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"Characterization of Biodiesel: A Review"

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Abstract

It is well known for us, biodiesel is an alternative substitute for fossil diesel. Biodiesel is basically Fatty Acid Methyl Ester Based Fuel, a long chain of Triglycerides and the Alcohol in the presence of Catalyst forms Ethyl Esters and the Glycerol that process is known as Transesterification, if the fatty acid content in the oil is more than 2.5% then the process by which the oil is converted to ethyl esters is known as Esterification followed by Transesterification.

This review paper mostly concentrates on the characterization of biodiesel; most of the Physio – Chemical properties like Density, Kinematic Viscosity, Flash Point, Cetane Number, and the heating value these are related to combustion. This paper is having the information about physio—chemical properties of biodiesel and fossil diesel and the availability of various feedstock for biodiesel production in the world.

Keywords: *Biodiesel, Transesterification, Esterification, Characterization of Biodiesel.*

1. Introduction

Now a days Energy Crises is one of the important issues for us, Fossil diesel has utilized everywhere in the world for production processes of the industry, transportation sectors, and also used in ships, motor Vehicle etc. But the emission produced by that fossil diesel after burning is very ineffective for our health and also for climate, it increases air pollution and global warming. Fossil diesel contributes almost 80% of the world's energy needs [*1*].

Most of the country in the world that are agricultural, due to fluctuating global prices of the crude oil has an adverse impact on the economy of many nations especially oil importing countries, apart from the fossil diesel is non – renewable source of energy, due to the depletion of fossil diesel fuels, the prices are also increasing day by day ultimately it leads to the economic recession in the various developing countries. If we see previous data the Diesel consumption of India in 2008 – 2009 was 51.7 million tons and 159.7 million tons of CO_2 was likely to be generated by such usage of fossil diesel [*9*].

So the next alternative available for this fossil diesel is Bio—diesel because it is clean and Renewable source of energy. Every country has specific variety of feedstock oil for their biodiesel production; some key countries and their feedstock has revealed in the Table 1.

Table 1: The Countries and Feedstock around the World: [*1, 3*].

Sr. No.	Country	Raw Product or Feedstock
1.	Mexico	Animal Fat, Waste Oil
2.	Canada	Canola Oil, Animal Fat
3.	USA	Soybean Oil, Waste Oil
4.	Brazil	Soybean Oil, Palm Oil, Caster Oil, Cotton Oil
5.	Spain	Sunflower Oil
6.	France	Rapeseed Oil, Sunflower Oil
7.	UK	Rapeseed Oil, Waste Oil
8.	Sweden	Rapeseed Oil
9.	Finland	Rapeseed Oil, Animal Fat
10.	Germany	Rapeseed Oil
11.	Italy	Rapeseed Oil
12.	India	Jatropha Oil, Karanja Oil, Mahua Oil
13.	China	Jatropha Oil, Waste Oil
14.	Thailand	Palm Oil, Jatropha Oil, Coconut Oil
15.	Malaysia	Palm Oil
16.	Indonesia	Palm Oil, Jatropha Oil
17.	Russia	Rapeseed Oil, Soybean Oil, Sunflower Oil
18.	Japan	Waste Oil
19.	Korea	Waste Oil
20.	Philippine	Coconut Oil, Jatropha Oil
21.	Australia	Waste Oil, Animal Fat
22.	New Zealand	Waste Oil, Animal Fat

As we have expected from the alternative fuel i.e. Biodiesel that must be technically feasible, economically competitive, environmentally acceptable, and easily available in the world. The current alternative fuel can be termed Biodiesel. Biodiesel can offer other benefits, including Greenhouse emissions, regional development, and social structure, especially to developing countries [*1, 3, 14*].

