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Biodiesel for Diesel Engines

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Abstract – *Biodiesel fuels are attracting increasing attention worldwide as a blending component or a direct replacement for diesel fuel in vehicle engines. The purpose of the transesterification process is to lower the viscosity of the oil. The most important variables affecting the methyl ester yield during the transesterification reaction are the molar ratio of alcohol to vegetable oil and the reaction temperature. Methanol is the commonly used alcohol in this process, due in part to its low cost. Methyl esters of vegetable oils have several outstanding advantages among other new-renewable and clean engine fuel alternatives. Biodiesel fuel is a renewable substitute fuel for petroleum diesel or petrodiesel fuel made from vegetable or animal fats. Biodiesel can be used in any mixture with petrodiesel as it has very similar characteristics but it has lower exhaust emissions. Biodiesel fuel has better properties than that of petrodiesel fuel such as renewable, biodegradable, non-toxic, and essentially free of sulfur and aromatics. Biodiesel has become more attractive recently because of its environmental benefits.*

Keywords – Biodiesel, transesterification, vegetable oil, viscosity.

1. INTRODUCTION

Biodiesel (Greek, bio, life + diesel rom Rudolf Diesel) refers to a diesel-equivalent, processed fuel derived from biological sources. Biodiesel is the name for a variety of ester-based oxygenated fuels from renewable biological sources. It can be made from processed organic oils and fats.

Chemically, biodiesel is defined as the monoalkyl esters of long-chain fatty acids derived from renewable biolipids. Biodiesel is typically produced through the reaction of a vegetable oil or animal fat with methanol or ethanol in the presence of a catalyst to yield methyl or ethyl esters (biodiesel) and glycerine [1]. Fatty acid (m)ethyl esters or biodiesels are produced from natural oils and fats. Generally, methanol is preferred for transesterification because it is less expensive than ethanol [2].

In general terms, biodiesel may be defined as a domestic, renewable fuel for diesel engines derived from natural oils like soybean oil that meets the specifications of ASTM D 6751. In technical terms (ASTM D 6751) biodiesel is a diesel engine fuel comprised of monoalkyl esters of long-chain fatty acids derived from vegetable oils or animal fats, designated B100 and meeting the requirements of ASTM D 6751. Biodiesel, in application as an extender for combustion in CIEs (diesel), possesses a number of promising characteristics, including reduction of exhaust emissions [3]. Chemically, biodiesel is referred to as the monoalkyl esters, especially (m)ethylester, of long-chain fatty acids derived from renewable lipid sources via a transesterification process. Technical properties of biodiesel are given in Table 1.

The possibility of using vegetable oils as fuel has been recognized since the beginning of diesel engines. Vegetable oil has too high a viscosity for use in most existing diesel engines as a straight replacement fuel oil. There are a number of ways to reduce vegetable oils' viscosity. Dilution, microemulsification, pyrolysis, and transesterification are the four techniques applied to solve the problems encountered with high fuel viscosity. One of the most common methods used to reduce oil viscosity in the biodiesel industry is called transesterification. Chemical conversion of the oil into its corresponding fatty ester is called transesterification [4], [5].

Transesterification (also called alcoholysis) is the reaction of a fat or oil triglyceride with an alcohol to form esters and glycerol. Figure 1 shows the transesterification reaction of triglycerides. A catalyst is usually used to improve the reaction rate and yield. Because the reaction is reversible, excess alcohol is used to shift the equilibrium to the product side [6].

Transesterification is extremely important for biodiesel. Biodiesel as it is defined today is obtained by transesterifying triglycerides with methanol. Methanol is the preferred alcohol for obtaining biodiesel because it is the cheapest alcohol. Base catalysts are more effective than acid catalysts and enzymes [7]. Methanol is made to react with triglycerides to produce methyl esters (biodiesel) and glycerol (Equation 1).

$$C_3H_5(OOCR)_3 + 3CH_3OH \rightarrow 3RCOOCH_3 + C_3H_5(OH)_3 \quad (1)$$

Triglyceride Methanol Methyl ester Glycerine

The production processes for biodiesel are well known. There are four basic routes to biodiesel production from oils and fats:

- Base-catalyzed transesterification
- Direct acid-catalyzed transesterification
- Conversion of the oil into its fatty acids and then into biodiesel
- Non-catalytic transesterification of oils and fats

Biodiesel produced by transesterification reactions can be alkali catalyzed, acid catalyzed, or enzyme catalyzed, but the first two types have received more attention because of the short reaction times and low cost compared with the third one. Most of the biodiesel

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produced today is made with the base-catalyzed reaction for several reasons [8]:

- It involves low temperature and pressure.
- It yields high conversion (98%) with minimal side reactions and reaction time.
- It allows a direct conversion into biodiesel with no intermediate compounds.
- It requires simple construction materials.

