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A Review on Dependence of Biodiesel Properties on the Structure of Fatty Acids

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Abstract: *In order to improve the economy of a country, we need to develop the Energy sector i.e., use age of the fossil fuels, because of depletion of the fuels leads to down the human leaving style. Therefore we are in need to search the alternate fuel for the substitute of the petroleum fuels to extend the life of the fossil fuels as well as to decreasing the global warming. In this present work the review of dependence of Biodiesel properties on the structure of Fatty acids is analyzed. Since the biodiesel gives less emission such CO, HC and* CO_2 *and whereas* NO_X *in a proportionate manner. The basic fuel properties depends upon the various free fatty acids which are present in the biodiesel (FFA) may be saturated or unsaturated, saturated is one which does not except any further addition of hydrogen and has single bond. Whereas unsaturated biodiesel excepts further addition of hydrogen and has double or triple bonds.*

Keywords—Fuel; Biodiesel blends; Emissions; FFA; Saturated; Unsaturated.

1. INTRODUCTION

Biodiesel is a renewable fuel, biodegradable and nontoxic. It is an ester based oxygenated fuel made from an any vegetable oil (edible oil or nonedible) or animal fat. Bio-Diesel is produced by a simple chemical reaction between the vegetable oil and alcohol in the presence of an acid or base as catalyst. It contains around 10% built in oxygen by weight and has no sulphur, biodiesel has an excellent lubricant properties. The built in oxygen makes more completely combustible in the combustion chamber, its energy is similar to that of the diesel fuel because of same number of cetane is present in it. It is defined as mono-alkyl esters of long fatty acids derived from vegetable oils or animal fat which conform to ASTM D6751. Diesel engines operated on biodiesel comparatively will have less emission of carbon monoxide (CO), unburned hydrocarbons (HC), particulate matter (PM) and air toxics than when operated on petroleum-based diesel fuel.

2. PROPERTIES OF BIODIESEL

The properties of biodiesel decides the performance and emission characteristics of diesel engine, it also influence the combustion characteristics. The physical chatcetrstics dealt in this paper are calorific value,viscosity, density, flash point, fire point, pour point and lubricity. The property of the biodiesel depends very much on the nature of its raw materials as well as the technologies related to biodiesel conversion process.

2.1 Calorific valve

It is the amount of heat realised by burning unit mass of fuel. The calorific value of the biodiesel is ranging from 39 to 43 MJ/kg, whereas the fossil diesel has ranging from 44 to 49 MJ/kg. It shows that biodiesel has lesser calorific value than the diesel fuel.

2.2 Viscosity

It is the flowablity of the fuel during the operating conditions, the viscosity of the biodiesel ranging from 5Cst to 7Cst, where the fossil fuel diesel has 3.5 to 4.5Cst. Since the biodiesel has higher viscosity which leads to poor atomization.

2.3 Density

It is the heaviness of the fuel, the density of the biodiesel ranging from 850 to 950 Kg/m^3, where has the fossil fuel diesel as ranging from 750 to 850 Kg/m^3. Since the biodiesel has higher density which leads to poor vaporization and incomplete combustion.

2.4 Flash point

It is the temperature at which the fuel will get first flash, since the biodiesel has higher density and poor vaporization by this the flash point of the biodiesel is higher than the diesel fuel by 10 to 15^0C. Similarly the fire point and pour point of the biodiesel are higher than the diesel fuel.

3. IMPORTANCE OF FREE FATTY ACIDS

The above fuel properties depend on the fatty acids present in the biodiesel. Fatty acid has either single bond or double bond. The important fuel properties of the biodiesel that are influenced by the fatty acid profile are cetane number, heat of combustion, cold flow properties, oxidative stability and lubricity. The structural formulae for the different fatty acids are listed in table 1.The fatty acids vary in their carbon chain length and in number of double bonds of carbons [Babu, et al 2003]. Fatty acids may be saturated or unsaturated. A saturated fat is one that cannotaccept additional hydrogen and contains only single carbon-carbon bonds. An unsaturated fat can be hydrogenated and contains one or more double bonds [Graboski, et al 1998]. Structural features that influence the fuel properties of a biodiesel are

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chain length, degree of unsaturation, and branching of the chain.

