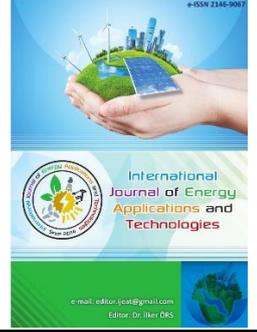




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Original Research Article

Comparison of fuel properties of biodiesels produced from different waste cooking oils

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ABSTRACT

In this study, it was investigated that the fuel properties of waste cooking oils by converting them to biodiesel and their suitability as diesel fuel according to these properties were investigated. However, differences in the separation or mixing of waste edible oils during collection are also presented. Waste cooking oils were obtained from cafeterias and dining hall kitchens in different regions of universities and serving different food product groups. Transesterification method was applied as a method of converting waste oils to biodiesel. Density, kinematic viscosity, flash point, cetane index, water content, calorific value and cold filter plugging point fuel properties of produced biodiesels were investigated. According to the results obtained, it has been revealed that the produced biodiesels comply with the standards, and because the fuel properties of the biodiesel produced from blended oils are within the standards, the waste cooking oils can be mixed during collection. Although the flow and cold flow properties and lower heating value of biodiesel produced with waste oil mixtures are disadvantageous compared to diesel fuel, the cetane index affecting combustion and the flash point value that emphasizes its safety are its important advantages. In addition, the fact that the water content of the produced fuels complies with the standards shows that the biodiesel production is successful and the results obtained can be used safely.

Keywords: Biodiesel; Diesel engine; Fuel properties; Transesterification; Waste cooking oil

1. Introduction

Waste cooking oils (WCOs) are contaminated or spoiled products that are harmful to human health and the environment, as they are processed foods. It has been determined that the production of waste cooking oil worldwide is over 16.54 million tons per year. The disposal of these harmful wastes has become a global problem due to the rising food demand due to the rapidly increasing population growth [1-7].

Evaluation of WCOs as engine fuel with minimum damage to nature is one of the most widely used methods today. However, it should be converted to biodiesel since it is not suitable for direct use as fuel due to its high density and

viscosity value. The use of WCOs as biodiesel has important advantages both environmentally and economically. Because WCOs is the most economical feedstock that can be used in biodiesel production. In addition, the positive effects of biodiesel on harmful exhaust emissions have been demonstrated by many researchers.

Transesterification is the most widely used biodiesel production method due to its economy and simplicity [8-12]. Although biodiesel is mostly used as a mixture fuel in diesel engines [13-16], it can rarely be used as a single fuel [17,18]. The researchers stated that the negative effects of the flow properties of biodiesel on the spray characteristics also affect the combustion parameters to some extent [19-21]. However, thanks to the high cetane number, it is seen that this negative

effect on combustion parameters is considerably reduced [22,23]. Especially the low calorific value causes a decrease in engine performance [24-27]. However, it has been observed that there is a noticeable increase in the performance of especially low biodiesel blended fuels, thanks to the somewhat positive effect of the oxygen it contains on combustion [28,29]. At the same time, it has also been found that the fuel properties of biodiesel improve engine performance by allowing some modifications on the engine. For example, it allows the compression ratio to be increased thanks to its high cetane number. The increase in compression ratio positively affects engine performance [30-32]. An increase in performance has been achieved with the preheating process, as the high flash point allows the biodiesel to be heated [33]. The fact that it can be injected at higher pressures due to its high viscosity also showed a positive effect on the performance [34,35]. It is seen that the oxygen content of biodiesel also has positive effects on exhaust emissions, and fuels with high biodiesel ratio have very low CO, HC and smoke emission values. However, as a disadvantage of this oxygen content, it has been stated that NO_x emissions are higher than diesel fuel [36-40]. In addition, some studies have stated that a decrease in NO_x emissions can also be seen, since the low heat release rate and low calorific value of biodiesel cause a decrease in the post-combustion temperature [41,42].

