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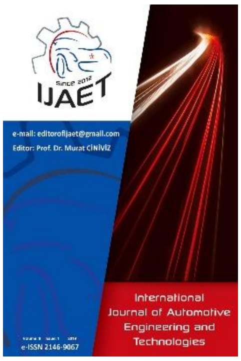

Original Research Article

Predicted fuel characteristics of prunus avium seed oil as a candidate for biodiesel production

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ABSTRACT

Energy is an indispensable requirement for both developed and developing societies today. However, most of the energy needs are met by fossil fuels, these resources are not renewable. Many countries are evaluating alternative sources to meet energy demand and to sustain development. In this study, oil was obtained by using Prunus avium kernels, also known as Turkish Cherry cultivated from Pozantı which is on the Taurus Mountains. Oil characterization was performed by gas chromatography (GC) and free fatty acids were determined. Oleic acid (C18:1) and Linoleic acid (C18:2) determined as 38.938 and 40.963 respectively. The free fatty acids were then evaluated using the Biodiesel Analyzer v1.2 program. The predicted results were the total percentage of monosaturated fatty acids (MUFA) 39.408, total percentage of polyunsaturated fatty acids (PUFA) 41.042, Allylic Position Equivalents (APE) 121.146, Bisallylic position equivalents (BAPE) 41.220 respectively. On the other hand, Long Chain Saturated Factor (LCSF) is calculated as 3.624. Higher Heating Value (HHV) was calculated as 37.65Mj/kg, Cloud Point (CP) 0.099, Cold Filter Plugging Point (CFPP) -5.091° C, Density (d) 0.838 (g/cm^3), Cetane Number (CN) 50.1, Iodine Value (IV) 109.878, Kinematic Viscosity 3.543, Flash Point (FP) 160.56, Saponification Value (SV) 191.354, and Oxidation Stability (OS) 5.468, respectively. As a result of this study, it was concluded that Prunus Avium kernel oil is a promising biodiesel candidate.

Keywords: Biodiesel, Fatty Acid, Fuel Property, Prunus avium

1. Introduction

Nowadays the world is rapidly moving towards an energy bottleneck. The reason behind this can be contributed to two main reasons; known fossil fuel resources are gradually decreasing while population increases hence the energy consumption increases; on the other hand, our world is faced with climate change due to the usage of fossil fuels. Therefore, the search for renewable energy sources has accelerated throughout the world. Biofuels gain importance at this point. The most important characteristics of biofuels are their renewability and their availability throughout the world. In the future, biofuels are expected to replace fossil-based fuels. Reducing the impacts of greenhouse gases, assisting regional development and maintaining sustainability are attractive aspects of biofuels.

Biodiesel is one of these alternative biofuels, which is methyl-esters of long-chain fatty acids [1]. It is biodegradable, non-toxic [2] which has very similar properties to fossil diesel and can be used without any modification in the vehicle engine. Using Biodiesel as an alternative to diesel fuel has been carried out for a long time. It can be produced from edible oils (sunflower, canola, sesame, sunflower oil, etc.), non-edible oils (Karanja, jatropha, eucalyptus, etc.), waste and recycled oils and also from algae [3]. There are four main methods of producing biodiesel. Blending, micro-emulsions, thermal cracking, and transesterification [4]. Scientists focused on evaluating different feedstocks, performance characteristics, appropriate blends, effects of additives in the literature. Şanlı [5] investigated biodiesel which is produced from waste chicken fat and waste fleshing oil. Exhaust emission characteristics were determined. The result showed that animal fat-based biodiesel had better total hydrocarbon and carbon monoxide emissions. However, carbon dioxide and nitrogen oxide emissions were increased. Ors et al [6] researched effects of blending biodiesel and bioethanol on performance, emission and combustion characteristics in a diesel engine. It was concluded that brake specific fuel consumption and volumetric efficiency are both increased. While using biodiesel NO emissions were increased, smoke opacity and Hydrocarbon emissions decreased. Kahraman et al [7] studied on the engine performance and exhaust emissions cotton oil methyl ester and its blends. The gained results showed that engine performance decreased and exhaust emissions were improved. Özgün and Eryılmaz [8] evaluated waste cooking oil biodiesel by applying a neutralizing process before transesterification. The result showed that maximum torque, maximum power, and minimum specific fuel consumption values increased. Exhaust emissions, CO, HC, and smoke intensity were lower, and NO and CO2 emissions were higher. The neutralization process improves the emission values. Can et al [9] prepared canola biodiesel and diesel blends with 5%, 10%, 15% and 20% v/v respectively. Authors stated that biodiesel blends showed shorter ignition delay time but decreased maximum heat release rate. Both NOx and CO2 emissions were higher however CO and Total Hydrocarbon emissions were lower than diesel. Kaya et al [10] investigated the peanut (Arachis hypogea L.) seed oil biodiesel. It was concluded that biodiesel has very close fuel properties to diesel. Salaheldeen et al [11] studied on the Moringaperegrina seed oil biodiesel. They reported that major fuel properties of Moringaperegrina biodiesel conformed to the ASTM D6751 standards and could be as a blend up to %20. Yeşilyurt et al [12] studied on biodiesel/diesel/1-butanol and biodiesel/diesel/n-pentanol fuel blends. They reported that as the amount of alcohol increased brake powers and torques are decreased. Also, n-pentanol blended fuels showed better performance and emission results than 1-butanol blends. Shivastayaa et al [13] evaluated different blends of Roselle and Karanja biodiesels. This study showed that brake thermal efficiency, exhaust gas temperature, indicated thermal efficiency, the maximum rate of pressure rise rate and ignition delay decreased. Besides NOx and smoke emissions also showed reductions.

