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Impacts of derivatization on physiochemical fuel quality parameters of fatty acid methyl esters (FAME) - A comprehensive review

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Abstract

Biodiesel is one of the possible alternations to overcome the recent energy crisis. Biodiesel is non-toxic, renewable and biodegradable and usually have low aromatic or sulfur contents. The use of variety of feedstocks is significant because of socio-economic issues however quality of biodiesel depends on the chemical composition of feedstock. Many feedstocks including edible oils, non-edible oils, fats and algae can be used but to attain the biodiesel of better quality, fatty acids can be derivatized in many ways that include transesterification and esterification, pyrolysis, thermal and catalytic cracking and polyester formation. Some of the most important physical and chemical properties of biodiesel are cetane number, kinematic viscosity, oxidative stability and inherent lubricity. These properties are mainly influenced by the chain length, position and number of double bonds. This review studied the effects of modification or derivatization of fatty acids on the properties of biodiesel.

Key words: Biodiesel, carbon chain length, fatty acids, derivatization, lubricity, physical properties, chemical characteristics

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1. Introduction

Now-a-days, world is facing worst energy crisis of the history. Over worldwide, most of the countries are mainly dependent on petroleum as the key source of energy for electricity and transportation fuel, so its price is increasing day by day. The only possible solution of this energy crisis is to find an alternative source of energy that is economically feasible and renewable in nature. There are many sources of energy that are substitute of fossil fuel and are renewable such as wind energy, solar power, geothermal and biomass derived energy. However, few of them are also economically feasible. One of these that fulfill both the criteria is biofuel as it is produced from the feedstock that is readily available [1]. Biofuels are gaseous or liquid fuels that are used mainly for transport sector; it can be produced from the variety of feedstocks that are sustainable, renewable, carbon neutral for the whole life cycle, environment friendly and biodegradable. Biofuels encourage the green industry and agriculture and are used as motor fuel with or without modification in engine. Biofuel include bioethanol, biomethanol, biodiesel and biohydrogen that are the attractive options for the future transportation sector [1].

Among all biofuel, one that is receiving the most attention is biodiesel because of its similarity with conventional fuel in terms of energy content and chemical structure [1]. Chemically biodiesel is fatty acid alkyl esters (FAAE), it can be derived by the reaction of triglycerides or free fatty acids with alcohol in the presence or absence of (acid or base) catalyst. The biodiesel qualities mainly depend on the concentration and type of free fatty acid, that is related to the type of feedstock used [2]. It is cleaner fuel, alternative to diesel fuel and like diesel fuel it operates in the compression ignition engines. Biodiesel have many advantages like it is portable, readily available, renewable, high combustion efficient, it have low sulfur and aromatic contents, high biodegradability and cetane number. Viscosity is important property because it has effect on the working of fuel injection equipment mostly at low temperature when the viscosity increases it affects the fluidity of fuel [3].

On the basis of source from which the biodiesel is derived, it can be classified into three generations. First generation biodiesel is produced from an edible oil like rapeseed or soybean oil. Biodiesel of second generation is produced from the non-edible oils like jatropha or neem oil. Feedstock having high oil content is best for the second generation biodiesel. The main benefit of biodiesel is that it eliminates the food imbalance, reduces the production cost, require less land for the cultivation and environmental friendly in nature [4-6]. Biodiesel produced from the non-edible oil are viscous in nature, does not fulfill the commercial demand and require more alcohol for production [6]. The third generation biodiesel is produced from microalgae [6]. The information about major cons and pros of biodiesel produced from different feedstock can be helpful to focus on the major challenges regarding the biodiesel production. For biodiesel characterization, spectroscopic and chromatographic analysis is used. Thin layer chromatography is used for simple qualitative analysis. It is initial method for the characterization of fatty acid methyl esters (FAME) but have low accuracy and sensitivity for humidity [7].

The compositional characteristics of FAME have great effect on the chemical and physical properties of biodiesel. Changes in one of the compositional properties like chain branching, chain length and unsaturation generally produces both wanted and unwanted changes in the properties of FAME. Biodiesel properties have incompatible relationship, for example the compositional characteristics that are favourable for good oxidative stability leads towards the poor performance at low temperature [8]. The fatty acid varies in their length of carbon chain and number of double bonds in carbon chain. The fatty acids can be saturated or unsaturated. The saturated fatty acids consist of only single carbon-carbon bond and chemically cannot accept more hydrogen atom while the unsaturated fatty acid have one or more double bonds and can accept one or more hydrogen atoms [9].