When the studies done so far are examined, it is seen that the fuel properties of biodiesel have direct effects on combustion, performance and emission parameters. In addition to the production process of biodiesel, the type of raw material also affects the fuel properties of biodiesel. Since the transesterification method is a standard procedure in general, the type of oil and the conditions of use can be said to be the most decisive features, especially for waste cooking oil biodiesel. Many parameters such as the feedstock of the frying oil, the type of the fried food (vegetable or animal), the usage time of the oil can change the properties of the waste oil. In this study, the fuel properties of biodiesels obtained from frying oils produced from different feedstocks, different food types subjected to frying process and mixtures of these oils used in different conditions were investigated.

2. Material and Methods

2.1. Test fuels

The waste cooking oils used for biodiesel were supplied from the central refectory and student cafeterias in Erciyes University and Aksaray University. This refectory is using frying oil for both cooking of vegetable products such as potato, eggplant, carrot, pepper and zucchini and animal products such as red meat, chicken and fish. The waste frying oils supplied have been classified according to their type and

intended use such as waste sunflower oil for vegetable (SOB_v) and animal (SOB_a), waste palm oil (POB) and waste cotton oil (COB). In addition, biodiesel (Mix) was created with the new oil mixtures obtained by mixing these collected oils in equal volumetric proportions. In the process of converting the collected waste oils to biodiesel, 0.99 purity methanol was used as alcohol and sodium hydroxide with 0.97 purity was used as catalyst.

2.2. Biodiesel production

Before the transesterification process, all oils were filtered with paper filters with a pore diameter of 0.45 µm in order to remove residues and foreign substances in the waste oils. A mixture of 200 ml of methanol (1/5 of the oil by volume) and 3.5 g of sodium hydroxide was prepared and added into 1 liter of oil. The mixture was stirred at 55°C at 800 rpm for 1.5 hours. After waiting for the glycerol to settle to the bottom, it was separated from the biodiesel with a separating funnel as seen in Figure 1. 0.5 L distilled water was added to the biodiesel to clean the unwanted residues that may remain in the biodiesel. During washing, the temperatures of water and biodiesel were equalized at 50 °C. After mixing at very low speed for 10 minutes, it was rested for 20 hours and the water and its contents were separated with a separating funnel as seen in Figure 2. The washing process was repeated until the separated pure water became clear, that is, 4 times. The biodiesel was heated up to 100-110 °C for 5 hours in possibility the washing water could remain in the biodiesel and the water in it was removed. After the obtained biodiesels were filtered again, they were also stored in glass bottles as seen in Figure 3.



Fig. 1. Separation of glycerol with a separatory funnel.



Fig. 2. Separation of washing water with a separating funnel.



Fig. 3. Biodiesels produced from different waste cooking oils

2.3. Determination of fuel properties

Density, Kinematic Viscosity, Lower Heating Value, Cold Filter Plugging Point, Flash Point, Water Content of the

obtained biodiesels were measured using industrial devices, and Cetane Index was calculated using Equation 1 according to ASTM-D4737 standards.

$$CCI = 45.2 + (0.0892)(T_{10N}) + [0.131 + (0.901(B))][T_{50N}] + [0.0523 - (0.420)(B)][T_{90N}] + [0.00049][(T_{10N})^2 - (T_{90N})^2] + (107)(B) + (60)(B)^2$$

where:

CCI= Calculated Cetane Index by Four Variable Equation,
D= Density at 15°C, g/mL determined by Test Methods D 1298 or D 4052,

DN= D - 0.85,

B= $[e^{(-3.5)(DN)}] - 1$,

T₁₀= 10% recovery temperature, °C, determined by Test Method D 86 and corrected to standard barometric pressure,
T_{10N}= T10- 215,

T₅₀= 50% recovery temperature, °C, determined by Test Method D 86 and corrected to standard barometric pressure,
T_{50N}= T50- 260,

T₉₀= 90% recovery temperature, °C, determined by Test Method D 86 and corrected to standard barometric pressure, and

T_{90N}= T90- 310.

Density; the densities of the fuels were determined with the Kem Kyoto DA-645 model density measuring device shown in Figure 4. The device, which measures according to EN ISO 3675 and EN ISO 12185 standards, can measure up to 3g/cm³ at 0-93°C with an accuracy of ±0.00005.



