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Biodiesel Production and Its Use in Diesel Engines as an Alternative Fuel

Mustafa Çanakcı,
Assistant Professor , *Department of Mechanical Education, Technical Education Faculty, Kocaeli University, Anıtpark Yanı İzmit, Kocaeli, TURKEY*

Necati Özsezen,
Department of Mechanical Education, Technical Education Faculty, Kocaeli University, Anıtpark Yanı İzmit, Kocaeli, TURKEY
e-mail: nozsezen@hotmail.com

Cenk Sayın
Department of Mechanical Education, Technical Education Faculty, Kocaeli University, Anıtpark Yanı İzmit, Kocaeli, TURKEY
e-mail: sayincenk@yahoo.com

Abstract

This paper is about biodiesel production, its properties and use in diesel engines as an alternative fuel. A primary path to produce biodiesel is transesterification. The transesterification reaction is affected by parameters such as free fatty acid level of oil, chemical structure of alcohol, catalyst type, reaction temperature and reaction time. Although the heating value of vegetable oils is smaller than that of diesel fuel, the main advantage of biodiesel fuel is lower concentration of greenhouse gases (especially CO_2) and other pollutants in exhaust emissions compared to petroleum diesel fuel.

Key words: Biodiesel Fuel, Transesterification, Diesel Engine, Alternative Fuel

1. Introduction

The concept of using vegetable oil-based fuel dates back to 1895 when Dr. Rudolf Diesel developed the first compression-ignition engine

specifically to run on vegetable oil [1]. With the advent of cheap petroleum, appropriate crude oil fractions were refined to serve as fuel, and diesel fuels and diesel engines evolved together. At the same time, the direct use of vegetable oils is unsatisfactory for both direct-injection and indirect-type diesel engines. The high viscosity, acid composition and free acid level of such oils, as well as gum formation due to oxidation and polymerization during storage and combustion, and lubricating oil thickening are some of the more obvious problems [2]. In the 1930s and 1940s vegetable oils were used as diesel fuels from time to time, but usually only in emergency situations. Recently, because of increases in crude oil prices, limited resources of fossil oil and environmental concerns, there has been a renewed focus on vegetable oils and animal fats to make biodiesel fuels.

In August 1982, the first International Conference on Plant and Vegetable Oils as fuels was held in Fargo, North Dakota. The primary concerns discussed were the cost of the fuel, the effects of vegetable oil fuels on engine performance and durability, biodiesel preparation, its specifications and additives [3].

Transesterification reaction can be used to reduce the viscosity of vegetable oils. The popularity of esters has contributed to the term "biodiesel" now usually referring to vegetable oil esters and not neat vegetable oils. Esters have significantly lower viscosities than the parent oils and fats (see Table 1). Accordingly, they improve the injection process and ensure better atomization of the fuel in the combustion chamber.

Biodiesel is defined as monoalkyl esters of long chain fatty acids derived from a renewable lipid feedstock such as vegetable oil or animal fat. "Bio" represents its renewable and biological source in contrast to traditional petroleum-based diesel fuel; "diesel" refers to its use in diesel engines. As an alternative fuel, biodiesel can be used in neat form or mixed with petroleum-based diesel fuel [4].

2. Production of Biodiesel (Transesterification)

The most common way to produce biodiesel is transesterification, which refers to a catalyzed chemical reaction involving vegetable oil and an alcohol to yield fatty acid alkyl esters (biodiesel) and glycerol. The first

transesterification of coconut oil was carried out by Haller and Youssoufin at the beginning of the 20th century [3]. The coconut oil was transesterified with methanol containing 2% hydrogen chloride as a catalyst. A simple molecular representation of the reaction is shown in Fig.1. Biodiesel may be produced in batch or continuous systems by transesterification. To complete a transesterification reaction stoichiometrically, a 3:1 molar ratio of alcohol to triglycerides is needed. In practice, the ratio needs to be higher to drive the equilibrium to a maximum ester yield.

