CHAPTER 2

LITERATURE REVIEW

In this chapter, a detailed literature review that was carried out on various topics of the present work is described. The topics include,

- Structural chemistry of biodiesel fuels
- Effect of fatty acid composition on biodiesel conversion ratio
- Properties and structural configuration of fatty acid methyl esters (FAMEs) and their effects on biodiesel properties
- Effects of structural configuration of FAMEs on combustion, performance, and emission parameters of biodiesel properties

2.1 STRUCTURAL CHEMISTRY OF BIODIESEL FUELS

Due to the rapid depletion of fossil fuel resources, researches have been directed to explore plant-based fuels (Agarwal 2007). Fuels derived from vegetable oils can be used as alternative fuels for the diesel engines. Biodiesel fuels are gaining more and more importance as an attractive alternative fuel in recent years and can be obtained when a vegetable oil is chemically reacted with an alcohol to produce monoalkyl ester in which glycerol is obtained as a co-product (Agarwal et al. 2006; Ejim et al. 2007; Pratas et al. 2010).
The basic composition of any vegetable oil is triglyceride that consists of three fatty acids and one glycerol molecule. The fatty acids vary in their carbon chain length and in number of double bonds of carbon atoms (Allen et al. 1999a). Fatty acids may be saturated or unsaturated. Saturated fatty acids form a straight chain homologous series of compounds characterized by the general formula $C_nH_{2n+1}COOH$. A saturated fat cannot chemically accept additional hydrogen and contains only single carbon–carbon bonds. The unsaturated fatty acids are characterized by the existence of one or more than one double bond between carbon atoms (Graboski & McCormick 1998; Knothe 2008). Unsaturation therefore refers to the presence of a double bond between two adjacent carbon atoms in the hydrocarbon chain.

Biodiesel is a mixture of various fatty acid ester compounds and is obtained through transesterification of vegetable oils with alcohol in the presence of a catalyst. Biodiesels are called fatty acid methyl esters (FAMEs) and fatty acid ethyl esters (FAEEs) when they are derived from transesterification of vegetable oils with methanol and ethanol, respectively. However, methanol is used most commonly because of its availability and relatively low cost. Biodiesel is a mixture of various fatty acid ester compounds; hence the properties of biodiesel are strongly influenced by the properties of individual fatty acid esters and their structural configuration. Supplementing a particular fatty acid(s) with desirable properties to obtain a fuel enriched with certain fatty acids in the biodiesel fuel to improve its overall fuel properties may be attainable in future by means of genetic engineering of the parent vegetable oils (Knothe 2005).
2.2 EFFECT OF FATTY ACID COMPOSITION ON BIODIESEL CONVERSION RATIO

Biodiesel is obtained through transesterification of vegetable oils. Transesterification is a process of producing a reaction in triglyceride and alcohol in the presence of a catalyst to produce alkyl ester and glycerol. Alkali (sodium hydroxide (NaOH) or potassium hydroxide (KOH)) and acids (sulphuric acid or hydrochloric acid) catalyse the reaction (Hass 2005). Alkali-catalysed transesterification is faster than acid-catalysed transesterification and is most used commercially (Gopinath et al. 2009a). If the free fatty acid (FFA) content and moisture content are less than 0.5%, good-quality biodiesel can be produced. Knothe (2008) has stated that the fatty acid profile of biodiesel is identical to that of the parent oil or fat.

Davis et al. (2009) have made a comparison to determine whether the fatty acid profiles of the oil feedstocks changed upon conversion to biodiesel. Nine different fatty acid methyl esters with their corresponding oil feedstock were compared. These comparisons showed that the fatty acid content of the oils was practically unchanged upon biodiesel conversion. However due to geographical origin and ecological conditions, fatty acid composition could vary to a greater extent even for a same type of oil (Marina 2009).