Many compositional characteristics of FAME have contradictory impact on the properties of fuel, thus it is not possible to specify the composition of fatty acid that is optimum with respect to other main qualities of fuel. The properties of biodiesel that explain the suitability of FAME as the engine fuel include lubricity, viscosity, oxidative stability, cetane number and cold flow properties. The properties that are more critical include oxidative stability and cold flow. Many researchers have investigated the FAME features to optimize the biodiesel performance with respect to oxidative stability and cold flow properties [8-10]. There is a view that optimum compositional characteristics of FAME would have low levels of saturated fatty acids in order to minimize the cold flow problems, relatively low level of polyunsaturated fatty acid to minimize the oxidative instability and high level of monounsaturated fatty acids. It is concluded that the oleic acid (18:1) and palmitoleic acid (16:1) provide the compromise between the properties of biodiesel like oxidative stability and cold flow properties without having impact on the cetane number. To chemically modify the properties of natural fatty acids of oils and algal lipids, there are many efforts in progress in laboratories to improve their suitability as the feedstock of biodiesel [8]. This paper reviews the previous work done by the researchers to derivatize the fatty acids for production of biodiesel with better stability. This review discuss in detail about the effect of fatty acid composition on properties of biodiesel and methods used to derivatize the fatty acid to improve the quality of biodiesel.

2. Types of Feedstock

The biomass or feedstock used for biodiesel production is vegetable oils that are generally plant based but it also includes fats that mainly consist of triglycerides. The most commonly used feedstock includes plant oils that can be edible or non-edible oils. Properties, qualities and other parameters of feedstock affect the yield of biodiesel [11]. Different countries use variety of feedstocks for the production of biodiesel that basically depends on the local availability of feedstock. Thus, choice of feedstock is mainly country specific, that depend on the domestic production and cost effectiveness [12].

3. Structures of Oils and Fats

Vegetable oils are also called triglycerides as they are composed of 98% triglycerides and small ratio of mono and diglycerides. Basically triglycerides are esters of three molecules of fatty acid and one molecule of glycerol, its structure contains significant quantities of oxygen. The alkyl chain of triglycerides mainly consists of oleic and linoceric fatty acids. Vegetable oils are distinguished by composition of their fatty acids. Myristic acid (14:0) palmitic acid (16:0), stearic acid (18:0), arachidic acid (20:0), behenic acid (22:0), linoceric acid (24:0), oleic acid (18:1), erucic acid (22:1), linoleic acid (18:2) and linoleinic acid (18:3) are commonly present fatty acids in vegetable oils in varying percentages. Different types of oils have different types of fatty acids. Triglycerides that are fully saturated, they are solid at room temperature, thus they cannot be used as regular fuel. Molecules of triglycerides have molecular weight in between 800 to 900 that is nearly four times larger than conventional fuel. The oils of vegetables have high molecular weight that is why they have low volatility and are more reactive than conventional fuel because of their unsaturation. Thus, they are more exposed to thermal polymerization and oxidation reactions.

4. Composition of Biodiesel

The composition of biodiesel depends on the feedstock that is used for the biodiesel production. Biodiesel is the blend of FAAE. When the reactant is methanol then it will be the mixture of FAME, if the reactant is ethanol then it will be the mixture of fatty acid ethyl esters (FAEE). In biodiesel production, methanol is commonly used because of its low cost [14].

5. Derivatization of Fatty Acids

Many efforts have been made to derivatize the vegetable oil in the way that it meets to the properties of conventional diesel fuel. Vegetable oils cannot be used in place of fuel because they have high viscosities, poly-saturation and low volatilities [3]. Vegetable oils can be derivatized through micro-emulsion, blending, pyrolysis, cracking, transesterification, esterification and polyester formation. Some of these derivatization techniques are described below.

