	19,3
2012	25930	6,1	26,6
2013	28968	11,7	41,4
2014	32541	12,3	58,8
2015	29294	-10,0	43,0
2016	33299	13,7	62,5
2017	34726	4,3	69,5
2018	40705	17,2	98,7
2019	44910	10,3	119,2
2020	43808	-2,5	113,8
2021	45712	4,3	123,1
2022	47429	3,8	131,5
Projected rate of development			
The Year	Production, mln l./year	Annual production growth, %	Growth compared to 2010, %
2023	52607	10,9	156,8
2024	58137	16,1	183,8
2025	60235	13,8	194,0
2026	62335	17,9	204,3
2027	63831	21,1	211,6

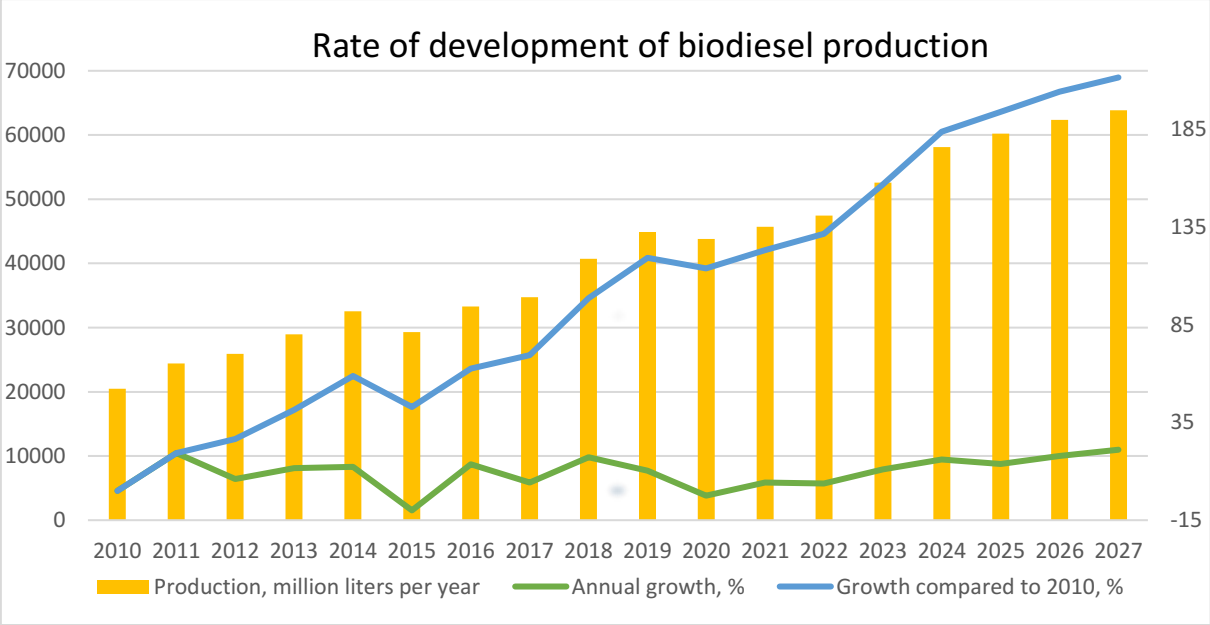


Figure 21. Rate of development of biodiesel production

The global biodiesel market is driven by the growing need for clean and renewable fuels. Environmental awareness is growing, leading to a preference for clean fuels. The skyrocketing prices of non-renewable energy sources, for example, due to their limited resources, are forcing attention to alternative fuels.

The most active rates of biodiesel consumption are in developing countries, due to their desire to reduce oil imports and use the production of biodiesel from local resources to strengthen the economic situation.

In developed countries, a major factor affecting economic growth is the growing concern about gas emissions from the use of fossil fuels. Biodiesel can be used as an additive to the main fuel, thus reducing greenhouse gas emissions. In addition, waste from other industries can be used as a feedstock, bringing us closer to the idea of a circular economy. In 2021, almost 70% of renewable diesel and biojet fuel in 2021 was derived from waste. (apk-inform.com, 2022).

The biodiesel market depends on a complex of factors, including the overall demand for engine fuels, since the main consumption of biodiesel is in the form of an admixture to petroleum diesel in an amount ranging from 2 to 100%, depending on the technological features of the engine, the quality of biodiesel and the requirements of each state.

The main producers of biodiesel are EU, the United States, Indonesia, Brazil, and Argentina (Figure 22).

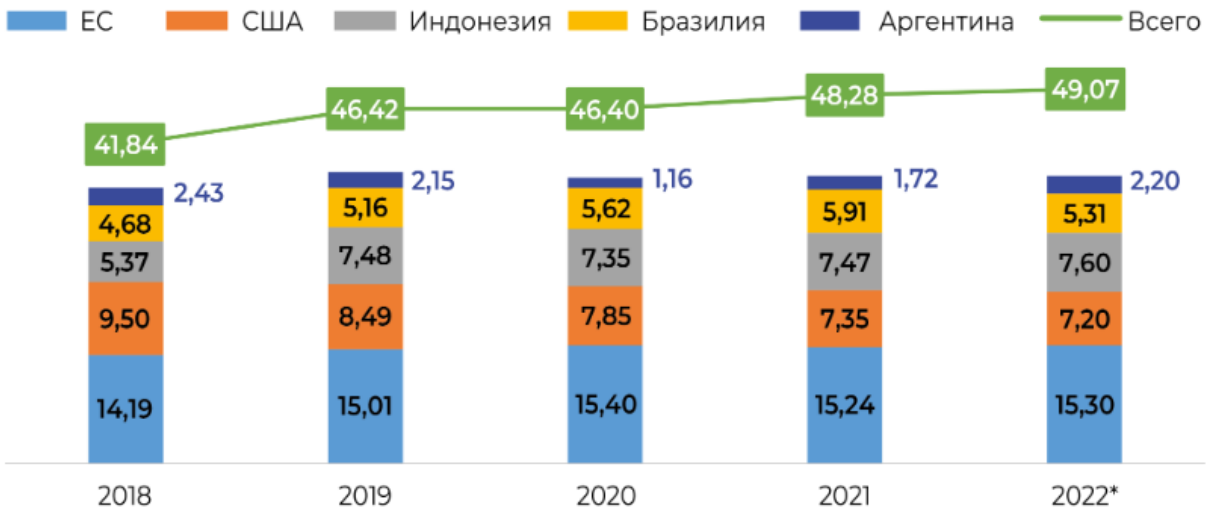


Figure 22. Dynamics of world biodiesel production, million tons

*** - projected value (Oil World)**

The development of biodiesel production largely depends not only on economic and environmental requirements, but also on a set of political measures taken in these countries.

Within the forecast period (until 2030), biodiesel consumption will depend on the available volumes of feedstock and the adopted regulations governing its use. China

is expected to maintain its B2 blending level, as the introduction of a national law increasing this value to 10% of biodiesel content in conventional fuels has been postponed since 2017. Proportional consumption growth is expected to continue in Brazil, the U.S. and Argentina due to the current standards. Argentina maintains the B10 standard and Indonesia has a 30% blending program since 2020.