Table 2 shows the typical proportions for the chemicals used to make biodiesel. The quantitative transesterification reaction of triolein obtained for methyl oleate (biodiesel) is given in Equation (2):

$$\underset{885.46\text{ g}}{\text{Triolein}} + \underset{192.24\text{ g}}{\text{6 Methanol}} \xrightarrow[\text{(Catalyst)}]{} \underset{889.50\text{ g}}{\text{Methyl oleate}} + \underset{92.10\text{ g}}{\text{Glycerol}} + \underset{96.12\text{ g}}{\text{3 Methanol}} \qquad (2)$$

Table 1: Technical properties of biodiesel

Common name	Biodiesel (bio-diesel)
Common chemical name	Fatty acid (m)ethyl ester
Chemical formula range	C_{14} - C_{24} methyl esters or C_{15-25} H_{28-48} O_2
Kinematic viscosity range (mm^2/s, at 313 K)	3.3-5.2
Density range (kg/m^3, at 288 K)	860-894
Boiling point range (K)	>475
Flash point range (K)	430-455
Distillation range (K)	470-600
Vapor pressure (mm Hg, at 295 K)	<5
Solubility in water	Insoluble in water
Physical appearance	Light to dark yellow, clear liquid
Odor	Light musty/soapy odor
Biodegradability	More biodegradable than petroleum diesel
Reactivity	Stable, but avoid strong oxidizing agents

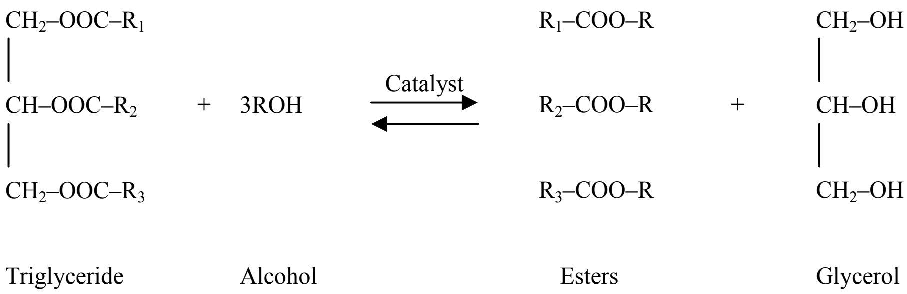

Fig. 1. Transesterification of triglycerides with alcohol

Table 2: Typical proportions for chemicals used to make biodiesel

Reactants	Amount (kg)
Fat or oil	100
Primary alcohol (methanol)	10
Catalyst (sodium hydroxide)	0.30
Neutralizer (sulfuric acid)	0.36

Table 3: Inputs and mass requirements for the Lurgi process

Input	Requirement/ton biodiesel
Feedstock	1,000 kg vegetable oil
Steam requirement	415 kg
Electricity	12 kWh
Methanol	96 kg
Catalyst	5 kg
Hydrochloric acid (37%)	10 kg
Caustic soda (50%)	1.5 kg
Nitrogen	1 Nm^3
Process water	20 kg

The Lurgi process is shown as a two-step reactor. Most of the glycerine is recovered after the first stage where a rectifying column leads to separation of the excess methanol and crude glycerine. The methyl ester output of the second stage is purified, to some extent, of residual glycerine and methanol by a wash column. Table 3 shows the inputs and mass requirements for the Lurgi process.

2. ADVANTAGES OF BIODIESEL

Biodiesel is a biodegradable, nontoxic, and clean-burning fuel that can be made from any fat or vegetable oil, including recycled cooking oil. Because it contains no petroleum or other fossil fuels, it emits virtually no sulfurs, aromatics, particulates, or carcinogenic compounds and is thus a safer and healthier alternative than petroleum diesel. Biodiesel can be used in all conventional diesel engines, delivers similar performance and engine durability as petroleum diesel, and requires virtually no changes in fuel handling and delivery systems.

The advantages of biodiesel as a diesel fuel are its portability, ready availability, renewability, higher combustion efficiency, lower sulfur and aromatic content [7], [9], higher cetane number, and higher biodegradability [10]-[12]. The main advantages of biodiesel given in the literature include its domestic origin, its potential for reducing a given economy's dependency on imported petroleum, biodegradability, high flash point, and inherent lubricity in the neat form [13], [14].

Biodiesel is the only alternative fuel in which low-concentration biodiesel-diesel blends run on conventional unmodified engines. It can be stored anywhere that petroleum diesel fuel is stored. Biodiesel can be made from domestically produced, renewable oilseed crops such as soybean, rapeseed, and sunflower. The risks of handling, transporting, and storing biodiesel are much lower than those associated with petrodiesel.

The combustion of biodiesel alone provides over a 90% reduction in total unburned hydrocarbons and a 75 to 90% reduction in polycyclic aromatic hydrocarbons. Biodiesel further provides significant reductions in particulates and carbon monoxide than petroleum diesel fuel. Biodiesel provides a slight increase or decrease in nitrogen oxides depending on the engine family and testing procedures. Many studies on the performances and emissions of compression ignition engines, fuelled with pure biodiesel and blends with diesel oil, have been conducted and are reported in the literature [15], [16].

