

THE STUDY OF BIODIESEL OBTAINED FROM POMEGRANATE PEEL AND SEED OIL AS AN ALTERNATIVE FUEL

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Abstract: Biodiesel is a type of an alternative fuel used in diesel engines, made from renewable raw materials such as vegetable oils. In the article, examines the process of obtaining biodiesel from pomegranate peel and seed oil. Biodiesel was produced in high yield by the method of transesterification of oils obtained from pomegranate peel and seed with KOH as a catalyst, temperature range of 40-60 °C as the optimal reaction condition and oil to ethanol ratio of 1:3 and 1:10 Mol. Biofuels were prepared by mixing biodiesel obtained from transesterification with different amount (80% diesel and 20% biodiesel; 40% diesel and 60% biodiesel) of the diesel fraction obtained from the low-pressure (0.4-3.0 Mpa) hydrocracking of fuel oil, which is heavy oil residue. The temperature dependence of the density and kinematic viscosity of fuel obtained from the mixture of diesel fuel and biodiesel obtained from pomegranate peel and seed oil in different ratios was studied comparatively. It was determined that the density and kinematic viscosity of mixed biofuels are higher than the density and viscosity of diesel fuel obtained from fuel oil.

Keywords: pomegranate, alternative fuel, diesel, biodiesel, transesterification, density

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Introduction

Depletion of natural fuels (oil, natural gas, coal, etc.), increased demand for fuel, and environmental pollution lead to a greater need for alternative fuels [1]. In the chemical industry, research on renewable fuels as an alternative to natural fuels has been ongoing for a long time. Various alternative fuels with both renewable and emission enhancing properties are being investigated for diesel engines. The use of alternative fuels without requiring much change in engine design and engine parameters is considered to be the main advantage factor. Additionally, fuels that are renewable, will lead to a decrease in the utilization of oil [2]. The use of alternative fuels in an engine, either alone or mixed with diesel fuel, depends on the application characteristics of the fuel. Biofuels are the most promising alternative fuel for replacing petroleum-based diesel fuels. Biodiesel, which belongs to the biofuel group, is a non-toxic,

biodegradable and renewable fuel. It is used as a replacement for conventional diesel fuel in existing engines without requiring any major modifications [3].

In diesel engines, when fuel is injected into the cylinder, it mixes with hot air and begins to form a diffusion flame structure as it rapidly evaporates, breaking down into hydrocarbons of lower molecular weight. As the fragmented fuel continues to combine with air, the temperature in the reaction zone rises to approximately 1800 K due to the heat released into the environment. An active zone forms around the base mix and diffusion flame, and as a result, there is not enough oxygen in these areas for the complete combustion of the fuel [4]. Since complete combustion cannot occur in this area, CO and soot-forming precursors form unsaturated and uncertain hydrocarbons (C₂H₂, C₂H₄, C₃H₃). As a result, it acquires a more stable state by forming polycyclic aromatic

hydrocarbon compounds, and the formation of the structure of the substance with nuclear structure begins. The first chain structure grows by undergoing dehydrogenation of propylene (C_3H_6) or acetylene (C_2H_2) radicals under the influence of high temperature, forming polycyclic aromatic hydrocarbon compounds, and then adding other soot formations to its composition. In the last stage of uncontrolled combustion, when the remaining fossil fuels are oxidized in a diffusion flame, all chemical energy is released, and in this case, the temperature of the field increases to approximately 2700 K. The aromatic structure reaches a critical size at high temperature, develops within substances with nuclear structure, and adsorbs hydrocarbons in the gas phase, leading to an increase in particle weight [5]. The first formed particles stack on top of each other and form the second larger structure. Adsorbed hydrocarbon molecules form a carbonaceous soot structure by chemical formation. The formation of substances with nuclear structure mostly affects the carbonaceous component in the combustion chamber. Subsequently, SO_3 formed as a result of oxidation of sulfur in the composition of diesel fuel, along with water vapor and lubricant oil residues are also added to this structure. Emission values vary depending on the amount of aromatic substances and sulfur contained in the fuel [6].

The factors that lead to the reduction of particulate and soot emissions in diesel engines by adding oxygen-containing fuels like biodiesel to diesel fuel can be grouped under three main headings.