In Europe, there has been a decrease in biofuel blending commitments due to the rising price of biofuels caused by the growing market for agricultural raw materials. However, countries continue to comply with existing regulations, such as the EU Fuel Quality Directive (FQD), which sets targets for reducing greenhouse gas emissions. (IEA, 2023).

Asia-Pacific demand growth for biofuels is expected to decline in 2023 as Indonesia had planned to begin a 40% blending mandate this year, but it has been delayed due to rising prices and market uncertainty.

5.2 Raw Materials Market Assessment

Biodiesel can be produced from a wide range of raw materials found around the world (Figure 24). Source virgin oil includes such products as soybean oil, rapeseed oil, sunflower oil, mustard oil, palm oil, tung oil, jojoba oil, cotton oil, rubber oil, Nahora oil, Nima oil, Jatropha oil, Karanji oil, Pongamia oil, and rice bran oil. Pork tallow, ghee, chicken fat, yellow fat, and fatty acid byproducts from linseed oil and fish oil were also used (Sales *et al.*, 2022). In addition, microalgae and algae oils with higher yields and cheaper costs have begun to be used in the last decade. Worldwide, the most common categories of raw materials are waste oil, animal fats, and vegetable oil (both edible and inedible) (Rezania *et al.*, 2019). Environmental conditions, farming practices, soil availability and quality, and geographic location all influence the choice of feedstock for biodiesel production (Manaf *et al.*, 2019). Palm oil, for example, is widely used in Malaysia because of its high soil properties, while soybean oil is widely used in the United States because of adverse weather and convenience (Mathew *et al.*, 2021).

Figure 23. World distribution of feedstock for biodiesel production

Because of the high cost of the process, technological problems, and regulatory restrictions, biodiesel production is still in its infancy (Maheshwari *et al.*, 2022). The feedstock used to produce biodiesel is an important factor to consider when calculating the total cost of production and profit. The choice of feedstock is expected to account for up to 75% of the total cost of biodiesel production.

First-generation oilseeds currently account for more than 95% of biodiesel synthesis (Akram *et al.*, 2022). In regions with significant soil and water resources, biodiesel derived from first-generation oils, such as sunflower and soybean oil, is more cost-effective. As a result, biodiesel derived from food sources such as oilseeds is 1.5-3 times more expensive than diesel fuel and accounts for 60-80% of total production costs (Al-Saadi, Eze and Harvey, 2022). Nevertheless, there is growing public concern in poor countries about food shortages and poverty resulting from the use of biodiesel derived from agricultural sources. In addition, various factors such as methanol and catalysts, labor, geographic location, and seasonal variations can affect biodiesel production costs (Julio *et al.*, 2022).

Biodiesel produced from non-edible ingredients such as waste vegetable oil, sewage sludge, animal fat waste and microalgae, as well as oil seeds such as Pongamia, Jatropha, Camelina and others has attracted much attention because it

has a better energy balance, economy and environmental aspects than diesel fuel and biodiesel based on traditional raw materials (Jafarihaghighi *et al.*, 2022). In addition, as stated earlier, many non-food sources are classified as waste, and using them to produce biodiesel would bring enormous economic and environmental benefits. Biodiesel derived from non-food feedstocks is of superior quality that can be used directly in diesel vehicles or blended with diesel fuel to produce biodiesel (Das, Ghatak and Mahanta, 2023).

5.3 Prospects for Biodiesel Market Development in Russia

The Government of the Russian Federation by the decree from October 29, 2021 № 3052-r approved the strategy of socio-economic development of the Russian Federation with low greenhouse gas emissions until 2050, according to which set a goal - by 2050 to reduce emissions by 60% compared to 2019 and by 80% compared to 1990.

One of the directions for achieving the goal is to develop the production of new types of energy carriers, including biodiesel, as well as the use of these new energy carriers.

If we consider the prevalence of biodiesel in Russia, it should be noted that so far there is no unified state program for the development of this direction. There is a bill of the Ministry of Agriculture, which creates conditions for active production of biodiesel in the country. Under the terms of the project up to 5.5 million tons of rapeseed oil should be produced annually, and 2.5 million tons will be allocated for biofuel production.

Oilseeds planted in Russia in 2020 amounted to 14.3 million hectares, which is 2% less than the previous season. Oilseeds were dominated by sunflower, which was planted on 8.48 mln ha (-1.2% compared to the previous season), soybeans - 2.83 mln ha (-8.0%), rape - 1.49 mln ha (-3.5%).

Rapeseed and soybean are the most promising crops in Russia for processing into vegetable oils with subsequent export. According to the Federal Customs Service, in 2019 Russia sold 668 thousand tons of rapeseed oil to foreign markets in more than 30 countries. With the gross harvest of rapeseed about 2.5 million tons in 2020, 1.9 million tons were used for processing, and more than 0.5 million tons were

exported without processing. Gross soybean harvest was 4.3 million tons in 2020, with 2.2 million tons imported and 1.2 million tons exported. About 4.8 million tons were processed.

According to the forecast of the Russian Oil and Fat Union in 2024 the area under rape will expand up to 2.5 mln ha, and the gross output - up to 4.1 mln tons, and according to the forecast of the CAR agency - up to 1.9 mln ha and 3 mln tons. Further growth of rapeseed production will be constrained by insufficient processing capacity even taking into account new investment projects, and the lack of capacity will be most acutely felt in Siberia with the development of oil exports to China (Goncharov S.V., 2020).

Large volumes of produced oilseeds provide an opportunity to develop production capacity and increase domestic processing of oils.

The development of the fuel and energy complex using fossil fuels, primarily gas and oil, remains a priority in Russia. However, it is necessary to work on the development of alternative energy sources, which include biodiesel. In this process, the development of vegetable oil production, a raw material for biodiesel production, and the development of production facilities for the production of alternative fuels should remain a priority (Research).

According to the forecast of INEI RAS, renewable sources of primary energy consumption in Russia should reach 6% of its structure by 2040, which implies the development of alternative energy and the use of biodiesel (Paptsov A.G., 2019). Because of the need to transition to a model of low-carbon development of the economy and the implementation of policies and measures to reduce carbon dioxide emissions in the importing countries, the demand for fossil fuels, together with the volume of imports from Russia, will fall, while the development of biodiesel production will open new economic development prospects.

6 Environmental safety

Biodiesel is becoming increasingly popular because it offers several advantages over petroleum diesel. The environmental aspects for which biodiesel should be preferred to petroleum diesel include a number of factors described below.

Reducing Pollution: Biodiesel can reduce emissions from vehicle tailpipes. Compared to diesel, a biodiesel-powered engine emits fewer pollutants, including hydrocarbons, carbon monoxide, and particulate matter. Although carbon dioxide emissions are similar to those of petroleum diesel, with biodiesel these emissions are offset by the absorption of carbon dioxide by growing plants, such as soybeans, during production. Taking the entire life cycle into account, pure biodiesel reduces carbon dioxide emissions by 74% compared to petrodiesel.

Renewability: Petroleum fuel, including diesel, is a non-renewable resource, while biodiesel is a renewable fuel, as it is produced from plant raw materials. The second generation of biodiesel is produced from household waste - waste household oil, effluent from alkaline refining of vegetable oils and a by-product of cellulose production - tall oil (Su, Zhang and Su, 2015). Thus, biodiesel is a more environmentally friendly option, which may become more in demand when there is a shortage of fossil fuels, as well as through the recycling of waste from other industries.

