

Article

Determination of the Effect of the Addition of Second-Generation Biodiesel BBuE to Diesel Fuel on Selected Parameters of “B” Fuels

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Abstract: Progressive and increasingly noticeable climate change is forcing the search for new energy sources to reduce greenhouse gas emissions, especially carbon dioxide. One way to reduce greenhouse gas emissions is by gradually replacing fossil fuels with biofuels. The authors of this work addressed the production of second-generation biofuel. The purpose of this study was to produce second-generation biodiesel from babassu palm oil (BBuE) and first-generation biodiesel from rapeseed oil (RME), to study their properties, and to determine the effect of the addition of these biodiesels to diesel fuel on selected properties of “B” fuels that affect the fuel–air mixture formation process and the combustion process. Biodiesel from babassu oil was produced because it is non-edible and has a different composition than canola oil. Then, fuels were prepared that were mixtures of diesel oil and biodiesel containing from 10 to 40% (*v/v*) BBuE or RME (B10, B20, B30, and B40). Tests were conducted on selected physicochemical properties of the obtained fuels. “B” fuels prepared with BBuE and DF were shown to have more favorable fuel properties than those obtained from RME and DF. Fuels that are blends of BBuE and DF have slightly higher heating values, higher cetane number values, a more favorable distillation curve, lower dynamic viscosity values as a function of temperature, and marginally lower flash point values compared to the corresponding blends of RME and DF. Esters with shorter molecules have been shown to have more favorable fuel properties.

Keywords: renewable fuels; biodiesel production; transesterification; non-edible fuel sources; babassu butyl esters; rapeseed methyl esters; second-generation biofuels; first-generation biofuel; improved fuel properties



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1. Introduction

Internal combustion engines are still the primary source of propulsion in transportation. They also have significant applications in other areas of the human economy. Demands to reduce their harmful environmental impact force the search for new fuels that could gradually replace conventional fuels derived from crude oil. Fuels obtained from organic matter are essential. Such fuels in liquid or gaseous form, used to power internal combustion engines, are called biofuels [1]. Biofuels can be obtained from both plant and animal organic matter. More common, of course, is using plant organic matter for fuel. Animal

fat waste is being tried for fuel purposes. Rudolf Diesel already used vegetable-derived oil to power the first compression-ignition engine. However, the availability of fuels from oil later met fuel needs for transportation and beyond for decades. Fatty acid esters are primarily sourced from vegetable oils and used to power compression-ignition engines. However, they satisfy the fuel requirements for these engines only to a small extent. Work is ongoing all the time to find new raw materials for obtaining esters for fuel purposes.

Palm oil is the most produced oil in the world. Its share of global production is approximately 37% [2]. Next in line is oil extracted from soybeans (approximately 27%). The next position is rapeseed oil, the most popular in Europe and Poland, with a share of 14%. Like several others, these oils are a food source for humans. For this reason, they cannot be used indefinitely to produce fuels used to power engines. This could cause food prices to rise. Nutritional requirements should take priority over fuel needs. Fuels derived from edible plants are now classified as first-generation biofuels. The technology for obtaining and using this type of biofuel is best recognized [3–8]. The use of edible raw materials for ester production is due to their high availability and ease of production. The most important disadvantage of this type of raw material is the possibility of an increase in its price and the cost of food products. The above disadvantage is due to the limited area of fuel crops.

The prospect of rising food prices and possible related social problems have necessitated the search for new raw materials for ester production. The concept of second-generation biofuels has been introduced. They are obtained from non-consumable vegetable oils and waste organic matter [3,4,9–14]. Inedible plants are not in direct competition with food crops. However, they may contribute to a reduction in the area under food crops and thus may impact food price formation. The raw materials for obtaining esters as second-generation biofuels also include distinct types of biological waste. This waste can come from agriculture, food preparation, the food industry, and other industries where organic matter is used. The raw materials to produce second-generation esters are waste oils used in food production and preparation [15–18]. Uddin et al. used oil from coffee grounds to produce the esters [19]. Animal waste also produces esters [20–22]. In the work [23], the feedstock for biodiesel production was a mixture of poultry and pig fat residues. A feature of the waste from which esters can be produced is the low cost of obtaining it. In addition, organic waste can be a problem due to the need to dispose of it. It can, therefore, be used to produce renewable fuel. The authors of the publication [9] made esters from waste animal fats from industries involved in the preparation of animal skins subsequently used in the production of footwear and clothing. The authors of the paper [24] show that the impact of using plant-based feedstocks to produce second-generation biofuels on food prices is unclear. They do not support the view that second-generation biofuels are sometimes presented as a solution to the problem of producing food and fuel from plants. Growing non-edible crops can compete for soil with crops grown for consumption.

Today, third- and fourth-generation biofuels are also distinguished. These are the fuels of the future, the production of which is currently being researched. Third-generation biofuels will be obtained from organic matter extracted from algae or other feedstocks from crops modified using molecular biological techniques [25]. For many years, research has been conducted on the use of algae in the energy industry, including in the production of biomass for energy and biofuel production [26–30]. Algae have high biomass yields and high oil content and do not require cultivation on agricultural land [31]. Microalgae can be grown on non-agricultural land, so they do not compete with crops grown for food. Forward-looking production technologies incorporating carbon capture, using plants with enhanced carbon assimilation at the cultivation stage, are considered the fourth generation of biofuels [32,33]. Fourth-generation biofuels result from efforts to close the carbon balance and eliminate its environmental impact. The technologies used must consider the possibility of capturing carbon dioxide from the atmosphere and offer the option of storing it. The fourth generation of biofuels will achieve a carbon-neutral economy [4]. Third- and fourth-generation biofuels can significantly increase the use of fuels derived from organic

matter and environmental improvements in the future. It should be emphasized that esters as engine fuel have a beneficial impact on the environment not only because they are renewable fuels. The positive impact is also reflected in the impact on the composition of exhaust gases. The ester molecule contains oxygen atoms, which is why esters are classified as oxygenated fuels. These types of fuels typically reduce exhaust emissions of particulate matter, carbon monoxide, and hydrocarbons [34–36].

The babassu palm grows in the natural forests of the Amazon. It is not an agricultural crop grown for the food industry. As the authors of publications [37,38] show, the possibility of extracting biomass from this palm (fruit, babassu oil) for use in electricity generation is being considered in Brazil. These resources are renewable and underutilized to a significant extent. Therefore, the economic benefit of these resources for electricity generation is being considered. In addition, fuel can be produced from palm fruit to power engines. Girardi et al., in their work, conclude that biodiesel from babassu has suitable physical and chemical properties and can become a commercial biofuel [39]. Ferreira et al. pointed out the high potential of babassu oil production in Brazil and the possibility of using it for biodiesel production [40].

The authors of publications [41–43] list the oil obtained from babassu palm as inedible and include it among the raw materials from which second-generation biodiesel is obtained. Babassu oil is characterized by unfavorable composition and arrangement of fatty acids and the content and ratio of omega 3 to omega 6 acids. Therefore, from the point of view of human health, this type of oil should not be applied in the food industry. Its intended use is the cosmetics industry. For such use, it has an excellent composition of fatty acids and other accompanying substances. Adequate content of omega 3 and omega 6 fatty acids is essential in vegetable oil as it is known that the human body can synthesize all the fatty acids needed for metabolism, except for two: C18:2 linoleic acid of the omega 6 group and α -linolenic C18:3 of the omega 3 group. The amount of C18:2 and C18:3 acids in edible oil are particularly essential to the body. Rapeseed oil is approximately 30% (*w/w*); meanwhile, in babassu oil, these acids are only about 3.2% (*w/w*), which is 10 times lower. Babassu oil, in its structure, contains few precious acids. Instead, it contains acids that are not important to the body. This is a critical argument for why babassu oil should not be used in the food industry. On the other hand, it can be used to produce esters as fuel for compression-ignition engines.