- Reduction of the fuel/air ratio in the field as a result of the presence of additional oxygen in the fuel during the initial mixing stage of combustion;

- Carbons prevent the formation of soot due to the bonds between C—O in the structure of oxygenated compounds;

- By developing a radical environment, soot formation reactions are prevented and the oxidation of molecules that can cause soot formation with the formed OH radicals is ensured [7].

Research on the utilization of biodiesel, which are renewable fuels, in diesel engines is ongoing. Although the renewability of these fuels and emission-enhancing properties are significant advantages, there are important considerations to take into account when they are used in engines. Though biodiesel is considered a type of green fuel, the production process is expensive due to the economic value of raw material resources. Alternatively, in order to reduce the financial cost of biodiesel, the possibility of using cheap raw materials such as oils from agro-industrial waste, used waste oil, non-edible oils and lipid-rich microalgae is being investigated [8-10].

The analysis of literature data showed that various studies have been conducted to investigate the use of plant waste as a potential source for biodiesel production. Mathews J.A. and other researchers [11-13] conducted comprehensive studies on the use of food raw materials in the production of biofuels. In this context, we can note that the increasing demand for fuel may lead to food shortages. The importance of using raw materials that consist of more waste materials compared to food raw materials for biofuel production should be investigated. Taking this into account, *the aim of this research* is to study the biodiesel production process from pomegranate peel and pith waste and various physico and chemical properties of biodiesel.

Experimental part

In the research work, the process of obtaining biodiesel from pomegranate peel and seed oil was studied. During the study, the pomegranate fruit was kept at a temperature of $+4^{\circ}C$. After the pomegranate juice was distilled, the waste part, consisting of the peel and seeds, was collected. After cleaning 10 kg of waste, 4970 g of peel and 5000 g of seed were

obtained. Washed with pure water and dried on drying papers in a drying oven for 72 hours at a temperature ranging from $25-40^{\circ}C$. After drying, 4670 g of peel and 4800 g of seed were obtained and grounded to 2-3 mm in a laboratory mill (SM-450L, MRCLab, Israel).

Oil from pomegranate peel and seed was obtained by extraction method with the presence

of ethanol as a solvent. Ethanol extraction was carried out according to the standard method in a Soxhlet extraction unit consisting of a counter-cooler at a temperature of 45-50°C for 6-7 hours. After the extraction process was completed, the solvent was separated from the oil by distillation. The samples were kept in an oven at 105±5°C for 30 minutes to completely evaporate the solvent and were weighed after cooling in a desiccator.

The transesterification method was chosen to convert the oils obtained from the waste of pomegranate peels and seeds into biodiesel. The process was carried out by adding different amounts of ethanol (147 µL and 457 µL) to a mixture of waste oil (1 g) and KOH (0.05 g, 5 wt %). The reactions were carried out by mixing oil to ethanol at 1:3 and 1:10 Mol ratios at 40°C and 60°C under counter-cooler. When a layer of

glycerin forms at the bottom of the reaction vessel (after about 2-2.5 hours), the mixture is placed in a separatory funnel. After waiting for 24 hours, two phases are formed. The lower phase is collected as glycerol and the upper phase, which is centrifuged, consists of ethyl esters of fatty acids (biodiesel) and residual alcohol. The mixture is filtered through anhydrous sodium sulfate to separate the aqueous phase. The obtained organic phase was washed with hot water until neutralized and dried in a desiccator under vacuum at 60°C.

Biodiesel fuel obtained by transesterification method was mixed with diesel fuel obtained from low pressure (0.4-3.0 MPa) hydrocracking of fuel oil, which is heavy oil residue (80% diesel and 20% biodiesel; 40% diesel and 60% biodiesel).

Results and discussion

The moisture content of the peel and seed according to the weight loss after the drying

process was calculated by using the following formula [14]:

$$\text{Moisture (\%)} = \frac{M_i - M_s}{M_s} * 100\%$$

M_i – mass of undried waste;

M_s – mass of the waste after drying.

According to the given formula, it was calculated that the moisture content of the pomegranate peel is 6.42%, and the moisture content of the seed is 4.16%.

The initial filtration of pomegranate peel and seed waste used as raw materials is

mandatory, otherwise, instead of the transesterification reaction, the hydrolysis of triglycerides will occur in the process, and the salts of fatty acids will be obtained instead of biodiesel.