5.1 Pyrolysis

The main purpose of the pyrolysis is to optimize the biomass products by catalytical or thermal means. The material that is subjected to pyrolyze can be any biomass like animal fats, vegetable oils, bio-waste or wood. The derivatization of vegetable oils through pyrolysis convert them to biodiesel [15]. Thermal decomposition of fatty acids produces hydrocarbon compounds like alkane, alkenes, aromatic and carboxylic acids. The nature of final product depends on the composition of oil. Thermal decomposition mechanism was proposed by the Schwab et al. This mechanism is complex because of many structures and variety of possible reactions of mixed triglycerides. Generally, these reactions involve carbonium ion or free radical mechanism. Diels-Alder addition of ethylene supported the formation of aromatics. Cleavage of glycerides molecules produces carboxylic acid. The properties liquid fractions produced through the pyrolysis of vegetable oils are likely to approach conventional fuel.

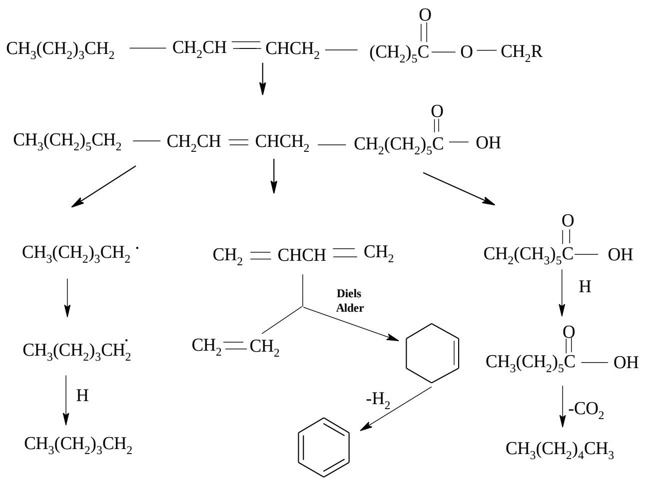


Fig 1 The mechanism of thermal decomposition of triglycerides

5.2 Transesterification

Transesterification is the reaction of vegetable oils and animal fats (triglycerides) with alcohols (primary), in presence or absence of catalyst. The following figure presents the basic transesterification reaction, which produces fatty acid alkyl esters known as biodiesel and glycerol as by products. This is reversible reaction however this reaction uses higher than stoichiometric quantity of alcohol in order to force the equilibrium of reaction on product side. Methanol and ethanol are most commonly used alcohol in this process [12].

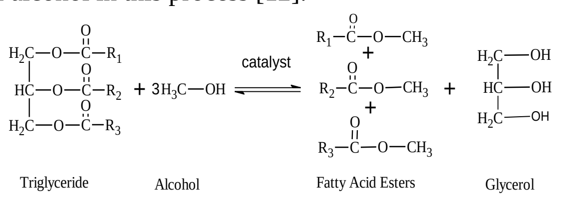


Fig 2 Transesterification reaction

5.3 Esterification

Esterification is the pretreatment of vegetable oils to convert the free fatty acids into FAME. The homogenous or heterogenous acid catalyst can be used to esterify free fatty acid like oleic acid or myristic acid. Liquid inorganic and mineral acids can also be used as a catalyst for esterification reaction, but they show many limitations. These catalysts are not environmental friendly, have high cost for purification and separation and proved to be corrosive for equipments.

5.4 Reactions on Fatty Acids

The alkyl ester's structure can be modified by reaction on its carboxylic group and double bonds. The polyesters with α-hydroxyeters and polyols are produced when reaction occur on carboxylic group. On double bonds, electrophilic addition reaction takes place that allows oxidation, hydroxylation, hydrogenation and polymerization [16]. It also include breakdown in which molecules having better cold flow properties are produced. Isomerization reaction takes place by two methods (a) hydrocarbon direct isomerization with mesoporous acid catalyst or epoxidation and its opening with carboxylates or alcohols [17].

5.5 Polyesters Formation

The polyester can be formed by acid transesterification using heteropoly acid salts [18]. These esters and their epoxides can be used as bio-lubricants because they have good tribological properties, the eaters that are derived from palm oil and pentaerythritol, pentaerythril monophenyl ether, pentaerythril monobutyl ether, pentaerythril monoethyl ether have shown better cold flow properties. Following figure shows the production of disasters from oleic acid and inorganic compounds (Mp: -42 ºC) [17].