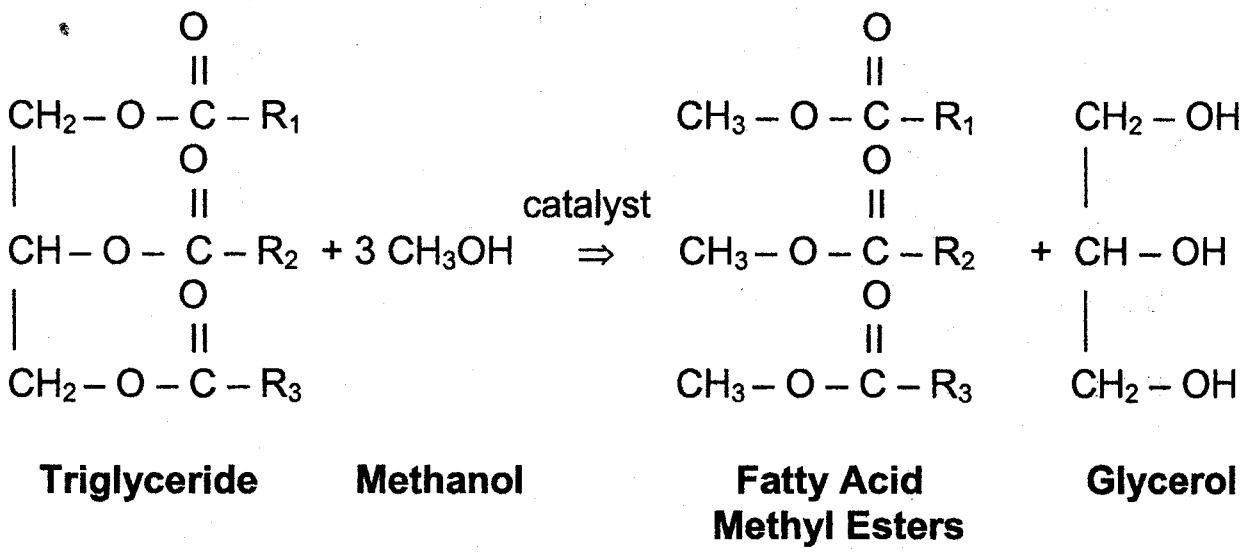


Fig.1. Transesterification of triglycerides with alcohol.

Triglycerides, as the main component of vegetable oil, consist of three long chain fatty acids esterified to a glycerol backbone. When triacylglycerols react with an alcohol (e.g., methanol), the three fatty acid chains are released from the glycerol skeleton and combined with the alcohol to yield fatty acid alkyl esters (e.g., fatty acid methyl esters). Glycerol is produced as a by-product [4,5].

After transesterification of triglycerides, the products are a mixture of esters, glycerol, alcohol, catalyst and tri-, di- and monoglycerides. Obtaining pure esters was not easy, since there were impurities in the esters, such as di- and monoglycerides [5].

The properties of vegetable oil based methyl esters and diesel fuels are compared in Table 1. Since the characteristics of biodiesel are generally similar to those of diesel fuel, therefore, it is a strong candidate to replace diesel if the need arises.

Table 1: Physical and chemical properties of vegetable methyl esters [6]

Vegetable oil methyl ester	**Kinematic viscosity (mm^2/s)**	**Cetane number**	**Lower heating Value (MJ/*l*)**	**Cloud point (^0C)**	**Flash point (^0C)**	**Density (g/*l*)**	**Sulfur (wt%)**
Peanut	4,9 ($37,8^0C$)	54	33,6	5	176	0,883	-
Soybean	4,5 ($37,8^0C$)	45	33,5	1	178	0,885	-
Soybean	4,0 (40^0C)	45,7-56	32,7	-	-	0,880 (15^0C)	-
Babassu	3,6 ($37,8^0C$)	63	31,8	4	127	0,879	-
Palm[a]	5,7 ($37,8^0C$)	62	33,5	13	164	0,880	-
Palm[b]	4,3-4,5 (40^0C)	64,3-70	32,4	-	-	0,872-0,877 (15^0C)	-
Sunflower	4,6 ($37,8^0C$)	49	33,5	1	183	0,860	-
Tallow	-	-	-	12	96	-	-
Rapeseed	4,2 (40^0C)	51-59,7	32,8	-	-	0,882 (15^0C)	-
Used Rapeseed	9,48 (30^0C)	53	36,7	-	192	0,895	0,002
Used Corn Oil	6,23 (30^0C)	63,9	42,3	-	166	0,884	0,0013
Diesel Fuel	1,2-3,5 (40^0C)	51	35,5	-	-	0,830-0,840 (15^0C)	-

