Original Research Article

Evaluation of biodiesel produced from tea seed oil in terms of fatty acid components

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ARTICLE INFO

ABSTRACT

Factors such as increased energy demand, environmental pollution, energy security and ensuring energy sustainability have accelerated the search for alternative energy. The interest in renewable energy sources has increased with the decrease of oil, oil crises and the increase of environmental awareness. Biodiesel is an alternative energy source that is renewable with chemical methods from vegetable and animal oils. It does not cause CO₂ release and greenhouse effect compared to petro diesel. It is an environmentally friendly fuel. The tea seeds used in this study have been selected as an alternative from the idle tea seed for biodiesel production without harming the cooking oil stock in Turkey, which is an agricultural country where tea growing and tea consumption is increasing. Biodiesel production was investigated with the transesterification method, which is a method that reduces the production cost and viscosity of the oil obtained from tea seeds by using less chemicals to bring the idle tea seeds to the economy in Turkey and in the world.

Keywords: Biodiesel; Tea seed oil; Transesterification

1. Introduction

Most of the world's energy needs are met from fossil origin primary energy sources such as oil, coal, natural gas; and nuclear and hydraulic energy are also used [1].

Due to the economic requirements and environmental effects of fossil fuel consumption, many studies have been conducted to find the best alternative fuels in internal combustion engines [2].

As energy demand of human beings increases, the effort to create an alternative energy source increases as well. Using biodiesel as a renewable fuel for an alternative to petro diesel (diesel) is an important transition strategy in the search for a new energy source [3].

Because there is no need for any changes in engines, no significant decreases in engine performance and because the unit prices are within reasonable limits; vegetable and animal carbo-hydrate compounds defined as biomass in engines are preferred. These fuels, which can be used as fuel in diesel engines and derived from renewable biological raw materials, are called biodiesel [4].

Today, the fuels produced as an alternative to gasoline and diesel fuel are ethanol and biodiesel. Biodiesel production gained speed especially in the world and in Turkey after 2000's. Biodiesel contributes to the growth of the agricultural industry, reduces migration from rural areas and it can be produced from agricultural products and wastes. It includes features such as contributing to ecology positively by providing diversity in agricultural production and creating a sustainable agricultural structure, providing continuity to the farmer's production, expanding the oil crops agriculture, meeting the deficit of the domestic oil and increasing soil fertility by expanding the crop rotation [5].

With the “Communique on Biodiesel Mixtures to Diesel Oil Types” prepared by the Energy Market Regulatory Authority
Biodiesel, one of the commonly studied liquid biofuels, can be obtained from vegetable or animal oils with methanol or ethanol by esterification and transesterification reactions on acid or base catalysts [12].

The basic composition of any vegetable or animal fat is triglycerides, consisting of three fatty acids and one glycerol (glycerin). By the way, fatty acids are grouped as saturated and unsaturated according to double bond number. If the fatty acid is saturated, there is no double bond. Unsaturated fatty acids can be grouped according to double bond number. Triglycerides are composed of these saturated and unsaturated fatty acid mixtures. Due to the properties of the fatty acids that make up triglycerides, the fuel characteristics may also differ [13].

In this study, the biodiesel production of the oil obtained from the tea seed was investigated by means of the transesterification method to bring the idle tea seeds to the economy.

2. Material and Method

When the tea plant is left to grow in nature, it looks like a tree. Growth height varies by species. Tea plant is an evergreen plant. Year-round shoot formation continues where there is sufficient temperature and humidity. There is