Safety: If spilled or otherwise released into the environment biodiesel is not harmful to animals and plants, unlike fuels of petroleum origin. Oil spills form oil slicks on the surface of water bodies. Their spreading over the area and the result of the impact on the environment is unpredictable, and the recovery of the affected biome can take a long time to several years (Allen and Ferek, 1993).

Biodiesel based on fatty acid esters is biodegradable, which on the one hand reduces the shelf life of the fuel, and on the other hand - the impact on the soil and water in the event of a spill or accident will be minimal. Microorganisms in water and soil process up to 99% of biodiesel within a month.

Biodiesel has superior performance characteristics compared to petrodiesel because it has a higher cetane number and additional lubricity. The high cetane number of biodiesel makes it easier to start the engine. Higher lubricity means less wear and tear on your engine over time. Even mixing just a small amount of biodiesel with petrodiesel can increase the lubricity of the fuel.

Biofuel does not contain sulfur, so its complete or partial use noticeably reduces sulfur oxide emissions. The toxicity of the exhaust gas is reduced.

Combustion of oil fuel is one of the main sources of dust emissions on a par

with coal combustion, biomass, black liquor in the pulp and paper industry, as well as processes of agglomeration and mechanical processing of solid materials. The use of biofuel as an additive to petroleum diesel reduces the smokiness of exhaust gas. The use of biodiesel reduces the emission of particulate matter PM10. Thus, the use of biodiesel B20 with the composition of 20% FAEE to 80% of diesel reduces particulate matter emissions by 30% compared to pure diesel, and the emission of hydrocarbons is reduced by 50% (V.A. Zvonov, 2008).

Table 5. Engine performance on biodiesel and petroleum fuel

Indicator	DT	PM:DT 30:70	BIO ECT	PB
Specific effective fuel consumption, g/(kWh)	349	366	337	374
Effective efficiency, %	24,2	23	25	22,6
Exhaust gas temperature, °C	289	571	841	765
NO_x , ppm	693	1028	841	765
CO, %	0,036	-	0,021	0,0348
CH, %	0,24	-	0,0323	0,0577
CO_2 ,%	5,87	5,39	-	-
Fuel composition: Oxygen, % S/H.	 0,4 6,9	 3,6 6,7	 - -	 - -

In work (V.A. Zvonov, 2008) the authors presented the results of tests of biodiesel from soybean oil (BIO EST), sunflower biofuel (SB), diesel fuel (DT), as well as a mixture of diesel fuel with sunflower oil in the ratio PM:DT = 30:70. The tests were conducted on the bench with the vortex chamber diesel engine 2Ch 8,5/11, the test results are presented in table 5. The results of work confirm the reduction of carbon monoxide and hydrocarbon emissions when using biodiesel with soybean oil, but the authors also identified an increase in nitrogen oxide.

7 Conclusion

Biodiesel is a clean-burning fuel with a chemical structure of fatty acid alkyl esters. Alkali-catalyzed transesterification of vegetable oils and animal fats is currently the most common method for biodiesel production.

Transesterification is essentially a sequential reaction. However, when raw materials (oils or fats) contain a high percentage of free fatty acids or water, the alkaline catalyst reacts with the free fatty acids to form soaps, and water can hydrolyze triglycerides into diglycerides and form more free fatty acids. These are undesirable reactions that reduce the yield of the biodiesel product. Therefore, after purifying the raw material, the acidic raw material should be pretreated to inhibit the saponification reaction.

The transesterification reaction requires alcohol as reagent and catalyst. The most commonly used alcohol is methanol, while sodium hydroxide and potassium hydroxide are the most commonly used catalysts. During the reaction, glycerol is formed as a byproduct. Because of its many industrial applications, crude glycerin must be purified to a purity above 99% to make it usable.

To purify the resulting crude biodiesel, the product should first be neutralized and then passed through an alcohol purifier before purification by one of the following methods: water washing, membrane extraction and dry washing. A very promising method of biodiesel washing is hollow fiber membrane extraction, which effectively prevents emulsification at the washing stage and reduces refining losses.

There are four main factors affecting the biodiesel yield, namely the amount of alcohol, reaction time, reaction temperature and catalyst concentration. To ensure a complete transesterification reaction, the molar ratio of alcohol to triglycerides should be increased to 6:1 using an alkaline catalyst. For used cooking oils or oils with a high percentage of free fatty acids, a higher molar ratio is required for acid-catalyzed transesterification. Because the conversion rate of fatty acid esters increases with reaction time, but the yield of the biodiesel product reaches a maximum at the optimal reaction time.

Higher reaction temperatures can reduce the viscosity of the oils, increasing the reaction rate. The optimal temperature ranged from 50°C to 60°C, depending on the

oil used. The optimal catalyst concentration condition is about 1.5 wt.% for NaOH, which is the most frequently used catalyst.

The highest yield of biodiesel can be obtained only by individual selection of optimal process parameters for the used feedstock. The following are the averaged values established by the results of the work:

1. The raw material for the biodiesel production process can be vegetable and animal fats, waste oils, microalgae and other sources of fatty acids.
2. The most efficient way of conducting the transesterification process is with alkaline catalysts.
3. Homogeneous catalysts give a higher product yield in the reaction, while heterogeneous catalysts can be separated and regenerated for reuse.
4. In industrial production the optimal solution is to use methanol (conversion up to 99%), but because of its high toxicity it is possible to replace it with ethanol.
5. Glycerol, a byproduct of biodiesel production, should be purified and used in the pharmaceutical and cosmetic industries to increase the economic viability of the process.
6. Selection of parameters for the selected purification method allows to optimize the technological process and increase the yield and quality of the biodiesel
7. Optimal parameters of the wet cleaning process for FAEE are:
    a. Process temperature 40-45°C
    b. Stirring speed 400-450 rpm

Given the growing concern about global warming, we can predict that the use of biodiesel will continue to grow at a rapid pace. This will spur the development of more sophisticated biodiesel production and processing methods to cope with the growing market demand.

8 Bibliography

REFERENCE LIST

Abo, B.O. *et al.* (2019) 'Microalgae to biofuels production: a review on cultivation, application and renewable energy', *Reviews on Environmental Health*, 34(1), pp. 91–99. doi: 10.1515/reveh-2018-0052

Abomohra, A.E.-F. *et al.* (2020) 'Potential of fat, oil and grease (FOG) for biodiesel production: A critical review on the recent progress and future perspectives', *Progress in Energy and Combustion Science*, 81, p. 100868. doi: 10.1016/j.pecs.2020.100868

Adama, K.K., Aluyor, E.O. and K, A.T. (2021) 'Component distribution associated with phase separation and purification of tropical almond biodiesel at different temperatures', *Renewable Energy*, 165, pp. 67–76. doi: 10.1016/j.renene.2020.10.117

Aghbashlo, M., Tabatabaei, M. and Hosseinpour, S. (2018) 'On the exergoeconomic and exergoenvironmental evaluation and optimization of biodiesel synthesis from waste cooking oil (WCO) using a low power, high frequency ultrasonic reactor', *Energy Conversion and Management*, 164, pp. 385–398. doi: 10.1016/j.enconman.2018.02.086

Akram, F. *et al.* (2022) 'Current trends in biodiesel production technologies and future progressions: A possible displacement of the petro-diesel', *Journal of Cleaner Production*, 370, p. 133479. doi: 10.1016/j.jclepro.2022.133479

Allen, A.A. and Ferek, R.J. (1993) *Advantages and disadvantages of burning spilled oil*. United States: American Petroleum Institute. Available at: http://inis.iaea.org/search/search.aspx?orig_q=RN:24063854.