Srivastava & Prasad (2000) have stated that the most important variables that influence transesterification reaction time and conversion are: reaction temperature, ratio of alcohol to oil, catalyst type and its concentration, mixing intensity, and purity of reactants. The studies of pure fatty acids indicate that the reaction rate for methyl linoleate is about 12 times greater than that of methyl oleate, whereas that of methyl linolenate is 24 times that of methyl oleate. Kirschenbauer (1960) has reported that reaction of paraffinic chains such as stearic acids that occur in saturated fatty acids, are
relatively inert, i.e., they are attacked by oxygen only under very severe conditions. The effects of particular fatty acid (s) on ester conversion ratio were not reported much in the previous research studies. But the oils containing high FFA cannot be effectively converted to biodiesel, since they reduce the process yield (Ma & Hanna 1999; Canacki & Van Gerpen 2001).

Berchmans & Hirata (2008) reported that high FFA content (>1%) will result in soap formation and the separation of products will be exceedingly difficult, and as a result, it has low yield of biodiesel product. It was also reported that it is required to reduce the FFA of the feedstock using an acid catalyzed pretreatment to esterify the free acids before the transesterification of triglycerides with an alkaline catalyst to complete the reaction.

Kinoshita et al. (2006) have found that the ester conversion ratio of an ethyl ester is lower than that of a methyl ester under same manufacturing conditions. The ester conversion ratio of ethyl ester of palm and rapeseed oils was found to be lower than that of their methyl esters and the authors stated that this could be due to the higher free glycerin contents and the mono-, di-, and tri-glyceride contents in the palm and rapeseed oil ethyl esters as compared to their methyl ester counterpart. However the percentage of yield was not reported in their study.

Similarly for a fixed fatty acid composition and alcohol, catalyst types and concentrations can have considerable differences in ester conversion ratio. The yield of biodiesel produced from soybean oil was higher in NaOH than in KOH while used 0.5% (% of parent oil quantity) as catalyst and the highest yield was obtained having 1% NaOH compared to 0.5 and 1.5% NaOH (Hossain & Mazen 2010).
2.3 PROPERTIES AND STRUCTURAL CONFIGURATION OF FATTY ACID METHYL ESTERS AND THEIR EFFECTS ON BIODIESEL PROPERTIES

As mentioned earlier, the overall biodiesel properties are strongly influenced by the properties of individual fatty acid esters, which are present in biodiesel. The properties of pure fatty acids and ester compounds and their effects on biodiesel properties are reviewed in this section. The properties which are reviewed in the present work are as follows; viscosity, density, cetane number, heating value, bulk modulus and compressibility, iodine value, oxidative stability, low temperature properties, boiling point, surface tension, and flash point.

2.3.1 Viscosity

Viscosity is one of the most critical fuel properties, which is closely related to the molecular structure and length of the hydrocarbon chain. It is one of the contributing factors, which affects the atomization of a fuel significantly. The magnitude of viscosity of biodiesel is lower about an order than that of its parent oil.

Researchers (Chiu et al. 2004; Hu et al. 2005; Monyem & Van Gerpen 2001; Ramadhas et al. 2005) have found that the biodiesel fuels those are largely composed of monoalkyl ester in the forms of the methanol esterifies to one fatty acid (carbon number less than or equal to C14), has good atomization characteristics. Whereas, the biodiesel fuels mainly based on the fatty acid methyl ester having carbon number greater than or equal to C16 show poorer atomization characteristics as compared with diesel fuel. The kinematic viscosity increases with carbon number and decreases with degree of unsaturation (Freedman et al. 1990; Saran & Narula 1995).
The viscosity increases with chain length (number of carbon atoms) and with increasing degree of saturation (Knothe 2005; Knothe & Steidley 2007). Knothe & Steidley (2005) have found that the factors like double bond configuration can also influence viscosity, i.e. “cis” double bond configuration giving lower viscosity than “trans”. The dynamic viscosity of pure FAMEs at 40°C increased with carbon number in a curvilinear trend for saturated esters (Allen et al. 1999a).

For unsaturated fatty acid esters, the viscosity (at 40°C) trend showed a sharp deviation from the trend of the saturated esters when 18:0 (Stearic acid) became 18:1 (Oleic acid). As the degree of unsaturation progressed from 18:1 to 18:3 (number of double bonds increased), a non-linear decrease in viscosity (at 40°C), with 21% difference between 18:0 and 18:1 (based on 18:0), 18% difference between 18:1 and 18:2 (based on 18:1) and 13% difference between 18:2 and 18:3 (based on 18:2) was observed (Allen et al. 1999a).