According to Turkish Institue of standards data, there are 4,621,993 diesel fulled vehicles on the road while gasoline fulled vehicle number reached to 3,086,192 in Turkey [14]. Diesel vehicles reached to a 37.1% percentage of the total vehicles. As a fuel, diesel is used extensively in the transportation sector in Turkey. Being an oil importer country the cost of diesel has a huge impact on the Turkish economy, besides concerns about climate change and exhaust emissions affect on human health plays an important role in the researches about biodiesel. On the other hand, the Energy Market Regulatory Authority of Turkey published the regulation for blending diesel with biodiesel in 1.1.2018. By this regulation, diesel fuel must be blended with 7% biodiesel. Turkey has produced 110,000 m^3 biodiesel in 2018 and used 33% of the production capacity. [15]

If biodiesel is to be put on the market as an alternative fuel, it is necessary to concentrate on the production of biodiesel from non-edible oils rather than oils that can be used as food. The oil which is not a part of human nutrition namely non-edible oils should be considered as biodiesel feedstock. According to 2018 Turkstadt data, there is a production of 627,132 tonnes of Turkish cherry (Prunus avium) and almost 41,000 tons were recorded as lost and disposed of as waste [14]. Therefore, the main objective of this study is evaluating the biodiesel production possibility of Prunus avium seeds as a feedstock by characterizing the fatty acid profile of oil and predicting the biodiesel fuel properties.

2. Material and Method

Prunus avium (figure 1) [16], which shows a widespread commercial sense in the world, is grown in countries such as Turkey, Iran, Italy, and the US. Although production levels vary according to the year and climate conditions, Turkey is located in the first row of cherry production. Prunus avium cultivation is carried out in various regions including İzmir (Kemalpaşa), Manisa, Konya (Aksehir, Hadim, Taşkent), Afyon (Sultandağı), Isparta (Uluborlu) and Denizli (Honaz).

Figure 1. Prunus avium (cherry) [16]

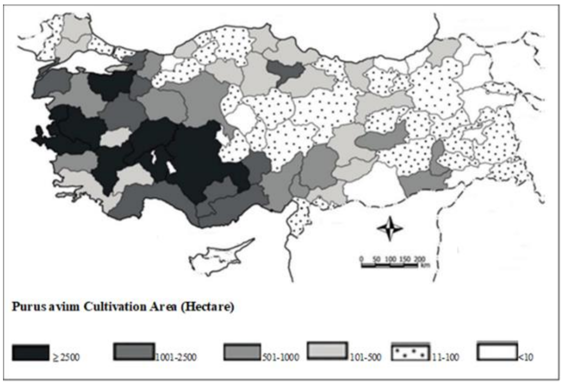

Figure 2. Prunus avium cultivation area [17]