Al-Saadi, L.S., Eze, V.C. and Harvey, A.P. (2022) 'A techno-economic analysis based upon a parametric study of alkali-catalysed biodiesel production from feedstocks with high free fatty acid and water contents', *Biofuels*, 13(4), pp. 401–413. doi: 10.1080/17597269.2020.1727688

Ambat, I., Srivastava, V. and Sillanpää, M. (2018) 'Recent advancement in biodiesel production methodologies using various feedstock: A review', *Renewable and Sustainable Energy Reviews*, 90, pp. 356–369. doi: 10.1016/j.rser.2018.03.069

Atadashi, I.M. *et al.* (2011) 'Refining technologies for the purification of crude biodiesel', *Applied Energy*, 88(12), pp. 4239–4251. doi: 10.1016/j.apenergy.2011.05.029

Atadashi, I.M. *et al.* (2012) 'Production of biodiesel using high free fatty acid feedstocks', *Renewable and Sustainable Energy Reviews*, 16(5), pp. 3275–3285. doi: 10.1016/j.rser.2012.02.063

Atadashi, I.M., Aroua, M.K. and Aziz, A.A. (2011) 'Biodiesel separation and purification: A review', *Renewable Energy*, 36(2), pp. 437–443. doi: 10.1016/j.renene.2010.07.019

Athar, M. and Zaidi, S. (2020) 'A review of the feedstocks, catalysts, and intensification techniques for sustainable biodiesel production', *Journal of Environmental Chemical Engineering*, 8(6), p. 104523. doi: 10.1016/j.jece.2020.104523

Ayu, D. *et al.* (2019) 'Catalytic Transesterification of Used Cooking Oil to Biodiesel: Effect of Oil-Methanol Molar Ratio and Reaction Time', *Automotive Experiences*, 2(3), pp. 73–77. doi: 10.31603/ae.v2i3.2991

Babadi, A.A. *et al.* (2022) 'Emerging technologies for biodiesel production: Processes, challenges, and opportunities', *Biomass and Bioenergy*, 163, p. 106521. doi: 10.1016/j.biombioe.2022.106521

Bashir, M.A. *et al.* (2022) 'Recent development of advanced processing technologies for biodiesel production: A critical review', *Fuel Processing Technology*, 227, p. 107120. doi: 10.1016/j.fuproc.2021.107120

Baweja, S., Trehan, A. and Kumar, R. (2021) 'Combustion, performance, and emission analysis of a CI engine fueled with mustard oil biodiesel blended in diesel fuel', *Fuel*, 292, p. 120346. doi: 10.1016/j.fuel.2021.120346

Bet-Moushoul, E. *et al.* (2016) 'Application of CaO-based/Au nanoparticles as heterogeneous nanocatalysts in biodiesel production', *Fuel*, 164, pp. 119–127. doi: 10.1016/j.fuel.2015.09.067

Catarino, M. *et al.* (2020) 'Dry washing biodiesel purification using fumed silica sorbent', *Chemical Engineering Journal*, 386, p. 123930. doi: 10.1016/j.cej.2019.123930

Cercado, A.P., Ballesteros, F., JR and Capareda, S. (2018) 'Biodiesel from Three Microalgae Transesterification Processes using Different Homogenous Catalysts', *International Journal of Technology*, 9(4), p. 645. doi: 10.14716/ijtech.v9i4.1145

Chimezie, E.C. *et al.* (2023) 'Yield optimization and fuel properties evaluation of the biodiesel derived from avocado pear waste', *Industrial Crops and Products*, 191, p. 115884. doi: 10.1016/j.indcrop.2022.115884

Chozhavendhan, S. *et al.* (2020) 'A review on influencing parameters of biodiesel production and purification processes', *Current Research in Green and Sustainable Chemistry*, 1-2, pp. 1–6. doi: 10.1016/j.crgsc.2020.04.002

Coniglio, L. *et al.* (2013) 'Combustion chemical kinetics of biodiesel and related compounds (methyl and ethyl esters): Experiments and modeling – Advances and future refinements', *Progress in Energy and Combustion Science*, 39(4), pp. 340–382. doi: 10.1016/j.pecs.2013.03.002

Das, A., Ghatak, M.D. and Mahanta, P. (2023) 'Production Optimization for a Biofuel Prepared from a High Acid Value Fuel like Nahar Oil, Its Properties and Feasibility to Use in a Four-Stroke DI Diesel Engine', in Pradhan, P. *et al.* (eds.) *Recent Advances in Mechanical Engineering.* (Lecture Notes in Mechanical Engineering). Singapore: Springer Nature Singapore, pp. 699–708.

Demirbas, A. (2008) 'Comparison of transesterification methods for production of biodiesel from vegetable oils and fats', *Energy Conversion and Management*, 49(1), pp. 125–130. doi: 10.1016/j.enconman.2007.05.002

Devarajan, Y. *et al.* (2022) 'Inedible oil feedstocks for biodiesel production: A review of production technologies and physicochemical properties', *Sustainable Chemistry and Pharmacy*, 30, p. 100840. doi: 10.1016/j.scp.2022.100840

Elango, R.K. *et al.* (2019) 'Transesterification of castor oil for biodiesel production: Process optimization and characterization', *Microchemical Journal*, 145, pp. 1162–1168. doi: 10.1016/j.microc.2018.12.039

Elgarahy, A.M. *et al.* (2023) 'Sustainable management of food waste; pre-treatment strategies, techno-economic assessment, bibliometric analysis, and potential utilizations: A systematic review', *Environmental Research*, 225, p. 115558. doi: 10.1016/j.envres.2023.115558

Elgharbawy, A.S. *et al.* (2021) 'Maximizing biodiesel production from high free fatty acids feedstocks through glycerolysis treatment', *Biomass and Bioenergy*, 146, p. 105997. doi: 10.1016/j.biombioe.2021.105997

Enweremadu, C.C. and Mbarawa, M.M. (2009) 'Technical aspects of production and analysis of biodiesel from used cooking oil--A review', *Renewable and Sustainable*

Energy Reviews, 13(9), pp. 2205–2224. Available at: https://ideas.repec.org/a/eee/rensus/v13y2009i9p2205-2224.html.