Viscosity was found to increase with increasing chain length (Rabelo et al. 2000; Ramirez-Verduzco et al. 2012) whereas branching appears to take part a secondary role (Knothe & Steidley 2005).

The viscosity increased with the increase in lengths of the acid and alcohol segments in the ester molecules. The effect becomes more apparent at lower temperatures, since the molecular movements are even more restricted (Rodrigues et al. 2006). Davis et al. (2008) have argued that the changes in the viscosity are attributed to both structural differences and differences in the potential for interactions among oil molecules as the fatty acid profile change. Pratas et al. (2010 and 2011) have measured the viscosity of seven ethyl esters and eight methyl esters at atmospheric pressure and temperatures from 273.15 to 363.15 K. The viscosities of all esters increase with the ester chain length.
and decrease with its level of unsaturation. The ethyl esters exhibit a higher viscosity than their corresponding methyl ester of the equivalent fatty acid.

2.3.2 Density

The engine performance and emissions can be largely affected by fuel density. Density was correlated with cetane number and in turn oxides of nitrogen (NO$_X$) emissions, with lower densities favoring lower NO$_X$ (McCormick et al. 2001). Some researchers (Encinar et al. 2005; Graboski & McCormick 1998) argued that the density of biodiesel has not changed much since the densities of alcohol (methanol in specific) and parent oil are near to that of the biodiesel produced.

Density increases with decreasing chain length and increasing number of double bonds, while it can be decreased by the presence of low-density contaminants, such as methanol (Alptekin & Canakci 2008; Pratas et al. 2010). Ejim et al. (2007) have performed an analytical comparison of atomization characteristics of D2 diesel at 80°C with seven pure biodiesels and 14 biodiesel-D2 blends. From the reported values of density, it was observed that density of FAMEs generally increases with increase in degree of unsaturation. In other words, density of FAMEs increases with increase in number of double bonds. Density of FAMEs decreases linearly with temperature (Swern 1979).

Yuan et al. (2009) have stated that the densities of individual fatty acid components decrease with increasing chain length and increase with decreasing saturation. Thus, the densities have smaller values when biodiesels contain longer chain components.

Hoekman et al. (2012) have stated that correlation between density and average chain length of FAMEs could not be established. However
biodiesels with higher densities imparting lower cetane numbers (McCormick et al. 2001).

Pratas et al. (2010 and 2011) have measured the density of seven ethyl esters and eight methyl esters at atmospheric pressure and temperatures ranging from 273.15 to 363.15 K. They found that the density of FAMEs decreases with increasing alkyl chain length and increases with the level of unsaturation, the same happening with FAEEs. The FAMEs exhibit a much higher value for density than the corresponding FAEEs with the same number of carbon atoms in acid side chain.

2.3.3 Surface Tension

Surface tension of a fuel is considered to be one of the basic properties which can affect its atomization characteristics. Higher fuel surface tension opposes the formation of droplets from the liquid fuel (Lefebvre 1989).

Allen et al. (1999b) have reported the surface tension of a series of methyl and ethyl esters of fatty acids. The surface tension of saturated fatty acid esters increased with increase in carbon number except ethyl ester of palmitic fatty acid (C16:0). For methyl ester, the trend was curvilinear. For unsaturated compounds, when compared to C18:0, the surface tension for C18:1 found to be decreased. As the degree of unsaturation progressed to 18:2 and 18:3 the surface tension increased rather than continuing to decrease. For methyl esters, the surface tension of 18:3 was higher than the saturated 18:0 (Allen et al. 1999b).

Surface tension increases with long fatty acid hydrocarbon chains and a level of unsaturated bonds; i.e. biodiesel fuels with more unsaturated fatty acids will present a higher surface tension (Shu et al. 2008).
From the relationship between molecular volume, density, and surface tension; it was found that less dense methyl stearate has a similar surface tension to that of methyl oleate, whereas the methyl linoleate which is having a higher density has an increased surface tension (Doll et al. 2007).