The use of biodiesel to reduce N_2O is attractive for several reasons. Biodiesel contains little nitrogen, as compared with petrodiesel, which is also used as a reburning fuel. The N_2O reduction is strongly dependent upon initial N_2O concentrations and only slightly dependent upon temperature, where increased temperature increases N_2O reduction. This results in lower N_2O production from fuel nitrogen species for biodiesel. In addition, biodiesel contains trace amounts of sulfur, so SO_2 emissions are reduced in direct proportion to the petrodiesel replacement.

One of the most common blends of biodiesel contains 20 volume percent biodiesel and 80 volume percent conventional diesel. For soybean-based biodiesel at this concentration, the estimated emission impacts for percent change in emissions of NO_x, PM, HC, and CO were +20%, –10.1%, –21.1%, and –11.0%, respectively (EPA, 2002). The use of blends of biodiesel and diesel oil are preferred in engines in order to avoid some problems related to the decrease of power and torque and to the increase of NO_x emissions (a contributing factor in the localized formation of smog and ozone) that occurs with an increase in the content of pure biodiesel in a blend [17].

Biodiesel fuels can be used as a renewable energy source to replace conventional petroleum diesel in CIEs. When degradation is caused by biological activity, especially by enzymatic action, it is called biodegradation. Biodegradability of biodiesel has been proposed as a solution for the waste problem. Biodegradable fuels such as biodiesels have an expanding range of potential applications and they are environmentally friendly. Therefore, there is growing interest in degradable diesel fuels that degrade more rapidly than conventional disposable fuels.

Biodiesel is non-toxic and degrades about four times faster than petrodiesel. Its oxygen content improves the biodegradation process, leading to a decreased level of quick biodegradation. In comparison with petrodiesel, biodiesel shows better emission parameters. It improves the environmental performance of road transport and reduces greenhouse emissions (mainly of carbon dioxide).

The biodegradabilities of several biodiesels in the aquatic environment show that all biodiesel fuels are readily biodegradable. In one study, after 28 d all biodiesel fuels were 77 to 89% biodegraded; diesel fuel was only 18% biodegraded [18]. The enzymes responsible for the dehydrogenation/oxidation reactions that occur in the process of degradation recognize oxygen atoms and attack them immediately [19].

The biodegradability data of petroleum and biofuels available in the literature are presented in Table 4. In 28-d laboratory studies, heavy fuel oil had a low biodegradation of 11% due to its higher proportion of high-molecular-weight aromatics [20], [21]. Gasoline is highly biodegradable (28%) after 28 d. Vegetables oils and their derived methyl esters (biodiesels) are rapidly degraded to reach a biodegradation rate of between 76 and 90% [19], [10]. In their studies [19] they have shown that vegetable oils are slightly less degraded than their modified methyl ester.

Table 4: Biodegradability data of petroleum and biofuels

Fuel sample	Degradation in 28 d (%)	Reference
Gasoline (91 octane)	28	[11]
Heavy fuel (Bunker C oil)	11	[20], [21]
Refined rapeseed oil	78	[19]
Refined soybeen oil	76	[19]
Rapeseed oil methyl ester	88	[19]
Sunflower seed oil methyl ester	90	[19]

3. DISADVANTAGES OF BIODIESEL

The major disadvantages of biodiesel are its higher viscosity, lower energy content, higher cloud point and pour point, higher nitrogen oxide (NO_x) emissions, lower engine speed and power, injector coking, engine compatibility, high price, and higher engine wear.

Important operating disadvantages of biodiesel in comparison with petrodiesel are cold start problems, lower energy content, higher copper strip corrosion, and fuel pumping difficulty from higher viscosity.

Biodiesel has a higher cloud point and pour point compared to conventional diesel [22]. Neat biodiesel and biodiesel blends increase nitrogen oxide (NO_x) emissions compared with petroleum-based diesel fuel used in an unmodified diesel engine [23]. Peak torque is lower for biodiesel than petroleum diesel but occurs at lower engine speed and generally the torque curves are flatter. Biodiesels on average decrease power by 5% compared to diesel at rated loads [24].

4. CONCLUSION

Alternative fuels for diesel engines have been becoming increasingly important due to diminishing petroleum reserves and the growing environmental concerns have made renewable fuels an exceptionally attractive alternative as a fuel for the future. Transesterification is a chemical reaction between triglyceride and alcohol in the presence of catalyst or without catalyst. The purpose of the transesterification process is to lower the viscosity of the oil.

The advantage in its usage is attributed to lesser exhaust emissions in terms of carbon monoxide, hydrocarbons, particulate matter, polycyclic aromatic hydrocarbon compounds and nitrited polycyclic aromatic hydrocarbon compounds. The main disadvantages of biodiesel are its higher viscosity, lower energy content, higher cloud point and pour point, higher nitrogen oxide emissions, lower engine speed and power, injector coking, engine compatibility, and high price.

Biodiesel is a biodegradable and renewable fuel. It contributes no net carbon dioxide or sulfur to the atmosphere and emits less gaseous pollutants than normal diesel. Carbon monoxide, aromatics, polycyclic aromatic hydrocarbons (PAHs) and partially burned or unburned hydrocarbon emissions are all reduced in vehicles operating on biodiesel.

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