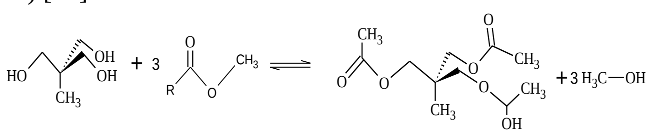
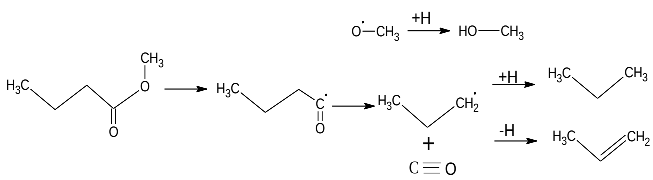


Fig 3 Trimethylolpropane ester formation by transesterification reaction

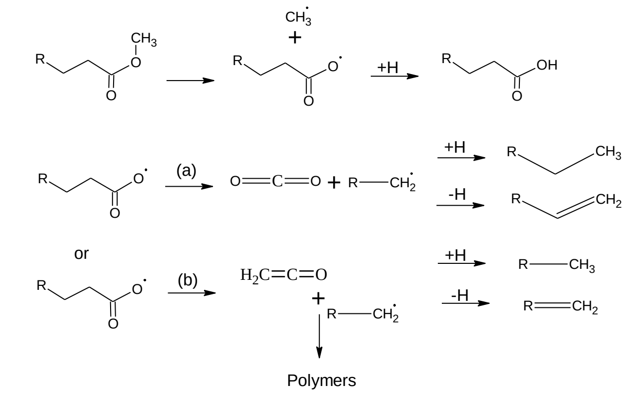
5.6 Cracking and Hydrothermal Oxidation Treatments

In order to improve the cold flow properties of biodiesel, hydrothermal oxidation and cracking of FAME have been investigated. These treatments produce molecules of low molecular mass, which shows improved cold flow properties and low viscosity [19]. Cracking is the breakdown of molecules as shown in the following figures.

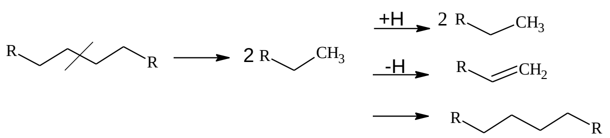
Decarboxylation



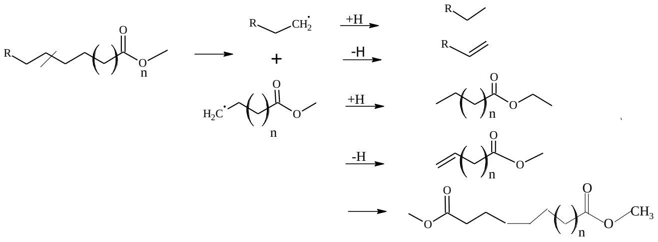
Demethylation and decarboxylation (a)/dekenezation (b) upon the ester bond cracking



Cracking of the hydrocarbons formed previously



Cracking of FAMEs



Diels-Alder reaction followed by dehydroxygenation

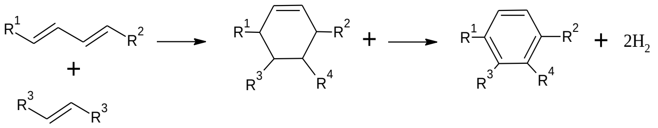


Fig 4 Radical mechanism of thermal cracking of fatty methyl esters

This process produces biodiesel of low cloud and pour point. Biodiesel of palm oil has been produced by dehydrogenation and catalytic cracking using catalyst SiO_2/Fe_3O_4, this process reduces the CFFP value in 12ºC [20]. The treatment of hydrothermal oxidation break the molecules through the double bonds, it generates compounds with high oxygen level [21] according to reaction that is shown in following figure.