Some of the researchers like [*Krawezyk et. al. 1966, Kerutzer et. al. 1984, schwab et. al. 1987, Daming Huang, 1*] have put the definition for biodiesels, Biodiesel is defined as oxygenated, sulfur free, Biodegradable, Non – Toxic, and ecofriendly diesel oil. [*Demirbas Ayhan, 3*] Biodiesel (Greek, Bio, Life + Diesel from Rudolf Diesel) refers to a diesel equivalent, processed fuel from biological sources. Biodiesel fuels are attracting increasing attention worldwide as blending component or direct replacement for the diesel fuel in the vehicle engine. Biodiesel comprises alkyl fatty acid (Chain length C_{14} – C_{22}) esters of short chain alcohols, primarily, methanol or ethanol. [*Connemann and Fischer et. al. 1998, Ma and Hanna et. al. 1999, Van Gerpen et. al. 2005, Canakci et. al. 2007, Daming Huang, 1, 13*] chemically, Biodiesel can be defined as a fuel composed of Mono – alkyl esters of long chain fatty acids derived from renewable energy sources, such as vegetable oil, animal fat, etc. designated as B100 and it must meet to the requirements of (American Society of Testing and Materials) ASTM D 6751 standards and (European Nations) EN 14214 standards.

Few of the Technical Properties of Biodiesels are same as that of Fossil Diesel and some properties are slightly higher than fossil diesel. The biodiesel is having Density is in the range of 860 – 900 kg/m^3 as per ASTM D6751 standard and Fossil Diesel is having 800 – 860 kg/m^3 as per ASTM D 975 standard. Kinematic Viscosity of Biodiesel is in the range of 1.9 – 6.0 mm^2/s as per ASTM D6751 standard and 3.5 – 5.0 mm^2/s as per EN 14214 standards and for Fossil diesel the range is given 1.3 – 4.1 mm^2/s as per ASTM D 975 standard. The Flash point of biodiesel is given 130^{0}C mini-mum as per ASTM D 6751 standard and for Fossil diesel is 52^{0}C as per ASTM D975 standard. The Copper Strip Corro-sion is same for both the fuels as per ASTM D 6751 and ASTM D 975 standards. The Cetane Number is slightly high-er for Biodiesel i.e. 47 minimum as per ASTM D 6751 stand-ard and for Fossil Diesel 40 minimum as per ASTM D 975 standard [15,17].

The Biodiesel is Insoluble in water and having light to Dark Yellow, clear liquid physical appearance. The Biodiesel is basically Light Musty or Soapy Odor and it is more biodegradable than fossil diesel. The general technical properties of Biodiesel have laid down in the Table 2.

Biodiesel is same as that of Fossil Diesel; as per the ASTM Standards comparison of Biodiesel with Fossil Diesel have laid down in the Table 3.

The Higher Heating or Gross Heating Values of Biodiesels are relatively high. The HHV's of Biodiesel is in the Range of 39 – 41 MJ/kg are slightly lower than of gasoline i.e. 46 MJ/kg, Petro – Diesel i.e. 43 MJ/kg but higher Coal, the Coal is having HHV's is in the Range of 32 – 37 MJ/kg [*3*].

Table 2: Technical Properties of Biodiesel [*3*].

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 40^{0}C)	1.9 – 6.0 as per ASTM and 3.5 – 5.0 as per EN
Density Range (kg/m^3 at 15^{0}C)	860 – 900
Boiling Point (:C)	>202
Flash Point Range (:C)	147 – 177
Distillation Range (:C)	197 – 327
Vapour Pressure (mm of Hg at 22^{0}C)	<5
Solubility in Water	Insoluble in Water
Physical Appearance	Light to Dark Yellow, Clear Liquid
Odor	Light Musty, Soapy Odor
Biodegradability	More Biodegradable than Fossil Diesel
Reactivity	Stable, but avoid oxidizing agents

Table 3: ASTM Standards of Biodiesel and Fossil Diesel [3].

