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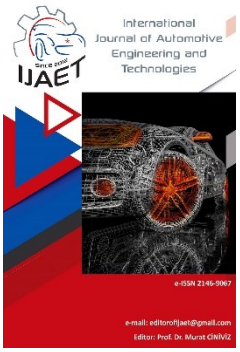

Original Research Article

Investigation of fuel properties of biodiesel produced from hemp seed oil

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ABSTRACT

Scientists continue to work in order to obtain clean and efficient energy in a sustainable and economical way. Biodiesel is an important research topic not only because it is a renewable energy source, but also because it is an environmentally friendly fuel that can be produced as efficiently as petroleum-derived fuels. The raw materials used are as important as the production parameters in the production of biodiesel fuels. Hemp is not a widely cultivated plant because its cultivation is subject to government control. However, by breeding, the production of species containing low amount of stimulant and high amount of seed and fiber can be realized. In case of an efficient fuel production in compliance with the determined standards, the hemp plant can be accepted as a raw material that can also be evaluated in the field of energy. In order to guide the studies to be carried out for this purpose, in this study, the conformity of the fuel obtained by producing biodiesel from hemp seed oil to the standards was examined. As a result of the fuel analysis, it has been seen that the fuel properties of the produced hemp biodiesel are largely compatible with the TS EN 14214 standards. The results obtained provided a sufficient starting point for the development of the study.

Keywords: Biodiesel, hemp, fuel properties, renewable energy, fatty acid.

1. Introduction

Due to population growth, industrialization and economic developments, the use of transportation, public transportation and personal vehicles is also increasing. Most of the internal combustion engines used in the transportation industry are compression ignition engines using petrodiesel. Accordingly, oil-based energy demand is increasing day by day in developed and developing countries [1, 2]. However, one of the most important disadvantages of using petroleum-based fuels is that it causes serious greenhouse gas emissions and the other is that it is not renewable and sustainable [3, 4].

The dependency on foreign resources in crude oil and the serious increases in oil prices constitute the basis of the energy crisis that the world has been in recently. In addition, when global climate change is taken into account, environmentally friendly, sustainable, domestic and economic energy resources play a great role in the development of the country. When Türkiye's energy situation is analyzed, it is seen

that Türkiye is dependent on foreign financial resources 70% and petrodiesel 90% in total energy. This negative situation creates the need accelerate the promotion of local resources and to diversify energy resources [5]. With the norms determined for fuel emissions and clean energy studies, biodiesel has developed and continues to develop as an alternative to diesel fuel over the years [4-7].

The most important feature that distinguishes biodiesel from other alternative fuels is that it contains oxygen in the range of 10-15% by mass in its structure. In this way, combustion efficiency increases and emissions of carbon monoxide, hydrocarbon, particulate matter and other pollutants are reduced [8-10]. In addition, it is a renewable, biodegradable energy source with low sulfur content and high cetane number [11]. The advantages as well as the disadvantages should be mentioned. The most important disadvantage of biodiesel production is its high cost [1].

In biodiesel production, the chemical structure of the raw material used is as important as the production method and parameters. Fatty acids are formed as a result of the hydrolysis of substances generally in the ester structure in oils, by chemical and/or enzymatic means. The best example of these are triglycerides. The degree of saturation of fatty acids differs according to the number of bonds between the carbon atoms forming the chain and whether these bonds are single or double bonds. When comparing saturated and unsaturated fatty acids with the same chain length, it is seen that there are serious differences in their physical and chemical properties [12].

The type and concentration of the fatty acid contained in the raw material affect many properties of biodiesel. Many of them are characteristics that directly affect the use of the fuel. For this reason, examining the effects of fatty acid composition on these properties is important in increasing the quality of biodiesel. Various studies have been carried out to investigate the relationship between the physicochemical properties of a biodiesel and its molecular structure. The type of fatty acid and the carbon chain length have an effect on the physical and chemical properties of many oils [13,14].