Kinematic viscosity is an important measure of the biodiesel's flow properties. Because high viscosity has been associated with poor atomization of the fuel spray from the injectors and engine deposits. The cetane number of biodiesel (45-70) is higher than petroleum diesel fuel (40-55). At the same time, the cetane number for saturated compounds is higher than that of unsaturated compounds. Higher cetane numbers indicate shorter times between the injection of the fuel and its ignition. Higher cetane numbers can impact the engine's start ability, noise level, and exhaust emissions. The most important compositional difference between diesel fuel (No.2) and biodiesel is oxygen content. Biodiesel contains 10-12 wt% oxygen, which lowers energy density and the particulate emission. Another parameter is cloud point which is the temperature where wax formation might begin to plug the fuel filter. All biodiesel fuels exhibit poor cold flow properties with cloud and pour points 20-25 ^{o}C higher than diesel fuel [7,8,9].

Influence of free fatty acids

Natural vegetable oils and animal fats are extracted or expressed to obtain crude oil. These oils usually contain free fatty acids, phospholipids, carotenes, sterols, water, odorants and other impurities. The free fatty acid and water contents have significant effects on the transesterification. They also interfere with the separation of fatty acid esters and glycerol [9].

Biodiesel typically contains up to 14 different types of fatty acids that are chemically transformed into fatty acid methyl esters. The chemical composition of fat and oil esters is dependent upon the length and degree of unsaturation of the fatty acid alkyl chains. Table 2 shows the chemical structure of the fatty acid chains found in the most common biodiesel source materials. High levels of saturates (C14:0, C16:0, C18:0) raise cloud point, raise cetane number, reduce NO_x, and improve stability. More polyunsaturates (C18:2, C18:3) will reduce cloud point and cetane number and stability (unless stability additives are used), and raise NO_x [9,10].

Table 2. Chemical structural formula for fatty acids and methyl esters [10]

Fatty Acid Name	No. of Carb.	Chemical Structure (= denotes double bond placement)	Fatty Acids		Methyl Esters	
			Melting points (^{0}C)	Boiling points (^{0}C)	Melting points (^{0}C)	Boiling points (^{0}C)
Caprylic	8	$CH_3(CH_2)_6COOH$	16,5	239	-40	193
Capric	10	$CH_3(CH_2)_8COOH$	31,3	269	-18	224
Lauric	12	$CH_3(CH_2)_{10}COOH$	43,6	304	5,2	262
Myristic	14	$CH_3(CH_2)_{12}COOH$	58	332	19	295
Palmitic	16	$CH_3(CH_2)_{14}COOH$	62,9	349	30	338
Palmitoleic	16	$CH_3(CH_2)_5CH=CH(CH_2)_7COOH$	33	-	0	-
Stearic	18	$CH_3(CH_2)_{16}COOH$	69,9	371	39,1	352
Oleic	18	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	16,3	-	-19,9	349
Linoleic	18	$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$	-5	-	-35	366
Linolenic	18	$CH_3CH_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_7COOH$	-11	-	-	-
Arachidic	20	$CH_3(CH_2)_{18}COOH$	75,2	-	50	-
Eicosenoic	20	$CH_3(CH_2)_7CH=CH(CH_2)_9COOH$	23	-	-15	-
Behenic	22	$CH_3(CH_2)_{20}COOH$	80	-	54	-
Erucic	22	$CH_3(CH_2)_7CH=CH(CH_2)_{11}COOH$	34	-	-	-

The boiling points and melting points of the fatty acids, methyl esters, mono-, di- and triglycerides increase as the number of carbon atoms in the carbon chain increase, but decreasc with increases in the number of double bonds. The melting points increase in the ordcr of tri-, di- and monoglycerides due to the polarity of the molecules and hydrogen bonding. Low free fatty acid content in triglycerides is required for alkali catalyzed transesterification. If more water and free fatty acids are in the triglycerides, acid-catalyzed transesterification can be used. The triglycerides can be purified by saponification (known as alkali treating) and then transesterified using an alkali catalyst.