Table 1. Biodiesel EN 14214 Standard [11]

| Properties                      | Units                  | Minimum | Maximum | Test Method |
|---------------------------------|------------------------|---------|---------|-------------|
| Estester Content                | % (m/m)                | 96.5    | -       | EN 14103    |
| Density, 15 °C                  | Kg/m³                  | 860     | 900     | EN ISO 12185|
| Kinematic Viscosity, 40 °C      | mm²/s                  | 3.50    | 5.00    | EN ISO 3104 |
| Flash Point                     | °C                     | 120     | -       | prEN ISO 369|
| Cetane Number                   |                        | 51      | -       | EN ISO 5165 |
| Copper Strip Corrosion          | -                      | 1       |         | EN ISO 2160 |
| Sulfur Content                  | mg/kg                  | -       | 10      | prEN ISO 20846|
| Water Content                   | mg/kg                  | -       | 500     | EN ISO 12937|
| Iodine Value                    | g tyot/100 g           | -       | 120     | EN 14111    |
| Methanol Content                | % (m/m)                | -       | 0.20    | EN 14110    |
| Monoglycerides Content          | % (m/m)                | -       | 0.80    | EN 14105    |
| Diglycerides Content            | % (m/m)                | -       | 0.20    | EN 14105    |
| Triglyceride Content            | % (m/m)                | -       | 0.20    | EN 14105    |
| Free Glycerol                   | % (m/m)                | -       | 0.02    | EN 14105    |
| Total Glycerol                  | % (m/m)                | -       | 0.25    | EN 14105    |
| Total Impurity                  | mg/kg                  | -       | 24      | EN 12662    |
| Oxidation Stability 110 °C     | Hour                   | 6.0     | -       | EN 14112    |
| Acid Value                      | mg KOH/g               | -       | 0.5     | EN 14104    |
| Carbon Residue                  | % (m/m)                | -       | 0.30    | EN ISO 10370|
no development in leaves and buds in places where there is not enough temperature and humidity and shoot formation pauses. During the shoot period, the rain must be abundant and the temperature must be sufficient, otherwise the plant will not be able to produce the expected shoot, the development will regress significantly and thus the amount of product will be significantly reduced [14].

Tea seed oil is obtained from tea seeds. In recent studies, tea seed oils have been an alternative to other oils due to the suitability of the acidity content. Tea seed oil lowers blood pressure and, accordingly, cholesterol [16]. Tea seed contains to make use of many ingredients. It contains 29–34% (v / v) fat content, 17-20% (v / v) starch, 11-15% (v / v) saponin, 10-16% (v / v) protein and 10-14% (v / v) fiber. Saponins are surfactant sterol or triterpene glycosides and are found in a wide variety of plants. Saponins prepared from various sources such as tea leaves have antimicrobial activity. More than 10% (v / v) of dry weight of tea seeds contains a large amount of saponins. Tea seed oil also contains rich foods such as antioxidants (vitamin E and polyphenol) [18]. Also, the obtained saponin is a very valuable raw material. It is a good cleaner because it foams a lot. Saponin is used as emulsifier in the production of pesticides, in the production of foams and detergents in fire trucks. Saponin is also used in making photographic film [16]. The ability of tea plant to seed increases with age. When rejuvenation pruning is not done and when there is no collection for the leaf, the amount of seeds becomes too much due to the flowering and fertilization [17].

In this study, the tea seeds obtained from Bilenköy, Hemşin district in Rize were annealed after the rolling process at 80 °C and the raw oil was obtained with the help of a press, and after this oil was filtered, it was transformed into Tea Oil Methyl Ester by transesterification method.

3. Research Findings and Discussion

Biodiesel production from tea seed oil was carried out by the transesterification method. For testing purposes, half a liter of tea seed oil was heated by stirring on a magnetic stirrer heater until it reached 55°C. In another beaker, 20% (v / v) methyl alcohol (100 ml) and 1.75 g NaOH were mixed for 0.5 liter of oil to form methoxide. Methoxide was slowly added to the oil reaching 55 ºC and it was mixed on the heater at approximately 700 rpm for 1 hour. In the last 10 minutes of the process, the temperature was raised to 70 °C to remove alcohol. The mixture was taken to rest and after waiting for 8 hours, the glycerin which collapsed to the bottom was removed and the washing process was started (Figure 3). For the washing process, 20% (v / v) pure water was sprayed on the raw biodiesel whose glycerin was taken and the process was carried out by showering. Afterwards, the washed biodiesel was rested for 8 hours and the washing water settled to the bottom.