Fig. 4. Density measuring device

Kinematic viscosity; in the measurement of kinematic viscosities of fuels, a viscosity measuring device with Ambient temperature with ±0.05 sensitivity, with Measuring tubes with ±0.5 and ±1 accuracy, and Timekeeper with ±0.01 accuracy, measuring according to EN ISO 3104 standards was used. Figure 5 shows the Standard Immersion Circulator of the viscosity meter.





Fig. 5. Standard Immersion Circulator of the viscosity meter

Lower heating value; the calorific values of the fuels were measured with the IKA C200 bomb model calorimeter shown in Figure 6. The device, which can measure values up to 40000 J with ± 0.1 accuracy, works according to DIN 51900 standards. Values measured by calorimeter are determined as lower heating value.



Fig. 6. Bomb calorimeter

Cold filter plugging point; the cold filter plugging point values were determined as the cold flow analysis of the fuels. Cold filter plugging points were measured with Labkits PT-SYD-510F1 multifunctional low temperature tester, as seen Figure 7, with $\pm 0.5^\circ\text{C}$ accuracy, according to GB/T510, GB/T3535, GB/T6986, SH/T0248 standards.



Figure 7. Multifunctional low temperature tester

Flash point; the flash point values of the test fuels were determined by the test device that with measures ± 1 accuracy in the range of $-30 - +300^\circ\text{C}$ in EN ISO 2719 and EN ISO 3679 standards seen in Figure 8.

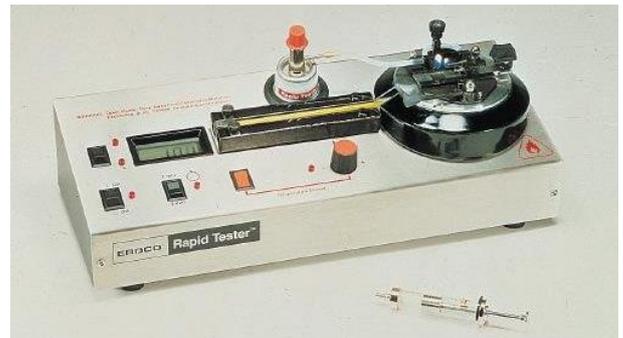


Fig.8. Flash point device determination: Rapid Tester RT-1

Water Content; the amount of water content in the produced biodiesel was controlled with the Kem Kyoto MKC-520 Karl-Fischer model moisture titrator with an accuracy of $\pm 0.1 \mu\text{g}$ in accordance with EN ISO 12937 standard. The moisture titrator device shown in Figure 9 can measure water content up to 300000 μg .



Fig. 9. Moisture titrator device



2.4. Standards

The investigated properties of the produced test fuels were evaluated according to ASTM D6751 and TS EN 14214 standards, and the properties of diesel fuel were evaluated according to the TS EN 590 standard. Table 1 shows the standard values of the investigated fuel properties.

Table 1. Standards and limits for measured fuel properties

Properties	Unit	Limits of ASTM D6751		Limits of TS EN 14214		TS EN 590	
		Min.	Max.	Min.	Max.	Min.	Max.
Density, at 15 °C	kg/m ³	-	-	860	900	820	845
Kinematic Viscosity, at 40°C	mm ² /s	1.9	6.0	3.5	5.0	2.0	4.5
Cold Filter Plugging Point	°C	-	-	-	-	-15 (wint.) +5 (sum.)	-
Flash Point	°C	93	-	101	-	55	-
Water Content	mg/kg	-	500	-	500	-	200
Cetane Number/Index		47/-	-	51/-	-	51/46	-

3. Results

The examined physical and chemical properties were chosen as the most important fuel properties affecting engine performance.

3.1. Density

When considered as a fuel property, density is a determining factor for the flow and cold flow properties of the fuel as well as related to other fuel properties such as cetane number and calorific value. In fact, the density value of the fuel is also needed in the calculation of the cetane index [43].