The amount of oil obtained from each sample during the extraction process (%) was calculated by the following formula [15]:

$$\text{Oil (\%)} = [M_2 - M_1] / m * 100$$

M_1 – Mass of empty receiver (g);

M_2 – mass of the receiver with oil (g);

m – mass of the obtained oil (g).

According to the given formula, it was calculated that 46% of oil was obtained from 4670 g of pomegranate peel, and 68% of oil was obtained from 4800 g of pomegranate seeds.

Pomegranate waste used in biodiesel production contains 46-68% oil (Fig. 1.)

Properties of pomegranate waste oil were determined by various physical and chemical methods and density, kinematic viscosity, heat of combustion, acid number, etc. parameters are shown in Table 1. As can be seen from the table, since the acid value of pomegranate peel and seed oil is less than 2 mg KOH g⁻¹, it was subjected to direct transesterification reaction in the presence of alkaline catalysts without preliminary treatment.

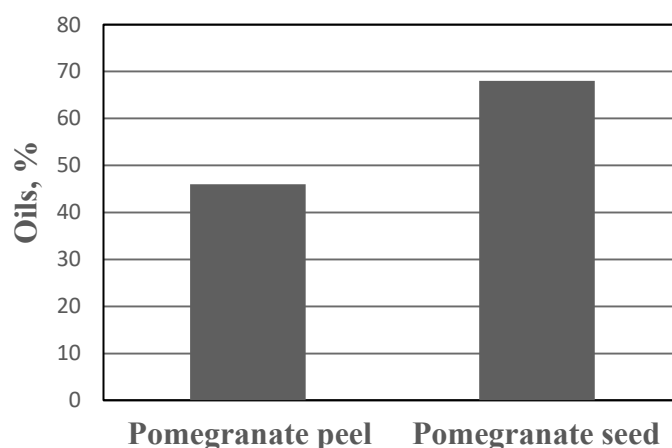


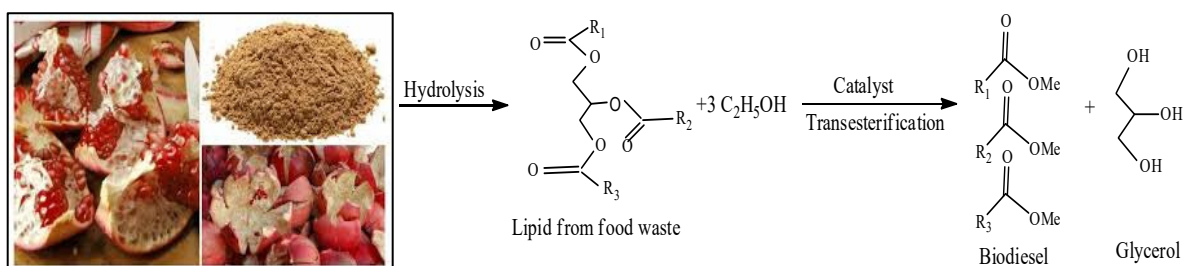
Fig. 1. The amount of oil in pomegranate peel and seed

Table 1. Physical and chemical indicators of pomegranate waste oil

Indicators	Pomegranate peel oil	Pomegranate seed oil
Density, 20°C, kg/m ³	0.9226	0.9121
Kinematic viscosity, 40°C, mm ² /s	3.218	3.141
Acid number, mg KOH g ⁻¹	0.3	0.2
Heat of combustion, kJ/kg	39.321	38.462
Peroxide number, mekv/kg	6.2	6.0
Iodine number, gJ ₂ /100g	11.3	11.5
Water composition, % (wt)	0.1	0.1
Total sulfur content, % (wt)	0.002	0.001
Cetane number	35	35
The surface tension coefficient, 20°C, mH/m	33.2	33.0
Ignition temperature, °C	311	315
Freezing temperature, °C	-20	-20
Composition % (wt)		
C	76.0	78.0
H	13.0	11.0
O	10.0	11.0
Coking of 10% residue, %	0.2	0.2

In the research work, the process of biodiesel production by transesterification method based on vegetable oil obtained from pomegranate peel and seed as raw materials of low technical and economic value was studied

(Scheme 1). For the production of high-yield biodiesel from waste oils, KOH was used as a catalyst, temperature range of 40-60°C and 1:3 and 1:10 Mol ratio of oil to ethanol were used as optimal reaction conditions.



