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The Investigation of Biodiesel Production Techniques

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Abstract
Today, increasing energy demand and consequent environmental pollution have made the search for alternative fuels compulsory. Biodiesel, which is one of the alternative fuels, can be produced from waste oils, vegetable oils and animal fats, and it is preferred since it is a clean fuel. In the production of biodiesel, the plants such as canola, sunflower, safflower, soy, cotton seed, poppy seed, flax seed and ground nuts; the fruits with high oil ratio such as nuts, olives, almonds, walnuts; animal oil and some algaes are made use of. Taken into account the advantages and disadvantages, it seems biodiesel will be an indispensable fuel for the future with some legal regulations.
In this study, the methods of biodiesel production are discussed. The method used in the production of biodiesel has five types: Dilution Method, Micro-Emulsion Method, Pyrolysis Method, Transesterification Method and Super Critical Method.
Generally, the most commonly used method is transesterification method since its production cost is low, it decreases the viscosity of vegetable oils best, and the biodiesel obtained through this method has closest features to diesel fuel.

Keywords: *Biodiesel, Biodiesel production methods, Methyl ester, Transesterification.*

1. INTRODUCTION

Energy resources are examined in two main categories as “Primary Energy Sources” and “Secondary Energy Sources”. Energy sources that are potentially available and that have just been utilized in parallel with technological developments are called “new”; and the sources that are everlasting or continually replenished in nature are called renewable energy sources (Öğüt and Oğuz, 2006).

Searches for alternative fuels are supported significantly around the world. In many developed countries, especially in European Union countries, serious works are carried out on this subject and positive results and ideas are put into practice. Alternative fuels that can be used in diesel engines need to have economic, renewable, nature friendly and easily obtainable advantages. Biodiesel is regarded as an alternative fuel type with characteristics that can meet these requirements for diesel engines (Uyar, 2013).

Biodiesel can be defined as ‘a kind of nature friendly and renewable liquid fuel which is converted into biofuels by mixing vegetable or animal oils with base or alcohol and petrodiesel in a certain extent by means of chemical methods’. Biodiesel does not contain any products of petroleum origin. However, biodiesel can be used as a fuel crudely or with mixtures which can be prepared with any amount of diesel fuel. Pure biodiesel and biodiesel mixtures can be used in diesel engines, with little or no change in the engine (Anonymous, 2005).

Biodiesel can be produced from the plants with oil content such as canola, sunflower, safflower, soybean, cottonseed, poppy seed, flax seed and ground nuts; and from high-fat fruits such as nuts, olives, almonds, walnuts and also from animal oil and some algaes.

Some of the criteria for the selection of the seed to be used in biodiesel production are; the amount of oil in the content, the chemical properties of the selected seed oil, oil acid, the physical properties of the selected seed oil, its agricultural suitability, climate and soil selectivity, irrigation desire, tendency for agricultural mechanization, storage conditions, portability, spoilage time, the protein amount of residue of the product after extraction of oil, the amount of production and the market share, whether the plant is single-year or double-year, the yield, usability in other sectors including food, agricultural costs and so on (Koç, 2011).

The characteristics of some oil plants are shown in Table1.1.

Table 1.1. Chemical properties of some vegetable oils (Gök, 2008)

Variety of vegetable oil	Viscosity (mm²/s)	Cetane Number	Calorific Value (kj/kg)	Flash Point (°C)	Density (kg/lt)	Carbon residue (%)	Sulfur (%)
Indian Oil	297	-	37274	260	0,9537	0,22	0,01
Corn Oil	34,9	37,6	39500	277	0,9095	0,24	0,01
Cotton Oil	33,5	41,8	39468	234	0,9148	0,24	0,01
Linseed Oil	27,2	34,6	39307	241	0,9236	0,22	0,01
Peanut Oil	39,2	41,8	39,782	271	0,9026	0,24	0,01
Colza Oil	37	37,6	39709	246	0,9115	0,3	0,001
Safflower Oil	31,3	41,3	39519	260	0,9144	0,25	0,01
Sesame Oil	35,5	40,2	39349	260	0,9133	0,25	0,01
Soybean Oil	32,6	37,9	39623	254	0,9138	0,27	0,01
Sunflower Oil	33,9	37,1	39,575	274	0,9161	0,23	0,01
No 2 Diesel	2,7	47	45343	52	0,84	0,35	0,01

Biodiesel-diesel mixture ratios are named in the forms shown in table 1.2.