2.3.4 Bulk Modulus and Compressibility

Bulk modulus, which can be thought of as a resistance to compression, is dependent on the amount of free space available between molecules (Szybist 2005a). A higher bulk modulus of a fluid indicates that the fluid is relatively incompressible. Biodiesel has a higher bulk modulus than conventional petro-diesel that has been shown to influence higher NO\textsubscript{X} emissions (Tat et al. 2000).

The advancement of injection timing will increase NO\textsubscript{X} emission and the bulk modulus can impact the fuel injection timing (Heywood 1988). McCormick et al. (2001) have studied the impact of biodiesel chemical structure, specifically, fatty acid chain length and number of double bonds, on emissions of NO\textsubscript{X} and particulate matter (PM). The authors have stated that the differences in the speed of sound and isentropic bulk modulus of biodiesel relative to petroleum diesel could advance the effective injection timing and thereby cause NO\textsubscript{X} to increase.

Tat & Van-Gerpen (2003) have stated that the more saturated a fatty acid methyl ester is, the lower the bulk modulus. Saturated FAMEs are more linear than unsaturated FAMEs, thus allowing for more flexibility and therefore a greater compressibility. The presence of double bonds would affect the linearity or packing of molecules in turn can affect compressibility.

Effects of unsaturation on higher order structure are evidenced by the fact that the addition of even a single double bond decreases the melting point of an 18 carbon fatty acid from 71 to 16°C (Hess et al. 2007; Knothe...
et al. 2005). A carbon-carbon double bond introduces a kink into, and thereby distorts the linearity of, a run of carbon-carbon single bonds. This kinked configuration may foster intra- or inter-molecular interactions in the fuel that reduce compressibility i.e. increase in bulk modulus, leading to earlier injection (Hess et al. 2007; Szybist et al. 2005b).

2.3.5 Cetane Number

Cetane number is the property, which specifies the ignition quality of a diesel engine fuel. The cetane number of biodiesel depends on the parent oil; however, both moieties, the fatty acid chain and alcohol functionality contribute to the ignition quality of biodiesel fuels (Knothe 2005).

The cetane number of neat fatty acid compounds decreases with increasing unsaturation and increases with increasing chain length, i.e. uninterrupted CH$_2$ moieties (Knothe 2005). The cetane number of saturated FAMEs increases with increase in the chain length, and that of unsaturated FAMEs decreases with increase in the degree of unsaturation or number of double bonds (Kinoshita et al. 2006). According to Graboski & McCormick (1998), the cetane number increases with increase in the chain length, decreases with increase in the number of double bonds, and decreases as the double bonds and carbonyl group move toward the centre of the chain. The more sequential CH$_2$ groups in the fatty compound would result in a higher cetane number (Zhang & Van Gerpen 1996).

The branched esters derived from alcohols such as iso-propanol have cetane numbers competitive with methyl or other straight-chain alkyl esters. One long chain suffices to impart a high cetane number even if the other moiety is branched. Branched esters are of interest because they exhibit improved low-temperature properties (Freedman & Bagby 1990).
Longer ignition delay with low cetane numbers and subsequent poorer combustion has been associated with more highly unsaturated components, such as the esters of linoleic and linolenic acids (Knothe et al. 2003). High cetane numbers were observed for esters of saturated fatty acids such as palmitic and stearic acids. The increasing number of double bonds and their positions in their chain cause lower cetane numbers.

Knothe (1997) has concluded that the cetane number of fatty acid esters generally increases with the following: (a) increasing number of methylene groups in the chain of a fatty compound; (b) increasing number of methylene groups in the ester moiety; (c) increasing saturation of the fatty compound.

Yamane et al. (2001) have studied the effect of FAMEs on the ignition delay of diesel engine using oleic acid methyl ester and linoleic acid methyl ester. The authors have concluded that the higher cetane number of oleic acid methyl ester as compared to linoleic acid methyl ester could be the possible reason for its shorter ignition delay.