Property	Test Method	ASTM D 975 (Petro-diesel)	ASTM D 6751 (Biodiesel, B100)
Flash point (in ^{0}C)	D93	52 min	130 min
Water & Sediments	D 2709	0.05 max % vol.	0.05 max % vol.
Kinematic Vis-cosity @ 40^{0}C	D 445	1.3 – 4.1 mm^2/s	1.9 – 6.0 mm^2/s
Sulfated Ash	D 874	-	0.02 max %wt.
Ash	D 482	0.01 max % wt.	-
Sulfur	D 5453	0.05 max % wt.	-
Sulfur	D 2622 /129	-	0.05 max %wt.
Copper Strip Corrosion	D 130	No. 3 max	No. 3 max
Cetane Number	D 613	40 min	47 min
Aromaticity	D 1319	35 max % vol.	-
Carbon Residue	D 4530	-	0.05 max % mass
Carbon residue	D 524	0.35 max % mass	-
Dist. Temp. (90 % vol. recycle)	D 1160	282^{0}C min – 338^{0}C max	-

The Specifications and Test Methods of Biodiesel as Per ASTM D 6751 Standards and as per EN 14214 Standards have shown in Table 4.

Table 4: Specification and Test Methods of Biodiesel as per ASTM D6751 & EN 14214 Standards.

Property	Unit	Limits		Test Method	
		ASTM D 6751	EN 14214	ASTM D 6751	EN 14214
Flash point	^{0} C	130 min	101 min	D93	ISO CD 3679e
Kinematic viscosity @ 40^0 C	mm^2/s	1.9 – 6.0	3.5 – 5.0	D445	EN ISO 3104
Cetane Number	-	47 min	51 min	D 613	EN ISO 5165
Sulphated Ash Content	% (m/m)	0.020 max		D874	ISO 3987
Copper Strip Corrosion	-	No. 3 max	Class 1	D 130	EN ISO 2160
Acid Value	mg KOH/g	0.80 max	0.5 max	D 664	pr EN 14104
Free Glycerol	% (m/m)	0.020 max		D 6584	pr EN 14105m pr EN 14106
Total Glycerol	% (m/m)	0.240 max	0.25 max	D 6584	pr EN 141101
Phosphorous Content					
Carbon Residue D 6751 (100% sample) EN 14214 (10% Bottoms)	% (m/m)	0.050 max -	- 0.3 max	D 4530 -	- EN ISO 10370
Cloud point	^{0} C	Report Customer	-	D 2500	-
Density at 15^0 C	Kg/m^3	-	860 – 900	-	EN SIO 3675 EN SIO 12185
Distillation T90 AET	^{0} C	360 max	-	D 1160	-
Sulfur (S 15 grade)	ppm	0.0015 max	-	D 5453	-
Sulfur (S 500 grade)	ppm	0.05 max	-	D 5453	-
Sulfur content	mg/kg	-	10 max	-	-
Water & Sediments	% vol.	0.050 max	-	D 2709	-
Water content	mg/kg	-	500 max	-	EN ISO 12937
Total contamination	mg/kg	-	24 max	-	EN 12662
Oxidation stability at 110^0 C	h	-	6 min	-	pr EN 14112
Iodine value	-	-	120 max	-	pr EN 14111
Linolenic acid methyl ester	% (m/m)	-	12 max	-	pr EN 14013d
Polyunsaturated (>= 4 double bonds) methyl esters	% (m/m)	-	1 max	-	pr EN 14103
Ester content	% (m/m)	-	96.5 min	-	pr EN 14103d
Methanol content	% (m/m)	-	0.2 max	-	pr EN 141101
Monoglyceride content	% (m/m)	-	0.8 max	-	pr EN 14105m
Diglyceride content	% (m/m)	-	0.2 max	-	pr EN 14105m
Triglyceride content	% (m/m)	-	0.2 max	-	pr EN 14105m
Alkaline metals (Na + K)	mg/kg	-	5 max	-	pr EN 14108 pr EN 14109

AET: Atmospheric Equivalence Temperature.