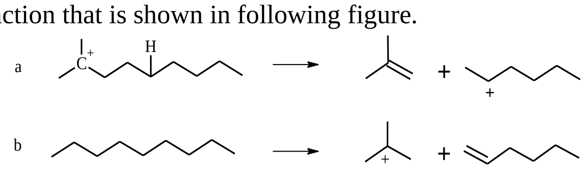


Fig 5 Proposed mechanism of β-scission

This process include the reactions like hydrocracking, deoxygenation and hydrogenation [22], which produces compounds with high lubricity, low viscosity and good cold flow properties. The products of these reactions have properties similar to conventional fuel with low production cost and great flexibility with raw materials. The disadvantages of cracking process are decarboxylation reaction and the production of light hydrocarbons formation, which results in the loss of gaseous products [17].

6. Effect of Fatty Acid Composition on Biodiesel Properties

The compositional profile of FAME material has great influence on the chemical and physical properties of biodiesel. Researchers have investigated the relationship between fuel properties and compositional characteristics of pure compound or the mixtures of pure compound [23]. The most important characteristics of FAME that have significant role in determining the properties of biodiesel are chain length of fatty acid and degree of unsaturation in fatty acid. Thus, the composition of fatty acid has much impact on many properties of biodiesel which is explained in detail below.

6.1 Cetane Number

Cetane number of biodiesel measures its auto-ignition quality. Biodiesel mainly consist of hydrocarbon groups having long chain which generally have no branching or aromatic groups, its cetane number is higher than the conventional fuel, increase in blending level also increase the cetane number of the blend [24]. However, there are exceptions, when biodiesel of low cetane number is blended with petroleum diesel of high cetane number. In this case, increase in blending level results in reduction in cetane number of this blend.

The biodiesel produced from the feedstock that have high proportion of saturated fatty acids like tallow and palm have high cetane number than the biodiesel produced from the feedstock that have less saturated fatty acids like rapeseed and soy. The effect of use of branching alcohol in production of biodiesel has less effect on the cetane number and this effect is difficult to explain. In pure FAME, cetane number increases with increase in the chain length, while this effect is covered when dealing with mixtures of FAME that are complex. The cetane number of biodiesel clearly varies with average of unsaturation. Some previous experimental investigations that are reported in literature also explain that increase in degree of unsaturation cause the decrease in cetane number [8].

The increase in double bond number and their position in their chain lower the cetane number. The increase in chain length or more consecutive methylene groups in fatty acid results in high cetane number. The CN of saturated FAME increases when there is increase in chain length, while the CN of unsaturated FAME decreases when there is decrease in number of double bond or degree of unsaturation. Thus, increase in the double bond lowers the cetane number, while increase in chain length increase the cetane number and it decreases with increasing unsaturation [9].

6.2 Ignition Quality

Fuel ignition quality is an important parameter for efficient and reliable operation of diesel. The molecular structure of fuel has significant impacts on the chemical and physical process that occurs during the vaporization, atomization and combustion of the biodiesel after it's injection to combustion chamber. It is stated that degree of unsaturation and chain length of pure FAME effect the ignition delay period of the fuel [25]. The saturated fatty acid and longer carbon chain lengths resulted in the shortened ignition delay. The saturated FAME and molecules with longer fatty acids have lower rate of heat release and pressure rise rate during the uncontrolled stage of combustion of CI engine than molecules of short chain length [25].

6.3 Oxidative Stability

It is one of the most important fuel properties of biodiesel. If the fuel is unstable it can lead to high viscosity along with the formation of sediments, gums and other deposits. Many commercially available biodiesels have to solve this problem that improve the stability but do not affect its composition. Unsaturation effect the oxidative stability as higher unsaturation causes the poor stability. The auto-oxidation of fatty compounds that are unsaturated occurs at different rates that depend on the position and number of double bonds. The process of oxidative degradation are initiated with the removal of hydrogen atom that is next to double bond (which is so called allylic position) [26-27]. When the hydrogen is removed, fast reaction with molecular oxygen take place and allylic hydroperoxides are formed. These consecutive reactions involve the radical chain propagation and isomerization that produce numerous alcohols, aldehydes and carboxylic acids. The molecule of FAME that contains carbon which is next to two double bonds is generally susceptible to oxidative instability. Researchers have identified the importance of polyunsaturated FAME for the stability of fuel. Ramos et al. defined the parameter of degree of unsaturation [27]. The biodiesel feedstock that has over 50% polyunsaturated FAME contents would have poor inherent oxidative stability. Thus, double bond of carbon-carbon is important for oxidative stability of biodiesel.

