International Journal of Science, Environment and Technology, Vol. 3, No 4, 2014, 1544 – 1562

ISSN 2278-3687 (O)

Review Article

PRODUCTION OF BIODIESEL FROM NON EDIBLE OIL AND ITS PROPERTIES

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Abstract: Due to the environmental problems caused by the use fossil fuels, considerable attention has been made to biodiesel production as an alternative to petrodiesel. Biodiesel is an ecofriendly, alternative diesel fuel prepared from domestic renewable resources i.e. produced from vegetable oils and animal fats. It is a renewable source of energy seems to be an ideal solution for global energy demands including Ethiopia as well. The general method to produce biodiesel is transesterification of non-edible oil with methanol in the presence of either base or strong acid catalysts. Transesterification reaction is quite sensitive to various parameters. An ideal transesterification reaction differs on the basis of variables such as fatty acid composition and the free fatty acid content of the oil. Other variables include reaction temperature, ratio of alcohol to vegetable oil, catalyst, mixing intensity, purity of reactants. This review paper describes the fuel properties of biodiesel, production process (transesterification) and the most important variables that influence the transesterification reaction.

Keywords: biodiesel; non-edible oil: transesterification.

Introduction

The worldwide worry about the protection of environment and the conservation of non-renewable natural resources, has given rise to alternate development of sources of energy as substitute for traditional fossil fuels. The major part of all energy consumed worldwide comes from fossil sources (petroleum, coal and natural gas). However, these sources are limited and will be exhausted in the near future. Thus, looking for alternative sources of new and renewable energy such as hydro, biomass (better sources of energy), wind, solar, geothermal, hydrogen and nuclear is of vital importance. Alternative new and renewable fuels have the potential to solve many of the current social problems and concerns, from air pollution and global warming to other environmental improvements and sustainability issues (Anitha and Dawn, 2010).

*Received June 27, 2014 * Published August 2, 2014 * www.ijset.net*

Manufacturing biodiesel from used vegetable oils and non-edible is relatively easy and possesses many environmental benefits. The use of vegetable oils as frying oils produces significant amounts of used oils which may present a disposal problem. The use of waste cooking oils and non-edible oil for biodiesel production has the advantage of their low price. Used vegetable oil is described as a 'renewable fuel' as it does not add any extra carbon dioxide gas to the atmosphere, as opposed to fossil fuels, which cause changes in the atmosphere (Mulimani *et al*., 2012).

Energy is the most fundamental requirement for human existence and activities. As an effective fuel, petroleum has been serving the world to meet its need of energy consumption. But the dependence of mankind entirely on the fossil fuels could cause a major deficit in future. The application of biodiesel to our diesel engines for daily activities is advantageous for its environmental friendliness over petro-diesel. The main advantages of using biodiesel is that it is biodegradable, can be used without modifying existing engines, and produces less harmful gas emissions such as sulfur oxide. Biodiesel reduces net carbon-dioxide emissions by 78% on a lifecycle basis when compared to conventional diesel fuel (Carvalho *et al*., 2011).

During recent years high activities can be observed in the field of alternative fuels, due to supply of petroleum fuels strongly depends on a small number of oil exporting countries. The demand for diesel and gasoline is increased drastically. It has been estimated that the demand for diesel will be increasing day by day (Mulimani *et al*., 2012). Alternative fuels, other than being renewable, are also required to serve to decrease the net production of carbon dioxide (CO_2), oxides of nitrogen (NO_x), particulate matter etc, from combustion sources (Topare *et al*., 2011). Hence, government of Ethiopia has taken necessary steps to fulfill future diesel and gasoline demand and to meet the stringent emission norms. These biofuels are being looked to provide employment generation to rural people through plantation of plants which produce non-edible oils (Mulimani *et al*., 2012).

As population is growing, transport becomes crucial part of life. The biggest problem is the growing population & depletion of fossil fuel. The large increase in number of automobiles in recent years has resulted in great demand for petroleum products. With crude oil reserves estimated to last only for few decades, there has been an active search for alternate fuels. The depletion of crude oil would cause a major impact on the transportation sector. Of the various alternate fuels under consideration, biodiesel, derived from vegetable oils, is the most promising alternative fuel to conventional diesel fuel (Jaichandarand and Annamalai, 2011).

Biodiesel is an alternative fuel made from renewable biological sources such as vegetable oils both (edible and non edible oil) and animal fats (Antony Raja *et al*., 2011). It can be defined as basically monoalkyl esters of fatty acids produced from animal fats or vegetable oils by transesterification or other methods with small chain alcohols, using different kinds of catalysts. Currently, more than 95% biodiesel are produced from edible oil feedstock (soya bean oil, sunflower oil, niger oil, rapeseed oil, palm oil, linseed oil and sesame oil), due to this there is a huge imbalance in the human nutrition chain versus fuel. This will make biodiesel economically unfeasible as compared to petroleum-derived fuels. To avoid these situations, non-edible oil seeds need to be used for commercial production of biodiesel. Many researchers have initiated work on the use of low cost non-edible oils as alternative feedstock for biodiesel production. Among non-edible oil feedstock, seeds of castor and jatropha, and microalgae oil are proved to be a one of the highly promising reliable source having high seed oil content (Sruthi, 2013). Algae are an economical choice for biodiesel production, because of its availability and low cost (Basumatary, 2013).