Table 1.2. The table of Biodiesel mixture

Biodiesel Name	Biodiesel Ratio	Diesel Rate
B_5	%5 Biodiesel	%95 Diesel
B_{20}	%20 Biodiesel	%80 Diesel
B_{50}	%50 Biodiesel	%50 Diesel
B_{100}	%100 Biodiesel	% 0 Diesel

Biodiesel has been accepted all over the world and standardized as in every product. The standards of biodiesel are given in Table 1.3.

Table 1.3. Biodiesel standards

Biodiesel	Units	Austrian Standard (C1190 Feb.9.11)	DIN 51606 September 1997	U.S. Quality Specification Nbb/ Astm	European Standard En 14214
Density (15 ^{0}C)	g/cm^3	0.86-0.90	0.875-0.90	/	0.86-0.90
Kinematic Viscosity (40^{0}C)	mm^2/s	6.5-9.0(20^{0}C)	3.5-5.0	1.9-6.0	3.5-5.0
Flash Point	^{0}C (F)	min. 55(131)	min. 110(230)	min. 100(212)	min 120(248)
Total Sulfur	mg/kg	max. 200	max. 100	max. 500	max. 10.0
Cetane Number	-	min. 48	min. 49	min. 40	min 51
Total Suspended Matter	mg/kg	/	max. 20	/	max. 24
Neutralization Value	mg	max. 1	max. 0.5	max. 0.8	max. 0.5
Methanol Content	%	max. 0.3	max. 0.3	max. 0.2	max. 0.2
Esther Content	%	/	/	/	min. 96.5
Monoglycerides	%	/	max. 0.8	/	max. 0.8
Diglycerides	%	/	max. 0.4	/	max. 0.2
Free glycerol	%	max. 0.03	max. 0.02	max. 0.02	max. 0.02
Total glycerol	%	max. 0.25	max. 0.25	max. 0.24	max. 0.25
Iodine number	/	/	max. 115	/	max. 120

Microalgae is also a source of raw material for biodiesel. In order for Migroalgler to be a source of raw material in biodiesel production, the lipid yields must be between 30-50% (Demirbaş, 2011).

When biodiesel is blended with diesel fuel in a proper composition, it can be used as an additive to reduce vehicle emissions, or it can be used crudely as renewable alternative fuel for diesel engines without engine modifications (Mehmood et al. 2017).

2. MATERIALS AND METHODS

Technical characteristics such as density, flash point, thermal value, kinematic viscosity, cold flow property, cetane number, carbon residue, iodine number and sulfur content determine biodiesel quality.

2.1. Density

Density is a parameter that affects fuel consumption and combustion temperature and it increases as the number of bond increases. The density of sunflower and soy is higher since they are more unsaturated than other vegetable oils.

2.2. Flash point

The flash point in fuels is a feature that affects safety. It is required that the flash point be high so that it can be safe in storage and transportation. The flash point of biodiesel was standardized as min.55 °C, max.248 °C. However, the flash point of vegetable oil is higher than 300 °C, whereas the diesel fuel has a flash point of around 74 °C.

2.3. Calorific Value

The calorific value refers to the energy given per kg. Calorific value of biodiesel is lower than diesel fuels depending on the amount of oxygen in it. The calorific value of diesel fuels ranges from 42 to 45 Mj / kg while the calorific value of biodiesel ranges from 32 to 35.

2.4. Viscosity

Viscosity is also the distinguishing feature of every fuel, such as density. The high viscosity makes fuel a poorly blended fuel and it makes it difficult to pump the fuel. It also creates negative effects such as carbon deposit in the segments and injector clogging and, as a result, poor engine performance. Purity and the ratio of oxidation products determine viscosity in biodiesel**.**

2.5. Cold Flow Property

The situation of the fuel in cold weather conditions affects its flow. Since biodiesel has higher flowability, it can cause difficulties in using the fuel in cold weather conditions and may cause fitler clogging. The viscosity values of biodiesel vary from 3,5 mm^2/s to 5 mm^2/s (Demirbaş and Karslıoğlu, 2007).