2. Genesis and Innovation of Research

The authors of this article are researching future biofuels in the form of new-generation esters for powering compression-ignition engines. They should be made from non-food raw materials and have the most favorable characteristics possible from the point of view of engine power. No widely known oilseed crops in the world have been modified to produce biofuels. Efforts should be made to obtain plants from which the oil grown would have properties that would predispose it to the efficient production of esters with favorable properties for powering engines. Oilseed crops have so far been modified for the food industry. In Europe, for example, the staple crop is rapeseed, which for many years has been modified solely for food so that in its structure, it does not have fatty acids that are unfavorable from the point of view of health and so that it contains a favorable arrangement of fatty acids that are part of the so-called omega 3 and omega 6 acids. What is known is that the hydrocarbons that make up diesel fuel consist of shorter chains, which are characterized by, among other things, better distillation properties, volatility, lower density, and kinematic and dynamic viscosity. All biodiesels have the inferior properties mentioned above. We wish to acquire a plant or, together with breeders and geneticists, develop a new plant dedicated to biofuels. This can be achieved by introducing shorter fatty acids into the structure, which would allow future biofuel production with more favorable properties than those currently produced. Therefore, as part of our ongoing work, we set ourselves the goal of finding a plant with short fatty acids in the oil structure, compared to plants commonly used for ester production, such as rapeseed. After analyzing the literature, we

selected the babassu plant, whose oil has substantial amounts of C-8 to C-12 fatty acids, which are not found in rapeseed. A different composition of fatty acids, including a high content of short-chain esters, will favorably affect the fuel properties of esters, on which the formation of the fuel–air mixture and its combustion process depend. The knowledge gained can be used in developing dedicated plants for biofuel production.

The research topic undertaken is innovative for several reasons. The oil obtained from the Babassu palm was selected for biodiesel production because its fatty acid composition is fundamentally different from the fatty acid composition of oil from the plants currently used for biodiesel production in Europe, North America, and Asia. In Poland and Europe, rapeseed oil with a different fatty acid composition than babassu oil is commonly used to produce biodiesel. Babassu oil comprises approximately 70% (*w/w*) C-6 to C-14 fatty acids. Meanwhile, rapeseed oil, for example, consists of roughly 90% (*w/w*) C-18:1 to C-18:3 fatty acids. Babassu oil contains short fatty acids, so we expected the resulting BBUe to have favorable properties, especially in distillation temperature, flash point, and viscosity. Another reason for our interest in this vegetable oil is that it is widely considered inedible, so the resulting biofuel has second-generation fuel status. Among other things, the publication's authors [44] state that babassu oil is considered inedible because of the high proportion of saturated fatty acids. Ferreira et al. report that there are between 84.4% and 96.6% saturated fatty acids in babassu oil [40].

In addition, the innovation of the research conducted is that we used sulfuric acid and n-butyl alcohol (C₄H₉OH) to prepare a mixture that catalyzes the transesterification process, that is, the production of biodiesel. Currently, on an industrial scale, the transesterification process uses methyl alcohol or, much less frequently, ethyl alcohol and a catalyst in the form of potassium hydroxide KOH or sodium hydroxide NaOH. Technologies for producing biodiesel from babassu oil are described in the literature [40,45–50]. The literature review found no papers that used n-butyl alcohol and sulfuric acid as a catalyst to produce biodiesel from babassu oil.

The issues presented in this publication focus on the effect of adding manufactured BBUe and RME esters to diesel fuel on selected properties of increasingly used “B” fuels (i.e., blends of diesel and biodiesel). The paper also compares selected fuel parameters of second-generation biodiesel BBUe with first-generation biodiesel RME and diesel DF. As part of the work already completed, laboratory tests on small samples were conducted on the possibility of producing biodiesel from babassu oil [51]. In contrast, in the work presented here, BBUe biodiesel was produced in a reactor under technical conditions, that is, those found in small refineries. Previously, a study of the effect on engine performance indicators fueled by new-generation biodiesel compared to first-generation biodiesel was also conducted, and the results have already been published [14].

“B” fuels testing is warranted. This is because there is currently no way to replace diesel fuel with biodiesel derived from organic matter. This is due to limited access to raw materials. In addition, manufacturers of modern compression-ignition engines do not recommend using pure esters to power them and are not willing to provide warranties for engines powered by pure esters. Increasingly, however, diesel fuels with ester blends are being used. Currently, according to the standard PN-EN 590:2022-08 [52], diesel oils with a volume share of esters of 7% (*v/v*) are used in Poland. This share will increase in the future. Testing “B” fuels with an ester content of 10% (*v/v*) or more is essential. This work aimed to study selected properties of blends of second-generation BBUe esters and diesel fuel and blends of first-generation RME esters and diesel fuel. Properties that affect the formation of the fuel-air mixture and the combustion process were studied. The esters selected for the study differ in their fatty acid composition, which significantly impacts their properties and those of their blends with diesel fuel.

3. Materials and Methods

3.1. Biodiesel Production

The first preliminary research evaluated the feasibility of making biodiesel from babassu oil. At first, KOH potassium hydroxide was used as a catalyst. The degree of over-reactivity obtained in most combinations of substrate amounts and process control parameters was unsatisfactory, and there was no repeatability. The quality of the esters obtained did not meet the requirements of the standard PN-EN 14214+A2:2019-05 [53]. It was only with the use of an acid catalyst, in the form of sulfuric acid (H_2SO_4), that a conversion rate of more than 97% (w/w) was achieved, so esters were obtained that could be biofuel for compression-ignition engines. Finally, the transesterification process of babassu palm oil was conducted using a catalytic mixture prepared with 15% (w/w) n-butanol and 3% (w/w) (H_2SO_4) sulfuric acid. The manufacturing process was completed at 115 °C and took 1.5 h. Sedimentary phase separation was then conducted. The resulting BBUe esters were neutralized by washing once with water containing potassium hydroxide. Water was removed from the BBUe, and the residue was dried with anhydrous magnesium sulfate. This way, pure BBUe was obtained and evaluated according to standards.

Producing biodiesel from babassu oil using the GW-200 reactor yielded high-quality esters, as the degree of conversion was 99.1% (w/w). To conduct their assessment as biodiesel as well, such esters must meet all the requirements of PN-EN 14214+A2:2019-05 [53]. One of the requirements is that the volume of esters in biodiesel be at least 96.5%. The use of n-butyl alcohol was dictated by its higher evaporation temperature of 117 °C, as the most used methanol for transesterification evaporates at 65 °C. Leaving some methanol in the esters can cause combustion anomalies through earlier ignition. Alcohol with a higher evaporation temperature will make the fuel more resistant to the anomalies mentioned earlier.

For comparison, esters were produced using the GW-200 reactor, from rapeseed oil, a raw material widely known and used in Poland and Europe for FAME production. Esters of this type are classified as first-generation biofuels. The RME production process used methyl alcohol, which is widely used on an industrial scale, and a base catalyst in the form of potassium hydroxide.

BBUe and RME biofuels were produced at the Renewable Energy Center of Lesser Poland “BioEnergia”. Grzegorz Wcisło constructed the GW-200 reactor. A photo of the GW-200 reactor used for biodiesel production is presented in Figure 1. The technology and reactor for FAME production are protected by the Polish patent office—no. P.218554. The GW-200 reactor can produce FAME or other such biofuels on a small scale. It is dedicated to farms, transport companies, and others that can produce biofuel for their use. It enables the production of FAME from crude, refined, and waste vegetable oils and animal fats. The primary technical parameters of the GW-200 reactor are presented in Table 1.

Table 1. Technical data of the GW-200 reactor.

Measured Parameter	Unit	Value
Efficiency per cycle	dm ³	50
Production time per cycle	h	1.5
Supply voltage	V	230
Rated power	kWh	5.15
Type of catalyst	-	basic/acidic
Rated power	kWh	5.15
Supply voltage	V	230
Process	-	periodic or semi-continuous
Type of process	-	single-stage or two-stage



Figure 1. GW 200 reactor making vegetable oil esters to fuel diesel engines.