6.4 Density

The fuel density is the main quality that is known to have long lasting impacts on the performance of engine. The fuel injection pumps the fuel by the volume not by the mass and the amount of mass that is injected depends upon the density of fuel. The fuel density has strong influence on total energy contents and air fuel ratio within the combustion chamber. Generally, densities of biodiesel are slightly higher than that of petroleum fuel. Nevertheless it has been found that increasing the blending level of biodiesel blends, the density of fuel increases [23]. The biodiesel density is affected by the chain length as higher chain lengths lowers the fuel density [8].

6.5 Kinematic Viscosity

Viscosity is a resistance measurement of flow of liquid due to the internal resistance of one part of a fluid moving over another [23]. The fuel injection behavior is affected by this critical property. Generally, higher viscosity causes poorer fuel atomization [28]. When the viscosity of fuel is higher it can cause narrower injection spray angle, larger droplet sizes, greater cylinder penetration of fuel spray and poorer vaporization [29] thus causes the poor combustion, increased oil dilution and higher emission. The biodiesel viscosity is higher than the viscosity of petroleum diesel by the factor of two. Similarly, increase in the blend level of biodiesel also increases the viscosity. The oil has much higher viscosity that is why it cannot be directly used as fuel. The higher viscosity of FAME causes increased injection variability, increased delay in time of ignition and reduction in injection volume [30]. Temperature have great effect on viscosity [31]. Hence, many problems arise due to higher viscosities that become even more prominent at low temperature. In case of reduced temperature, distribution of biodiesel among injectors becomes very unequal [32]. This cause problem related to toxic emission and improper engine’s performance. The viscosity of FAME molecules increases with increase in carbon number of fatty acids [31]. Viscosity is mainly related to degree of unsaturation as higher unsaturation leads towards the low viscosity (there is exception for coconut derived FAME). Viscosity is also affected by double bond configuration as the trans-configuration gives high viscosity than cis configuration. The position of double bond have less influence on the viscosity [8].

6.6 Lubricity

The reduction of resistance between the surfaces of solid in relative motion is known as "lubricity". Generally, there is contribution of two mechanisms to overall lubricity that includes boundary lubrication and hydrodynamic lubricity. Good lubricants are critical to protect the system of fuel injection systems. The biodiesel lubricity is mostly due to the ester group within the FAME molecules but increase in lubricity is because of traces of impurities present in biodiesel. Mostly, monoglycerides and free fatty acids are good lubricants. Biodiesel purification by distillation causes reduction in its lubricity because impurities are removed in this process. The effect of unsaturation on lubricity is not clear however some researchers reported the positive effect of carbon-carbon double bonds [33] while others reported that there is no effect of unsaturation. Thus, impurities have positive impact on the lubricity, but there are some impurities like monoglycerides that are responsible for the poor low temperature working problems. The effort to reduce these impurities for improvement of low temperature properties have resulted in worsening of lubricity [8].

6.7 Iodine Value

The iodine value (IV) is related to the unsaturation of FAME, this is the measurement of the value of I_2 that is added to carbon-carbon double bonds. This property of biodiesel is simply the measure of fatty acid unsaturation. This value was set as a specification in the standard of European biodiesel, EN 14214, to ensure reasonable oxidative stability of the fuel. The iodine value (IV) is a measure of total unsaturation in contrast to oxidative stability that is more strongly influenced by the amount of FAME molecules that have multiple double bonds. This is the reason that there is some controversy for the requirement for an IV standard at all, and certainly about the rather restrictive maximum IV value of 120 g I_2/100 g biodiesel set by EN 14214 [8].

6.8 Cold Flow Properties

Biodiesel properties related to low temperature are of most importance and significant consideration. Poor low temperature properties can cause several problems mainly including filter plugging because of wax formation as the reduced fuel flow cause engine starving. The cause of poor flow properties is the presence of long chain, saturated FAME present in the biodiesel. The cold flow properties include pour point (PP) and cloud point (CP). The methyl esters that are saturated and longer than C_{12} increase the pour point and cloud point, even when it is blended with conventional fuel. In general, when the carbon chains are longer then the melting point increases which results in poor low temperature flow properties.