Etim, A.O., Musonge, P. and Eloka-Eboka, A.C. (2022) 'Process optimization of bio-alkaline catalysed transesterification of flax seed oil methyl ester', *Scientific African*, 16, e01275. doi: 10.1016/j.sciaf.2022.e01275

Fadhil, A.B., Al-Tikrity, E.T.B. and Ibraheem, K.K. (2019) 'Transesterification of Bitter Almond Oil as a New Non-edible Feedstock with Mixed Alcohols System: Parameter Optimization and Analysis of Biodiesel', *Waste and Biomass Valorization*, 10(6), pp. 1597–1608. doi: 10.1007/s12649-017-0172-y

Falowo, O.A. and Betiku, E. (2022) 'A novel heterogeneous catalyst synthesis from agrowastes mixture and application in transesterification of yellow oleander-rubber oil: Optimization by Taguchi approach', *Fuel*, 312, p. 122999. doi: 10.1016/j.fuel.2021.122999

Fayyazi, E. *et al.* (2021) 'Biodiesel fuel purification in a continuous centrifugal contactor separator: An environmental-friendly approach', *Sustainable Energy Technologies and Assessments*, 47, p. 101511. doi: 10.1016/j.seta.2021.101511

Feng, L. *et al.* (2022) 'Techno-economic and profitability analysis of plant for producing biodiesel from fresh vegetable oil and waste frying oil on large-scale', *Fuel*, 323, p. 124304. doi: 10.1016/j.fuel.2022.124304

Ganesan, N. and Masimalai, S. (2020) 'Experimental investigation on a performance and emission characteristics of single cylinder diesel engine powered by waste orange peel oil biodiesel blended with antioxidant additive', *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 42(11), pp. 1412–1423. doi: 10.1080/15567036.2019.1604856

García-Martín, J.F. *et al.* (2018) 'Biodiesel production from waste cooking oil in an oscillatory flow reactor. Performance as a fuel on a TDI diesel engine', *Renewable Energy*, 125, pp. 546–556. doi: 10.1016/j.renene.2018.03.002

Gaurav, A. *et al.* (2019) 'A kinetic model for a single step biodiesel production from a high free fatty acid (FFA) biodiesel feedstock over a solid heteropolyacid catalyst', *Green Energy & Environment*, 4(3), pp. 328–341. doi: 10.1016/j.gee.2019.03.004

Goncharov S.V. (2020) 'National rapeseed breeding in accordance with agribusiness export needs'.

Hadhoum, L. *et al.* (2022) 'Experimental Investigation on the Supercritical Rapeseed Methanolysis for Biofuel Production: Effects of the Operating Conditions on the Bio-oil Viscosity', *BioEnergy Research*, 15(2), pp. 1304–1315. doi: 10.1007/s12155-021-10330-z

Hadiyanto, H. *et al.* (2020) 'Multi-Feedstocks Biodiesel Production from Esterification of Calophyllum inophyllum Oil, Castor Oil, Palm Oil and Waste Cooking Oil', *International Journal of Renewable Energy Development*, 9(1), pp. 119–123. doi: 10.14710/ijred.9.1.119-123

Hájek, M. *et al.* (2020) 'The description of catalyst behaviour during transesterification of rapeseed oil – Formation of micellar emulsion', *Renewable Energy*, 159, pp. 938–943. doi: 10.1016/j.renene.2020.06.082

Hosseinzadeh-Bandbafha, H. *et al.* (2022) 'Environmental life cycle assessment of biodiesel production from waste cooking oil: A systematic review', *Renewable and Sustainable Energy Reviews*, 161, p. 112411. doi: 10.1016/j.rser.2022.112411

IEA (2023) *Transport biofuels – Renewables 2022 – Analysis - IEA,* 24 May. Available at: https://www.iea.org/reports/renewables-2022/transport-biofuels (Accessed: 24 May 2023).

Isah, A.G. *et al.* (2022) 'Oxidation stability and cold flow properties of biodiesel synthesized from castor oil: Influence of alkaline catalysts type and purification techniques', *Materials Today: Proceedings*, 57, pp. 748–752. doi: 10.1016/j.matpr.2022.02.220

Ishak, S. and Kamari, A. (2019) 'A review of optimum conditions of transesterification process for biodiesel production from various feedstocks', *International Journal of Environmental Science and Technology*, 16(5), pp. 2481–2502. doi: 10.1007/s13762-019-02279-6

Jafarihaghighi, F. *et al.* (2022) 'Comparing among second, third, and fourth generations (genetically modified) of biodiesel feedstocks from the perspective of engine, exhaust gasses and fatty acid: Comparative assessment', *Cleaner Chemical Engineering*, 2, p. 100025. doi: 10.1016/j.clce.2022.100025

Jeyaseelan, T. *et al.* (2023) 'A techno-economic assessment of waste oil biodiesel blends for automotive applications in urban areas: Case of India', *Energy*, 271, p. 127021. doi: 10.1016/j.energy.2023.127021

Jisieike, C.F. *et al.* (2023) 'Crude rubber seed oil esterification using a solid catalyst: Optimization by hybrid adaptive neuro-fuzzy inference system and response surface methodology', *Energy*, 263, p. 125734. doi: 10.1016/j.energy.2022.125734

Joshi, S.M., Gogate, P.R. and Suresh Kumar, S. (2018) 'Intensification of esterification of karanja oil for production of biodiesel using ultrasound assisted approach with optimization using response surface methodology', *Chemical Engineering and Processing - Process Intensification*, 124, pp. 186–198. doi: 10.1016/j.cep.2017.12.010

Julio, A.A.V. *et al.* (2022) 'Techno-economic and environmental potential of Renewable Diesel as complementation for diesel and biodiesel in Brazil: A comprehensive review and perspectives', *Journal of Cleaner Production*, 371, p. 133431. doi: 10.1016/j.jclepro.2022.133431

Karacan, S. and Karacan, F. (2015) 'Steady-state optimization for biodiesel production in a reactive distillation column', *Clean Technologies and Environmental Policy*, 17(5), pp. 1207–1215. doi: 10.1007/s10098-015-0964-3

Kayode, B. and Hart, A. (2019) 'An overview of transesterification methods for producing biodiesel from waste vegetable oils', *Biofuels*, 10(3), pp. 419–437. doi: 10.1080/17597269.2017.1306683

Khan, I.A. *et al.* (2020) 'Efficient production of biodiesel from Cannabis sativa oil using intensified transesterification (hydrodynamic cavitation) method', *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 42(20), pp. 2461–2470. doi: 10.1080/15567036.2019.1607946

Kondrasheva, N. and Eremeeva, A. (2023) 'Production of biodiesel fuel from vegetable raw materials', *Journal of Mining Institute*, 260, pp. 248–256. doi: 10.31897/PMI.2022.15

Kondrasheva N. K. (2017) 'Study of the influence of additives and supplements for performance and environmental performance diesel fuel', *Bulletin of the Saint Petersburg State Institute of Technology (Technical University) | Bulletin of St PbSIT(TU)* (38 (64)), pp. 86–89. Available at: https://cyberleninka.ru/article/n/izuchenie-vliyaniya-prisadok-i-dobavok-na-ekspluatatsionnye-i-ekologicheskie-harakteristiki-dizelnogo-topliva.

Kondrasheva N. K. (2018a) 'Development of domestic technologies of produsing high quality clean diesel fuel', *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.*, 61(9-10),

pp. 76–82. Available at: https://cyberleninka.ru/article/n/razrabotka-otechestvennoy-tehnologii-polucheniya-vysokokachestvennogo-ekologicheski-chistogo-dizelnogo-topliva.