Table 1: Structural Formula for fatty acids

Acid Chain	C:N	Type	Structure
Caprylic	C8:0	S	CH_3 $(CH_2)_6$ COOH
Capric	C10:0	S	CH_3 $(CH_2)_8$ COOH
Lauric	C12:0	S	CH_3 $(CH_2)_{10}$ COOH
Myristic	C14:0	S	CH_3 $(CH_2)_{12}$ COOH
Palmitic	C16:0	S	CH_3 $(CH_2)_{14}$ COOH
Palmitoleic	C16:1	US	CH_3 $(CH_2)_5$ CH=CH $(CH_2)_7$ COOH
Stearic	C18:0	S	CH_3 $(CH_2)_{16}$ COOH
Oleic	C18:1	US	CH_3 $(CH_2)_7$ CH=CH (CH_2) COOH
Linoleic	C18:2	US	CH_3 $(CH_2)_4$ CH=CHCH $_2$ CH=CH (CH_2) COOH
Lenolenic	C18:3	US	CH_3 CH_2CH=CH CH_2CH=CH CH_2CH=CH $(CH_2)_7$ COOH
Arachidic	C20:0	S	CH_3 $(CH_2)_{18}$ COOH
Eicosenoic	C20:1	US	CH_3 (CH_2) CH=CH (CH_2) COOH
Behenic	C22:0	S	CH_3 $(CH_2)_{20}$ COOH
Erucic	C22:1	US	CH_3 (CH_2) CH=CH $(CH_2)_{11}$ COOH

Important fuel properties of biodiesel that are influenced by the fatty acid profile are cetane number, heat of combustion, cold flow properties (pour point and cloud point), oxidative stability, viscosity, and lubricity.

In Table 1, C: N, indicates, C the number of carbon atoms and N the number of double bonds of carbons in the fatty acid chain, US= unsaturated fatty acids and S= Saturated fatty acids. The four major fatty acid alkyl esters that influence the fuel properties are, Palmitic, Stearic, Linoleic and Linolenic [Gerhard Konthe].

3.1 Fuel Properties And The Influencing Structural Features

3.1.1. Cetane number

- Higher cetane numbers were observed for esters of saturated fatty acids Such as palamitic and stearic acids [GerahardKonthe, et al 2003]
- Low cetane numbers were observed with more highly unsaturated fatty acids such as linoleic and linoleic acids [GerahardKonthe et al 2003]
- The increasing number of double bonds and their positions in the chain causing lower cetane number.[A.Gopinath, et al 2010]
- Ceatane number generally increases with number of methylene groups (CH_2)In the chain of fatty acid[G.konthe et al 2005]
- Cetane number also dependence on the double bond and increases if the double bond moves towards one end of the molecule.
- Cetane number increase in molecular weight of fatty acids non linearly[Yamane K 2001]
- The Ceatne number increases with increase in lauric, myristic, Palmitic, and stearic fatty acids, wheras cetane number decreases with increase in olelic, linoleic and linolenic fatty acids[A Gopinath, et al 2010]

3.1.2. Heat of combustion

- Heat of combustion increases with increase in chain length and decreases with an increasing unsaturation[Gerhard konthe 2008]

3.1.3. Cold flow Properties

- Cold flow properties(cloud point and pour point) saturated fatty acids have significantly higher melting points than unsaturated fatty compounds and in mixture they crystallize at higher temperature than the unsaturates.Thus biodiesel fuels with significant amount of saturated fatty acids compounds will displace higher cloud points and pour points[Gerhard Konthe 2005]
- Cold flow properties increases with increasing number of CH_2 and decrease with an increasing unsaturation [Gerhard Konthe 2008]

3.1.4. Kinematic viscosity

- Viscosity increases with chain length (number of carbon atoms) and with increasing degree of saturation. Number of double bonds and position of the double bonds affects the viscosity. Branching of fatty acids has less or no influence on viscosity[G.Konthe et al 2005]
- Viscosity increases with increasing in number of CH_2 group in the fatty acids[Gerhard Konthe 2008]

3.1.5. Lubricity

- Unsaturated fatty acids exhibited better lubricity than saturated fatty acids[G.Konthe, et al 2005]

3.1.6. Oxidative stability

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- The unsaturated fatty acids like linoleic and linolenic acids influence the oxidative stablility. The number and position of the double bond influence the oxidative stability [G. Konthe, et al 2005]

- Saturated fatty acids are very oxidative stable, while double bonds are susceptibility to reaction with oxygen. Fatty acid chains with CH_2 interrupted fatty acids are very oxidative stable, while double bonds are susceptibility to reaction with oxidative stable, while double bonds are susceptibility to reaction with oxygen. Fatty acids chains with CH_2 interrupted double bonds are susceptibility to oxidation[Gerhard Konthe 2008].