Cloud point is the temperature when the least soluble components of the biodiesel crystallize from the solution. When the biodiesel is in pure form than the cloud point is determined by amount and type of FAME [34]. Wax crystallization is because the molecules are closely packed. The factors that inhibit the close packing of molecules decrease the cloud point of biodiesel. This arrangement is disturbed due to the high proportion of branching in fatty acid chain or the alcohol proportion of FAME. When double bond is introduced it also disturbs the close packing of molecules. The double bond orientation also has significant influences on the cold flow properties. When the configuration is cis it provide better low temperature performance than the trans configuration [8].

The use of feedstock with higher saturated fatty acids produces biodiesel having poor cold flow properties, while the feedstock that have highly unsaturated fatty acid produces biodiesel of better quality. There is strong relationship between low temperature properties for pure FAME and carbon chain length. The analysis of complex FAME molecules does not indicate the strong relationship between low temperature properties and chain length because the average length of chain does not differentiate between saturated and unsaturated fatty acid chains. The unsaturation degree has strong influence on low temperature properties while the high unsaturation has better impact on low temperature properties.

Table 1 Fatty acid composition of vegetable oils [13]

	Fatty Acid Composition (Weight Percentage)														
Plant Oil	**12:0**	**14:0**	**14:1**	**16:0**	**16:1**	**18:0**	**18:1**	**18:2**	**18:3**	**18:4**	**20:0**	**20:1**	**22:0**	**22:1**	**24:0**
Cottonseed	-	-	-	28.7	-	0.9	13.0	57.4	-	-	-	-	-	-	-
Rapeseed	-	-	-	3.5	-	0.9	64.1	22.3	8.2	-	-	-	-	-	-
Soybean	-	-	-	13.9	0.3	2.1	23.2	56.2	4.3	0	-	-	-	-	
Neem	-	0.2-0.26	-	13.6-16.2	-	14.4-24.1	49.1-61.9	2.3-15.8	-	-	0.8-3.4	-	-	-	-
Corn	-	0	-	12	-	2	25	6	Tr	-	Tr	-	0	0	0
Karanja	-	-	-	3.7-7.9	-	2.4-8.9	-	44.5-71.3	10.8-18.3	-	-	-	-	-	1.1-3.5

Table 2 Biodiesel properties of biodiesel produce from different feedstock

Biodiesel	**Density (Kg/m³) at 40°C**	**Kinematic Viscosity (mm²/s)**	**Cetane Number**	**Iodine Value (g Iodine/100 g Oil)**	**Saponification Value (mg KOH/g oil)**
Sunflower	841	4.87	47.8	136	193
Rubber Seed	839	4.88	51	120	196
Jatropha	836	4.91	54	105	198.8
Cottonseed	837	4.95	52.1	113.2	202.7
Karanja	837	5.00	52	92	198
Neem	832	5.16	58.7	83.2	201
Palm	830	5.39	64	59	205

7. Conclusion

The main technical problems in the use of biodiesel is related to the composition of fatty acid. Biodiesel stability, kinematic viscosity, cetane number and cold flow properties of fuel generally depend on fatty acid profile of feedstock. Properties of biodiesel are affected by chain length, number of double bonds, position of double bonds and number of branches. Biodoesel produced from the feedstock have high proportion of saturated fatty acid that usually have high cetane number. Cetane number increases with increase in the chain length while increase in double bond lowers the cetane number. Viscosity is mainly related to the degree of unsaturation. Density is affected by chain length. These properties of biodiesel are influenced by chain length and number and position of double bonds in fatty acids. In order to improve the properties of biodiesel, diffierent reactions have been studied in detail because these poperties have complex reltionship with these reaction intermediates. The properties of biodiesel can be improved by modification in the structure of fatty acids or FAME molecules. These modification includes esterification, transesterfication, isomerization, pyrolysis, polyester formation, cracking and hydrothermal oxidation treatments. Pyrolysis produces the fractions of oil that have properties closely related to conventional fuel. Formation of polyester improves the cold flow properties. Hydeothermal oxidation treatment and cracking improvres the low temperarure properties and improves the satbility as these reactions break the larger molecules and produce molecules of low molar mass. Hydrothermal oxidation treatment breaks molcules through hyrocracking, hydrogenation and deoxygenation that produces the compunds which shows low viscosity and relatively higher lubricity.

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