Scheme 1. Transesterification of oils with ethanol in the presence of a chemical catalyst

Vegetable oils have higher density, viscosity and lower thermal values, volatility than diesel fuel [16]. Therefore, the utilization of biofuel instead of diesel fuel, either entirely or partially, in diesel engines is limited by problems such as flow issues, poor atomization, and injector clogging, and thickening of the lubricating oil, incomplete combustion, and loss of power. Various techniques were developed to solve these problems. These include preheating, mixing and solubilization with other fuels, esterification or transesterification, and thermal cracking/pyrolysis processes [17]. Biodiesel obtained from the transesterification of pomegranate peel and seed oil was mixed with diesel fuel obtained from fuel oil in different percentages (80% diesel and 20% biodiesel; 40% diesel and 60% biodiesel) and the studies were conducted to solve the problems limiting

the use of biofuel. Before mixing, the physical and chemical indicators of the diesel fraction, which is the product of direct hydrocracking of fuel oil – heavy oil residue under low pressure, and biodiesel fuel obtained from the transesterification process were comparatively studied by different methods (Table 2). The density, kinematic viscosity and cetane number of biodiesel obtained from pomegranate peel and seed are higher than diesel fuel obtained from direct hydrocracking of fuel oil at low pressure, and at the same time, the sulfur content of the biofuel is lower by a certain percentage. This is due to the difference in the composition of the fuels; that is, the biodiesel obtained from pomegranate peel and seed consists of complex esters, while the diesel obtained from fuel oil mainly consists of saturated and unsaturated hydrocarbons.

Table 2. Physical and chemical indicators of fuel

Indicators	Diesel fuel	Biodiesel fuel of pomegranate peel	Biodiesel fuel of pomegranate seed
Density, 20°C, kg/m ³	805.0	810.0	820.4
Kinematic viscosity, 20°C, mm ² /s	2.5	4.4760	4.4645
Refractive coefficient, 20°C	1.4777	1.9654	1.9876
Heat of combustion, kJ/kg	44.631	39.811	39.493
Coking of 10% residue, %	0.4	0.4	0.4
Cetane number	49	56	57
Sulfated ash, % (wt)	0.02	0.02	0.02
Water, % (wt)	-	0.001	0.001
Sulfur, % (wt)	0.18	<0.001	<0.001
Ignition temperature, °C	55	125	125
Freezing temperature, °C	-25	-10	-10
Iodine number, gJ ₂ /100g	12	99.5	100.4
Free glycerin, % m/m	-	<0.1	0.2
Composition, % (wt)			
C	86.2	76.1	77.3
H	13.8	11.8	10.7
O	-	12.1	12.0

The utilization of biofuels made from vegetable oils is based on the difference in their physical and chemical properties from the properties of diesel fuel obtained from fuel oil, which is heavy oil residue [17, 18]. Therefore, the temperature dependence of the density and kinematic viscosity of diesel fuel and the mixture of diesel fuel and pomegranate peel and seed biodiesel in different ratios with diesel was studied.

As can be seen from the Figures 2 and 3, the temperature dependence of the density of diesel fuel is analogously the same as the temperature dependence of the density of fuels mixed with biodiesel in different ratios, that is, it becomes linear with increasing temperature, the value of density decreases. The density of the mixed fuel increases when biodiesel obtained from pomegranate peel and seed oil is

added in different ratios (80% diesel and 20% biodiesel; 40% diesel and 60% biodiesel).