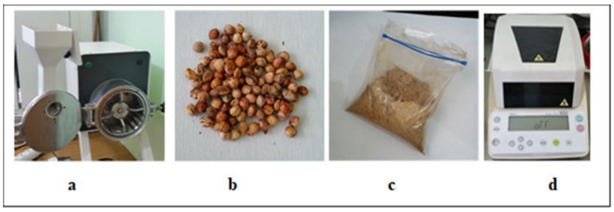

Figure 3. a-Grinding machine b- Prunus avium seeds c- Grounded Seeds d- Moisture Analyzer

2.1. Oil extraction

The Prunus avium seeds (fig 3 b) were ground into powder using ground machinery (figure 3a). The grounded seeds (figure 3c) placed in the Shimadzu moisture analyzer (figure 3d) and the moisture of the grounded seeds were measured as 8,47 %. The oil was extracted by using soxhlet figure 4.

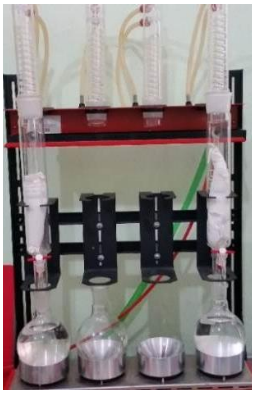

Figure 4. Soxhlet used for oil extraction

The Prunus avium seed oil (PO) was analyzed by gas chromatography (GC-MS QP-2010, SHIMADZU Japan) and figure 5 shows the results of this analysis. The results were tabulated in table 1. Biodiesel analyzer software v.2 was used for predicting the properties of Prunus avium biodiesel by using fatty acid profile.

2.2. Prediction of biodiesel characterization

Biodiesel fuel quality characterized cetane number, viscosity, flashpoint, heating value, iodine value, density, cold flow properties, etc. By using Biodiesel Analyzer V.1.2 some of the properties could be calculated. Empirical equations presented in Biodiesel Analyzer v1.2 software was used for the calculation of biodiesel properties [18,19].

The predicted biodiesel characteristics are calculated with the given formulas [18,19]:

The cetane number influenced by iodine and saponification values.

SV: Saponification Value

$$SV = \sum (560 \times N)/M \quad (1)$$

IV: Iodine Value

$$IV = \sum (254 \times D\ N)/M \quad (2)$$

where

M: Molecular mass of fatty ester,

N: percentage of Fatty Acid Ester in the oil sample,

D: Number of double bonds

CN: Cetane Number

$$CN = 46.3 + \left({}^{5.458}/_{SV} \right) - (0.225 \times IV) \quad (3)$$

DU: Degree of Unsaturation

$$DU = MUFA + (2 \times PUFA) \quad (4)$$

where
MUFA: % monosaturated fatty acids,
PUFA: % polyunsaturated fatty acids.
The oxidation stability of biodiesel was calculated using the given formulas below.
APE: Allylic position equivalents

$$APE = \sum(ap_n \times A_{cn}) \quad (5)$$

ap_n: number of allylic position equivalents
A_{cn}: Amount of Fatty Acid in the mixture.
Bisallylic position equivalents (BAPE)

$$BAPE = \sum(bp_n \times A_{cn}) \quad (6)$$

Bp_n: number of Bisallylicposition equivalents
Oxidation stability (OS)

$$OS = (117.9295/(C18:2 + C18:3) + 2.5905) \quad (7)$$

One of the main handicap for using biodiesel as a fuel is its cold flow properties. The cold flow properties that predicted are Cold Filter Plugging Point, Cloud Point, and Pour Point, respectively.
Long-chain saturated factor (LCSF)

$$LCSF = (0.1 \times C_{16}) + (0.5 \times C_{18}) + (1 \times C_{20}) + (1.5 \times C_{22}) + (2 \times C_{24}) \quad (8)$$

Cold Filter Plugging Point(CFPP)

$$CFPP = (3.1417 \times LCSF) - 16.477 \quad (9)$$

Cloud Point (CP)

$$CP = (0.526 \times C_{16}) - 4.992 \quad (10)$$

Pour Point (PP)

$$PP = (0.571 \times C_{16}) - 12.24 \quad (11)$$

The kinematic viscosity estimated at 40 °C as

$$\ln(v) = \sum N_i\,(-12.503 + 2.496 \times \ln Mw_i) - 0.178 \times D_i \quad (12)$$

where
Mw_i molecular weight of FA,
N_i is the percentage of the given FA,
D_i denotes the number of double bonds.
The density of the biodiesel estimated at 20° with the following equation.