Biodiesel, (the mono alkyl (mainly methyl) esters of long-chain fatty acids, derived from a renewable lipid feedstock (Cholakov, 2013), is advised for use as an alternative fuel for conventional petroleum-based diesel chiefly because it is a renewable, domestic resource with an environmentally friendly emission profile and is readily biodegradable. Biodiesel, a promising substitute as an alternative fuel has gained significant attention due to the predicted shortness of conventional fuels and environmental concern. The amount of greenhouse gas emissions, generating energy from renewable resources is being possessed a high priority gradually to decrease both over-reliance on imported fossil fuels (Hossain and Boyce, 2009).

Generally, biodiesel is produced by means of transesterification. Transesterification is the reaction of a lipid with an alcohol to form esters and a byproduct, glycerol. It is, in principle, the action of one alcohol displacing another from an ester, referred to as alcoholysis (cleavage by an alcohol). Transesterification consists of a sequence of three consecutive reversible reactions. The first step is the conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides, and finally monoglycerides into glycerol, yielding one ester molecule from each glyceride at each step. The reactions are reversible, although the equilibrium lies towards the production of fatty acid esters and glycerol (Anitha and Dawn, 2010). This reaction proceeds well in the presence of some homogeneous catalysts such as potassium hydroxide (KOH)/sodium hydroxide (NaOH)

and sulfuric acid, or heterogeneous catalysts such as metal oxides or carbonates. Depending on the undesirable compounds (especially FFA and water), each catalyst has its advantages and disadvantages. Sodium hydroxide is very well accepted and widely used because of its low cost and high product yield. The most common alcohols widely used are methyl alcohol and ethyl alcohol. Among these two, methanol found frequent application in the commercial uses because of its low cost (Carvalho *et al*., 2011).

Base-catalyzed transesterification, however, has some limitations among which are that it is sensitive to FFA content of the feedstock oils. A high FFA content (> 1 % w/w) will lead to soap formation which reduces catalyst efficiency, causes an increase in viscosity, leads to gel formation and makes the separation of glycerol difficult.

Also, the oils used in transesterification should be substantially anhydrous (0.06 % w/w). The presence of water gives rise to hydrolysis of some of the produced ester, with consequent soap formation. Other drawbacks of the base-catalyzed transesterification is that the process is energy intensive, recovery of glycerolis difficult, alkaline catalyst has to be removed from the product and alkaline waste water requires treatment (Anitha and Dawn, 2010).

The main advantage in biodiesel usage is attributed to lesser exhaust emissions in terms of carbon monoxide, hydrocarbons and particulate matter. Biodiesel is said to be carbon neutral as more carbon dioxide is absorbed by the biodiesel yielding plants than what is added to the atmosphere when used as fuel (Jaichandar and K. Annamalai, 2011). Biodiesel is gaining increasing acceptance in the market as an environmental friendly alternative diesel fuel. It is non-toxic, biodegradable, and free of sulphur or any carcinogenic compounds. The demand and cost of edible oils prevents its use in the production of biodiesel. So, a large variety of plants that produce non-edible oils are considered for biodiesel production (Vuppaladadiyam *et al*., 2013). Other advantages of biodiesel over fossil fuel are higher flash point and higher lubricity (Alnuami *et al*., 2014).

The aim of this review paper is to assess biodiesel production from non-edible oil with a view to determine its performance in Internal Combustion engine and investigate the fuel properties of bio-diesel. Additionally, physicochemical properties and factors affecting biodiesel production were discussed.

Production of biodiesel

Vegetable oils are chemically complex esters of fatty acids. These are the fats naturally present in oil seeds, and known as tri-glycerides of fatty acids. The molecular weight of these tri-glycerides would be of order of 800 kg/m^{3}or more. Because of their high molecular

weights these fats have high viscosity causing major problems in their use as fuels in CI engines. These molecules have to be split into simpler molecules so that they have viscosity and other properties comparable to standard diesel oils. Modifying the vegetable oils (to make them lighter) can be achieved in many ways, including; Pyrolysis, Micro emulsification, Dilution and Transesterification. Among these, transesterification is the most commonly used commercial process to produce clean and environmentally friendly light vegetable oil fuel i.e. biodiesel (Antony Raja, 2011).

Transesterification

Biodiesel, an alternative diesel fuel is derived from a chemical reaction called transesterifcation of plant-derived oil. It is the chemical conversion of oil to its corresponding fatty ester in the presence of a catalyst. The reaction converts esters from long chain fatty acids into mono alkyl esters. Chemically, biodiesel is a fatty acid methyl ester. Transesterification process helps reduce the viscosity of the oil. The process proceeds well in the presence of homogenous catalysts such as sodium hydroxide (NaOH), potassium hydroxide (KOH), sulphuric acid (Demirbas, 2008). The formation of fatty acid methyl esters (FAME) through transesterification of seed oils requires raw oil, 15% of methanol & 5% of sodium hydroxide on mass basis. However, transesterification is an equilibrium reaction in which excess alcohol is required to drive the reaction very close to completion (Ahmad *et al*., 2011). .