Density changes of the produced biodiesels are shown in Figure 10. The biodiesel with the highest density is COB, while the lowest density is SOBv. It is seen that the density value of biodiesel obtained with the oil used in frying animal products is approximately 0.3% higher than that of biodiesel obtained by frying vegetable products. It can be said that the differences in the physical properties of the animal fats transferred to the frying oil by frying animal products cause this increase. However, the density values of all biodiesels are higher than that of diesel fuel.

An increase in fuel density will cause more fuel to be injected into the cylinders by mass. While this situation is theoretically expected to increase the engine power parameter, in practically, spraying more fuel in mass into the cylinder will cause a rich mixture, so the injected fuel will not be able to penetrate homogeneously into the air taken into the cylinder and negatively affect on the combustion. Therefore, the fuel density must be suitable for the fuel system elements used.

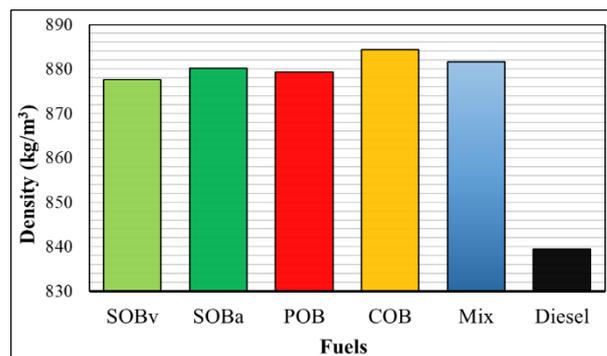


Fig. 10. Density variation of test fuels

3.2. Kinematic viscosity

In order for vegetable or animal oils to be used efficiently as fuel in reciprocating engines, their viscosity must be reduced. Reducing the viscosity of oils to be used as fuel is relatively cheaper and easier than modifying the engine. Transesterification is the most widely used method to reduce the viscosity of the oils used as waste frying oil as in this study, to be used as fuel. Thus, glycerol, which causes high viscosity in the oil, is separated. Figure 11 shows the viscosity changes of the test fuels. When the viscosity values are examined, it is seen that POB has a significantly lower value compared to other biodiesels. However, it is approximately 47.61% higher than that of diesel fuel. Sunflower oil-based fuels have the highest viscosity value. In particular, the viscosity value of SOBa is approximately 15.7% higher than POB.

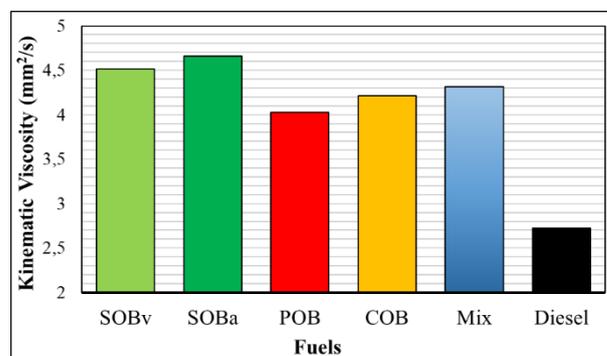


Fig. 11. Kinematic viscosity variation of test fuels

High viscosity has significant negative effects, especially at the time of injection of fuels. High viscosity causes insufficient atomization at the time of spraying and worsening combustion efficiency. Besides, high viscosity will create additional resistance to the operation of the parts that have the task of increasing the fuel pressure, and will adversely affect the operation of the fuel system elements.

3.3. Lower heating value

Lower heating value is one of the most important fuel properties that affect the performance of the engine. Because, the lower calorific value shows the amount of energy released

at the end of the combustion of the fuel. Thanks to this energy, the engines create work. As can be seen in Figure 12, the heating values of all biodiesel produced are lower than that of diesel fuel. However, there is no significant difference between the lower heating values of biodiesels. However, the fuel with the lowest lower calorific value is POB, while the fuel with the highest lower calorific value is SOBv. Animal product fried oils appear to be disadvantageous compared to vegetable fried oils.