4. Literature Survey

A**GehardKnotheet, al (2005)**, Analysed the most important fuel properties of biodiesel and conventional diesel fuel derived from petroleum is viscosity, which is most important property of lubricants. The allowable ranges of kinematic viscosity are specified in various biodiesel and petrol diesel standards.

The kinematics viscosity of various fatty compounds as well as components of petrol diesel were determined at 40^0C (ASTM D 445) as this is the temperature prescribed in biodiesel and petrol diesel standards. The kinematic viscosity increases with chain length of either the fatty acid or alcohol moiety in fatty acid ester or in aliphatic hydrocarbons.

The kinematic viscosity of unsaturated fatty compounds strongly depends on the nature and number of double bonds with double bond in aliphatic hydrocarbons has a comparatively small viscosity reducing effect. Branching in alcohol moiety does not significantly affect viscosity compared to straight line chain analogues.

Free fatty acid or compounds with high hydroxyl groups possess significantly higher viscosity. The viscosity range of fatty acid compounds is greater than that of various hydroxyl groups possess significantly higher viscosity.

The viscosity range of fatty compounds is greater than that of various hydrocarbons comprising petrol diesel. The effect of dibenzothiophene, a sulphur-containing compound found in petrol diesel fuel, on viscosity of Toluene is less than that of fatty esters or compounds with 10 carbon and varying oxygenated moieties were founded. A reversal viscosity of the carboxylic of influence on kinematic viscosity of oxygenated moieties is

COOH= C-OH>COOCH=C=>C-O-C> number of O_2.

While biodiesel faces some technical challenges such as reducing of NO_x exhaust emissions, improving oxidative stability and cold flow properties.Biodiesel having good properties reduces the 1.Exhaust emissions 2. Improved biodegradability 3.Higher flash point 4.Domestic origin.Because of reducing viscosity is the major reason why vegetable oil or animal fats are transesterified to biodiesel because the high viscosity of neat vegetable oils or fats ultimately leads to operational problems such as engine deposits.With the advent of low–sulphur petro-diesels the issue of fuel lubricity has become increasingly important as hydrodesulphurization removes polar compound responsible for the lubricity of petrol diesel. It has been stated that sulphur compounds are not among the compounds imparting to lubricity of diesel fuel in contrast to nitrogen and oxygen-containing compounds.Biodiesel added at low blends levels (1-2%) has been stated to restore lubricity to low sulphur petrol diesel.

The compound structure of a fatty acid of a biodiesel fuel will have the significantly influence of the temperature prescribed in the biodiesel and petro-diesel standard.Influencing factors are chain length, position number and nature of double bonds, as well as nature of oxygenated moieties. Generally, the hydrocarbons in petro-diesel exhibits lower viscosity in a narrow range than the fatty esters comparing biodiesel fuel.Branched esters, which have improve low temperature properties, are competitive with other ester in terms of kinematic viscosity and cetane number.

Malaya Naik et al (2007), used the production of biodiesel from a karanja oil containing a FFA upto 20%, acid of 0.5% H_2SO_4 is catalysed by esterification and alcohol 6:1 molar ratio with respect to high FFA karanja oil to produce methyl ester by lowering the acid value and next step is catalyzed transesterification. Hence the biodiesel is obtained from FFA karanja oil by dual step process has been observed upto 96.6%-97%. Since the presence of high FFA makes transesterfication reaction difficult because of the formation of soap with alkaline catalyst. The viscosity of karanja-based biodiesel is found to be 4.33Cst which is required standard of ASTM and calorific value of fuel was found to be less than that of biodiesel because lake of oxygen content in it, the flash point is 174^0C than diesel. Therefore storing of biodiesel and biodiesel blends are safe as compare to storing diesel alone. If the FFA content is high in the feed sock, the dual step production of biodiesel is effective in producing higher quality of biodiesel.