Transesterification transform the large branched molecule structure of the oils into smaller, straight chained molecules similar to the standard diesel hydrocarbons. Transesterification is the process of exchanging the organic group R" of an ester with the organic group R’ of an alcohol. These reactions are often catalyzed by the addition of an acid or base. Transesterification is common and well-established chemical reaction in which alcohol reacts with triglycerides of fatty acids (non-edible oil) in the presence of catalyst. The transesterification reaction scheme is shown below (Ojolo, *et al*., 2011).

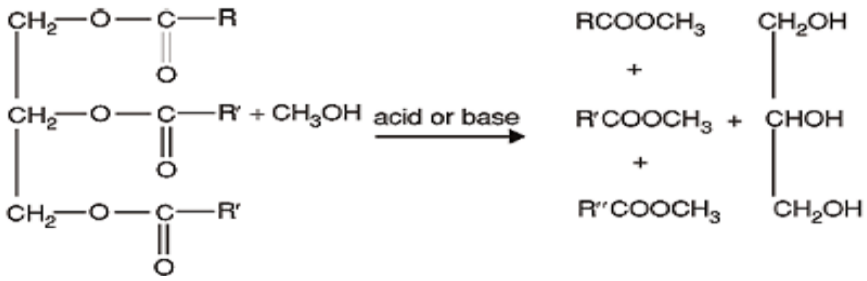

Figure1: Transesterification Reaction Scheme

Methanol and ethanol are used most frequently; especially methanol is preferred because of its low cost and its physical and chemical advantages (polar and shortest chain alcohol). It can quickly react with triglycerides and NaOH gets easily dissolved in it. Ethyl ester and methyl ester almost has same heat content (Ojolo, *et al*., 2011).

The two methods preferred for the industrial production of biodiesel from non-edible oils are base catalyzed and acid catalyzed transesterification.

Base-Catalyzed Transesterification Process

This is the traditional technology commonly employed for the commercial production of biodiesel from the refined vegetable oils/fats that are low in free fatty acids (FFAs < 0.1 wt %). It involves the transesterification of triglycerides present in oil/fat with a lower alcohol (mostly methanol) in the presence of a catalytic amount of a base (alcoholic solution of KOH/ NaOH or sodium methoxide) at the atmospheric pressure under the reflux condition for alcohol (60-70 °C). This reaction proceeds through the well known mechanism as shown in Fig. 2 and could produce the fatty acid methyl ester (FAME, called biodiesel) in an amount almost equal to that of the oil used. This reaction is fast and reversible. Therefore, one requires adding an excess amount of both methanol and the catalyst to drive the reaction to completion. Since this reaction is sensitive to the moisture, it essentially requires drying of all the reagents, particularly methanol, such that their moisture content is reduced to below 0.1% by weight (Tyagi *et al*., 2010). To complete a transesterification reaction stoichiometrically, a 3:1 molar ratio of alcohol to triglycerides is necessary. In practice, the ratio needs to be higher to drive the equilibrium to a maximum ester yield (Sarıbıyık, *et al*., 2010). Further, prior to using oil in the transesterification process, its FFA content must be reduced to below 0.1 wt % by neutralizing oil with an alkali, to prevent the formation of soap in the transesterification reaction (Tyagi *et al*., 2010). Base catalyzed transesterification is preferred over acid catalyzed transesterification reactions for the production of biodiesel at industrial level because it provides better conversion rates and efficiencies. The basic parameter reflecting the extent of the reaction could be the viscosity, since it is directly related with the fatty acid methyl ester (FAME) content of the product and is one of the specifications to comply with in biodiesel production (Aransiola *et al*., 2012).