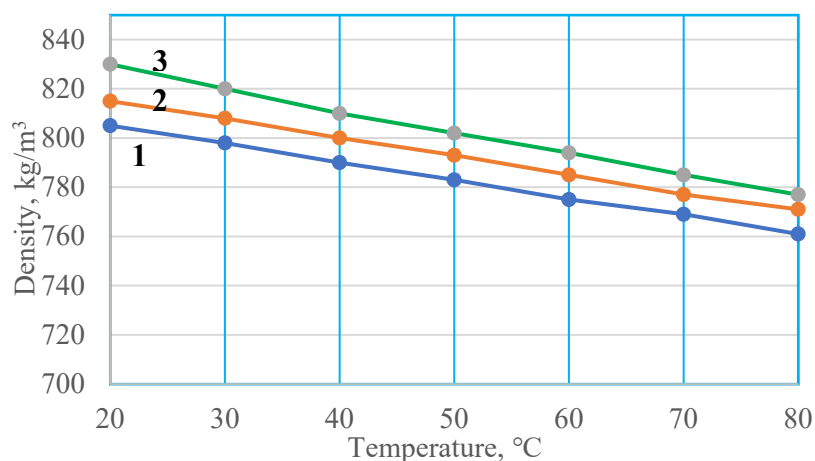


Fig. 2. Dependence of fuel density on combustion temperature: 1— diesel fuel; 2— 80% diesel fuel + 20% biodiesel obtained from pomegranate peel oil; 3— 40% diesel fuel + 60% biodiesel obtained from pomegranate peel oil

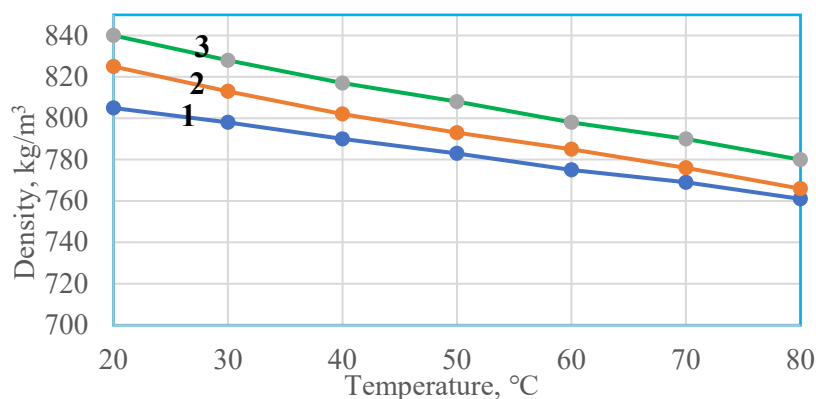


Fig. 3. Dependence of fuel density on combustion temperature: 1— diesel fuel; 2—80% diesel fuel + 20% biodiesel obtained from pomegranate seed oil; 3— 40% diesel fuel + 60% biodiesel obtained from pomegranate seed oil

One of the main problems that arise when diesel fuel is used in engines is their increased viscosity. Figures 4 and 5 show the temperature dependence of the kinematic viscosity of diesel, and also the fuel obtained from the mixture of pomegranate peel and seed biodiesel in different ratios with diesel. As can be seen from the figures, the temperature dependence of the kinematic viscosity of diesel fuel is analogously the same as the temperature dependence of the kinematic viscosity of fuels mixed with biodiesel in different ratios and it has an exponential character. Fuel obtained from a mixture of diesel in different ratios (80% diesel and 20% biodiesel; 40% diesel and 60% biodiesel) with biodiesel obtained from

pomegranate peel and seed oil has a viscosity closer to diesel fuel at low temperatures. At normal temperature ($t = 20^{\circ}\text{C}$), the viscosity of fuel obtained from a mixture of pomegranate peel and seed biodiesel is much higher than that of diesel fuel [19, 20]. In particular, in the presented studies, diesel fuel has a viscosity of $2.5 \text{ mm}^2/\text{s}$; a mixture of 80% diesel fuel and 20% biodiesel obtained from pomegranate peel oil has a viscosity of $4.3 \text{ mm}^2/\text{s}$; a mixture of 40% diesel fuel and 60% biodiesel obtained from pomegranate peel oil has a viscosity of $5.1 \text{ mm}^2/\text{s}$; a mixture of 80% diesel fuel and 20% biodiesel obtained from pomegranate seed oil has a viscosity of $4.5 \text{ mm}^2/\text{s}$; and a mixture of 40% diesel fuel and 60% biodiesel obtained

from pomegranate seed oil has a viscosity of 5.5 mm²/s. The density and kinematic viscosity, which are the main physical and chemical

properties of the obtained mixed biofuel, are higher than the density and viscosity of petroleum-based diesel fuel.