2.6. Cetane Number

It is a parameter that directly affects ignition property. High cetane number ensures ignition in the fuels in a shorter time. The cetane number of biodiesel varies depending on the selected raw material.

2.7. Carbon Residue

Carbon deposits in combustion chambers and injectors is a factor affecting the engine performance. Experiments have shown that biodiesel has the ability to recycle the carbon that it releases.

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2.8. Iodine Number

It is a property that indicates the unsaturation of oils. Fuels with a high iodine number causes the injectors to be clogged and causes deformation in the combustion chambers, so this affects the engine performance badly.

2.9. Sulphur Content

Sulfur content is a property that affects lubricating properties in fuels. The use of vegetable oils in biodiesel causes the lubrication of biodiesel to be high compared to diesel fuel. It is foreseen that the sulfur content will be reduced to the levels lower than 10 ppm by the European Standard EN 14214.

Direct use of vegetable oils or blending of oils is unsatisfactory and impractical for diesel engines. High viscosity, acid composition, free fatty acid content, storage and combustion cause oxidation and polymerization problems during carbon storage and thickening of lubricating oil.

When producing biodiesel, the following points should be observed;

- Methyl alcohol is a health hazard material and should be used with caution.
- Since sodium hydroxide is very basic and has moisture retention properties, it should be stored in a moisture free environmen. It may cause permanent damage if it is not used carefully.
- When waste oils are used in the production of biodiesel, the used oil should be heated before the chemicals are added if these oils are concentrated at 20 °C and coagulated.
- Chemical materials to be used in production must be resistant to heat and corrosion (Uyar, 2013).

2.10. The comparison of biodiesel to diesel fuel

The advantages of biodiesel over other petrodiesel fuels:

- It is renewable and reduces dependence on fossil resources.
- It creates a new market for agricultural activities.
- Carbon monoxide (CO), particulate matter, unburned hydrocarbons are less in their emissions and aromatic compounds and sulfur are almost non-existent.
- It does not cause greenhouse effect when compared to petrodiesel since carbon dioxide (CO_2), which is the result of the use of biodiesel, is again used by the plants in the production of biodiesel.
- Flash point is higher compared to Petrodiesele. This makes biodiesel more reliable for handling and use.
- Combustion efficiency of biodiesel is higher than petrodiesel since its O_2 content is higher.
- Biodiesel is not only used as engine fuel. It is also used as a heater and lubricant, as a solvent, in brickwork and ceramics, in construction moldings, in hydraulic fluids (Öğüt and Oğuz, 2006).
- They are not poisonous and can easily decompose. It was found out in the tests that 99,6% of biodiesel obtained from rapeseed decomposes within 21 days (Zhang, 2002).

The disadvantages of biodiesel over other petrodiesel fuels

- Its calorific value is lower than petrodiesel. In this case, it reduces engine power to some extent.
- In cold weather, it is affected more quickly than petrodiesel. This is a factor which limits the use of biodiesel in cold climate regions. Biodiesel B_{20} using form should be preferred to overcome this (With newly developed processes, biodiesel can be used smoothly up to -20 °C).
- Fuel Consumption is 11% more during volume and 5-6% more at overweight.
- When B_{100} (pure biodiesel) is used, the engine hose, the gaskets and connection components of the engine should be changed with appropriate equipment.
- 75% of the cost of biodiesel belongs to the raw material. For this reason, the cost of biodiesel increases as the price of raw materials increases (Öğüt and Oğuz, 2006).
- Nitrogen oxide emissions are slightly higher than petrodiesel. However, this problem can be overcome by reducing the combustion temperature (by delaying the combustion at 1-3 °C or using a catalytic converter) (Zhang, 2002).