3.2. Research Scope

In the first stage, chromatographic tests were conducted on the second-generation biodiesel BBUe produced from babassu palm oil and first-generation biodiesel RME obtained from rapeseed oil. This research aimed to check the quality of the biodiesels obtained. This was conducted by determining which fatty acid esters the biodiesels produced and determining the degree of rich acid conversion into esters. Determination of the fatty acid composition of BBUe and RME biodiesels was carried out per the PN-EN 14103:2020-06 standard [54]. The experiments were conducted on a bench with a Thermo TRACE gas chromatograph. Identification ranges for butyl esters in BBUe and methyl esters in RME have been established from C6:0, hexanoic acid esters, to C:24.1, tetracosanoic acid esters. Density at 15 °C was determined according to the requirements of PN-EN ISO 3675:2004 [55] using a Mettler Toledo DA-100M oscillating density meter. The iodine count was determined under PN-EN 14111:2022-11 [56]. The acid number was determined under PN-EN 14104:2021-06 [57]. The Pensky–Martens method determined the flash point under PN-EN ISO 3679:2015-04 [58] on a test stand equipped with a semi-automatic Herzog HFP 380. The fractional composition was determined by PN-EN ISO 3405:2019-05 [59] by standard distillation using a semi-automatic Herzog HDA 620. The cetane number of the tested fuels was investigated by PN-EN ISO 5165:2021-02 [60]. The heat of combustion was determined by the calorimetric method by PN-C-04375-1:2013-07 [61], using a KL10 Precision BIT calorimeter. The dynamic viscosity of the tested fuels was determined in the temperature change range from -20 °C to 50 °C on a bench equipped with an Anton Paar Reolab QC rotational rheometer and a Grant thermostatic bath.

EcoDiesel ULTRA diesel fuel (DF) without adding FAME fatty acid methyl esters was used for the comparative study, as part of the further research was to determine the effect of adding BBUe and RME biodiesels to diesel fuel on selected properties of the fuels evaluated. The fuel comes from PKN ORLEN S.A., Poland's largest fuel company. The produced biodiesels were added to diesel fuel in up to 40% of their volume (v/v) share in the resulting mixtures. Four types of "B" fuels were composed: B10, B20, B30, and B40 for BBUe biodiesel and diesel. B10, B20, B30, and B40 have also been prepared for RME biodiesel and diesel.

The properties of all fuels were assessed under current Polish and European fuel requirements. The quality of biodiesel BBUe and RME was assessed per PN-EN 14214+A2:2019-05,

while diesel and biofuel type “B” were assessed per PN-EN 590+A1:2017-06. For “B” fuels, the properties that significantly affect the fuel–air mixture formation and combustion process were determined: the heat of combustion, calorific value, flash point, fractional composition, cetane number, change in dynamic viscosity with temperature, and density.

4. Results and Discussion

The first stage of the study was to determine the type of fatty acids included in the produced butyl esters from babassu palm oil BBUe and methyl esters from rapeseed oil RME. Figures 2 and 3 show the fatty acid composition identified in the BBUe and RME biodiesels. The structure of BBUe biodiesel contains 67.7% (*w/w*) by weight fatty acid esters from C:8 to C14, which are absent from the structure of the other RME biofuel evaluated. BBUe biodiesel has the highest amount of lauric acid (C12:0)—39.2% (*w/w*). Ferreira et al. report that there may be 40 to 55% (*w/w*) C12:0 acid in babassu oil [40]. Bouaid et al. found a C12:0 acid content of 51.8% (*w/w*) in the babassu oil evaluated [45]. In addition, the composition of the BBUe biodiesel produced includes C16:0 acid esters at 10.0% (*w/w*). C18:0, C18:1, C18:2, and C18:3 fatty acids in BBUe total 21.6% (*w/w*). Biodiesel RME, on the other hand, consists of 89.9% (*w/w*) fatty acid esters of oleic acid (C18:1) at 61.9% (*w/w*), linoleic acid (C18:2) at 19.0% (*w/w*), and linolenic acid (C18:3) at 9.0% (*w/w*). Therefore, fuel parameters in RME depend primarily on the properties of these three fatty acid esters. Fatty acids with shorter chains dominate the esters obtained from babassu BBUe oil compared to esters from canola oil. This has a favorable effect on the properties of biofuels responsible for creating the air–fuel mixture in the engine, its self-ignition, the rate of combustion, and heat release. This will be proven by the results of tests on selected properties of BBUe and RME biodiesels given later in the paper.

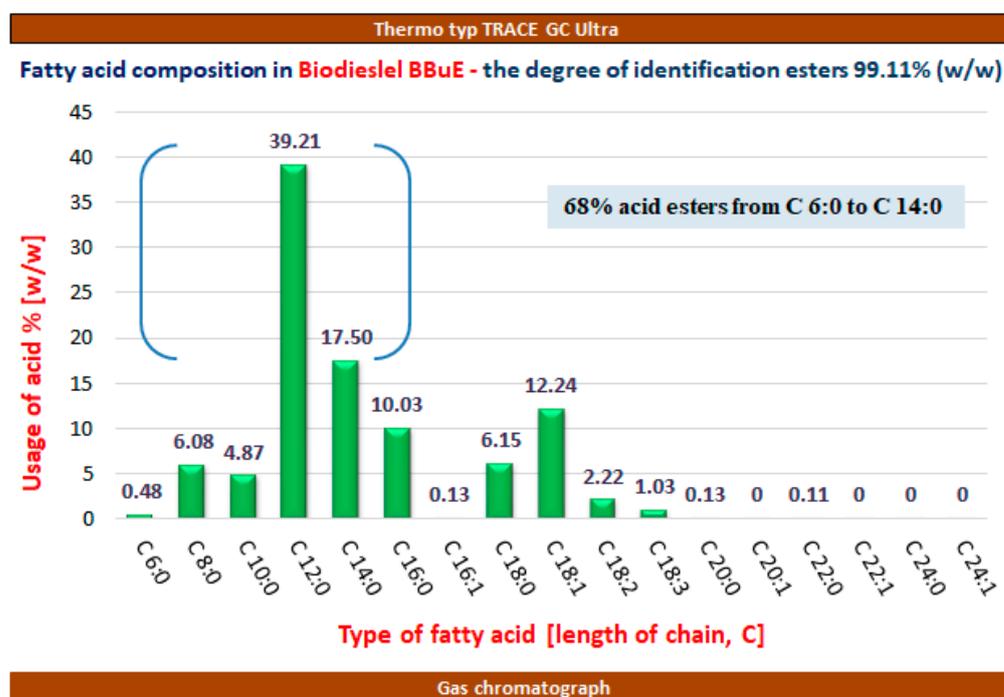


Figure 2. Composition of fatty acids contained in biodiesel II generation BBUe.

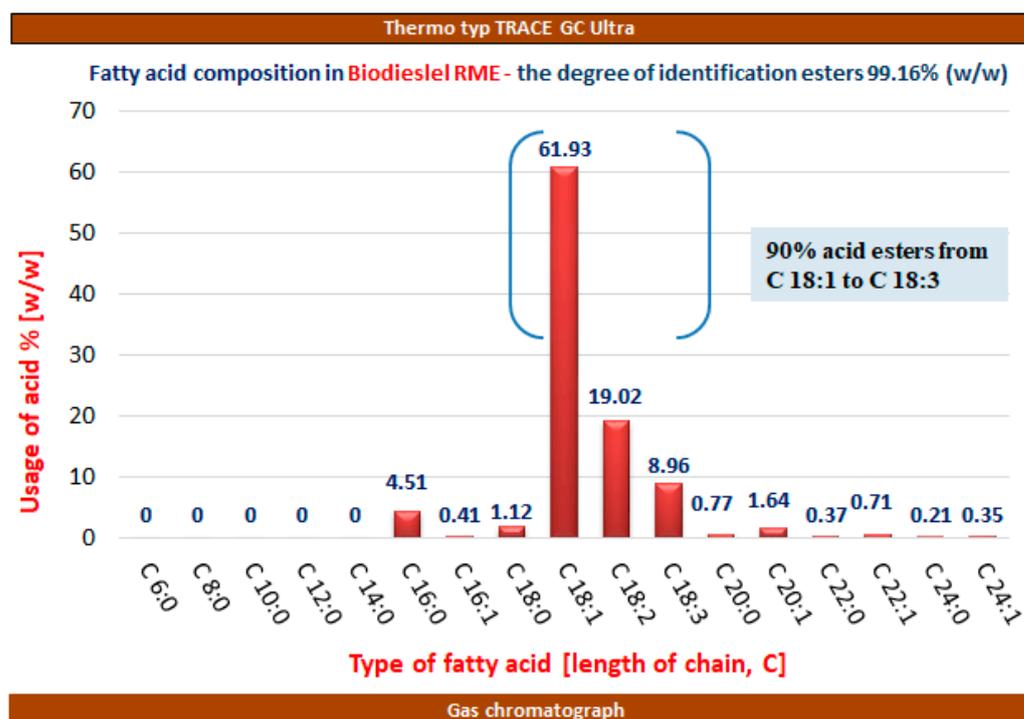


Figure 3. Composition of fatty acids contained in biodiesel I generation RME.