Influence of Alcohols

Alcohols are primary and secondary monohydric aliphatic alcohols having 1–8 carbon atoms. Among the alcohols that can be used in the transesterification process are methanol, ethanol, propanol and butanol. These alcohols present slight differences in suitability for transesterification. While both methanol and ethanol can be easily obtained from plant materials, ethanol has the drawback that the ethyl esters are less stable and leave a greater carbon residue. As methanol is also cheaper, it is the most commonly employed alcohol [11].

Influence of Catalyst Type

The reaction can be catalyzed by alkalis, acids, or enzymes. The alkalis include NaOH, KOH, carbonates and corresponding sodium and potassium alkoxides such as sodium methoxide, sodium ethoxide, sodium propoxide and sodium butoxide. Sulfuric acid, sulfonic acids and hydrochloric acid are usually used as acid catalysts. Lipases also can be used as biocatalysts.

Alkali-catalyzed transesterification is much faster than acid-catalyzed transesterification and is most often used commercially. An alkaline catalyst concentration in the range of 0.5-1 wt % yields 94-99% conversion of vegetable oil into esters. For an alkali-catalyzed transesterification, the glycerides and alcohol must be substantially anhydrous because water makes the reaction partially change to saponification, which produces soap. The soap lowers the yield of esters and renders the separation of ester and glycerol and the water washing difficult [5,6,10].

If the vegetable oil had free fatty acid content higher than 1%, the alkaline catalyst would be destroyed, whereas the acid catalyst would still be effective. Further increase in catalyst concentration does not increase the conversion and leads to extra costs because it is necessary to remove it from the reaction medium at the end.

Influence of Reaction Time

The conversion rate increases with reaction time. Freedman et al. [12] transesterificed peanut, cottonseed, sunflower and soybean oils under

the condition of methanol to oil ratio of 6:1, 0.5% sodium methoxide catalyst and 60°C. An approximate yield of 80% was observed after 1 min for soybean and sunflower oils. After 1 h, the conversions were almost the same for all four oils (93-98%).

Canakci and Van Gerpen [13] constructed a pilot plant to produce biodiesel from soybean oil. The ingredient amounts for the batch was prepared methanol to oil ratio of 6:1 with potassium hydroxide as catalyst (1% of oil by weight). They started the transesterification reaction by dissolving the potassium hydroxide catalyst in methanol at room temperature in the main reaction tank. Then, the mixture was agitated for 8 hours at room temperature. Samples of the mixture were extracted at one hour intervals and the total glycerin level of the ester fraction was measured. They founded total glycerin change during transesterification of soybean oil that it's shown in table 3.

Table 3. Total Glycerin Change During the Transesterification of Soybean Oil [13]

	Time, hours								
	0	1	2	3	4	5	6	7	8
Total Glycerin (%)	11.07	1.09	0.79	0.69	0.62	0.56	0.54	0.53	0.52

The Effect of Reaction Temperature

The rate of reaction is strongly influenced by the reaction temperature. The rate of transesterification increases with increasing temperature. However, the maximum operating temperature cannot exceed the boiling point of the reactants. Generally, the reaction is conducted close to the boiling point of alcohol at atmospheric pressure. Nevertheless, the reaction may be carried out at room temperature.