Klopfenstein (1985) has reported that the cetane number increases in a non-linear manner with increase in the chain length of fatty acid for methyl esters. It was also reported that the cetane number increases with increase in the molecular weight for esters of the normal alcohols when the fatty acid was kept constant. The cetane number increase resulting from an increase in the molecular weight of the alcohol of the ester was less than that for the same increase in the molecular weight of the fatty acid portion of the ester (Klopfenstein 1985).

### 2.3.6 Heating Value

The heating value or heat of combustion of a fuel is measured by the lower and higher heating values, while the heat of vaporization of water is
the difference between them (Nag 2002). As compared to diesel, biodiesel exhibits a lower magnitude of heating value due to the presence of oxygen (10 to 12% on average) in it.

The energy content of fatty acid esters is directly proportional to the chain length (Knothe 2008). Freedman & Bagby (1989a) have measured and reported the gross heats of combustion for three classes of fatty acid esters and two classes of triglycerides. For a given chain length, the heat of combustion values of saturated compounds increased in going from the alcohol to the methyl and ethyl esters. Within a given class, heat of combustion values increased with increasing chain length. Also, heat of combustion values of triglycerides were three times that of their single chain counterparts. Increasing unsaturation for a given chain length for both esters (methyl & ethyl) and triglycerides resulted in a decrease in heat of combustion due to loss of hydrogen (Freedman & Bagby 1989a).

The heat of combustion increases with an increasing chain length and decreases with an increasing unsaturation (Ali et al. 1995; Knothe 2008; Moser et al. 2009) whereas fatty alcohols possess heats of combustion in the same range (Freedman & Bagby 1989b).

The heating value of a fuel increases with increasing carbon number in fuel molecules and also increases as the ratio of carbon and hydrogen to oxygen and nitrogen increases (Demirbas 1997). Methyl esters of fatty acids with similar carbon to oxygen ratio but lower carbon to hydrogen ratio (that means added hydrogen) display greater heating value (Freedman & Bagby 1989b).

2.3.7 Iodine Value

The iodine value or iodine number can be directly related to the degree of unsaturation or number of double bonds in the oil. It is a parameter
used to establish the degree of unsaturation in a vegetable oil or animal fat. The iodine value designates the mass of iodine in grams that is necessary to completely saturate the molecules of 100g of a given oil/fat through a stoichiometric reaction.

A high degree of correlation coefficient was found between iodine value and biodiesel unsaturation level in the correlation analysis (Hoekman et al. 2012; Gopinath et al. 2009b; Ramos et al. 2009). Knothe (2002) has reported iodine values of common unsaturated fatty acids and their triacylglycerol, methyl, ethyl, propyl, and butyl esters. The free fatty acids have the highest iodine value, while the iodine value of triacylglycerol and methyl esters is nearly identical. The iodine value of higher esters decreases with increasing size of the alcohol moiety and hence iodine value is dependent on the molecular weight of the fatty compound.

2.3.8 Oxidative Stability

Oxidation is one of the key considerations in the use of vegetable oil based fuels. The mechanism of oxidative degradation of vegetable oil/biodiesel is a bit complex process to define and in general it can be divided into two stages. Primary process is the one in which the lower-molecular-weight compounds in the fuel were produced; this is then followed by a secondary process where higher-molecular-weight species form, resulting in increases in viscosity and solid deposits (Fang & McCormick 2006; Ogawa et al. 2008).

The oxidation rate and products formed from all these processes are temperature and light dependent as well as dependent on the original fatty acid profile (Bannister et al. 2001). As oxidation deterioration advances, change of relative volumetric fraction of the methyl ester components was observed with different biodiesel samples. Linolenic and linoleic acids
decrease, and the fraction of oleic acid become relatively high as oxidation deterioration advances. In other words, linolenic and linoleic acids are oxidized continuously (Yamane et al. 2007).

As compared to saturated fatty acids, oxidation of unsaturated fatty acids might occur easily (Canaki 2007; Gopinath et al. 2012; Yamane et al. 2007). Reported study shows that the density has increased after oxidation for oils with poor oxidation stability (Du Plessis et al. 1985). Polyunsaturated fatty acids are more sensitive to autoxidation than monounsaturated fatty acids as they contain more allylic methylene positions (Dunn 2008; Frankel 1984; Knothe 2006). Especially, fatty acid chains with methylene-interrupted double bonds (linoleic and linolenic acids) are susceptible to oxidation. If methyl oleate is assigned to a relative oxidative rate of 1, then methyl linoleate and methyl linolenate exhibit relative oxidation rates of 41 and 98, respectively (Knothe 2008). The bis-allylic methylene positions of esters composed of linoleic and linolenic acids in specific are vulnerable to oxidation (Knothe 2005; Neff et al. 1992).