Mohamed Fawzy Ramadan et al (2015), investigation shows the studied and investigated the raw material of biodiesel as madhucalongifolia. Syn. Madhuca indica (Sapapotacecae) and exact composition of Mahua butter from the fruit seed of better cup or madhuca tree. In this Madhuca longifolia, the main importance to know the chemical composition, nutritional value, antioxidative properties. The raw material of biodiesel, FAME are environmentally safe non-toxic and biodegradable, saponification value (SV) iodine value (IV) and cetane number were used to predict the quality of FAME of oil for use as biodiesel. Saponification depends upon the percentage of concentration of fatty acid components.

The obtained biodiesel from mahua FAME can be used as a biodiesel by trans-esterified method and methanol as a catalyst using sodium hydroxide to get a pure biodiesel and it can be used in engine as B100 fuel. Such that these

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properties of biodiesel are very close to the diesel fuel according to the standard of ASTM D 6751 and European standard and shows a very less in emission CO and HC when NO_x will be more if 30% of the blend is exceed.

GauravDwivedi et, al (2016), He noticed that the biodiesel have a major issue with the cold flow property and performance, so the cold flow properties will effect the performance of the engine in colder climatic regions. The cold flow properties are

- Cloud point (CP)
- Pour point (PP)
- Cold filter Plugging (CFPP)

These are responsible for solidification of fuel causing blockage in fuel lines filter which will further leads to fuel starvation in engine operation during starting condition. The low temperature properties are most important property for a biodiesel to be considered for practical usage. The inferior cold flow properties are existed of longer chain saturated fatty acids in feedstock.

The saturated fatty acid having chain longer than C12 have significant impact Cold Point (CP) and Pour Point (PP) which tends to increase non-edible oils having complex saturated fatty acid context like Palm oil and flow properties.

The best method to solve complications linked to the biodiesel compaction, are the mixing biodiesel with petrol diesel in various percentage to get that is blending mixture cold flow point (CFP) of fuel represents its behavior in specific climatic conditions.

The partial solidification of the fuel in colder temperature conditions can result in choking of fuel supply pipes and filters that will lead to improper ignition.

Fatty acids that include long carbon chains also affect cold flow properties. These fatty acids also crystalline at higher temperature and exhibit poor properties.

A biodiesel prepared with non–edible oil of large proportions of fatty acids with high melting points, like palm oil (43.9% palmatic acid, methyl ester melting point of 30.5^0C) will be having a higher cold point (16^0C).

The oils like canola, soybean and sunflower have better CFP'S as compared to other oils so these can be recommended for cold flow properties operations.

Many problems associated with the biodiesel, while we are using it as fuel in engine. The cold flow properties (CFP) of biodiesel are the major problems associated with engine operation during cold climates.

The inferior CFP'S of biofuel quality and it will not be in condition to be used in cold climatic regions because of ignition problem and there will be an incomplete combustion of fuel which will further lead to starting problem in the engine.Therefore to improve these CFP'S of biofuel using different methods like winterization, blending with petroleum diesel and solvents, use of additives. The biodiesel prepared with higher alcohols have better cold flow properties are obtained. Out of various methods, use of alcohols like blending of fuel with ethanol is recommended for various types of oils.

Jon Van Grepenet, al (2005), showed theprocess of complicity originates from contaminants in the feedstock, such as water and free fatty acids, or impurities in the final product, such as methanol, free glycerol, and soap.

Process have been developed to produce biodiesel from high free acid feed stocks, such as recycled restaurant grease, animal fats and soap stock. The reaction conditions generally involve a trade-off between reaction time and temperature as reaction completeness is the most critical fuel quality parameters.The biodiesel obtained from its primary feed stock of a vegetable oil or animal fat from its, biodiesel is generally considered to be renewable. Since carbon in oil or fat originated mostly from CO_2 in the air. Diesel engines operated on biodiesel will have lower emission of CO_2, unburnt hydrocarbon, Particulate matter and air toxics than when operated on petroleum based diesel fuel.