Selected determined properties of biodiesel from babassu palm oil BBUe and biodiesel from rapeseed oil RME and diesel DF are shown in Table 2. The analysis of the contents of Table 2 indicates that BBUe biodiesel has more favorable properties as a fuel for compression-ignition engines than RME biodiesel. BBUe esters, compared to RME, have a lower dynamic viscosity, a slightly higher cetane number, a higher calorific value, and a lower flash point. BBUe esters contain noticeably fewer longer fatty acids than RME esters. The physicochemical properties of BBUe biodiesel, shown in Table 2, are more similar to those of diesel fuel than those of RME biodiesel. From this, it follows that the right direction for research is searching for and using biodiesels that include shorter-chain fatty acids. Research on the search for new raw materials for biodiesel production should be conducted in this direction.

Distillation of the produced BBUe and RME biodiesels and commercial diesel was conducted. Figure 4 compares the distillation curve of BBUe biodiesel with diesel fuel. Meanwhile, Figure 5 compares the distillation curves of RME biodiesel and DF. Table 3 summarizes the distillation process parameters of BBUe biodiesel, RME, and diesel and counts the differences in these parameters for biodiesels and DF. The distillation onset temperature for biodiesels is significantly higher than for diesel. For BBUe, it was 243 °C, while for RME, it was 285 °C, and for DF, it was 160 °C. For BBUe, it is still noticeably higher than for DF but lower by 42 °C compared to its value for RME. This is a result of the fact that BBUe contains acids with shorter molecules than in RME. This is a favorable characteristic for BBUe esters as a fuel for compression-ignition engines. The distillation temperatures of 10% and 50% by volume of BBUe biodiesel are lower than those for RME. This will have a beneficial effect on the fuel-air mixture process. The end temperature of the BBUe distillation process is 6 °C lower compared to this temperature for RME and 4 °C higher compared to DF. From the point of view of fuel properties, all the distillation process parameters determined for BBUe biodiesel are more favorable than those determined for RME biodiesel. The BBUe distillation process curve is more like the diesel distillation process curve than the RME and DF distillation curves.

Table 2. Values of fuel parameters of BBuE, RME, and DF were determined following the requirements of the PN-EN 590:2022-08 [52] and EN-PN 14214+A2:2019-05 [53] standards.

Property	Standard	BBuE	RME	DF
Content of fatty acid methyl esters, % (w/w)	PN-EN 14103 [54]	99.11	99.20	-
Density at 15 °C, g/cm ³	PN-EN ISO 3675 [55]	0.884	0.872	0.839
Dynamic viscosity 40 °C, mPa·s	EN ISO 3104 [62]	3.8	4.1	2.8
Cetane number	PN-EN ISO 5165 [60]	57.4	56.1	51.8
Flashpoint, °C	PN-EN ISO 3679 [58]	102	105	58
Higher heating value, MJ/kg	PN-C-04375 [61]	43.41	42.23	46.32
Lower heating value, MJ/kg	PN-C-04375 [61]	39.45	38.27	43.07
Acid number, mg KOH/g	PN-EN 14104 [57]	0.42	0.40	-
Iodine number, g iodine/100 g	PN-EN14111 [56]	12.4	103	-
Water content, mg/kg	PN-EN ISO 12937 [63]	206	221	132
Sulphur content, mg/kg	EN ISO 8754 [64]	1	3	7
Oleic acid ester content C18:1, % (w/w)	PN-EN 14103 [54]	12.26	60.91	-
Linoleic acid ester content C18:2, % (w/w)	PN-EN 14103 [54]	2.19	19.25	-
Alcohol content, % (w/w)	PN-EN 14110 [65]	0.18	0.19	-
Monoacylglycerol content, % (w/w)	PN-EN 14105 [66]	0.5	0.6	-
Diacylglycerol content, % (w/w)	PN-EN 14105 [66]	0.13	0.11	-
Glycerol content, % (w/w)	PN-EN 14105 [66]	0.22	0.20	-

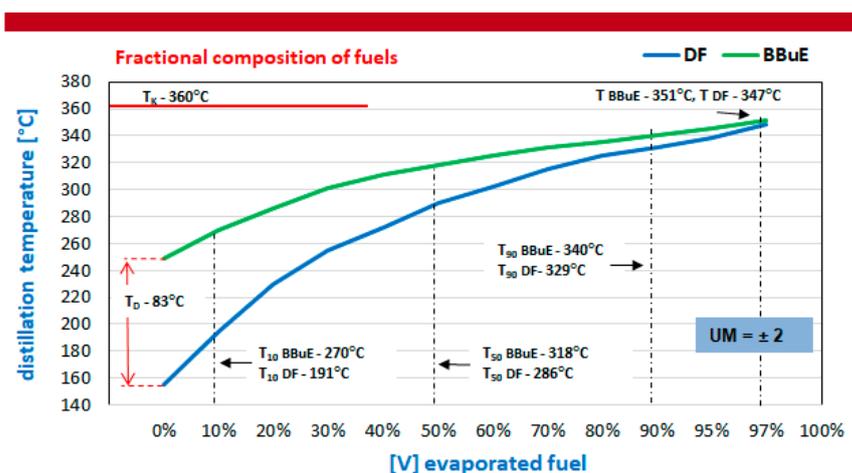


Figure 4. BBuE and DF biodiesel distillation curves.

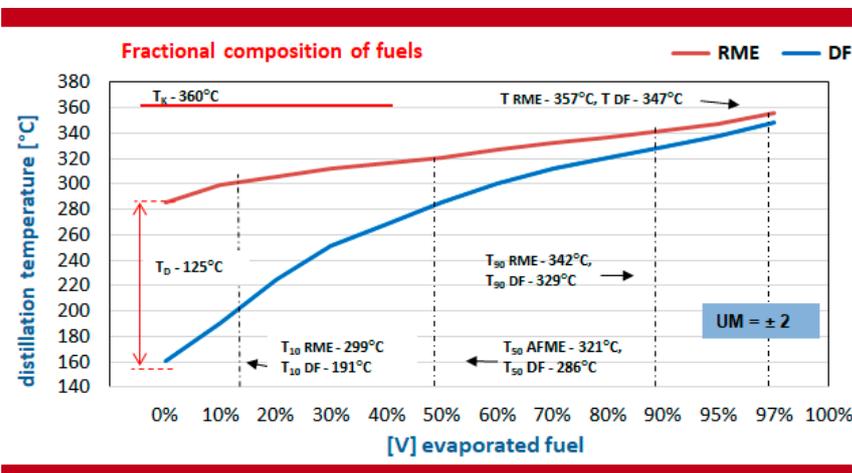


Figure 5. RME and DF biodiesel distillation curves.

Table 3. Distillation process parameters of biodiesel BBuE, biodiesel RME, and diesel DF.