Moser (2009) has reported oxidative stability index (OSI) and oxidation onset temperature (OT) of pure fatty acid methyl and ethyl esters. The author has conducted experiments in which several fatty acid alkyl esters were subjected to accelerated methods of oxidation, including EN 14112 (Rancimat method) and pressurized differential scanning calorimetry (PDSC). With respect to PDSC, a correlation was found in which the OT of saturated fatty acid esters increased with decreasing molecular weight ($R^2 0.7328$). In the case of the monounsaturates, a very strong inverse correlation was detected between molecular weight and OT ($R^2 0.9988$). Oxidation onset temperature is a relative measure of the degree of oxidative stability of the material evaluated at a given heating rate and oxidative environment.
The content of natural antioxidants like tocopherols was found to be a critical factor for the oxidative stability of biodiesel other than the fatty acid composition (Knothe 2005). Tocopherols can lead to the reduction in the biodiesel oxidation rate by more than a factor of 10 (Knothe et al. 2005). Similarly, moisture content in biodiesel will increase biodiesel degradation due to hydrolysis (Bouaid et al. 2007).

2.3.9 Low Temperature Properties

One of the major problems associated with the use of biodiesel in countries with cold climate is poor cold flow properties (Durrett et al. 2008). The melting point is the parameter used to assess the suitability of individual fatty acid esters regarding the low-temperature properties, whereas parameters such as cloud point (CP), pour point (PP), and cold-filter plugging point (CFPP) are used for assessing low-temperature properties of biodiesel.

The CP is the temperature at which the first solids become visible when cooling a diesel fuel; the PP is the temperature at which the fuel ceases to flow; and the CFPP is a low temperature filterability test for cooled fuels already containing some solids. Melting points of fatty acid esters generally increase with an increasing number of CH$_2$ moieties and decrease with an increasing unsaturation (Knothe 2008).

The methyl or ethyl esters forms of biodiesel have CP and PP that are 15-25°C higher than those of No. 2 diesel fuel (Schwab et al. 1987). The length of the fatty acid chain can have a noticeable effect on the crystallization temperature of the biodiesel. Longer chain fatty acids that are completely saturated have shown lesser time to promote crystallization, both in oils, where the fatty acids are predominately in the triglyceride form (Davis et al. 2009; Davis and Sanders 2007; Dunn 2005) and in biodiesels, where the fatty acids are most typically methyl esters (Lee et al. 1995). If branched or
medium chain (C\textsubscript{2} to C\textsubscript{4}) alcohols are used in the process of transesterification to produce biodiesel, then such biodiesels generally have better cold flow properties (Foglia et al. 1997; Lang et al. 2001; Lee et al. 1995). Although crystallization temperature and viscosity depend upon the molecular interactions; crystallization depends not only on interaction, but also on molecular packing to reach the adequate entropy level (Rodrigues et al. 2006).

Knothe & Dunn (2009) have measured and reported the melting points of pure methyl, ethyl, propyl, and butyl esters of pure fatty acids and compared with the existing literature values. They found that the melting point increases with increasing chain length for saturated compounds. In case of unsaturated fatty compounds, the introduction of one “cis” double bond in a fatty acid chain reduces the melting point considerably compared to the saturated chain with the same number of carbon atoms. A “trans” double bond has comparatively little effect on the melting point compared to the saturated chain with the same number of carbon atoms. This is a result of a “cis” double bond introducing a bend in the hydrocarbon chain while in the case of a “trans” double bond, the chain is propagated in a fashion close to that of the corresponding saturated species (Knothe & Dunn 2009).