Kondrasheva N. K. (2018b) 'Reduction of harmful emissions from the operation diesel engine', *Известия Санкт-Петербургского государственного технологического института (технического университета)* (42 (68)), pp. 54–57. Available at: https://cyberleninka.ru/article/n/snizhenie-vrednyh-vybrosov-pri-rabote-dizelnogo-dvigatelya.

Korshunov, G., Eremeeva, A. and Drebenstedt, C. (2021) 'Justification of the use of a vegetal additive to diesel fuel as a method of protecting underground personnel of coal mines from the impact of harmful emissions of diesel-hydraulic locomotives', *Journal of Mining Institute*, 247, pp. 39–47. doi: 10.31897/PMI.2021.1.5

Kumar, A., Singh, V.P. and Srivastava, A. (2022) 'Quality biodiesel via biotransesterification from inedible renewable sources', *Journal of Cleaner Production*, 379, p. 134653. doi: 10.1016/j.jclepro.2022.134653

Kumar, L.R. *et al.* (2020) 'Cost, energy and GHG emission assessment for microbial biodiesel production through valorization of municipal sludge and crude glycerol', *Bioresource Technology*, 297, p. 122404. doi: 10.1016/J.BIORTECH.2019.122404

Kumar, S., Singhal, M.K. and Sharma, M.P. (2022) 'Predictability of Biodiesel Fuel Properties from the Fatty Acid Composition of the Feedstock Oils', *Arabian Journal for Science and Engineering*, 47(5), pp. 5671–5691. doi: 10.1007/s13369-021-05564-0

Läubli, M.W. and Bruttel, P.A. (1986) 'Determination of the oxidative stability of fats and oils: Comparison between the active oxygen method (AOCS Cd 12-57) and the rancimat method', *Journal of the American Oil Chemists' Society*, 63(6), pp. 792–795. doi: 10.1007/BF02541966

Li, R. (2022) 'Integrating the composition of food waste into the techno-economic analysis of waste biorefineries for biodiesel production', *Bioresource Technology Reports*, 20, p. 101254. doi: 10.1016/j.biteb.2022.101254

Liu, X. *et al.* (2021) 'Recent progress on biodiesel production from municipal sewage sludge', *Renewable and Sustainable Energy Reviews*, 135, p. 110260. doi: 10.1016/j.rser.2020.110260

Maheshwari, P. *et al.* (2022) 'A review on latest trends in cleaner biodiesel production: Role of feedstock, production methods, and catalysts', *Journal of Cleaner Production*, 355, p. 131588. doi: 10.1016/j.jclepro.2022.131588

Manaf, I.S.A. *et al.* (2019) 'A review for key challenges of the development of biodiesel industry', *Energy Conversion and Management*, 185, pp. 508–517. doi: 10.1016/j.enconman.2019.02.019

Maroušek, J. *et al.* (2023) 'Techno-economic identification of production factors threatening the competitiveness of algae biodiesel', *Fuel*, 344, p. 128056. doi: 10.1016/j.fuel.2023.128056

Mathew, G.M. *et al.* (2021) 'Recent advances in biodiesel production: Challenges and solutions', *The Science of the Total Environment*, 794, p. 148751. doi: 10.1016/j.scitotenv.2021.148751

Mohadesi, M. *et al.* (2019) 'Production of biodiesel from waste cooking oil using a homogeneous catalyst: Study of semi-industrial pilot of microreactor', *Renewable Energy*, 136, pp. 677–682. doi: 10.1016/j.renene.2019.01.039

Nabgan, W. *et al.* (2022) 'Sustainable biodiesel generation through catalytic transesterification of waste sources: a literature review and bibliometric survey', *RSC Advances*, 12(3), pp. 1604–1627. doi: 10.1039/d1ra07338a

Nawaz, K. *et al.* (2023) 'Optimised transesterification of used frying oils: production and characterisation of biodiesel', *International Journal of Environmental Analytical Chemistry*, 103(7), pp. 1615–1632. doi: 10.1080/03067319.2021.1878164

Nježić, Z.B. *et al.* (2023) 'Kinetics and optimization of biodiesel production from rapeseed oil over calcined waste filter cake from sugar beet processing plant', *Fuel*, 334, p. 126581. doi: 10.1016/j.fuel.2022.126581

Noriega, M.A. and Narváez, P.C. (2020) 'Scale-up and cost analysis of biodiesel production using liquid-liquid film reactors: Reduction in the methanol consumption and investment cost', *Energy*, 211, p. 118724. doi: 10.1016/J.ENERGY.2020.118724

Paptsov A.G. (2019) 'Forecast of scientific and technical development of crop production, including seed production and organic farming in Russia, in the period up to 2030'.

Paul, A.A.L. and Adewale, F.J. (2018) 'Data on optimization of production parameters on Persea Americana (Avocado) plant oil biodiesel yield and quality', *Data in Brief*, 20, pp. 855–863. doi: 10.1016/j.dib.2018.08.064

Pooja, S. *et al.* (2021) 'Efficient production and optimization of biodiesel from kapok (Ceiba pentandra) oil by lipase transesterification process: Addressing positive environmental impact', *Renewable Energy*, 165, pp. 619–631. doi: 10.1016/j.renene.2020.11.053

Pydimalla, M. *et al.* (2023) 'Sustainable biodiesel: A comprehensive review on feedstock, production methods, applications, challenges and opportunities', *Materials Today: Proceedings*. doi: 10.1016/j.matpr.2023.03.593

Rajkumari, K. and Rokhum, L. (2020) 'A sustainable protocol for production of biodiesel by transesterification of soybean oil using banana trunk ash as a heterogeneous catalyst', *Biomass Conversion and Biorefinery*, 10(4), pp. 839–848. doi: 10.1007/s13399-020-00647-8

Research, A.M. 'Biodiesel Market to grow at 4.7% CAGR to hit US $47.90 billion by 2025 – Global Insights on Key Stakeholders, Leading Players, Value Chain Analysis, Regulatory Framework and Business Opportunities: Adroit Market Research', *Adroit Market Research*. Available at: https://www.globenewswire.com/news-release/2020/06/25/2053297/0/en/Biodiesel-Market-to-grow-at-4-7-CAGR-to-hit-US-47-90-billion-by-2025-Global-Insights-on-Key-Stakeholders-Leading-Players-Value-Chain-Analysis-Regulatory-Framework-and-Business-Oppo.html (Accessed: 24 May 2023).