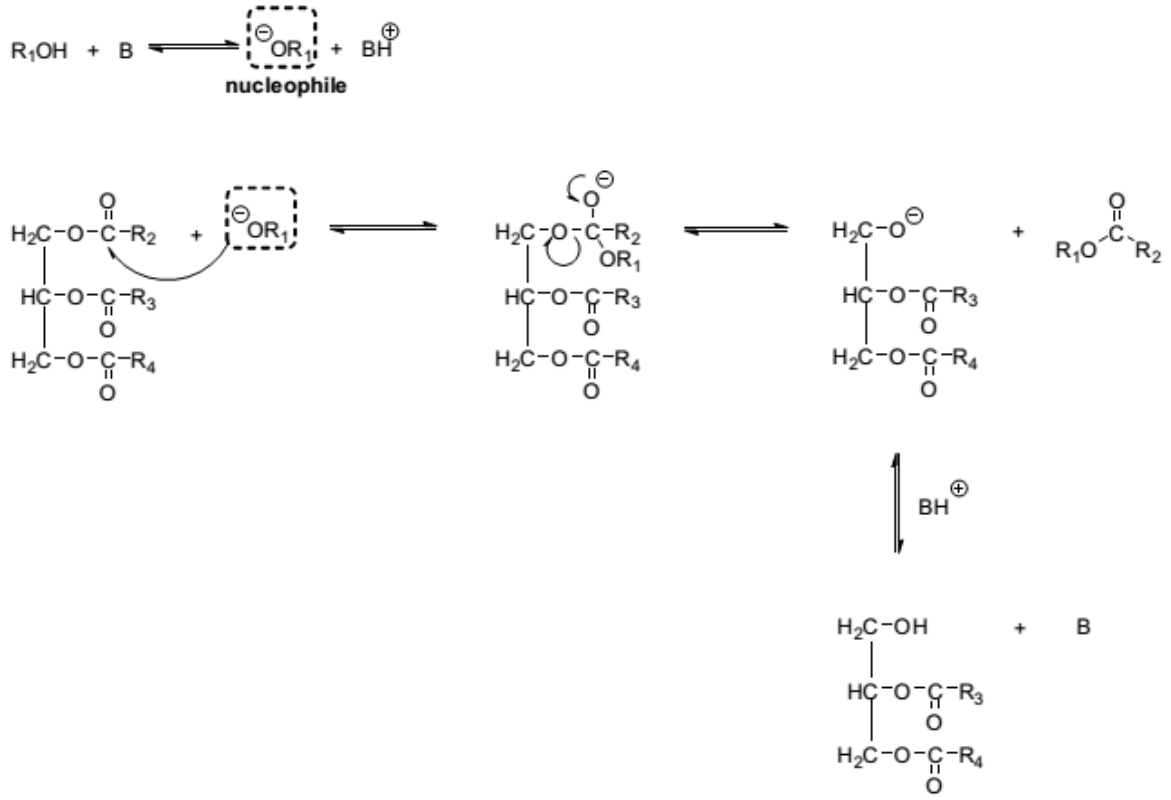

Figure 2: Reaction mechanism for base-catalyzed transesterification during biodiesel production. Where B is a base and R1-4 are hydrocarbon groups

Acid-Catalyzed Transesterification process

This process is especially suitable for the feedstocks like unrefined or waste cooking oils that are high in FFAs. It uses an acid (commonly sulfuric acid) as the catalyst and follows the well known mechanism as shown in **figure 3**. This process does not require the pretreatment of oil with an alkali for reducing its FFA content. However, it has the following drawbacks. It is very slow and needs a very high methanol-to-oil molar ratio. The water produced by the reaction of FFA with the alcohol inhibits the transesterification of triglycerides in this process. The acid, if added in large amounts, would burn some oil, thus reducing the overall yield of biodiesel (Tyagi et al., 2010).

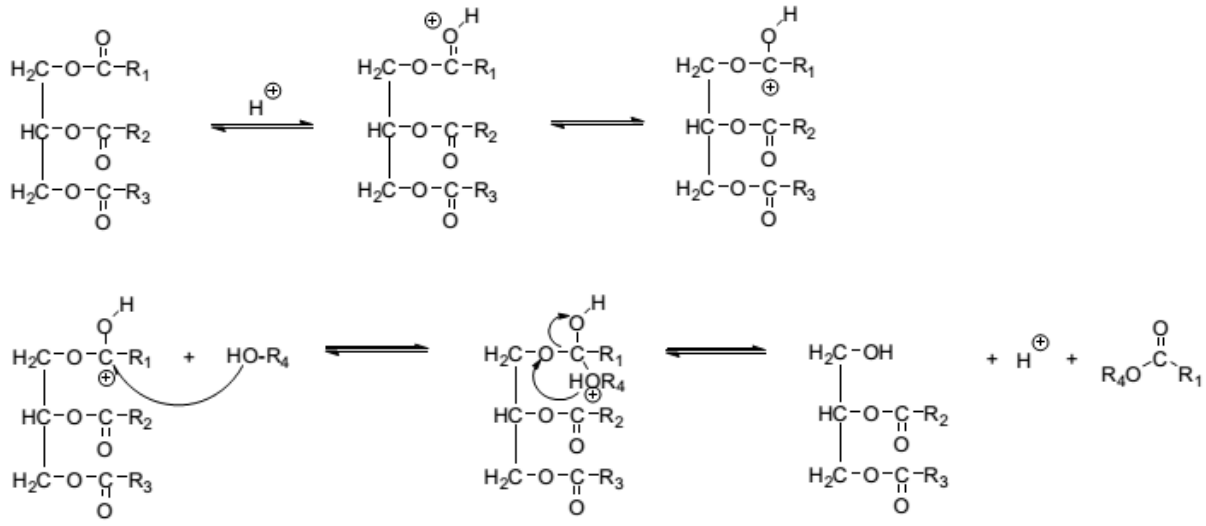

Figure 3: Reaction mechanism for acid-catalyzed transesterification during biodiesel production. Where R1-3 are hydrocarbon groups

Properties of Biodiesel Fuels

Since biodiesel is produced from vegetable oils of varying origin and quality, the pure biodiesel must meet before being used as a pure fuel or being blended with conventional diesel fuels. Various parameters which define the quality of biodiesel are discussed below.