In this study, biodiesel was produced from hemp seed oil, which is promising in terms of being a new source in biodiesel production for Türkiye. The aim of the study is to determine whether hemp seed oil is a suitable raw material for biodiesel production. For this purpose, the fuel properties of the biodiesel fuel produced will be analyzed with the relevant devices, and its compliance with the standards will be examined and the fatty acid composition of the raw material will be determined.

2. Material and Method

2.1. Material selection

Although the production of biodiesel from edible oils is successful, it is not sustainable in the long term. The rapid increase in the world population and food prices necessitates the production of biodiesel from non-edible oils [15,16]. Since the use of domestic raw materials will contribute to the national economy, countries are looking for ways to produce efficient biodiesel from the oil of inedible plants that they can grow in their own climate conditions. The fact that we live in a country suitable for agriculture plays an important role in the supply of clean energy [16]. In recent years, energy agriculture has gained speed with the planting of plants that can be grown even in harsh climatic conditions and infertile soils and provide the highest yield per unit area [17,18]. Despite the high yield these plants provide, the production costs are quite low. Making the necessary infrastructure works for biodiesel production from these raw material sources and switching to large-scale production will enable our country to produce more economical, clean and sustainable energy with its own means [17]. Industrial hemp is a promising renewable and sustainable source for biodiesel production [2, 19]. It is one of hundreds of plants grown and yielding crops for industrial purposes in the world. The cultivation of hemp plant is largely banned in many countries, which hinders research into the hemp plant. It can be cultivated in Türkiye subject to permission [1].

Hemp seeds and oil are as in Fig. 1 Hemp seed oil has been purchased commercially.

Hemp seeds contain 20-25% protein, 20-30% carbohydrates, 10-15% fiber, minerals and 25-35% oil [1,15]. When the oil content of hemp seed is compared to cotton (15-24%), soybean (17-21%) and olive (20-25%) grown in the

United States, Brazil, China and other Asian and European countries, it appears to be an alternative raw material [15]. It can be grown in various climatic conditions water consumption is very low. It is a very economical plant to grow since there is no need for pesticides and fertilization processes [1, 20]. When considered in terms of economic efficiency, the cultivation of hemp plants and the production of biodiesel from its oil are a good alternative in the field of energy.

a) b)

Fig. 1. a) Hemp seed b) Hemp oil.

2.2. Biodiesel production

It is known that the most suitable method to obtain biodiesel fuel from vegetable oils is the transesterification process. Biodiesel is obtained as a result of the reaction of alcohol with triglycerides of fatty acids in the presence of a suitable catalyst [1,18,21].

Glycerin, which is bound to fatty acids, causes vegetable oil to be thicker and sticky. Since the low viscosity of the fuel is an important criterion for engine performance and life, the glycerine is removed from the vegetable oil by the transesterification reaction and the oil is converted into a fuel with lower viscosity and fine structure.

The basis of biodiesel production is the separation of ester and glycerine in the oil [17]. The reaction mechanism is as in Fig. 2 and Fig. 3.

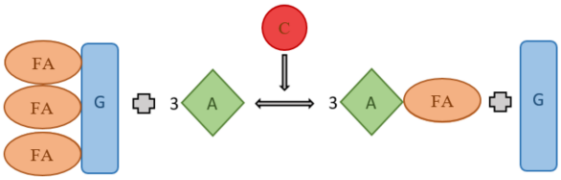
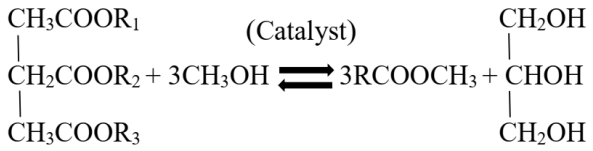


Fig. 2. Schematic illustration of transesterification reaction. (FA: Fatty Acid, G: Glycerin, A: Alcohol, C: Catalyst [22].