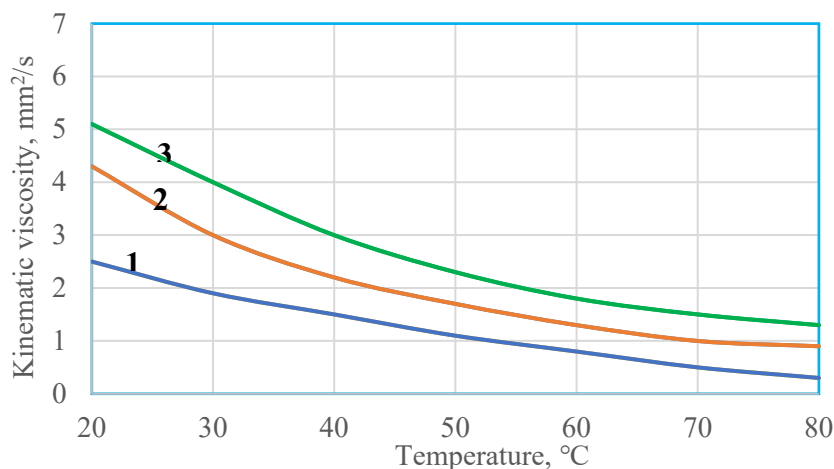


Fig. 4. Dependence of kinematic viscosity of fuels on combustion temperature: 1— diesel fuel; 2— 80% diesel fuel + 20% biodiesel obtained from pomegranate peel oil; 3— 40% diesel fuel + 60% biodiesel obtained from pomegranate peel oil

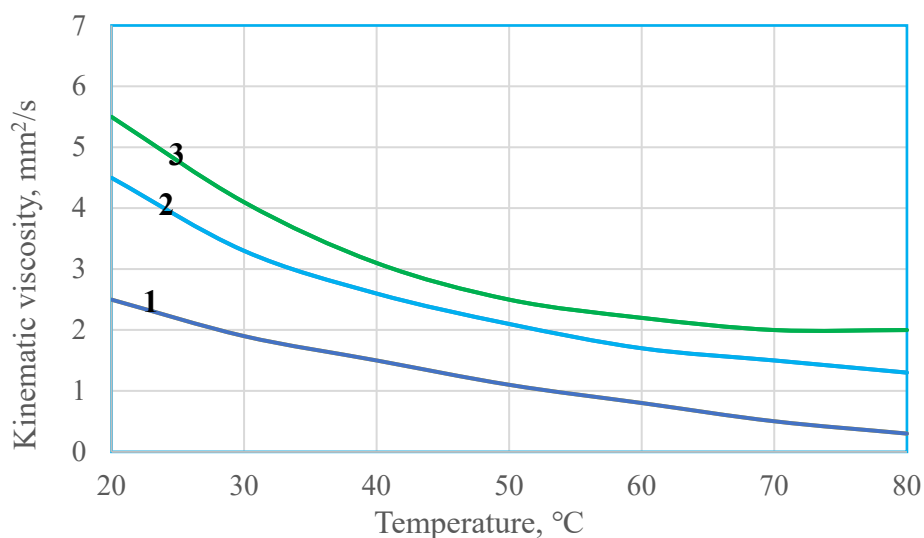


Fig. 5. Dependence of kinematic viscosity of fuels on combustion temperature: 1— diesel fuel; 2— 80% diesel fuel + 20% biodiesel obtained from pomegranate seed oil; 3— 40% diesel fuel + 60% biodiesel obtained from pomegranate seed oil

Conclusion

We can note that pomegranate peel and seed oil can be used as an economically favorable and environmentally friendly source of natural raw materials in the production of biodiesel as an alternative fuel. Biodiesel was produced in high yield by the method of transesterification of oils obtained from the waste of pomegranate peels and seeds with KOH as a catalyst, temperature range of 40-

60°C as the optimal reaction conditions and oil to ethanol ratio of 1:3 and 1:10 Mol. Mixed biofuels were prepared by mixing the obtained biodiesel with petroleum-based diesel fuel in different amounts (80% diesel and 20% biodiesel; 40% diesel and 60% biodiesel). As a result of the analysis, we can note that the density and kinematic viscosity of mixed

biofuels are higher than the density and viscosity of diesel fuel obtained from fuel oil.

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