Viscosity

The viscosity of a liquid is a measure of its resistance to flow due to internal friction; this is a very important property of a diesel fuel because it affects the engine fuel injection system predominantly at low temperatures. A highly viscous fuel will result in poor atomization hence a loss of power of the engine and production of smoke. Biodiesel is slightly viscous but their viscosities are still close to that of the petroleum diesel. This is an advantage of biodiesel over its source oils (Alnuami *et al.,* 2014).

High values of kinematic viscosity give rise to poor fuel atomization, incomplete combustion, and carbon deposition on the injectors. Therefore, the biodiesel viscosity must be low. Biodiesel fuel blends generally have improved lubricity; however, their higher viscosity levels tend to form larger droplets on injection which, can cause poor combustion and increased exhaust smoke. Moreover this high viscosity generates operational problems like difficulty in engine starting, unreliable ignition and deterioration in thermal efficiency. Converting to biodiesel is one of the options to reduce the viscosity of vegetable oils (Alnuami *et al.,* 2014). The viscosity of fatty acid methyl esters can go to very high levels

and hence it is important to control it within an acceptable level to avoid negative impacts on fuel injector system performance. Therefore, biodiesel viscosity must be nearly same to that of the diesel fuel (Sanjay, 2013).

Density

Density is a key fuel property, which directly affects the engine performance characteristic. It affects the mass of fuel injected into the combustion chamber and thus, the air-fuel ratio. This is because fuel injection pumps meter fuel by volume not by mass and a denser fuel contains a greater mass in the same volume. Thus, the changes in the fuel density will influence engine output power due to a different mass of fuel injected. It is known that biodiesel density mainly depends on its esters content and the remained quantity of alcohol; hence this property is influenced primarily by the choice of vegetable oil (Encinar *et al*., 2010).

The density of diesel fuels is another important property of the fuels that affects the fuel injection system, density is usually measured at $15^{o}C$. Density of biodiesel is the weight of a unit volume of fluid while the specific gravity is the ratio of the density of a liquid to the density of water. The fuel injection equipment meters the fuel volumetrically and high densities translate into a high consumption of the fuel. it can be seen that biodiesel has densities between $0.860g/cm^3$ and $0.897g/cm^3$ at $15^{o}C$ which is higher than that of the petroleum diesel, however this high density can be said to make up for the low volumetric energy content of biodiesel (Alnuami *et al*., 2014).

Flash point

Flash point of a fuel indicates the minimum temperature at which the fuel will ignite (flash) on application of an ignition source under specified conditions. Flash point varies inversely with the fuel's volatility. Flash point minimum temperatures are required for proper safety and handling of fuels. It is noted that the biodiesel component must meet a flash point criteria, prior to blending, for the purpose of assuring that the biodiesel component does not contain methanol. The flash point of biodiesel is higher than the petro diesel, which is safe for transport purpose. High values of flash point decreases the risk of fire (Sanjay, 2013; Vuppaladadiyam *et al*., 2013).

Biodiesel's have higher flash and fire points than the petroleum diesel meaning that they are less flammable hence they are safer to handle. However, biodiesel has worse oxidation stability than petroleum diesel and will deteriorate under prolonged storage due to oxidation in the presence of air (Alnuami *et al*., 2014).

Cloud point and Pour point

The two most important criteria are the cloud and pour points. The cloud point is the temperature at which is the fuel starts to form crystals, with further decrease in temperature these crystals increase in size and quantity until the fuel gels and does not move again. The pour point is the lowest temperature at which the oil specimen will flow. Both parameters are often used to specify cold temperature usability of fuel oils. The cloud and pour points are related to the cold start of the motor. Biodiesel's have been reported to have relatively high cloud and pour point. Both points must be sufficiently low, because if the biodiesel is frozen, the motor will not start (Sanjay, 2013; Alnuami *et al*., 2014).

The cloud point for Diesel is 4^0C which is very low and the fuel performs satisfactorily even in cold climatic conditions. The higher cloud point can affect the engine performance and emission adversely under cold climatic conditions. The pour point for Diesel is -4^0C. In general higher pour point often limits their use as fuels for Diesel engines in cold climatic conditions. When the ambient temperature is below the pour point of the oil, wax precipitates in the vegetable oils and they lose their flow characteristics, wax can block the filters and fuel supply line. Under these conditions fuel cannot be pumped through the injector (Antony Raja *et al*., 2011).

Lubricity and Cold flow

Biodiesel's have higher lubricity than the petroleum diesel which means that an engine run on biodiesel will be less prone to wear and will last longer. However, the major property of biodiesel, which hampers its use as a neat fuel (B100), is the cold flow property otherwise known as the low temperature flow property. Biodiesel's have been reported to have relatively high cloud and pour point. The cloud point is the temperature at which is the fuel starts to form crystals, with further decrease in temperature these crystals increase in size and quantity until the fuel gels and does not move again. The cloud point is of more importance because it indicates the onset of filterability problems of the fuel in the fuel filter equipment (Alnuami *et al*., 2014).