Rezania, S. *et al.* (2019) 'Review on transesterification of non-edible sources for biodiesel production with a focus on economic aspects, fuel properties and by-product applications', *Energy Conversion and Management*, 201, p. 112155. doi: 10.1016/j.enconman.2019.112155

Rocha-Meneses, L. *et al.* (2023) 'Recent advances on biodiesel production from waste cooking oil (WCO): A review of reactors, catalysts, and optimization techniques impacting the production', *Fuel*, 348, p. 128514. doi: 10.1016/j.fuel.2023.128514

Rodriguez, N.E. and Martinello, M.A. (2021) 'Molecular distillation applied to the purification of biodiesel from ethanol and soybean oil', *Fuel*, 296, p. 120597. doi: 10.1016/j.fuel.2021.120597

Sahar *et al.* (2018) 'Biodiesel production from waste cooking oil: An efficient technique to convert waste into biodiesel', *Sustainable Cities and Society*, 41, pp. 220–226. doi: 10.1016/j.scs.2018.05.037

Sajjad, N. *et al.* (2022) 'Biodiesel Production from Alkali-Catalyzed Transesterification of Tamarindus indica Seed Oil and Optimization of Process Conditions', *Molecules (Basel, Switzerland)*, 27(10). doi: 10.3390/molecules27103230

Sales, M.B. *et al.* (2022) 'Sustainable Feedstocks and Challenges in Biodiesel Production: An Advanced Bibliometric Analysis', *Bioengineering (Basel, Switzerland)*, 9(10). doi: 10.3390/bioengineering9100539

Šalić, A. *et al.* (2020) 'Biodiesel purification in microextractors: Choline chloride based deep eutectic solvents vs water', *Separation and Purification Technology*, 242, p. 116783. doi: 10.1016/j.seppur.2020.116783

Sandouqa, A., Al-Shannag, M. and Al-Hamamre, Z. (2020) 'Biodiesel purification using biomass-based adsorbent manufactured from delignified olive cake residues', *Renewable Energy*, 151, pp. 103–117. doi: 10.1016/j.renene.2019.11.009

Saputra Nursal, R. *et al.* (2021) 'Autoignition behavior and emission of biodiesel from palm oil, waste cooking oil, tyre pyrolysis oil, algae and jatropha', *Fuel*, 306, p. 121695. doi: 10.1016/j.fuel.2021.121695

Selemani, A. and Kombe, G.G. (2022) 'Glycerolysis of high free fatty acid oil by heterogeneous catalyst for biodiesel production', *Results in Engineering*, 16, p. 100602. doi: 10.1016/j.rineng.2022.100602

Silviana, S. *et al.* (2022a) 'A Review on the Recent Breakthrough Methods and Influential Parameters in the Biodiesel Synthesis and Purification', *International Journal of Renewable Energy Development*, 11(4), pp. 1012–1036. doi: 10.14710/ijred.2022.43147

Silviana, S. *et al.* (2022b) 'A Review on the Recent Breakthrough Methods and Influential Parameters in the Biodiesel Synthesis and Purification', *International Journal of Renewable Energy Development*, 11(4), pp. 1012–1036. doi: 10.14710/ijred.2022.43147

Sokač, T. *et al.* (2020) 'Purification of biodiesel produced by lipase catalysed transesterification by ultrafiltration: Selection of membranes and analysis of membrane blocking mechanisms', *Renewable Energy*, 159, pp. 642–651. doi: 10.1016/j.renene.2020.05.132

Stojković, I.J. *et al.* (2014) ‘Purification technologies for crude biodiesel obtained by alkali-catalyzed transesterification’, *Renewable and Sustainable Energy Reviews*, 32, pp. 1–15. doi: 10.1016/j.rser.2014.01.005

Su, Y., Zhang, P. and Su, Y. (2015) ‘An overview of biofuels policies and industrialization in the major biofuel producing countries’, *Renewable and Sustainable Energy Reviews*, 50, pp. 991–1003. doi: 10.1016/j.rser.2015.04.032

Suthar, K., Dwivedi, A. and Joshipura, M. (2019) ‘A review on separation and purification techniques for biodiesel production with special emphasis on Jatropha oil as a feedstock’, *Asia-Pacific Journal of Chemical Engineering*, 14(5). doi: 10.1002/apj.2361

Tarasevich B.N. (2012) *Basics of IR spectroscopy with Fourier transform. Sample preparation in IR spectroscopy*. Moscow: Lomonosov Moscow State University.

Tebas, S.d.O.G. *et al.* (2021) ‘Mild conditions in the transesterification reaction of babassu oil and purified fusel oil’, *Chemical Engineering Communications*, 208(3), pp. 432–440. doi: 10.1080/00986445.2019.1710495

Utami, M. *et al.* (2022) ‘Synthesis of biodiesel from castor oil catalyzed by sodium hydroxide dispersed on bentonite’, *Sustainable Energy Technologies and Assessments*, 53, p. 102526. doi: 10.1016/j.seta.2022.102526

V.A. Zvonov (2008) ‘Investigation of the effectiveness of the use of fuel mixtures and biofuels in diesel engines’.

Vávra, A., Hájek, M. and Skopal, F. (2018) ‘Acceleration and simplification of separation by addition of inorganic acid in biodiesel production’, *Journal of Cleaner Production*, 192, pp. 390–395. doi: 10.1016/j.jclepro.2018.04.242

Velvizhi, G. *et al.* (2023) ‘Carbon credit reduction: A techno-economic analysis of "drop-in" fuel production’, *Environmental Pollution (Barking, Essex : 1987)*, 316(Pt 1), p. 120507. doi: 10.1016/j.envpol.2022.120507

Verma, P., Sharma, M.P. and Dwivedi, G. (2016) ‘Impact of alcohol on biodiesel production and properties’, *Renewable and Sustainable Energy Reviews*, 56, pp. 319–333. doi: 10.1016/j.rser.2015.11.048

Xu, H. *et al.* (2022) ‘Life Cycle Greenhouse Gas Emissions of Biodiesel and Renewable Diesel Production in the United States’, *Environmental Science & Technology*, 56(12), pp. 7512–7521. doi: 10.1021/acs.est.2c00289

Yaashikaa, P.R. *et al.* (2022a) 'A review on biodiesel production by algal biomass: Outlook on lifecycle assessment and techno-economic analysis', *Fuel*, 324, p. 124774. doi: 10.1016/j.fuel.2022.124774

Yaashikaa, P.R. *et al.* (2022b) 'A review on biodiesel production by algal biomass: Outlook on lifecycle assessment and techno-economic analysis', *Fuel*, 324, p. 124774. doi: 10.1016/j.fuel.2022.124774

Zahan, K. and Kano, M. (2018) 'Biodiesel Production from Palm Oil, Its By-Products, and Mill Effluent: A Review', *Energies*, 11(8), p. 2132. doi: 10.3390/en11082132

Zhang, Y. *et al.* (2003) 'Biodiesel production from waste cooking oil: 1. Process design and technological assessment', *Bioresource Technology*, 89(1), pp. 1–16. doi: 10.1016/S0960-8524(03)00040-3

Zulqarnain *et al.* (2021) 'A Comprehensive Review on Oil Extraction and Biodiesel Production Technologies', *Sustainability*, 13(2), p. 788. doi: 10.3390/su13020788

https://www.apk-inform.com/ru/exclusive/topic/1528162 (2022), 16 July (Accessed: 24 May 2023).