The process of producing and production of biodiesel mainly by reacting soybean oil or used cooking oil with methanol. Biodiesel is renewable and does not contribute to global warming due to its closed carbon cycle. A life cycle analysis of biodiesel showed that overall CO_2 emission test has shown a slight increase in oxides of NO_x. Biodiesel if added to a regular diesel fuel in an amount equal to 1-2% it can convert a fuel with poor lubricating properties such as modern ultra-low sulphur diesel fuel into an acceptable fuel. Biodiesel is an important new alternate transport fuel. It can be produced from many vegetable oil or animal fat feedstock.Conventional processing involves an alkali-catalysed process, but this is unsatisfactory for lower cost high free fatty acid feed stock due to soap formation. Pre-treatment process using strong acid catalyst has been shown to provide good conversion yields and high-quality final products. These techniques have even been extended to allow biodiesel production from feedstock like soap that is often considered to be waste.

The total glycerol is defined as the sum of free and bound glycerol, and the bounded glycerol is equal to the glycerol portion of the residual mono, Di and tri-glycerides. The amount of residual methanol, Fuels, flash point ash level and free glycerol. When there limits are met, the biodiesel can be used in most modern engines without any modification while maintain the engines durability and reliability.

AderrahimBouaidet, al(2016), found that the quantity of biodiesel may be improved by using a used fry oil (UFO) samples with different free acids (FFA) contents upto 4%. There is a slightly increase in the yield of the biodiesel and purity by used fry oil (UFO).With the content of FFA as a Mono, Di, and Triglycerides (MG,OG and TG). From the use of any (UFO) the yield of methyl ester (ME) is decreased from 97.2% to 95% by increasing the FFA content of the oil. When the FFA content of the oil is decreased, hence there is a gradual reduction in the content of (DG, MG) decreased. And finally the (MG) is increased in biodiesel sample. Which will meet the required standard of the biodiesel.

G.S. Anastacioet, al (2013), He observed that the main by-product of biodiesel is glycerine in biodiesel industry. The estimated of glycerine produced will be 40,000 tons by the year 2020. Yeast enzyme is used for production of biodiesel from crude glycerol from soybean oil as carbon source for heterologous protein production using the yeast pichidpastoris. Here the cell growth experimented showed that crude glycerol containing either KOH and NAOH resulted in 1.5 to 2 times higher final densities, when the comparison to the glycerol P.A. Yeast by batch fermentation consumes residual methyl esters, fatty acids and monocyglycerols and yeast uses these compounds as carbon sources for the growth cell by its density nearly doubled

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FaeghehMoazeniet, al (2019), analyse of the conversion of UCO to biodiesel by enzymatic can be made. The production of biodiesel by used cooking oil to yield higher biodiesel production various microorganisms that are capable of producing the enzymes required to convert used cooking oil to biodiesel.The transesterification methods including homogenous alkali-catalysed, homogenous acid catalysed, non–catalytic reaction under super critical conditions and enzyme catalysed reactions.The enzymatic reactions have more advantages than that of the other methods because lipases are most promising enzymes currently known for conversion. The physiological and physical properties of microbial lipases, the catalytic mechanisms of the enzymes and the various methods of enzyme immobilization such as adsorption, covalent and affinity binding, entrapment and whole-cell immobilization.

A. Restitogluet, al (2012), He investigated to yield biodiesel quantity more from the WCO or (trap Grease), Sulphuric acid is used as a catalyst and esterification process. The analysis of more yield of biodiesel was concentrated on the molar ratio of methanol/WCO and an amount of acid catalyst, reaction time and reaction temperature are FFA'S above 65% which is been preferred for esterification process. Meanwhile methanol is used because of its low cost and sulphuric acid is used as a catalyst because it gives very high yields in alkyl esters. The optimum conditions for this esterification process were obtained with molar ratio of methanol/WCO in 9/1 with 9 wt% sulphuric acid catalyst and a reaction time 120 min and the reaction temperature was absorbed at 60^0C. The yield of biodiesel was 93.98% at optimum esterification process.
The biodiesel blends were characterized for their physical characteristics referring to the substitute for biodiesel fuel. The blending percentage of biodiesel below 40 vol% had their physical properties within EN590 standards is similar to that of diesel fuels and its blends can be used in the diesel engines without any modification of the engine.
Hence the WCO which is having a high FFA'S in which the molar ratio of methanol/WCO 9:1 of 9wt% acid catalyst amount,60^0C temperature and 120 min reaction time, the maximum efficiency can be obtained 93.98% at these conditions.The biodiesel was mixed with diesel in different volumetric ratio and their characteristic was observed such that they have a similar to that of EN590 standard. It showed that 30 vol% could be applied to the engine without any modification and hence the WCO can be used as addition fuel to diesel fuel and environmental effects such as emission of CO and other PM matter will be solved with the WCO.