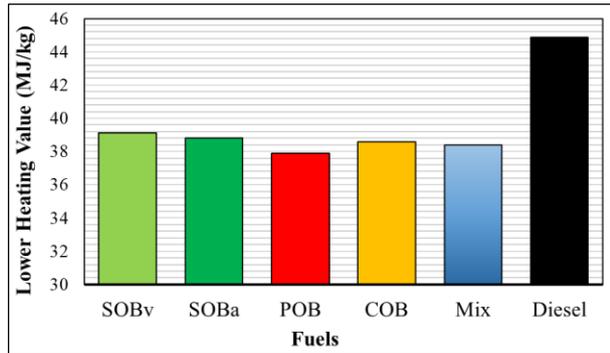


Fig. 12. Lower heating value variation of test fuels

3.4. Cold filter plugging point

The cold flow properties of the fuel are an indication of its geographical availability. Density and viscosity values of fuels are also parameters that enable cold flow properties to be predicted. Generally, cloud point, cold filter plugging point, pour point and freezing point parameters are examined as cold flow properties. Among these parameters, the cloud point is the temperature at which particles called wax crystals begin to form in the fuel. At cloud point temperature, the engine continues to run, albeit with problems. However, the cold filter plugging point is the first indicator of the temperature at which the fuel cannot pass through the filter. Afterwards, pouring and freezing point temperatures are important parameters especially for the storage and transportation processes of the fuel. Cold filter plugging point values of test fuels are shown in Figure 13. Due to the vegetable oil content of biodiesels, it is seen that the filter clogs at lower temperatures than diesel fuel.

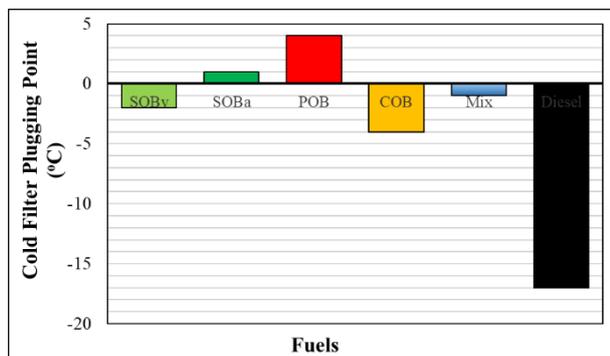


Fig. 13. Cold filter plugging point value variation of test fuels

Among the produced biodiesels, the lowest cold filter plugging point temperature is for COB, while the highest is for POB. The high properties of fatty acids and triglycerides in POB reduced its cold flow properties despite its low density and viscosity. Therefore, this chemical structure of POB shows that it is not suitable for use in cold conditions.

3.5. Water content

There can be many reasons for the presence of water in the fuel. The most important reason for the water in biodiesel is the water remaining after the washing process. Even if biodiesel is subjected to drying process, it is normal to have in standards amount of water in its content, since the fatty acids and some molecules in the fuel do not allow it to evaporate by holding the water. The amount of water higher than the standards causes a decrease in the quality of the fuel, especially the cold flow properties of the fuel, worsening of the combustion characteristics and corrosion in the fuel system. Figure 14 shows the water content values of the test fuels. The fact that the amount of water content in all produced fuels complies with the standards is an indication of the correct and successful production.

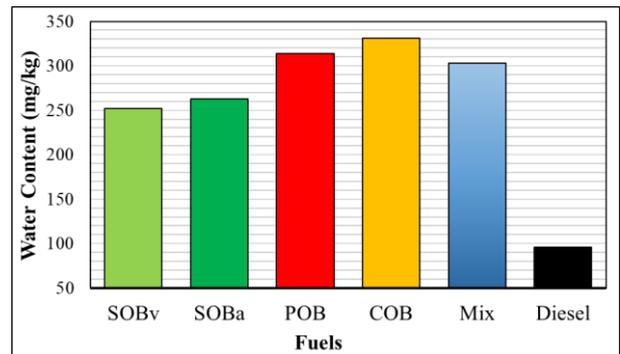


Fig. 14. Water content value variation of test fuels

3.6. Cetane index

The cetane number is the self-igniting tendency of the fuel. The cetane number is a very important property for the combustion characteristics of the fuel. It is a parameter that directly affects the ignition delay. Since the start of ignition of fuels with high cetane number will be shortened, they allow controlled combustion. The cetane indexes of the test fuels calculated according to Equation 1 are shown in Figure 15.