Encinar et al. [14] investigated the influence of temperature. They tested the methyl esterification of cynara oil at 25, 40, 55, and 60°C in order to determine the effect of reaction temperature on the methyl ester formation

(see Table 4). In all these experiments, a concentration of 15% in methanol and 1% in NaMeO (as catalyst) was used. As can be observed, for the same final reaction time, the percentage of esters obtained increases with temperature.

Table 4. Influence of Temperature on Characteristics Parameters of the Process[14]

	Temperature, °C			
Parameter	25	40	55	60
Density, (kg/m^3)	885	881	880	878
Viscosity(30 °C), (cSt)	6.21	5.10	4.90	4,55
HHV, (Mj / kg)	39.60	39.73	39.80	39,78
Cloud point, (°C)	0	-1	-1	-1
Pour point, (°C)	-2	-3	-3	-3
Flash point, (°C)	177	176	176	175
Combustion point, (°C)	182	180	180	179
Yields of esters, (%)	86	90	93	94

(NaMeO = 1%, Methanol = 15%)

3. Using Biodiesel in Diesel Engines

Compared with petroleum diesel fuel, the use of biodiesel fuel reduces the concentration of pollutants in motor exhaust gases: sulphur dioxide practically completely, carbon monoxide on the average of 20%, hydrocarbons on the average of 30%, soot and particulate matter of 40–50%. Because of a lower concentration of polycyclic aromatic hydrocarbons in the emissions of biodiesel fuel the emissions are many times less carcinogenic than those of petroleum diesel fuel. But slightly increases levels of oxides of nitrogen (NO and NO_2, collectively termed NO_x) [15].

Goodrum [16] was tested by 200 hr EMA (Engine Manufacturers Association) durability test using 20% and 80% peanut methyl ester/D2 blends and compared to No.2 diesel fuel at the laboratory of University of

Georgia. Engine performance with peanut methyl esters differed little from that with diesel fuel. In that work, also a slight power loss was observed together with an increase in fuel consumption due to the lower heating values of the esters. The emissions for the two fuels were similar, with the exception of NO_x which are higher for the methyl ester as mentioned above. Engine wear and fuel-injection system tests showed no abnormal characteristics for any of the fuels. Deposit amounts in the engine were comparable, however, the methyl ester showed greater varnish and carbon deposits on the pistons. Operating direct injection engines with neat peanut oil esters under certain conditions produced lubricating oil dilution which was not observed with an indirect injection engine.

Yu et al. [17] investigated biodiesel in form of esters from used cooking oils in diesel engine. They founded that biodiesel made from used cooking oil as a fuel for diesel engines has combustion characteristics generally similar to those of diesel. The premixed combustion phase was less intense than for diesel owing to the shorter ignition delay. However, the peak pressures were about 1.5 bar higher and the times of occurrence of the peak pressures were in the range 1.1°–3.8° earlier than those for diesel. The mixing-controlled combustion phase was similar to that of diesel. The energy released at the late combustion phase is higher, which is due to heavier molecular weight materials present in the used cooking oil. The emissions of CO, NO and SO_2 were higher for used cooking oil as compared with diesel. The average emission of CO was 29.4 per cent higher for used cooking oil owing to local rich mixtures.

4. Conclusions

Biodiesel is an alternative fuel produced from vegetable oils, used cooking oils, or animal fats. The most common path to produce biodiesel is by transesterification, which refers to a catalyzed chemical reaction involving vegetable oil and an alcohol to yield fatty acid alkyl esters (biodiesel) and glycerol. Biodiesel can help cut emissions of carbon dioxide (CO_2), the primary greenhouse gas contributing to global warming. Biodiesel reduces lifecycle CO_2 emissions by almost 80% compared to

petroleum diesel. Biodiesel contains almost no sulfur, so burning it creates no sulfur dioxide.

Biodiesel can be used in diesel engines with few or no modifications. Biodiesel has a higher cetane number than petroleum diesel fuel. Biodiesel fuel exhibits chemical and thermodynamic properties that are quite similar to those of petroleum diesel fuel. Biodiesel fuel is affected by the contents of the fatty acids, which may cause the difference in the characteristics of ignition, combustion emission between it and petroleum diesel fuel.

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