Bezerigianni et al (2008), the feed stock oil (UCO) will be converted into biodiesel through chemical reactions of transesterification and esterification.
The transisterification is the catalyzed process of trading the alkyl group an ester by an alcohol such as methanol and ethanol to convert the triglycerides (TG) of the UCO to fatty acid methyl ester (FAME) and glycerol.
A direct esterification could also generate biodiesel, in which free fatty acid. (FFA'S) with alcohols produce FAME and water as a by-product. The yield of biodiesel conversion increased in all types of UCO feedstock as the reaction temperature was increased.
The type of catalyst used in the transesterification reaction is another critical element affecting the biodiesel production. They are chemical compounds, such as acids and/or bases and enzymes depending on the method used for biodiesel product.The overall process involves three consecutive reversible reactions which produce intermediate molecules of di and mono glycerides.

$$\text{FFA+ MeOH} \longrightarrow \text{FAME+H}_2\text{O}$$

The biodiesel production yield under the optimum reaction conditions of methanol FFA molar ratio 1:10, amount of hexane of 1.33ml/g acidified UCO, and 40^0C. The result should that an initial increase in the biodiesel production yields as methanol, FFA molar ratio increased above a certain level due to harmful effects of methanol on the enzyme active center. Also the biodiesel production yield increased with solvent n-hexane concentration, but then it decreased once the solvent concentration reached a level at which the substrate become too dilute.

The enzymatic transesterification methods are more advantages because of environment friendly, the operational conditions are moderate and operational conditions are moderate and ambient conditions. The ratio of alcohol to oil is lower than previous methods (which can lower the cost of production) and the quality of the by-product glycerine is decent (>90%) purity. The purity of the final product is high and thus to no polishing process is necessary at the end.

The enzymatic method allows for higher free fatty acids content in feedstock which will permit the usage of a board variety of oils as a feedstock. The enzymatic method is enables utilizing the used cooking oil, containing high free acids content, which otherwise would have been difficult or infeasible to process due the economical and operational burdens it import on the process of biodiesel. Such is greatly beneficial to biodiesel production became of UCO'S abundant availability, Low cost and not competing with food and agriculture.

Knothe et al (2005), Many researchers have found the alkyl esters rather than ethyl esters mainly because of methanol is less costly than ethane Tranesterfication can be done by both heterogeneously and homogenously by acid and base catalyst. Alkali catalysts in the form of sodium or potassium hydroxide are more common in homogenous transesterfication reactions. Fatty acids in general, general contain the very polar carboxyl group at one end of a hydrocarbon molecule. Fatty acids are of two types saturated and unsaturated fatty acids.

Bezerigianni et, al (2009), the feed stock oil (UCO) will be converted into biodiesel through chemical reactions of transisterfications and esterification .The transisterfication is the catalyzed process of trading the alkyl group an ester by a convert the triglycerides (TG) of (UCO) to fatty acid methyl ester (FAME) and glycerol.

A Direct esterification could also generate biodiesel, in which free fatty acid (FFA'S) with alcohols produce FAME and water as a by-product. Temperature is one of key element affecting the production yield of biodiesel through transisterfication. The yield of biodiesel conversation increased in all types of UCO feed stocks as the types of UCO feed stocks as the reaction temperature was increased.

5. Conclusion

The detail literature survey reveals that the physical and chemical properties of the biodiesel depend upon the chemical composition and number of bonds present in the biodiesel fuel.The most of the properties depends upon the type of free fatty acids and esters present in the biodiesel. The researcher Gerhard Konthe reveals that the four major fatty acids that influences very much on the fuel properties are Palmitic, Stearic, Linoleic and Linolenic. The researcher Mallya Naik observed that the presence of higher FFA makes transesterification reaction difficult because of the formation of the soap with alkaline catalyst. Gaurav Dwivedi observed that fatty acids that include the long carbon chains also affect cold flow properties. These fatty acids also crystalline at higher temperature and exhibits pour properties. In overall free acids influence very much on the basic fuel properties and hence on the performance, combustion and emission characteristics of the diesel engine.

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