The biodiesel left on top due to the difference in density was transferred to another beaker again and finally the washed biodiesel was mixed on magnetic stirrer heater for 10 to 15 minutes at 110 ° C to remove the water remaining in the
biodiesel and the water was evaporated. Thus, biodiesel was produced from tea seed oil.

Fig. 3. Glycerin and biodiesel formation

Fig. 4. Washing water settling down

Fig. 5. Separation of water remaining in biodiesel

Saturated fatty acids are long chain fatty acids that do not contain double bonds between carbon atoms [19]. Fats that are rich in fatty acids are called saturated fats [20]. The most common saturated fatty acids found in animal and vegetable oils are butyric acid, caproic acid, caprylic acid, lauric acid, myristic acid, palmitic acid, stearic acid, arachidic acid, behenic acid, lignoceric acid, serotic acid, montanic acid [19]. Properties of biodiesel produced from tea seed oil and fatty acid composition were given in Table 2. Saturated fatty acids are synthesized in the human body; even if no fat is consumed, these types of fatty acids can be synthesized from molecules formed by carbohydrate metabolism [20]. Fatty acids containing one or more double bonds in the molecule are called unsaturated fatty acids. Oleic acid, the most common unsaturated fatty acid in nature, contains a single double bond. Unsaturated fatty acids can easily be oxidized. Especially, the increase in the number of double bonds facilitates oxidation [19].

The two most important members of monounsaturated fatty acids are palmitoleic acid (C16:1) and oleic acid (C18:1). Oleic acid has been included in the structure of all known natural oils up until now. Linoleic (C18:2), linolenic (C18:3), arachidonic (C20:4), eicosapentaenoic (C22:5) and docosahexaenoic (C22:6) acids are the most important of polyunsaturated fatty acids [20]. Polyunsaturated fatty acids are important essential fatty acids in nutrition. These are desired to be present at certain levels in oils and various oil products [21]. The main unsaturated fatty acid is oleic acid, followed by linoleic acid [18].

Re-esterification is easier in oils with high linoleic acid content. Phosphorus removal is carried out to obtain quality biodiesel during the processing of raw oils for both food and biodiesel. The phosphorus ratio of the oil which is processed to produce biodiesel should not be more than 10 ppm. Since caustic is used during neutralization and degum (phosphorus removal) processes, a loss of approximately 2-3% (v/v) occurs in vegetable oil. These loss values of raw oil vary according to acidity and phosphorus values [22]. When the fatty acid composition of tea seed oil is examined, it is seen that it contains the highest amount of oleic acid. Oleic - linoleic acid group oils are the oils that can be adapted to all solid and liquid oils by technological processes and they have a wide range of uses. These oils are oils that can be consumed as first-class edible oils. Since tea seed oil does not contain higher levels of unsaturated fatty acids than linoleic acid, it is also resistant to serious taste and aroma deterioration. Palmitic acid, compared to the other saturated fatty acids, is the one that tea seed oil contains most. This fatty acid is followed by stearic acid, arachidic acid and myristic acid, respectively [23].
Vegetable oils have a different chemical structure than petroleum-based fuels. Although diesel fuel consists of large amounts of paraffins and aromatics, vegetable oils are the esters made by fatty acids with glycerin. These esters are called glycerides. The 3 alcohol groups that make up the glycerin molecule are called triglycerides. The type and amount of fatty acids in triglycerides constitute the properties of vegetable oil [24]. The composition of biodiesel produced from tea seed oil was given in Table 3.

Table 3. Composition of biodiesel produced from tea seed oil [17]

| Properties                        | Units       | TS EN 14214 Standard Values |
|-----------------------------------|-------------|-----------------------------|
| Methyl Ester, %                   |             | ≥ 96.5                      |
| Monoglycerides, %                 |             | ≤ 0.8                       |
| Diglycerides, %                   |             | ≤ 0.2                       |
| Triglycerides, %                  |             | ≤ 0.2                       |
| Free Glycerol, %                  |             | ≤ 0.02                      |
| Total Glycerol, %                 |             | ≤ 0.25                      |
| Oxidation Stability, h            |             | ≥ 6.0                       |
| Iodine Number                     |             | ≤ 120                       |

Tea seed oil can be used in biodiesel production alone or in mixtures with other high-iodine oils both in terms of iodine number and oxidation stability [17]. Tea seed oil properties were given in Table 4.