3. RESULT AND DISCUSSION

Biodiesel, whose raw material is vegetable and animal oils, is a renewable energy source and obtained by various chemical methods. The viscosity problem of biodiesel must be solved in order to use it properly in engines. High viscosity can cause poor fuel, bad combustion, clogged injectors, carbon deposits and deterioration in the lubrication (Karaosmanoğlu et al., 1996).

To solve high viscosity problem; dilution, microemulsion formation, pyrolysis, transesterification and supercritical methods are applied to biodiesel. The most common of these methods is the method of transesterification.

3.1. Dilution Method

The dilution method is the method in which biodiesel is obtained by mixing it with diesel fuel at certain ratios. In dilution method, the viscosity of biodiesel which is mixed with diesel fuel reduces at a certain rate.

The most preferred vegetable oils in the application of dilution technique are sunflower oil, soy oil, safflower oil, rapeseed oil, groundnut oil, palm oil and used frying oils. The chemical composition of these oils, as well as their high viscosities, can cause problems in their evaluation as fuel. The degree of unsaturation of oil acids that make up the oil directly affects combustion. Depending on the degree of unsaturation, some complex oxidative thermal polymerization reactions can occur as a result of combustion. Thus, carbon deposits occur in the spray nozzles, the spraying deteriorates, the viscosity of the lubricating oil increases and changes its property.

Volumetrically, the viscosity of the 75% diesel fuel and 25% high oleic acid safflower oil mixture was determined as 4,92 mm^2/s at 40 ^0C. Safflower oil contains less unsaturation, which makes this mixture superior to the mixture formed with sunflower oil (Kaplan, 2001).

In another study related to this, rapeseed oil was added to diesel fuel by 10% ratio and it was observed that this oil did not cause significant changes in diesel fuel properties. The laboratory works performed with this mixture on diesel engines gave positive results and it was also stated that some improvements were made in the exhaust gas (Çildir, 2003).

With the dilution method, the viscosity of sunflower oil with 120.9 Redwood / second at 38°C was diluted by mixing it with diesel fuel at the rate of 20%, 50% and 70%; and in these mixture rates, the viscosity of biodiesel was reduced to 35,5, 48,8 and 64,7 Redwood/second respectively. The fuel obtained by reducing the viscosity could be used in engines (Oğuz H., 1998).

3.2. Micro-Emulsion Method

Microemulsification is a process used to formulate hybrid diesel fuels by dissolving vegetable oil / alcohol mixtures by adding amphiphiles. In this process, the cetane number of the microemulsion is also low because the cetane numbers of the alcohols are low. At the same time, the mixture tends to decompose at low temperatures. These two situations are seen as the disadvantages of the method (Erdoğan, 1991).

By the evaporation and explosion of the components with low boiling point during the reaction, the spray characteristics are improved. In all microemulsions carried out with butanol, hexanol and octanol, the lowest viscosities suitable for diesel fuels are obtained. With this method, it is possible to generate alternative diesel fuels completely free from petroleum (Kaplan, 2001).

In investigating the use of animal fats as compression ignition (CI) engine fuel by forming water and CH_3OH (Methyl-Alcohol) stable emulsion through micro emulsion method; span 83 (sorbitan sesquiolate) and 80 (sorbitan sesquioleate) surfactants were used to prepare and stabilize animal oil - water emulsions. It was concluded that animal fats could be converted into balanced biofuel emulsions with improved physical and chemical properties and could be used as a fuel applicable to diesel engines. As a diesel engine fuel based on stability, structure, viscosity, oil content and economic properties, the effects of the formulation and other variable parameters on CH_3CH_2OH (Ethanol)- animal fat emulsion were investigaetd. Optimum emulsion conditions were determined as 36.4% CH_3CH_2OH, 3.6% SPAN 83, 10% water and 50% animal fat by volume, diesel engine tests were performed on the fuels based on CH_3CH_2OH animal fat emulsion. It was found that at high power outputs there was a significant reduction in smoke, nitric oxide, hydrocarbon and carbon monoxide emulsions when comparing fuel emulsion to smooth oil and clean diesel (Peter et al., 2015).