The Cetane number

The cetane number of a fuel is a measure of the ignition quality of the fuel, the higher the cetane number the better the ignition quality, which is conceptually similar to the octane number used for gasoline. Generally, a compound that has a high octane number tends to have a low cetane number and vice versa. The cetane number measures how easily ignition occurs and the smoothness of combustion. Higher is the cetane number better it is in its

ignition properties. Cetane number affects a number of engine performance parameters like combustion, stability, drivability, white smoke, noise and emissions of CO and hydrocarbons (Sanjay, 2013). On the basis of ignition quality, biodiesel can be said to be better than the petroleum diesel because they have cetane numbers higher than that of the petroleum diesel, this high cetane number is due to higher oxygen contents. This means that they will burn smoothly and with less noise in a diesel engine than petroleum diesel (Alnuami *et al*., 2014; Bello and Agge, 2012).

Acid number and Free Fatty Acid value

Acid number is a measure of acids in the fuel. These acids emanate from two sources: acids utilized in the production of the biodiesel that are not completely removed in the production process; and degradation by oxidation (Sanjay, 2013). This is the quantity of base required to titrate a sample to a specified end point. It is a measure of free fatty acid in biodiesel. Excessive free fatty acid in the fuel can be corrosive and may be a symptom of water in the fuel or poor production or subjected to oxidative degradation. Excessive free fatty acid in the fuel can inhibit the transesterification process and lead to soap formation. The acid values of the oil and FAME are 15.37 mg KOH/gm and 3.37 mg KOH/gm respectively (Bello and Agge, 2012). For biodiesel blends the acid number will change as a result of the normal oxidation process over time. Biodiesel fuel blends that will not be utilized immediately should be monitored for changes in acid number as an indicator of fuel degradation. A high acid value will damage fuel pumps and fuel filters (Sanjay, 2013).

Iodine number

Iodine number is a measure of total unsaturation within a mixture of fatty material. Its value only depends on the origin of the vegetable oil, the biodiesel obtained from the same oil should have similar iodine values (Encinar *et al*., 2010). It is related to the chemical structure of the fuel. Higher iodine value indicates higher unsaturation in fats and oils. Standard iodine value for biodiesel is 120 for Europe's EN 14214 specification. This requirement is limited by the standard limits of linolenic acid methyl ester composition for biodiesel. The limitation of unsaturated fatty acids is necessary due to the fact that heating higher unsaturated fatty acids results in polymerization of glycerides. This can lead to the formation of deposits or deterioration of the lubricating property. Fuels with this characteristic are also likely to produce thick sludges in the sump of the engine, when fuel seeps down the sides of the cylinder into the crank (Sanjay, 2013).

Sulfated Ash and Phosphorus content

This is the alkaline catalyst residue remaining after a fuel sample has been carbonized, and the residue subsequently treated with sulfuric acid and heated to a constant weight. It is a measure of the mineral ash residue when a fuel is burned. It is an important test for biodiesel because it is an indicator of the quantity of residue metals in the fuel that came from the catalyst used in the transesterification process. Especially for base catalyzed transesterification in which the sodium hydroxide and potassium hydroxide commonly used have low melting points and may cause engine damage in combustion chamber, injector deposits or fuel system fouling. The sulfated ash for FAME is 0.010 % (mol/mol) and lower than the 0.05 ASTM maximum limit (Bello and Agge, 2012).

Phosphorus in biodiesel originates from phospholipids (animal and vegetable material) and inorganic salts contained in the feedstock. Phosphorus has adverse effect on long term activity of exhaust emission catalytic systems and therefore limited by specification. The value for the oil is less than the maximum of 10 mg/kg specified by EN standard (Bello and Agge, 2012).

Table 1: Properties of vegetable oil (adapted from Jaichandar and Annamalai, 2011).

Vegetable oil	Kinematic viscosity at 38°C (cSt)	Cetane No.	Heating value (MJ/kg)	Cloud point (°C)	Pour point (°C)	Flash point (°C)	Density (kg/l)
Diesel	3.06	50	43.8	–	–16	76	0.855
Corn	34.9	37.6	39.5	- 1.1	- 40.0	277	0.9095
Cottonseed	33.5	41.8	39.5	1.7	-15.0	234	0.9148
Crambe	53.6	44.6	40.5	10.0	- 12.2	274	0.9048
Linseed	27.2	34.6	39.3	1.7	-15.0	241	0.9236
Peanut	39.6	41.8	39.8	12.8	-6.7	271	0.9026
Rapeseed	37.0	37.6	39.7	-3.9	-31.7	246	0.9115
Safflower	31.3	41.3	39.5	18.3	-6.7	260	0.9144
Sesame	35.5	40.2	39.3	-3.9	-9.4	260	0.9133
Soya bean	32.6	37.9	39.6	-3.9	-12.2	254	0.9138
Sunflower	33.9	37.1	39.6	7.2	-15.0	274	0.9161
Palm	39.6	42.0	–	31.0	–	267	0.9180