Biodiesel is not a simple vegetable oil and the biodiesel properties can very according to the feedstock used. All major U.S. manufacturers of diesel engine endorse the use of biodiesel.

2. Literature Survey:

A. Density:

The density of a material or liquid is defined as its mass per unit volume. Many researchers prefer the dimensionless term specific gravity, which is defined as the ratio of the density of a substance to the density of a reference substance (usually water) [20]. Density of the biodiesel, diesel fuel and their blends can be measure by ASTM Standard D 941 or as per European Standard of EN ISO 3675 and EN ISO 12185 test methods. Most of the Researchers have used Anton Paar density meter, Pycnometer, and Hydrometer in the measurement of Density at room temperature or at stated temperature i.e. 15^0 C [20, 22, 30]. From various researcher papers The (average) densities of the 25 investigated methyl esters, again excluding castor, range from 870.8 to 891.5 kg/m^3, with the overall average value being 880.2 kg/m^3 (i.e. almost 5% higher than the corresponding fossil diesel value). Density increases with the decrease in chain and with unsaturation [20,22]. Density can impact on fuel consumption as fuel introduced into the combustion chamber is determined by volumetrically [6]. Biodiesel fuels are, in general, characterized by higher density than conventional fossil diesel, which means that volumetrically-operating fuel pumps will inject greater mass of biodiesel than fossil diesel fuel [11,24]. Since the flow is controlled by volume, the expected peak power reduction for engines using B100 is only 5 to 7 % less than the fossil diesel because more (g/ml) would flow and vaporize more efficiently given a set throttle (volume) [12,23]. It should be noted that biodiesel produces more than three times the energy as the same amount of fossil fuel. Biodiesel's higher Specific gravity and Density relative to fossil diesel means that on road biodiesel blends are normally made by splash blending the biodiesel fuel on top of the conventional diesel fuel or fossil fuel [12]. The biodiesel has an average density i.e. Crude oil density is 12% higher than the fossil diesel [11]. Actually, it has been argued that there exists a correlation between density and NOx emissions, with lower densities favoring lower NOx, although other researchers have not confirmed such an unequivocal trend [11].

B. Viscosity:

Kinematic viscosity is the primary reason why biodiesel is used as an alternative fuel instead of neat vegetable oils or animal fats [5]. Viscosity is a measure of the internal fluid friction or resistance of oil to flow, which tends to oppose any dynamic change in the fluid motion [6,25]. Kinematic Viscosity of the biodiesel, diesel fuel and their blends can be measure by ASTM Standard D 445 or as per European Standard of EN ISO 3104 and EN ISO 3105 test methods [31]. The Viscosity ranges have given as per the ASTM D445 standard 3.5 to 5.0 mm^2/s and as per the EN ISO 3104, 05 standard 1.9 to 6.0 mm^2/s [25,31]. Most of the researchers have used Redwood Viscometer, Setavis Kinematic Viscometer, and Canon – Fenske Viscometer Tube of size No. 75, 100 used in the Viscometer Bath for Viscosity measurement [6,27]. The kinematic viscosity was determined at 40^0C by multiplying the constant of viscometer tube and the measured efflux time, which is the time for a known volume of liquid flowing under gravity to pass through a calibrated glass capillary viscometer tube. **Kinematic viscosity = Calibration constant (mm^2/s^2) x mean time of flow (s) in mm^2/s.** Crude Vegetable oils have high viscosity (one order of magnitude higher than the acceptable diesel fuel values), which means that they cannot be used safely as fuels in a compression ignition engine, at least not without prior heating (viscosity decreases exponentially with increasing temperature), and only for relatively small blending ratios[11]. The Crude vegetable oils have highest viscosity than biodiesel and biodiesel have higher viscosity than fossil diesel, the crude vegetable oil have viscosity 10 to 17 times higher than that of Biodiesel [18]. Several structural features influence the kinematic viscosities of FAME, such as chain length, degree of unsaturation, double bond orientation, and type of ester head group. Factors such as longer chain length and larger ester head group result in increases in kinematic viscosity[11]. Increasing the degree of unsaturation results in a decrease in kinematic viscosity and as the temperature of oil is increased its viscosity decreases and it is therefore able to flow more readily. Double bond orientation also impacts kinematic viscosity[5,6]. Viscosity is the most important property of lubricating oil, as it affects the wear rate of engine components. Relatively higher viscosity of biodiesel helps in plugging the clearance between piston rings and cylinder liner effectively, thus reducing blow-by losses and fuel dilution of lubricating oil[27]. In a diesel engine, higher viscosity leads to less accurate operation of the fuel injectors, and to poorer atomization of the fuel spray, increase in the Sauter mean diameter of the fuel droplets and of the jet break -up time; these inefficiencies are exaggerated during cold starting. Due to the large molecular size of the triglycerides making up about 98 % of plant oils, viscosity is higher and volatility is lower than fossil diesel[5]. The Brake Power of an engine working with plant oils or blends varies in the range of +10% to -18% compared to engines running on fossil diesel under similar operating conditions. However, according to most reports there is power decrease around 2% to 18%. Possible problems are:

- Higher viscosity interferes with the injection process and leads to poor atomization, leading in turn into inefficient mixing of air and fuel which contributes to incomplete combustion.
- It also causes some plant oil to be left unburnt and penetrate the engine crankcase which can cause loss of power [5].

C. Flash Point:

Biodiesel and diesel have a common boiling point, but biodiesel has higher flash point – the temperature at which a fuel will catch fire – because biodiesel has higher number of FAMEs which are generally not volatile [6]. Flash point varies inversely with the fuel's volatility. Thus, biodiesel is safer to handle at higher temperature than fossil diesel. Flash Point of the biodiesel, diesel fuel and their blends can be measure by ASTM Standard D 93 or as per European Standard of EN ISO 3679 and IP 523 & IP 524 test methods[31]. Most of the researchers have used Pensky Marten Closed Cup Apparatus in the measurement of Flash Point[5,6,11]. The minimum temperature ranges have given as per the ASTM D 6751 standard 130^0C and 101^0C as per EN 14214 standards. The Flash Point of Non – Edible oils is much higher than that of fossil diesels [31].

It also can be transported conveniently and more safely than fossil diesel, due to its high flash point which enables it to be identified as safe goods[14,15]. Flash point temperature indicates the overall flammability hazard in the presence of air, higher flash point makes for safe handling and storage. Especially Methanol which is a particular hazard to its invisible flame [5,17,18]. As the impurities increases in the Biodiesel and Diesel Blends ultimately the Flash Point also increase [6].

D. Cetane Number:

One of the most influential properties of the diesel fuel is the dimensionless cetane number (CN), which represents the ignitability of the fuel, particularly critical during cold starting conditions [5]. Cetane number of the fuel is defined as the percentage by volume of the normal cetane in a mixture of normal cetane and α – methyl naphthalene which has the same ignition characteristics (ignition delay) as the test fuel, when combustion has carried out in a standard engine under specified operating conditions [6]. The cetane number of the Biodiesel and fossil diesel can be measured by D 613 as per the ASTM D6751 standard and EN ISO 5165 as per the EN 14214 standard. The limit is giv-en for Cetane Number as per the ASTM D6751 standard 47 minimum and as per EN 14214 standard 51 minimum for Biodiesel and cetane number limit is given for fossil diesel 40 minimum as per ASTM D975 standard [31]. The physical and chemical properties of the fuel play very important role in the delay period. The cetane number (CN) of the fuel is one such important parameter which is responsible for the delay period [29,30]. The ignition quality of the fuel is measured by cetane number (CN) and it measures how easily ignition occurs. A fuel with good ignition quality has higher Cetane Number, where the ignition delay period between the start of the fuel injection and the onset of auto ignition is short [27]. The higher Cetane Number, Shorter the Ignition delay time and vice versa. The cetane number assists in the smooth combustion with lower knocking characteristics in the diesel engine [5]. The cetane number requirement for the engine depends on the fuel composition and influences the beginning of the process of combustion and emissions. The cetane number of methyl esters depends on fatty acids of feedstocks [11]. Cetane number decreases as the number of double bonds (or the unsaturation) increases [11]. Low cetane number lead to long ignition delay, i.e. long time between fuel injection and start of combustion [12]. A fuel of higher cetane number gives lower delay period and provides smoother engine operation[27]. Biodiesel has a higher cetane number because of its higher oxygen content [31].