Distillation Process Parameters	BBuE	RME	DF	BBuE-DF	RME-DF
Distillation start temperature T_0 , °C	243	285	160	83	125
Distillation temperature of 10% by volume of fuel T_{10} , °C	270	299	191	79	108
Distillation temperature of 50% by volume of fuel T_{50} , °C	318	321	286	32	35
Distillation temperature of 90% of the fuel volume T_{90} , °C	340	342	329	11	13
Distillation temperature of 95% of the fuel volume T_{95} , °C	345	350	338	7	12
Distillation end temperature T	351	357	347	4	10
Volume of the fuel sample distilled to a temperature of 250 °C, % (v/v)	4	0	27	−23	−27
The volume of the fuel sample distilled to a temperature of 350 °C, % (v/v)	96	94	100	−4	−6

The next stage of the work performed was the preparation of “B” fuels, that is, blends of DF diesel and BBuE biodiesel and blends of DF and RME. The further study aimed to determine the effect of adding BBuE and RME biodiesels at 10 to 40% (v/v) to diesel fuel on selected fuel parameters. The following were determined for BBuE and RME and their blends with diesel fuel (B10, B20, B30, and B40): the heat of combustion, calorific value, flash point, cetane number, change in dynamic viscosity versus temperature, and density.

The heat of combustion was determined under PN-C-04375-3:2013-07 [61] using a KL10 calorimeter from Precision BIT, while the calorific value of the tested fuels was calculated based on the equation:

$$W_u = Q - r (W^a + 8.94 H^a); \left[\frac{\text{MJ}}{\text{kg}} \right], \quad (1)$$

Q—heat of combustion of fuel MJ/kg;

W^a —moisture content in biodiesel BBuE is 0.206%, and in biodiesel RME it is 0.221%;

H^a —hydrogen content in BBuE biodiesels and RME is 12% (w/w), while in diesel, it is 13% (w/w);

r—heat of vaporization of water contained in the fuel (assumed—2.934 MJ/kg);

8.94—is the conversion rate of hydrogen to water.

Combustion heat and heating values of DF diesel and its blends with BBuE biodiesel (B10, B20, B30, and B40) are shown in Figure 6. These values are smaller for mixtures of BBuE and DF compared to DF. This is an effect of the oxygen content of the esters. The heating value of BBuE was approximately 8.4% lower than that of DF. Adding BBuE biodiesel to DF decreases the heating value of BBuE and DF mixtures relative to DF. The degree of reduction in the calorific value of B-type fuels relative to DF is insignificant. For B40 BBuE fuel, the calorific value decreased by approximately 4.6% compared to DF. Figure 7 shows the heat of combustion and calorific values of DF diesel and its blends with RME biodiesel: B10, B20, B30, and B40. The calorific value of RME is approximately 11.1% lower compared to DF. The resulting calorific value for BBuE is slightly higher than RME's (3.1%). The calorific value of B40 BBuE fuel is marginally higher (1.5%) than B40 RME fuel.

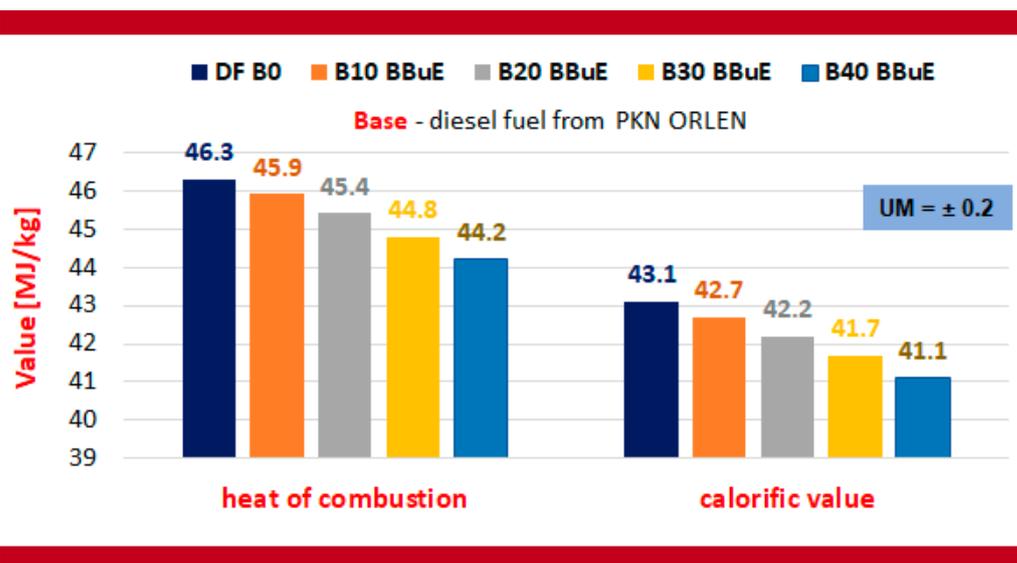


Figure 6. Combustion heat and calorific value of DF and its mixtures with BBuE: B10, B20, B30, and B40.

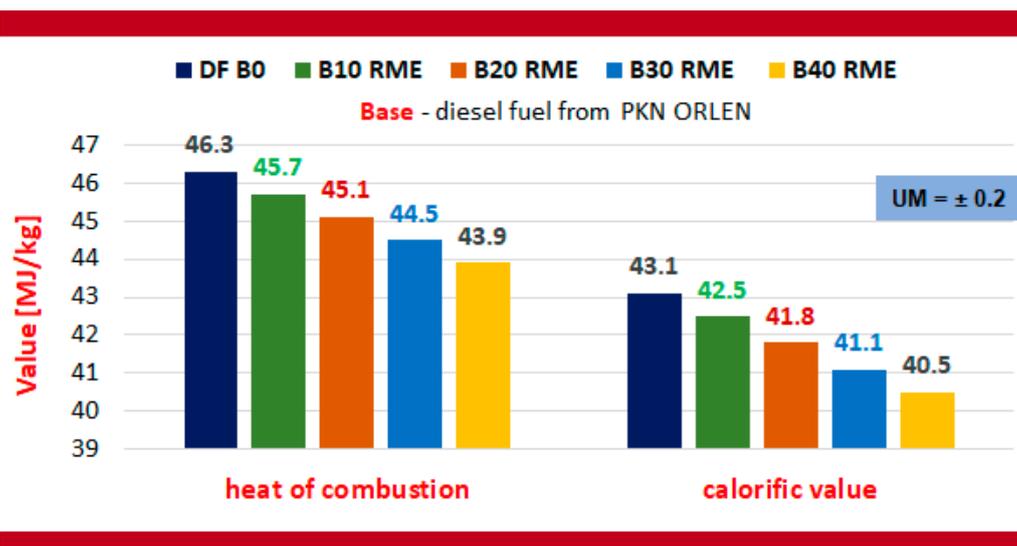


Figure 7. Combustion heat and calorific value of DF and its mixtures with RME: B10, B20, B30, and B40.

Ignition temperature values were determined for the fuels assessed. Figure 8 shows the flash point values for BBuE, DF, and their mixtures. For BBuE biodiesel, the ignition temperature was 102 °C, and for DF, it was 58 °C. Ferreira et al. determined a flash point value of 112 °C for babassu oil methyl esters, and 122 °C for babassu oil ethyl esters [40]. On the other hand, the paper [47] reported a flash point value for babassu oil methyl esters of 126 °C. Increasing the proportion of BBuE in the DF increases the ignition temperature. Figure 9 shows the flash point values for RME, DF, and their mixtures. For RME biodiesel, the ignition temperature was 105 °C, slightly higher than for BBuE biodiesel.