Table 2: Biodiesel properties (adapted from Alnuami *et al*., 2014)

property	unit	Jatropha	soybean	Oil palm	WCO	Biodiesel standards ASTM D 6751-02	DIN EN 14214	Diesel fuel
Density at 20 c°	Kg/m^3	880	885	880	884	870-900	875-900	850
Viscosity at 40 c°	Mm^2/s	2.37	4.5	5.7	4.5	1.9 - 6.0	3.5-5.0	2.60
Cloud point	C°	--	1	13	1	--	--	4
Flash point	C°	135	178	164	180	130	120	68
Pour point	C°	2	-7	12	-5.0	-15 to 10	-15 to 10	-20
Water	%	0.025	-	-	0.4	0.03	0.05	0.02
Sulfur	PPM	-	-	-		50	50	500
Carbon residue	Wt.%	0.20	-	-	0.3	-	0.3	0.17
Cetane number	--	61	45	62	57.2	48 - 60	49	49
Calorific value	Mj/kg	39.2	33.5	33.5	32.9	-	-	42

Edible versus Non-edible oils

There are two types of oils; edible and non-edible oils. Edible oils are the major sources to produce biodiesel fuel like sunflower, soybean, and palm oils. Due to higher prices of edible vegetable oils compared to diesel fuel, waste vegetable oils and non-edible crude vegetable oils are now being used as biodiesel sources. There are disadvantages of using edible oil such as: higher viscosity, lower volatility, the reactivity of unsaturated hydrocarbon chains. Due to these disadvantages, vegetable oils are not used directly as biodiesel, so there are methods to enhance the vegetable oil's characteristics for biodiesel production (Alnuami *et al*., 2014).

To evaluate for materials that are more suitable for biodiesel production, there are three important points to consider:

- ✓ Availability of these materials.
- ✓ Properties closer to the standard diesel.
- ✓ Economic value of biodiesel in comparison with fossil diesel.

Also, in comparing edible and non-edible materials, that is oil palm and soybean oil as edible oil with jatropha and waste cooking oil as non-edible oil, it could be seen from the result that non edible oils are more suitable to produce biodiesel because they are

not competitive with the food material, this will preserve the food sources alone even though biodiesel from edible oils have properties closer to standard diesel properties. Also, biodiesel from edible oils are not economical compared with non-edible oils. Jatropha oil and waste cooking oil are more readily available than edible oils. Jatropha appears to have several advantages as a renewable diesel feedstock, because it is non-edible and can be grown on marginal lands; it is potentially a sustainable material for biofuel production. The high oil content of Jatropha curcas indicates that Jatropha curcas is suitable as non-edible plant oil feedstock in oleo chemical industries. Jatropha has been planted in several arid regions, in these regions it only yields about 0.5 ton per hectare. The seeds contain about 30% oil. Biodiesel from Jatropha curcas so obtained is found to be comparable to those of fossil diesel conforming to the American and European standards (Alnuami *et al*., 2014).

Purification of Biodiesel

The crude biodiesel (FAME) contains many impurities like FFAs, soaps, water, glycerol, sterols, unsaponifiable matter, mono- and di-glycerides, triglycerides, alcohol, metal ions, etc. These impurities are detrimental to the storage stability of biodiesel, storage tanks and combustion systems. Therefore, there are two washing processes to purify it.

a. Wet Washing Process

This classical method involves repeated washing of biodiesel with clean water followed by the removal of aqueous phase. It removes most of the impurities from biodiesel since a majority of them are water soluble. This washing process carried out using biodiesel/water volume ratio of 1: 0.5 under stirring at 2000 rpm at ambient temperature for 10 minutes. They found no advantage in using acidified or deionized water as compared to clean tap water, a higher temperature or a more rigorous stirring. Since the solubility of water in biodiesel is about 1500 mg/kg at 20-22° C, a FAME-water emulsion is often formed in the wet washing process. In such a situation, the additional steps are needed to first demulsify FAME and then demoisturize it. This makes the wet washing a costly and time consuming process. Further, the wet washing is not eco-friendly because it requires a large amount of clean water and generates highly contaminated effluents (Tyagi *et al*., 2010).

b. Dry Washing Process

In this water-less purification method, a synthetic adsorbent or an ion exchange resin is employed to bind and remove the ionic salts, traces of catalyst, soaps, glycerin and water from biodiesel. Three commercial products are being promoted as an eco-friendly alternative

to the water washing process. The first is Magnesol®, which is a synthetic magnesium silicate adsorbent promoted by Hydrotechnik, UK and Dallas Corporation, USA. The second product is 'BD10 Dry', which is an ion exchange resin promoted by Rohm and Hass. The third product is 'PD206', which is also an ion exchange resin from Purolite. All these three methods remove glycerin and soaps, but methanol could be effectively removed only by the water-washing process. They found none of these methods capable of significantly decreasing the concentration of glycerides and FFAs in biodiesel or improving the oxidation stability index (OSI) of biodiesel. In the ion exchange method, the contaminants in the feed whenever present in high concentrations can bind permanently with the resin bed and cause a sudden and irreversible loss of the column efficiency. In the dry wash method, the fine particles of resin/adsorbent continuously elute from the column and have to be removed by post-elution ultra filtration of biodiesel. This increases the cost and time of biodiesel production ((Tyagi *et al*., 2010).).