9 List of Figures

10 List of Tables

11 List of Abbreviations

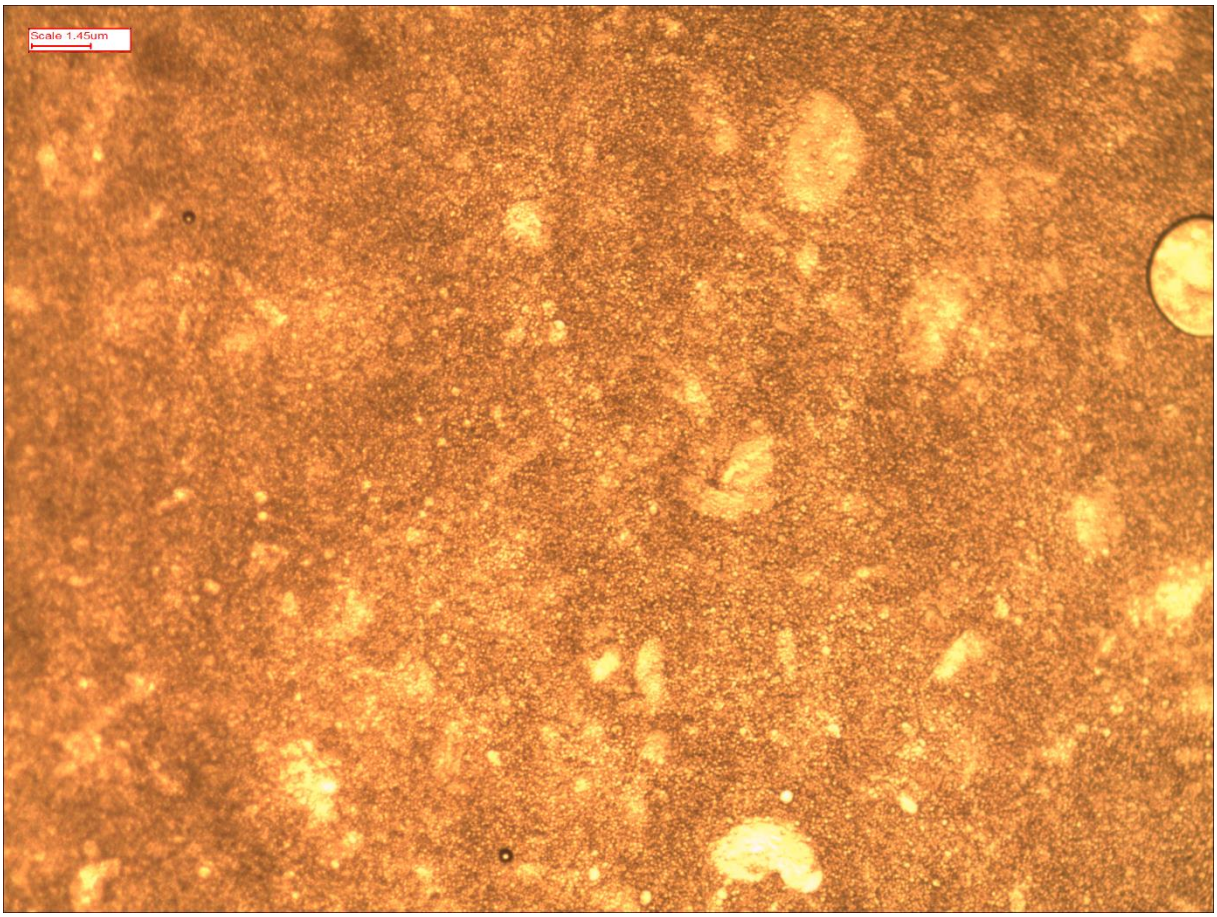
FFA	Free Fatty Acids
FAME	Fatty Acids Methyl Esters
FAEE	Fatty Acids Ethyl Esters
OAEE	Oleic Acid Ethyl Ester

Annex Table of Contents

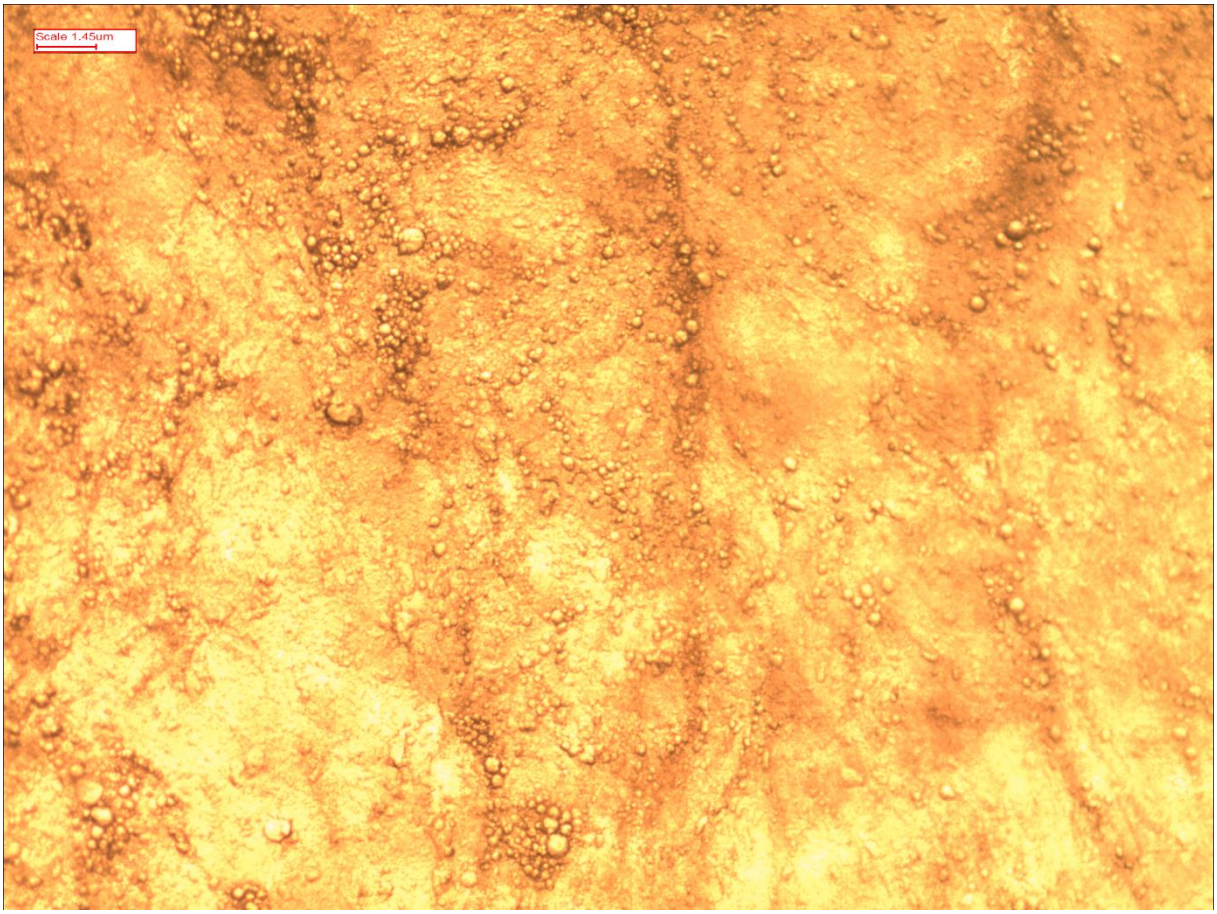
Annex 1. Photographs of emulsions

The annex contains photographs of emulsions obtained with the LOMO MSP-2 microscope camera

Photograph of a homogeneous phase-water emulsion



Photograph of the Ether-phase-water emulsion



Photograph of the glycerin phase-water emulsion