In this study, cold pressed hemp oil was used for biodiesel production. Experiments were carried out in the fuel analysis laboratory of Selçuk University, Faculty of Agriculture, Department of Agricultural Machinery and Technologies Engineering. Experimental parameters were kept constant since it was investigated whether the biodiesel obtained from hemp oil had physicochemical properties in accordance with the standards. Biodiesel production was carried out by transesterification method.



(Trigliserid) (Methanol) (Methyl Ester) (Glycerol)

Fig. 3: Transesterification reaction.

Alcohol (methanol)/oil molar ratio was 6:1 and sodium hydroxide (NaOH) was used as catalyst. The reaction took place in the range of 50-55 °C in 1 hour. At the end of the reaction, the washing process was carried out by pulverization method using distilled water. In the absence of a catalyst, the transesterification reaction between triglyceride and alcohol (methanol or ethanol) is very slow and sometimes the reaction does not occur. For this reason, the reaction is accelerated with the help of an acidic or basic catalyst. The bases used are usually NaOH and potassium hydroxide (KOH) [23,25]. NaOH must be pure. KOH has a less toxic effect [17]. The reason why most basic catalysts are preferred today is that they give good results under relatively low temperature and pressure. According to efficiency principles, the economic dimension of production is also very important [22].

The biodiesel obtained from hemp oil after the transesterification reaction is shown in Fig. 4.

Fig. 4: Hemp biodiesel.

2.3. Fuel analysis

Produced biodiesel fuels were analyzed with related devices. Devices in which fuel properties are analyzed have a sensitivity of ±1%. The

devices used in the measurement are given in the Table 1.

Table 1: Fuel Analysis Equipments.

Device	Trademark/Model
Density measuring device	Kem Kyoto DA-130N
Kinematic viscosity measuring device	Koehler K 23377
Cetane number analyzer	Shatox SX
Calorimeter	IKA C 200
Cloud and pour point measuring device	Polyscience
Cold filter plugging point measuring device	Tanaka AFP-102
Flash point determination device	Koehler K16270
Copper strip corrosion tester	Koehler K 25330
Water content measuring device	Kem Kyoto MKC-501
Colorimeter	Lovibond PFX 195

2.3.1. Density

Density is the key property for biodiesel. The amount of fuel injected into the engine is determined from its volume, so the density of the fuel directly affects the fuel injection process as it changes the air/combustion ratio. This is because the fuel injection pump measures on the basis of the volume of the fuel, not the mass. Therefore, the fuel with high density will be more in mass than the fuel with less density in the same volume [26,27]. In addition, the density of the fuel is important because it is related to viscosity, calorific value and cetane number [28,29]. The density of the fuel is also closely related to the amount of particulate matter emitted from the exhaust and NO_x emissions. With the increase in density, such emissions will also increase [30,31]. ASTM D6751 standards did not impose any limitation on density, but according to EN 14214 standards, the density of biodiesel should be in the range of 860-900 kg/m^3 [29,32]. The density of petroleum diesel is about 0.85 g/cm^3, which is lower than biodiesel with a density of 0.88 g/cm^3. According to the standards, the density of vegetable oil varies between 0.88-0.93 g/cm^3 at 15 °C, while it decreases to 0.86-0.89 g/cm^3 after the reaction [17,29].

2.3.2. Kinematic viscosity

Kinematic viscosity, like density, is a characteristic property of biodiesel. The main problem with biodiesel is that its viscosity is higher than petroleum diesel. Compared to petroleum diesel, vegetable oils are 9-17 times more viscous and biodiesel is 1.6 times more viscous [29]. With the decrease in temperature, an exponential increase in viscosity is observed, which adversely affects the flow properties [33]. Except for the viscosity increase caused by cold air, since a high viscosity fuel will mix slowly with the air, complete combustion does not occur, and the exhaust smoke and emission value increase. On the other hand, a low-viscosity fuel cannot provide sufficient lubrication for the fuel injection pumps to be fully seated, so wear and leaks increase [34]. For this reason, optimum viscosity values were determined at certain intervals. According to ASTM D6751 standards, the viscosity value for biodiesel should be in the range of 1.9-6.0 mm^2/s. The EN 14214 standard has determined this range as 3.5-5.0 mm^2/s [29,32].