$$\rho = \sum N_i(0.8463 + (4.9/(Mw_i)) + 0.118 \times D_i \quad (13)$$

Higher heating value is estimated as follows:

$$HHV = \sum Ni(46.19 - (1794 / Mw_i - 0.21 \times Di) \quad (14)$$

Flashpoint was estimated by using the formula below [3]

$$FP\,(°C) = 205.226 + 0.083x_p - 1.727x_s - 0.5717x_o - 0.3557x_{LI} - 0.467x_{LN} - 0.2287x_E \quad (15)$$

where
x_p mass fraction of palmitic acid
x_s mass fraction of stearic acid
x_o mass fraction of oleic acid
x_{LI} mass fraction of linoleic acid
x_E mass fraction of erucic acid

4. Results and Discussion

The gained oil sample was tested in gas chromatography and Figure 5 shows the gas chromatography spectra of Prunus avium seed oil. The corresponding data were tabulated in table 1 as the fatty acid profile.

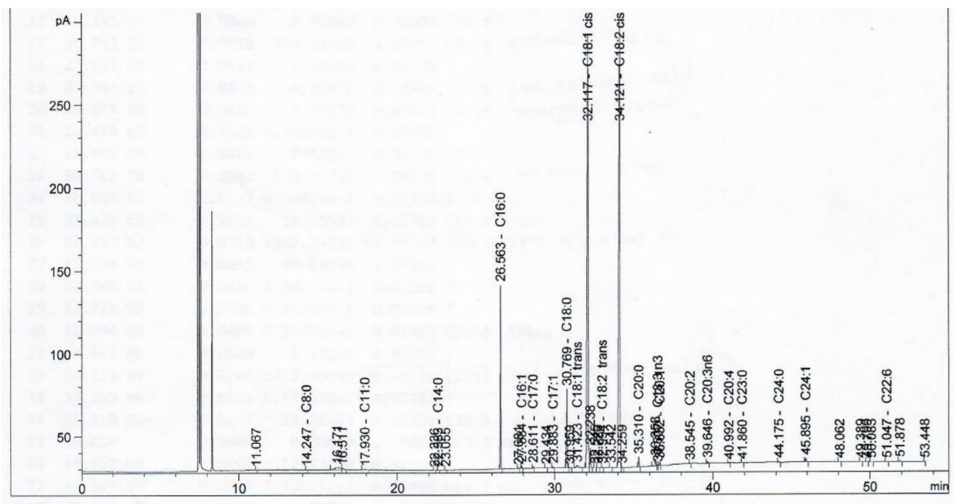

Figure 5. GS result of Purus avium seed

Table 1. Fatty acids profile of Prunus avium seed

Fatty Acid	% by weight	Fatty Acid	% by weight	Fatty Acid	% by weight
Caprylic(C8:0)	0.017	Stearic (18:0)	5.001	Arachidonic (20:0)	0.538
Myristic(14:0)	0.017	Oleic (18:1)	38.938	Docosahexaenoic (22:6)	0.033
Palmitic (16:0)	9.679	Linoleic (18:2)	40.963	Ervonic(24:1)	0.328
Palmitioleic (16:1)	0.143	Linolenic (18:3)	0.021	Lignoceric(24:0)	0.078
Margaric (17:0)	0.094				

Table 2. Estimated physicochemical values of Prunus avium biodiesel

Property	Diesel (EN 590) [20]	Biodiesel (EN 14214) [20]	POB
Oxidation Stability	25 g/m^3 max	8 hrs min	5.468
Cetane Number	51	51	50.1
Cold Filter Plugging Point	Location and season dependent	Location and season dependent	-5.091
Iodine Value		120^1 g lod/100g	109.878
Cloud Point	Location and season dependent	Location and season dependent	-0.099
Pour Point	-	-	-6.713
Kinematic Viscosity (mm^2/s)	2.0-4.5	3.5-5.0	3.543
Higher Heating Value (HHV)	-	-	37.650
Density (kg/m^3)	820-845	860-900	838
Saponification Value	-	-	191.354
Flash Point (C)	55	101	160.56

The main fatty acids in Prunus avium seed oil were Linoleic acid 40.963% by weight, Oleic acid 38.938 % by weight, Palmitic acid 9.679 % by weight and Stearic acid 5.001 % by weight. According to table 1 Linoleic acid and Oleic acid are the main fatty acid that affects the properties of the resulting biodiesel since these fatty acids have the maximum % by weight. The biodiesel analyzer V1.2 was used to predict the fuel properties of Prunus avium seed oil biodiesel.