E. Heating Value:

The lower (LHV) and the higher (HHV) heating values are measures of a fuel's heat of combustion, with the difference between them being the water's heat of vaporization [20,21]. Biodiesel contains on average 10 – 12% w/w oxygen, which leads to proportionally lower energy density and heating value, thus more fuel needs to be injected in order to achieve the same engine power output [30]. Some of the Researchers have measured the Heating Value of the biodiesel, and their blends can be measure by ASTM Standard D 240 or as per DIN Standard of DIN 51900, DIN 51900-1, and DIN 51900-2, DIN 51900-3 test methods [31]. Most of the researchers have used Bomb Calorimeter Apparatus in the measurement of Heating Value but there is no specification as regards the biodiesel heating value, neither in the EU nor in the US [5]. Previous research has shown that the energy content of fatty acid methyl esters is directly proportional to chain length (again for pure fatty acids), whereas FAME with similar C:O but lower C:H ratios (i.e. more hydrogen) exhibit greater LHV [11]. As a result, lower energy content is obtained from progressively greater levels of unsaturation for methyl esters of similar chain length [26]. Increasing the unsaturation or the number of double bonds, results in a moderate increase in the FAME heating value [30]. The higher the oxygen content, hence the lower the heating value, the higher the potential for PM reduction [27]. On the other hand, the fact that greater mass of biodiesel needs to be injected in order to achieve the same engine power as with conventional diesel fuel is responsible for an increase in NOx emissions in EGR equipped engines/vehicles; the latter engines rely on the mass flow signal in order to determine the appropriate EGR valve position [27]. The low heating value of Crude Vegetable oil, the maximum peak pressure of the cylinder reduced than fossil diesel and heat release diagram reveals that the oil vaporizes and burns at a slower rate than fossil diesel. Due to higher oxygen content of the biodiesel that produces more complete combustion of the fuel and soot. B100 has lower energy content than the diesel fuel by 11% [27,31].

3. Conclusion:

a. As the various kinds of feedstocks available in the world every country has its own biodiesel types in that every country is having their own feed stocks. The biodiesel is having some properties similar to the fossil diesel but some properties higher than the fossil diesel.

b. As we see the density of biodiesel is slightly higher than the fossil diesel and less than the water. The density decreases as the temperature increases and vice—versa. It has also cleared that every feed stock having different densities.

c. The biodiesel is having higher density that's why ASTM D6751 standard says use biodiesel for blending purpose up 20 % only because 20 % biodiesel is having kinematic viscosity similar to the fossil diesel. Other blends like B30 to B100 are having more kinematic viscosity than the fossil diesel.

d. The biodiesel is having high flash point than the fossil diesel because fossil diesel is HC based fuel and Biodiesel is FAME based. Due to high flash point it is easy in the transportation.

e. Fossil diesel is having 47 dimensionless Cetane number as per the ASTM D975 standard and Biodiesel is having 51 as per the ASTM D6751 standard and 52 as per the EN 14214 standard, so higher cetane number means clean burning of the fuel with lesser time.

f. The biodiesel is having 10 to 12 % less higher heating value because of more oxygen content and the efficiency of the engine decreases 2 to 12 % because of less heating value.

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