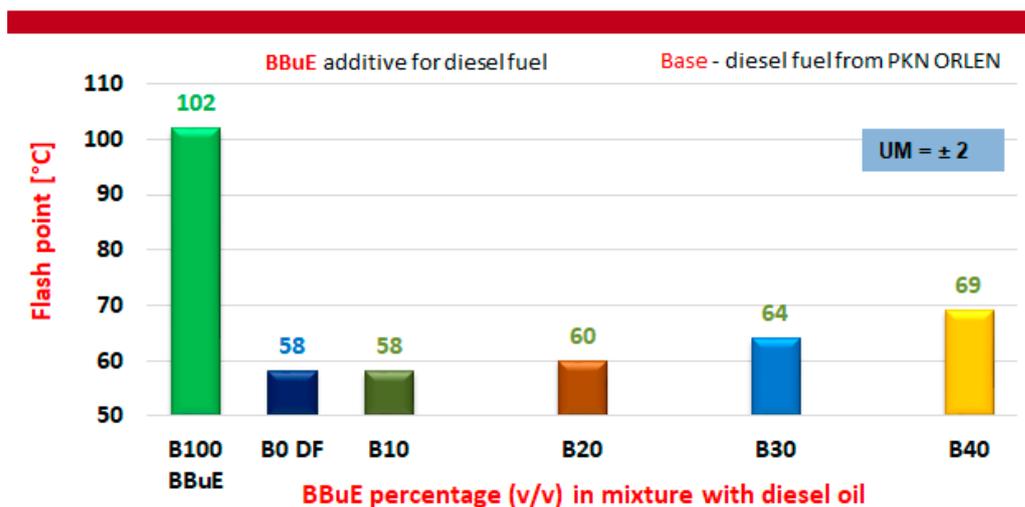


Figure 8. The flash point of BBUe, DF, and their mixtures: B10, B20, B30, and B40.

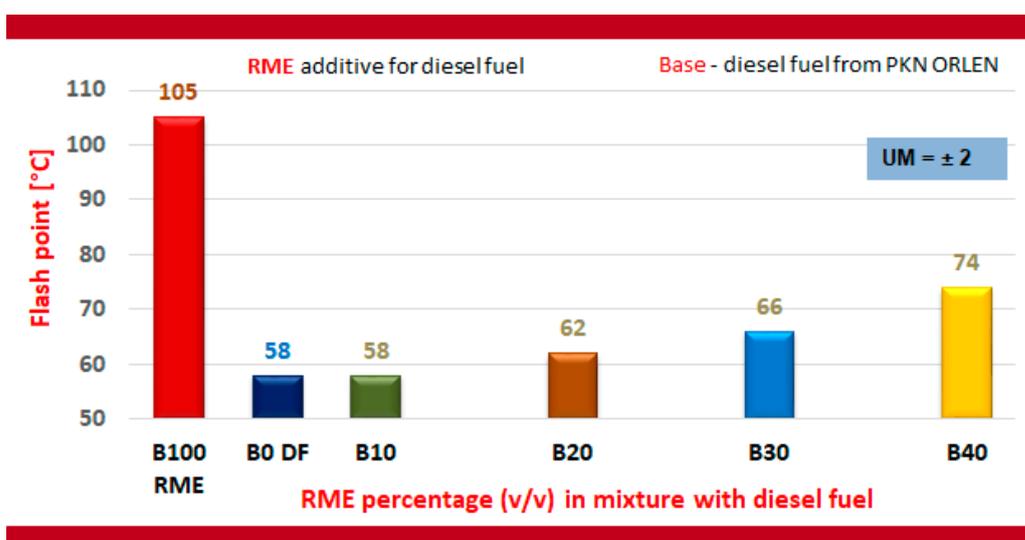


Figure 9. The flash point of RME, DF, and their mixtures: B10, B20, B30, and B40.

For compression-ignition engines, the cetane number is an essential property of the fuels that can be used to power them. Among other reasons, biodiesels can power compression-ignition engines because they often have a higher cetane number than diesel fuels [67,68]. Biodiesels have a high cetane number value without the need for additives to increase it. Figure 10 shows the cetane number values for DF, B10 BBUe, B20 BBUe, B30 BBUe, and B40 BBUe. Introducing the BBUe additive into the oil increases the cetane number value of the "B" fuel relative to diesel fuel. B40 fuel achieved a cetane number value 3.2 units higher than diesel. Figure 11 shows the cetane number values obtained for DF and its mixtures with RME. The cetane number values for BBUe and DF mixtures are higher than the corresponding RME and DF mixtures. This is another beneficial effect of BBUe biodiesel consisting of fatty acid esters with shorter molecules.

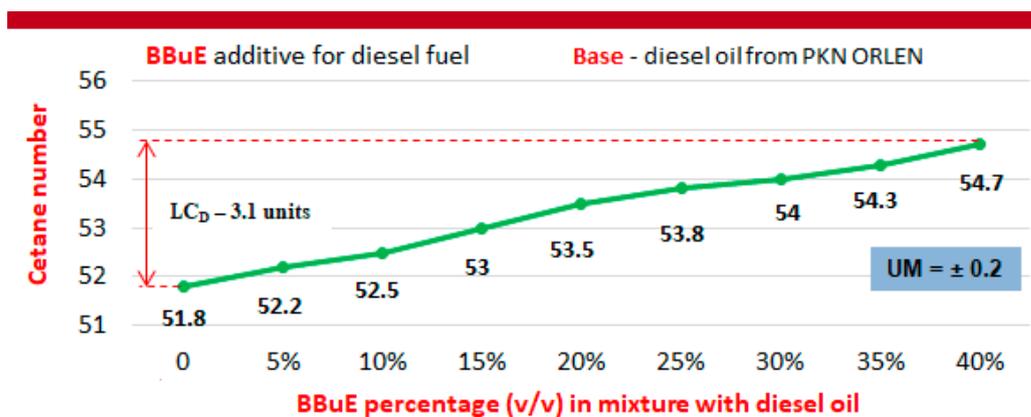


Figure 10. Effect of biodiesel BBUe addition to DF on cetane number.

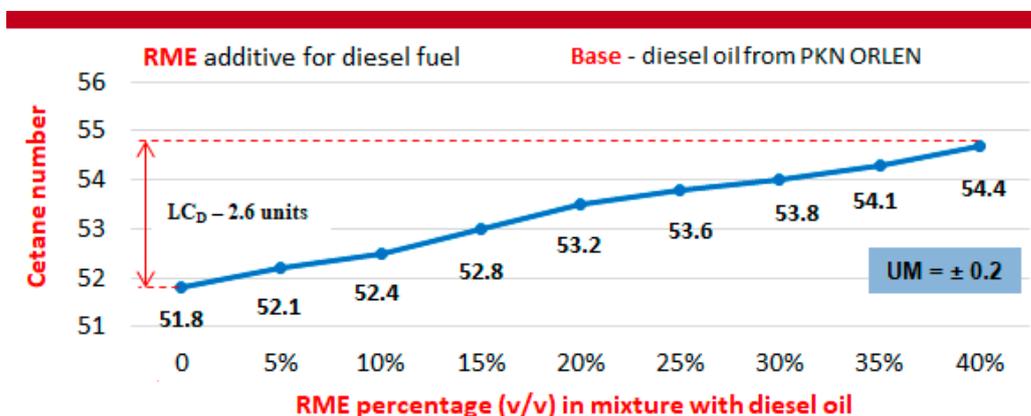


Figure 11. Effect of biodiesel RME addition to DF on cetane number.

The viscosity of the fuel has an incredibly significant impact on the fuel–air mixture formation and its combustion process, as well as engine starting, especially at low temperatures. Dynamic viscosity tests were conducted for BBUe and RME biodiesels, DF diesel, and prepared “B” fuels. The dynamic viscosity of the fuels was determined at temperatures ranging from $-20\text{ }^{\circ}\text{C}$ to $+50\text{ }^{\circ}\text{C}$. Figure 12 shows the temperature dependence of dynamic viscosity for BBUe, DF, and their mixtures. Meanwhile, Figure 13 shows the temperature dependence of dynamic viscosity for RME, DF, and their mixtures. The graphs clearly show that the temperature has a powerful effect on the dynamic viscosity value. Dynamic viscosity values for biodiesels are higher than for DF. With decreasing temperature, the increment in dynamic viscosity values for biodiesels is more significant than the values obtained for diesel fuel. The same trend of change is seen for “B” fuels. The higher the proportion of biodiesel in the mixture with DF, the higher the dynamic viscosity value and the greater its increase with decreasing temperature. For a temperature of $-20\text{ }^{\circ}\text{C}$, the dynamic viscosity for BBUe was $142\text{ mPa}\cdot\text{s}$, and for DF it was $26\text{ mPa}\cdot\text{s}$. The dynamic viscosity for RME biodiesel at $-20\text{ }^{\circ}\text{C}$ was $164\text{ mPa}\cdot\text{s}$. The dynamic viscosity for biodiesel BBUe and its blends with diesel is lower than that of biodiesel RME and its blends with diesel over the entire range of temperature variation. This is an obvious advantage of using BBUe biodiesel with shorter fatty acid molecules.