Table 4. Tea seed oil properties [25]

| Properties                        | Units       | Tea Seed Oil |
|-----------------------------------|-------------|--------------|
| Free Fatty Acid                   | %           | 2.7          |
| Kinematic Viscosity (40 °C)       | mm²/s       | 127.0        |
| Density at (15 °C)                | kg/m³       | 907          |
| Cetane Number                     |             | 43.8         |
| Higher Heating Value              | kl/kg       | 37141        |

The high cetane number ensures that the fuels are ignited in a shorter time and the knocking tendency is low. As the amount of unsaturated fatty acids in the oil increases, cetane number and oxidation stability decrease, iodine number increases and cold flow properties improve [11]. The fact that animal oils used in biodiesel production consists of saturated fatty acids such as C14: 0, C16: 0 and C18: 0 ensures high cetane number and less susceptibility to oxidation than unsaturated fats. However, it is an important disadvantage that this feature tends to crystallize at high temperatures [26].
Kinematic viscosity is the resistance of a fluid to flow under the influence of gravity. High viscosity is an indication that the transesterification process has not been successfully completed [27].

The length of the hydrocarbon chain in the oil affects the viscosity. As the length of the hydrocarbon chain increases, the viscosity increases; and as the number of double bonds increase, that is, the unsaturation increases, the viscosity decreases. As the viscosity decreases, the flow resistance in the pipes decreases and the fuel droplet diameters decrease, combustion improves. Diesel fuel thickens in cold weather, so its viscosity increases. This causes problems in injectors [11].

Tea seed oils have lower pour point and viscosity than other vegetable oils. Diesel fuel's pour point indicates the lowest temperature at which oil flows. This is an important feature because it defines the lowest temperature at which fuel can be moved before it solidifies [18]. Biodiesel has 5-8% (v/v) lower energy than diesel. As the chain length of saturated hydrocarbons increases, the heating value also increases. As the saturation increases (the number of hydrogen decreases) the heating value decreases [28].

In addition, oils containing high unsaturated fatty acids, especially oils with high oleic acid content, have low viscosity and low melting point, so it is a good raw material for the production of high quality biodiesel with microbial oils in cold climatic conditions [29]. Oxidation resistance is better in vegetable oils with high oleic acid [30]. If the oil to be used as a raw material in biodiesel production contains a large amount of free fatty acids such as oleic acid, the alkali catalyst reacts with free fatty acids to form soap, which is undesirable. Because this will deactivate the catalyst that accelerates the transesterification reaction [26].

4. Conclusions

It was observed that it is possible to bring the oil obtained from the tea seed into the economy by producing biodiesel with suitable methods to bring the idle tea seeds to the economy in Turkey and in the world. The high oleic acid content of tea seed oil indicates that it has low viscosity and low melting point. Based on these results, it can be said that tea seed oil is a suitable raw material for biodiesel production. As the viscosity decreases, the flow resistance in the pipes decreases and the fuel droplet diameters decrease. The low viscosity of tea seed oil will improve combustion.

The fact that tea seed oil consists of saturated fatty acids such as myristic acid, palmitic acid and stearic acid at normal temperatures shows that it has a high cetane number and will make it less susceptible to oxidation than unsaturated fats. The high cetane number of tea seed oil will have high ignition ability and low knocking tendency.

Acknowledgment

This work was financially supported by the Scientific Research Council (BAP) of Necmettin Erbakan University. Sema ÇALIŞKAN is a master student at the Department of Energy Systems Engineering, the Graduate School of Natural and Applied Science of Necmettin Erbakan University (Advisor: Dr. Fatih AYDIN).

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