The primary purpose of the biodiesel washing step is to remove any soaps formed during the transesterification reaction. In addition, the warm diluted water with acetic acid provides neutralization of the remaining catalyst and removes product salts. The use of warm water prevents precipitation of saturated fatty acid esters and retards the formation of emulsions with the use of a gentle washing action. Slightly acidic water eliminates calcium and magnesium contamination and neutralizes remaining base catalysts. Gentle washing prevents the formation of emulsions and results in a rapid and complete phase separation (Sarıbıyık *et al*., 2010; Thirumarimurugan *et al*., 2012).

Most Important Variables That Influence the Transesterification Reaction

Transesterification of oil or fat to produce a high yield of biodiesel is typically investigated by optimizing the following reaction variables: alcohol/oil molar ratio, catalyst concentration, reaction temperature, and reaction time involved in the process (Betiku and Adepoju, 2013).

i. Reaction temperature

The literature has revealed that the rate of reaction is strongly influenced by the reaction temperature. However, the reaction is conducted close to the boiling point of methanol (60–70°C) at atmospheric pressure for a given time. Such mild reaction conditions require the removal of free fatty acids from the oil by refining or pre-esterification. Therefore, degummed and deacidified oil is used as feedstock. Pretreatment is not required if the reaction is carried out under high pressure (9000 kPa) and high temperature (240°C), where

simultaneous esterification and transesterification take place with maximum yield obtained at temperatures ranging from 60 to 80 ^{o}C at a molar ratio of 6:1(Shereena and Thangaraj, 2009)

ii. Ratio of alcohol to oil

Another important variable is the molar ratio of alcohol to vegetable oil. As indicated earlier, the transesterification reaction requires 3 mol of alcohol per mole of triglyceride to give 3mol of fatty esters and 1 mol of glycerol. In order to shift the reaction to the right, it is necessary to either use excess alcohol or remove one of the products from the reaction mixture. The second option is usually preferred for the reaction to proceed to completion. The reaction rate is found to be highest when 100% excess methanol is used. A molar ratio of 6:1 is normally used in industrial processes to obtain methyl ester yields higher than 98% (w/w) (Shereena and Thangaraj, 2009)

iii. Catalysts

The concentration of the catalyst is an important parameter of the transesterification reaction and a strong influence on the yield of the isolated methyl esters. Excess catalyst reacted with the oil, leading to the formation of soap, thus as the catalyst concentration increased, the separation of esters became difficult (Babajide *et al*., 2009). The most suitable catalyst for this process proved to be potassium methoxide. The other basic catalyst, potassium hydroxide, achieved similar results but its methyl esters contents were slightly lower. On the other hand, the acid catalysts studied, sulfuric and phosphoric acid, obtained yields in methyl esters are poor, even with higher catalyst concentrations. In the case of phosphoric acid, its yield was negligible. The optimum concentration of potassium methoxide catalyst is 1 wt. % (Encinar *et al*., 2010). A catalyst is used to hasten up the process and Sodium hydroxide (NaOH) and potassium hydroxide (KOH) are the common catalyst used in the reaction process (Ojiego *et al*., 2014). High concentrations of alkaline catalyst form soaps in the presence of large residues of fatty acids resulting in emulsion formation between soaps and water molecules, thus leading to low yields of methyl esters (Babajide, 2009).

iv. Mixing intensity

Most literatures indicate that during the transesterification reaction, the reactants initially form a two-phase liquid system. The mixing effect has been found to play a significant role in the slow rate of the reaction. As phase separation ceases, mixing becomes insignificant. The effect of mixing on the kinetics of the transesterification process forms the basis for process scale-up and design (Shereena and Thangaraj, 2009).

v. Purity of reactants

Impurities in the oil affect the conversion level considerably. It is reported that about 65–84% conversion into esters using crude vegetable oils has been obtained as compared to 94–97% yields refined oil under the same reaction conditions. The free fatty acids in the crude oils have been found to interfere with the catalyst. This problem can be solved if the reaction is carried out under high temperature and pressure conditions (Shereena and Thangaraj, 2009).

Conclusion

Biodiesel is a good alternative fuel for diesel engines because it is environmentally friendly and renewable in nature. There are different methods of producing biodiesel but transesterification of vegetable oil and fats are predominantly used method these days. Researchers focus more on the production of biodiesel using edible oils but the use of non-edible oil for biodiesel production has contributed immensely to its cost reduction. The governments should make full use of these biodiesel resources and ensure international diesel security as a long lasting supplement. The combustion characteristics of biodiesel are similar as diesel and the engine power output with biodiesel is found to be equivalent to that of diesel. Moreover, the use of biodiesel in diesel engine results in drastic reduction engine emissions. Therefore, from this review, we concluded that the biodiesel is a better alternative renewable fuel for the diesel.

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