2.3.3. Cetane number

Cetane number is a dimensionless parameter related to the ignition delay time of the fuel injected into the combustion chamber in diesel engines [35,36]. It is an indicator of the self-ignitability of the fuel. The ignition characteristics of the fuel are important in terms of engine performance, noise level and exhaust emissions [29,33]. The most efficient and high quality combustion of the fuel depends on the high cetane number and low ignition delay time [29]. The high cetane number of the fuel used in diesel engines is extremely important as it provides some improvements in combustion in the cylinder. For this reason, the addition of cetane improver to diesel fuel has been highly preferred in recent years [37]. For this purpose, biodiesel is added to diesel fuel to improve the combustion performance of the fuel. According to EN 14212 standards, the cetane number should be at least 51. ASTM standards say that this value should be in the range of 48-67 [29,35]. The cetane number above 70 increases the soot and carbon deposits in the engine, while at values below 70 it shortens the ignition delay and improves combustion [38].

2.3.4. Calorific value

It is the amount of heat released during the combustion of one unit (one gram) of fuel to produce H_2O and CO_2 at the initial temperature. This feature characterizes the energy content of

the fuel and thus its efficiency [29]. There is no limitation in ASTM D6751 and EN 14214 standards regarding the combustion heat or the calorific value of the fuel. However, European standards have determined the lower calorific value for the biodiesel used for heating as 35 MJ/kg [17,33]. The heating value is important in determining the fuel consumption. The higher the heat obtained as a result of combustion, the lower the fuel consumption will be.

2.3.5. Cold flow properties

Cold filter plugging point and low temperature flow test can be used to determine the low temperature properties of biodiesel [36,39]. Cold filter plugging point varies in proportion to the degree of saturation calculated based on the melting point of fatty acids [35]. Biodiesel standards contain conditions related to low temperature properties. The cloud point is take part in ASTM D6751, but no limit has been set. The reason for this is the sharp changes in weather conditions in the USA. The cold filter plugging point is take part in EN 14214 standards. Each country can choose one of these two standards according to its own climatic conditions and seasonal conditions [28].

2.3.6. Flash point

The flash point is the minimum temperature at which a volatile fuel ignites when it comes into contact with fire under a pressure of 101.325 kPa (1 atm). Flash point is a key parameter for safety during storage, transportation, distribution of fuel and in NFPA (National Fire Protection Association) classifications [29]. The flash point is related to the volatility value, which is an important fuel property for the engine to start and warm up. According to ASTM D6751 standards, the flash point should be above 130 °C, but according to EN 14214 European standards, this value is a minimum of 120 °C [21,29,40]. Most vegetable oils have a very high flash point and decrease to the range of 120-220 °C at the end of the transesterification reaction. Since these values are higher than petroleum diesel, biodiesel is safer than petroleum diesel during storage and transportation [17,29].

2.4. Fatty acid analysis

The chemical content of the oil used in biodiesel production affects fuel production and the performance of the produced fuel. Type and ratio of fatty acids in the content of the oil used in biodiesel production, affects the conversion efficiency and the physiochemical properties of the produced fuel [14]. Therefore, gas chromatography-flame ionization detection (GC-FID) analyzes were carried out to examine the effect of unsaturation. GC-FID analysis method was applied for the fatty acid composition analysis of hemp oil. Appropriate parameters for the analysis were determined and measurements were made using the Agilent HP-88 capillary GC column in the device [41,42].

3. Results and Discussion

Fuel properties of biodiesel produced from hemp oil are given in Table 2.