Higher Heating Value measures the energy content of the fuel per unit mass [21]. The predicted result is 37.650 () which is in the limits of EN 14214.

The density of a fluid is defined as its mass per unit volume [22]. The predicted result shows that POB has a density of 838. That is below the limits of the standards. This result shows that the POB could only be used as blended forms.

Viscosity is a measure of the resistance of a fluid which is being deformed by either shear or tensile stress. The calculated viscosity of POB is 3.543 which is within the limits of biodiesel standards. Since the low values of viscosity are favorable for faster atomization of the fuel spray which reduces the ignition delay period [22].

Cloud point is the temperature in which cloudy appearance occurs in liquid lipid material [23]. Although it is not given in the biodiesel standard, a cloud point that is below zero makes the biodiesel preferable hence -0,099 is close to -1 C it is not preferable for use in cold climate region unless blended with diesel fuel.

Cold Filter Plugging Point is the highest temperature at which a fuel sample cannot pass through a standard filter in a specific time under certain experimental conditions [23]. The POB has a CFPP of -5.091.

Pour Point is the lowest temperature that the fuel can still be moved [24]

Oxidation stability is the unsaturation in the biodiesel ester molecule accounts for biodiesel instability. As the unsaturation in the Fatty Acid (FA) chain portion increases, the biodiesel becomes more unstable. Therefore, the position of and the number of allylic and bis-allylic methylene moieties adjacent to the double bond determines the rate of oxidation. Having oxidation stability of 5.468. During long-term storage, biodiesel can be easily affected by air oxidation due to its lower resistance capacity to oxidation.

The self-ignition of the air-fuel mixture is essential in a compression ignition engine. Therefore, the ignition delay time of the fuel is extremely important. The property that quantifies the ignition delay time is called cetane number [25]. The calculated cetane number of POB 50.1 which is so close to the Biodiesel standard. A high cetane number means and quick self-ignition. Contrarily, a low cetane number means a long ignition delay.

The iodine value indicates the stability to oxidation. High iodine value means that biodiesel can easily be oxidized when contact with air [26] POB has an iodine value of 109.878 that is below the maximum iodine value of the biodiesel standard.

The saponification value is inversely proportional to the mean molecular weight of the glycerides in an oil [18] POB has a saponification value of 191.354.

Flashpoint is the minimum temperature at which the fuel will flash upon the application of an ignition source. The flashpoint of POB is predicted as 160.56 which is higher than the minimum value in TS14214 which means POB is safe for storing and transporting.

5. Conclusion

Today, many countries are trying to reduce their dependence on foreign sources to meet their energy needs. At the same time, considering the negative effects of fossil fuels on the environment and human health, biofuels have become a necessity. Using the raw material of biodiesel from the so-called oil would be a more realistic quest. If biodiesel is to be put on the market as an alternative fuel, it is necessary to concentrate on the production of biodiesel from non-edible oils rather than oils that can be used as food. Because the increase in prices should be expected with the withdrawal of oils used as foodstuffs, which will prevent sustainable economic stability. At this point, using different feedstocks such as Prunus avium which were recorded as lost and disposed of as waste would be used. It will be possible to contribute a new feedstock for producing biodiesel from these wastes which do not have economical value currently.

In this study, Prunus avium seeds were evaluated and the fatty acid composition was determined numerically. The main fatty acid in Prunus avium seed oil were Linoleic acid, Oleic acid, Palmitic acid, and Stearic acid since the Linoleic acid and the Oleic acid are the main fatty acid that affects the properties of the resulting biodiesel, it was concluded that the Prunus avium seed is to be a promising candidate for biodiesel production. For future studies, it is suggested to produce the Prunus avium seed oil biodiesel experimentally and to evaluate engine performance characteristics.

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