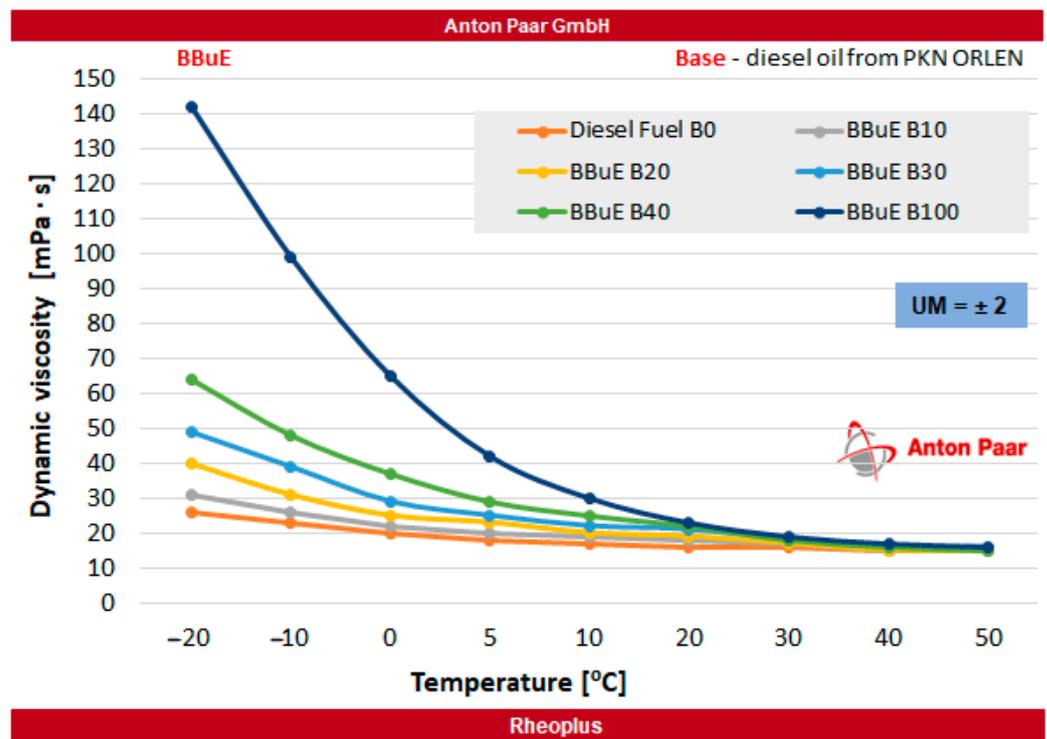


Figure 12. Temperature dependence of dynamic viscosity for DF, BBuE, and their mixtures.

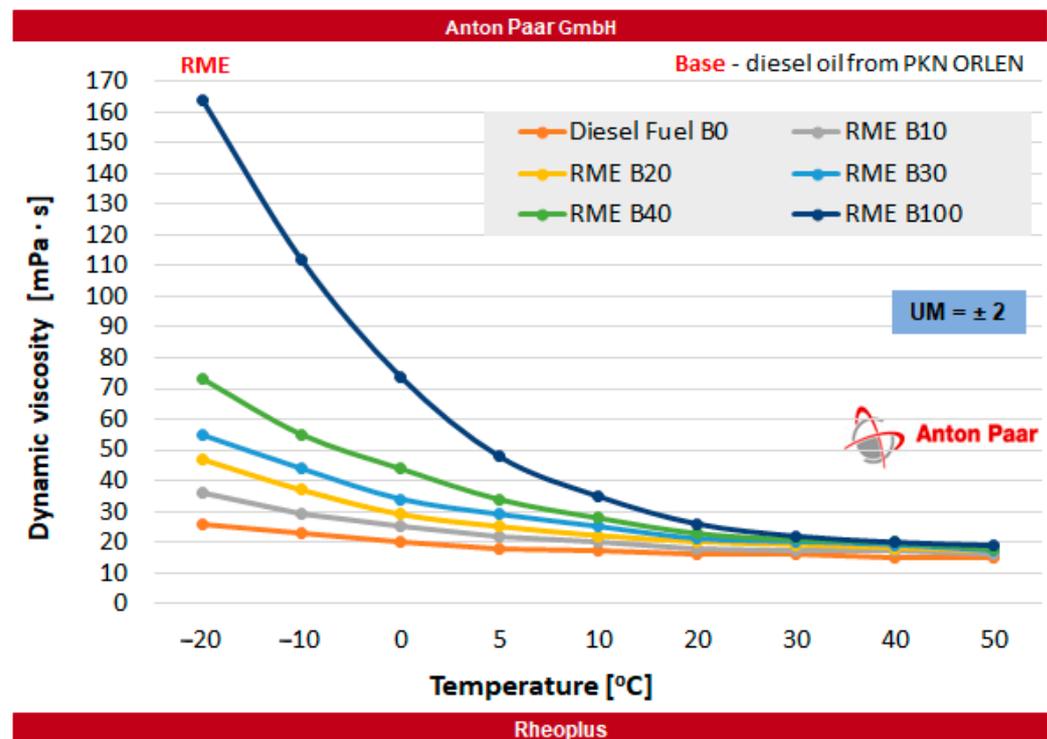


Figure 13. Temperature dependence of dynamic viscosity for DF, RME, and their mixtures.

Figure 14 presents the density values of biodiesel BBuE, diesel DF, and blends of BBuE and DF. The density of DF diesel at 15 °C was just over 829 kg/dm³, while that of BBuE biodiesel was over 884 kg/dm³. Based on the information presented above, the density of BBuE is approximately 6.6% higher than that of DF. Adding biodiesel to diesel fuel increases the thickness of the resulting mixtures. For B10 BBuE fuel, the density increased by approximately 0.64%, and for B40 BBuE, by about 2.7% compared to DF. Figure 15 shows

the density values of biodiesel RME, diesel DF, and mixtures of RME and DF. The density of RME biodiesel at 15 °C was 872.5 kg/dm³. Based on above, the thickness of RME is higher by approximately 5.2% compared to DF. For B10 RME fuel, the density is about 0.5% higher; for B40 RME, it is about 2% higher than diesel.

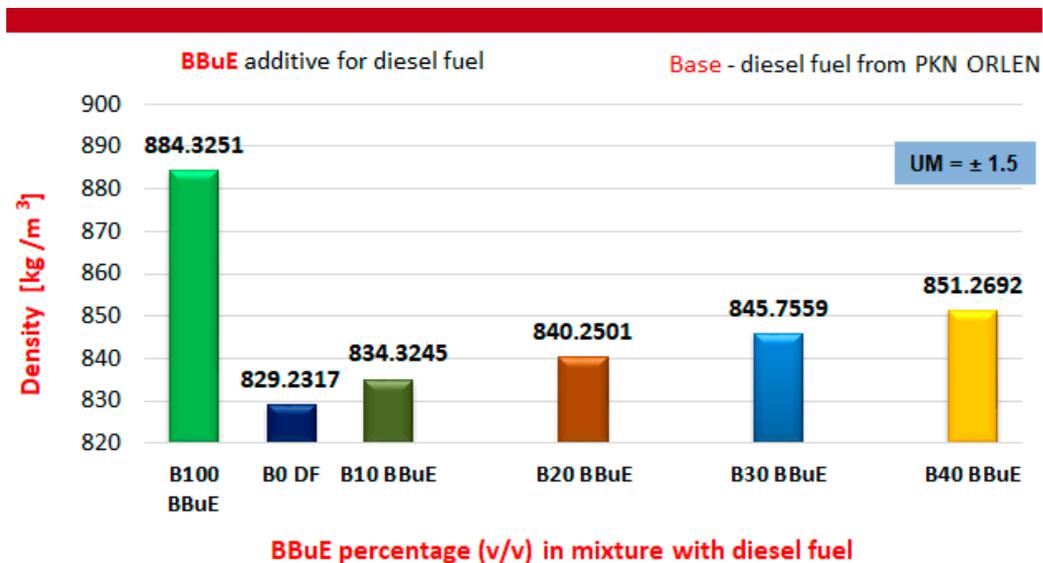


Figure 14. Density of BBUe, DF, and their mixtures at 15 °C.