3.3. Pyrolysis Method

Pyrolysis is the thermal decomposition of organic substances in an oxygen-free environment in order to produce gas, liquid and solid products. Pyrolysis has been used for centuries in the production of active carbon. The amount of produced material depends on the applied method and reaction parameters. In order to obtain a high amount of solid product, the raw material is slowly reacted at low temperatures. Fast or flash pyrolysis is applied to obtain maximum liquid product (Mesut, 2011).

The yield of liquid product in the pyrolysis process depends on the reaction rate. Generally, if very high heating speeds are 1000 - 10000 °C/s in the temperatures such as 450 - 650 °C, liquid product yield is high in flash and fast pyrolysis methods performed in a short time. In the pyrolysis process applied in this way, it is possible to prevent the breakdown of the products into smaller molecules in the gas state by means of the formed large molecular liquids and so, liquid product yield increases (Açıkgöz, 2001).

3.4. Transesterification Method

Transesterification is a method of esterification of vegetable oils with alcohols such as methanol or ethanol by means of acidic, basic catalysts and enzymes. It is the best way to reduce the viscosity of vegetable oils. The biodiesel obtained by applying this method shows the closest properties to diesel fuel. This biodiesel production technique has been reported to have certain advantages over other processes:

- Reaction conditions are easy.
- Production method is eco-friendly.
- A wide variety of feedstocks can be processed with this technique.

When the transesterification method is used in the production of biodiesel, sodium hydroxide, potassium hydroxide, sodium methoxide, potassium methoxide, sodium hydride, potassium amide and potassium hydride are used as alkaline catalysts. Sulfuric acid, phosphoric acid and hydrochloric acid are used as the acid catalyst. Alkali catalysts are faster than acid catalysts (Düzgün, 2015).

In biodiesel production, the reaction temperature, reaction time, alcohol / oil molar ratio, catalyst type and amount, alcohol type and quantity, free fatty acids in vegetable oil and the amount of water affect the product yield in transesterification method. The rate of reacting products is affected by the reaction temperature. If there is enough time for the reaction, the reaction may be completed or proceeded at room temperature (Srivastava and Prasad, 2000).

The increase in temperature has a positive effect on the ester conversion yield in the reaction (Demirbaş and Karslıoğlu, 2007).

Depending on the alcohol and oil used in the reaction, transesterification reaction should be kept at a different temperature close to the boiling point of the alcohol where the reaction can take place (Marchetti et al. 2007).

In the reactions with higher molar proportions, higher ester conversion takes place in a much shorter time (Anonymous, 2011).

If there is no free fatty acid in the vegetable oil content, the alkali-catalyzed transesterification is more effective than the acid-catalyzed reaction. However, acid-catalyzed reaction is inevitable if the vegetable oil contains high levels of free fatty acids or water, because free fatty acids and water can cause the reaction to result in saponification (Agarwal, 2007).

3.5. Supercritical Method

Unlike the transesterification method, only methanol is used in the super critical method without catalyst, and methanol and oil are reacted at high temperatures such as 350 °C and in a short time like 240 seconds (4 minutes). The increase in temperature also enhances the reaction rate. In this method, the reaction products can be easily separated and the oil which contains free fatty acids can be converted into methyl esters (***Öğüt*** and Oğuz, 2006, Anonymous, 2017).

4. CONCLUSIONS

Today, biodiesel is considered as an eco- friendly alternative fuel. It will be a very important part of the energy supply in the future. Because the production and use of biodiesel have high production costs when compared to fossil fuels, future efforts should be directed to low-cost and non-edible feedstocks, advanced technologies that reduce overall production costs, and profitable production capacity. Instead of edible vegetable oils used as a source of biodiesel production, it is particularly important to replace waste and used oils with biodiesel raw materials. For biodiesel production, the non-edible plants that are grown on insufficient arable land or that do not require land use must be made use of in the future.

Among the various methods available for producing biodiesel, transesterification is the most preferred method. If there is enough time in the transesterification process, the reaction can take place at room temperature. However, if the reaction period is shortened, then the reaction temperature should be increased. Since a wide variety of vegetable oils can be used in the transesterification process, it can be preferred in the production of biodiesel. The purpose of the process is to reduce the viscosity.

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