Table 2: Fuel properties of hemp biodiesel.

Fuel Properties	The Units	Hemp Biodiesel	En14214 Limits	Test Procedure
Density, (at 15 °C)	g/cm^3	0.887	0.86-0.90	DIN EN ISO 3675 DIN EN ISO 12185
Kinematic Viscosity, (at 40 °C)	mm^2/s	6.09	3.5-5.0	DIN EN ISO 3104 ISO 3105
Cetane Number	-	59	≥ 51	EN ISO 5165
Calorific Value	cal/g	9230	-	DIN 51900-3
Cloud Point	°C	-7.5	≤ -4/3	EN116
Pour Point	°C	-8,.8	-	EN 116 ISO 3016
Freezing Point	°C	-11.1	-	-
Cold Filter Plugging Point	°C	-8.0	-	EN 14107
Flash Point	°C	110	≥ 120	DIN EN ISO 3679
Water content	ppm	481.91	≤ 500	EN ISO 12937
Copper Strip Corrosion (3 hours at 50 °C)	1a	1a	≤ 1	EN ISO 2160

When the fuel properties are examined in Table 2; Density value of the obtained biodiesel is 0.887 g/cm^3, kinematic viscosity is 6.09 mm^2/s, cetane number is 59, calorific value is 9230 cal/g, cloud Point, -7.5 °C, pour point, -8.8 °C, freezing point, -11.1 °C, cold filter plugging

point, -8,0 ºC, flash point, 110 °C, water content 481.91 ppm and copper strip corrosion (3 hours at 50 °C), 1a.

The fuel properties of the produced hemp biodiesel were within the limit values specified in TS EN 14214, excluding the kinematic viscosity and flash point. Limit values specified in TS EN 14214 are respectively density (860-900 kg/m^3), copper strip corrosion Class 1, flash point min. 120 °C, cold filter plugging point, temperate climates Type a Max. +5 Type E max. -15, max. Water content 500 mg/kg, max. is in the form. Although the viscosity value is in the range of 3.5-5 mm^2/s in the TS EN 14214 standards, the viscosity value was measured as 6.09 mm^2/s, slightly above the standard in biodiesel.

Table 3 summarizes the results of gas chromatography analysis of hemp seed oil.

Table 3: GC–FID fatty acid profile analysis results of the sample (%) [g fatty acid/100 g total fatty acid].

Fatty Acids	Hemp Seed Oil
∑SFA	11.66
∑MUFA	17.35
∑PUFA	70.55
trans FAs	0.44

When the fatty acid analysis results of hemp seed oil given in Table 3 are examined, it is seen that the sum of monounsaturated (MUFA) and polyunsaturated fatty acids (PUFA) is considerably higher than saturated fatty acids (SFA). The fact that it consists of 87.9% unsaturated fatty acids shows that hemp seed oil is in the unsaturated oil group. It is known that an increase in the level of unsaturation increases the ester conversion efficiency [17]. When the GC-FID and fuel analysis results were evaluated, it was concluded that hemp seed oil could be used as a raw material in biodiesel production.

4. Conclusion

In this study, biodiesel production was carried out in order to evaluate hemp in the field of energy. The production was carried out with the traditional method and the results showed that hemp is a quite efficient raw material in obtaining energy. It can be considered as a preliminary study on obtaining efficient energy with a raw material that can be grown within the borders of our country and will reduce the production cost. Based on this study, it is planned to carry out new studies in which the test parameters are optimized in order to increase the fuel performance of biodiesel to be obtained from hemp oil. In addition, the fuel performance of hemp seeds grown under different conditions or of different types is also worth examining.

CRediT authorship contribution statement

Hidayet Oğuz: Investigation, Supervision, Resources, Conceptualization, Writing - review & editing.

Merve Çelik Tolu: Writing - original draft, Investigation, Visualization, Supervision, Resources, Formal analysis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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