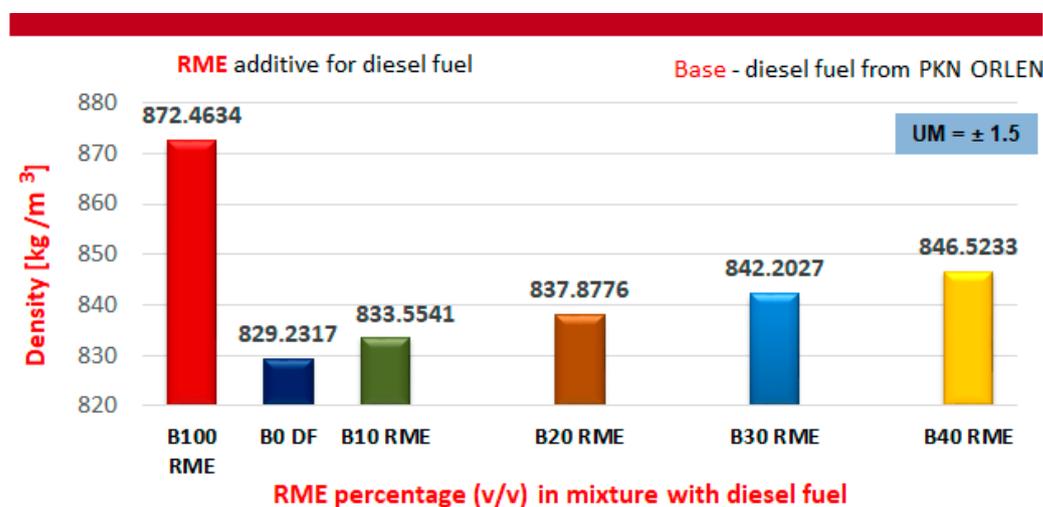


Figure 15. Density of RME, DF, and their mixtures at 15 °C.

5. Conclusions

As part of the work, a plant (babassu palm) was selected from whose fruits an oil is obtained that has a different composition than the rapeseed oil commonly used in Poland and Europe for biodiesel production. Biodiesel BBUe was produced as butyl esters of babassu palm oil and compared to biodiesel RME (i.e., rapeseed oil methyl esters). Biodiesel from babassu oil, containing acid esters with shorter molecules, has more favourable fuel properties compared to biodiesel obtained from rapeseed oil. It has been shown that:

- BBUe biodiesel comprises fatty acids with shorter molecules than those in RME biodiesel. In BBUe, C₆:0 to C₁₆:1 fatty acids are approximately 78.3% (*w/w*), while the same fatty acids in RME are approximately 4.9% (*w/w*). However, fatty acids

from C18:0 to C18:3 in BBUe are approximately 21.6% (w/w); in RME, these acids are 91.0% (w/w).

- BBUe biodiesel has a slightly higher heat of combustion, higher calorific value, and higher cetane count value than RME biodiesel. The data specified above show that the density of RME is higher by approximately 3.1% compared to RME. The resulting BBUe cetane number is 5.6 units higher than DF and 1.3 units higher than RME.
- The parameters of the BBUe biodiesel distillation process have more favourable values from the point of view of their use as a fuel for compression-ignition engines, compared to the parameters of the RME biodiesel distillation process. The onset temperature for the distillation of BBUe biodiesel is 14.7% lower than that for RME.
- The density of BBUe and RME biodiesels at 15 °C is higher than that of DF diesel. BBUe biodiesel has a slightly higher density compared to RME. The density of BBUe is 6.6% higher, and RME 5.2% higher, than that of diesel.
- The properties of BBUe biodiesel are more like those of diesel fuel than those of RME biodiesel.

The produced BBUe and RME biodiesels were added to diesel fuel, and “B” fuels were obtained. For BBUe and RME, mixtures were composed of DF with biodiesel contents of 10, 20, 30, and 40% (v/v) by volume. Blends of BBUe and DF have mostly more favorable fuel properties than RME and DF blends. The tests conducted on selected fuel properties showed:

- The dynamic viscosity of BBUe and DF mixtures is lower than that of RME and DF mixtures in the temperature range from -20 °C to $+50$ °C.
- The combustion heat and calorific values of BBUe and DF mixtures are slightly higher than those of RME and DF mixtures. The resulting calorific value of B40 BBUe fuel is only approximately 1.5% higher than that of B40 RME fuel.
- The addition of BBUe and RME up to 40% (v/v) resulted in a slight increase in density. For B40, BBUe was increased by approximately 2.7%, while for B40, RME was increased by about 2% relative to DF.
- Slightly higher cetane number values were obtained for BBUe and DF mixtures than for RME and DF mixtures.
- Mixtures of BBUe and DF achieved slightly lower flash points.
- Fuels obtained from blending BBUe biodiesel with DF have more comparable properties to pure DF diesel than fuels obtained as blends of RME biodiesel with DF.

There is a need for further work in the search for new raw materials for biodiesel production. These raw materials should be characterized by properties that will allow the production of fuels with properties like, or even better than, those of the diesel fuels still commonly used to power compression-ignition engines. The research shows that such raw materials should be oils that include fats with shorter chains.

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Nomenclature

B10, B20, B30 and B40	blends of esters and diesel
BBuE	babassu butyl esters
B0 DF	olej napędowy bez dodatku FAME
B10 BBuE	fuel composed of 10% (v/v) BBuE and 90% (v/v) DF
B20 BBuE	fuel composed of 20% (v/v) BBuE and 80% (v/v) DF
B30 BBuE	fuel composed of 30% (v/v) BBuE and 70% (v/v) DF
B40 BBuE	fuel composed of 40% (v/v) BBuE and 60% (v/v) DF
B10 RME	fuel composed of 10% (v/v) RME and 90% (v/v) DF
B20 RME	fuel composed of 20% (v/v) RME and 80% (v/v) DF
B30 RME	fuel composed of 30% (v/v) RME and 70% (v/v) DF
B40 RME	fuel composed of 40% (v/v) RME and 60% (v/v) DF
C6:0	caproic acid
C8:0	caprylic acid
C10:0	capric acid
C12:0	lauric acid
C14:0	Muriatic acid
C16:0	palmitic acid
C16:1	palmitoleic acid
C18:0	stearic acid
C18:1	oleic acid
C18:2	linoleic acid
C18:3	linolenic acid
C20:0	arachidic acid
C20:1	eicosanoic acid
C22:0	behenic acid
C22:1	erucic acid
C24:0	lignoceric acid
C24:1	nervonic acid
C ₄ H ₉ OH	n-butyl alcohol
DF	diesel fuel
FAME	fatty acid methyl ester
H ₂ SO ₄	sulphuric acid
KOH	potassium hydroxide
NaOH	sodium hydroxide
RME	rapeseed methyl esters
T	distillation end temperature, °C
T _D	distillation temperature difference for the compared fuels for a specific temperature, °C
T _K	temperature to which the whole volume of fuel should be distilled, °C
T ₀	distillation start temperature, °C
T ₁₀	distillation temperature of 10% by volume of fuel, °C
T ₅₀	distillation temperature of 50% by volume of fuel, °C
T ₉₀	distillation temperature of 90% of the fuel volume, °C
T ₉₅	distillation temperature of 95% of the fuel volume, °C
v/v	volumetric share
w/w	weight share
UM	measurement uncertainty

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