Among all fuels, the highest cetane index belongs to COB. In addition, it is seen that the cetane index of biodiesel is higher than that of diesel. It is seen that the cetane index of biodiesel obtained from frying oil of animal origin is slightly higher than that of vegetable-based frying oil. The high cetane number is one of the important advantages of biodiesel over diesel fuel.

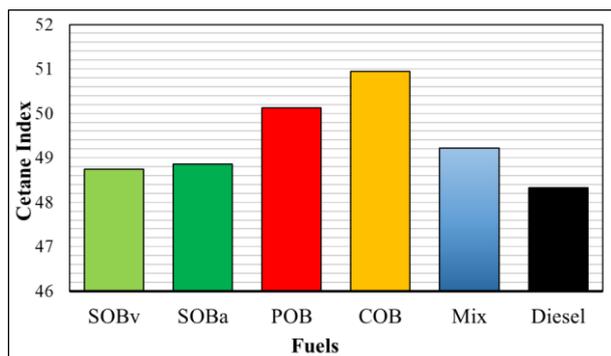


Fig. 15. Cetane index value variation of test fuels

3.7. Flash point

Flash point is a parameter that determines the transportation and storage safety of fuels. Biodiesel has a significantly higher flash point value than diesel fuel, as long as there is no methanol residue during its production, and this is one of its most important advantages. Table 2 shows the measured fuel properties parameters of the test fuels. As can be seen from the table, especially biodiesels produced from sunflower oil-based waste oils have very high flash point values.

Table 2. Fuel properties of all biodiesels and diesel fuel

Properties	Unit	SOBv	SOBa	POB	COB	Mix	Diesel
Density, at 15 °C	kg/m ³	877.6	880.1	879.3	884.3	881.6	839.4
Kinematic Viscosity, at 40°C	mm ² /s	4.517	4.656	4.024	4.211	4.315	2.726
Lower Heating Value	MJ/kg	39.1	38.8	37.9	38.6	38.4	44.86
Cold Filter Plugging Point	°C	-2	1	4	-4	-1	-17
Flash Point	°C	>120	>120	95	112	>120	72
Water Content	mg/kg	252	263	314	331	303	96
Cetane Number/Index		48.75	48.86	50.12	50.94	49.22	48.32

4. Conclusion

When the fuel properties of the produced biodiesels are examined;

- It is seen that the density values of all waste cooking oil biodiesel comply with TS EB 14214 standards, and even the COB, which has the highest density value, is 5.35% higher than diesel fuel.
- The viscosity values of the produced fuels comply with both ASTM D6751 and TS EN 14214 standards. SOBa with the highest viscosity is 1.71 times higher than diesel fuel, and POB with the lowest viscosity is 1.48 times higher.

- Although there is no significant difference between the calorific values of biodiesels, the SOBv, which has the highest lower calorific value, is 12.84% lower than that of diesel fuel.

In this study, although waste edible oils are collected according to their type and usage, in practice, oil collecting institutions will not take such a situation into consideration. For this reason, the collected oils will be mixed. It can be said that the fuel properties of the Mix biodiesel, which is obtained after being formed with a mixture of 4 different types of waste oil, are within the standards and it will be suitable for use as diesel fuel.

In order to minimize the negative effects of the density and viscosity of biodiesel, detailed studies such as increasing the injection pressure, changing the injection advance, and changes in the compression ratio can be done. In addition, the fuel quality of biodiesel produced from waste oils can be increased with different chemical methods before biodiesel production by examining the changes in fatty acids and components before and after using the oils as frying oil.

Authorship contribution statement for Contributor Roles Taxonomy

Enver Demir: Writing - original draft, Investigation, Visualization, Conceptualization, Methodology, Experimental study.

İlker Örs: Investigation, Supervision, Visualization, Conceptualization Writing - Review & editing, Funding acquisition.

Conflict of interest

The authors declares that he has no conflict of interest.

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