Imahara et al. (2006) have reported that the methyl esters of saturated fatty acids such as C16:0 (Palmitic) and C18:0 (Stearic) have relatively high CP and are considered to be a precursor for crystallization. The authors have reported the cloud points of series of samples with various fatty acid compositions (i.e. mixture of C16:0, C18:0, C18:1, and C18:2). For pure methyl oleate the CP was found to be 259 K and increased largely with methyl palmitate added even in its low mole fraction. It was then increased gradually and monotonously at higher fraction of C16:0 and finally reached at the intrinsic value of C16:0 (301 K). More similar behaviors were observed for binary mixtures of other saturated and unsaturated esters. These results
mean that saturated esters having higher CP than unsaturated ones can have a significant effect on characterizing its cold properties. Unsaturation within the hydrocarbon chain of a fatty acid or FAME represents a point at which the relatively linear chain is ‘‘kinked’’ as a result of the double bond geometry (Oda et al. 2002). As a result, escalating levels of unsaturation within a fatty acid or mixture of FAME usually lowers the crystallization temperature as these ‘‘kinks’’ hamper the ordering of the fatty acid hydrocarbon chains into crystals (Davis & Sanders 2007).

For a multi-component mixture, i.e. biodiesel, the CP depends mostly on the saturated ester content and unsaturated ester composition can be negligible (Imahara et al. 2006).

Interestingly, Nascimento et al. (2005) have argued that the unsaturation can also influence the crystallization temperature, because the molecule spatial configuration can obstruct with crystal packing efficiency. It was observed from the previous studies that cis-unsaturation, different chemical structures, and low molecular weights of glycerides favor solidification temperatures (Asadauskas & Erhanb 1999; Dunn & Bagby 1995; Dunn et al. 1997; Lee et al. 1996). It would be desirable to reduce the content of long chain saturated fatty acids to improve low temperature utilization.

2.3.10 Boiling Point and Flash Point

Volatility refers to the ease with which a liquid vaporizes. A liquid that vaporizes at a relatively low temperature has a high volatility. On the other hand, if the boiling point of the liquid is high, its volatility is low (Gopinath et al. 2012; Ramalingam 2005).
The normal boiling points (boiling points at atmospheric pressure) increase with increase in fatty acid carbon numbers. For the fatty acid chains with more than one double bond, the normal boiling point depends on both the number and position of these double bonds. Graboski & McCormick (1998) have stated that the normal boiling points are independent of the degree of unsaturation of the fatty acid.

The flash point is the minimum temperature at which there is a sufficient concentration of evaporated fuel in the air for flame to propagate after an ignition source has been introduced. Flash point is the lowest temperature at which there is enough fuel vapors to give a momentary flash. It is one of the major flammability indices used to establish the fire and explosion hazards of liquids (Katritzky et al. 2007). The values of flash points increase with increasing chain length and thus biodiesels contain longer chain components have higher value of flash points (Yuan et al. 2009).

2.4 EFFECTS OF PROPERTIES AND STRUCTURAL CONFIGURATION OF BIODIESEL FUELS ON THEIR COMBUSTION, PERFORMANCE, AND EMISSION CHARACTERISTICS

From the structural and chemical point of view, each biodiesel is unique since the fatty acid profile and the configuration of each biodiesel are different. As reviewed in the previous section, the structural features of fatty acids of biodiesels can greatly influence their physicochemical properties. Similarly, the combustion, performance, and emission characteristics of biodiesel fuels are significantly affected by their properties. In this context, the effects of the properties and structural configuration of biodiesel on their combustion, performance, and emission parameters are discussed in this section.
There has been a growing interest to broaden the potential feedstock for biodiesel production worldwide. This has led the researchers for a deeper investigation to understand the significance of the effect of biodiesel structure on diesel engine’s combustion, performance, and emission characteristics. A significant number of research studies have been taken place in this context; the outcomes are not conclusive yet, and differing in some cases.

The fuel viscosity and density effects on injection characteristics have been studied by Grimaldi & Postrioti (2000). An inverse correlation was found between the viscosity and spray cone angle, while the viscosity has a positive correlation with the sauter mean diameter. The authors have stated that the viscosity effects on injection rate and penetration length are not so appreciable, whilst the injection rate and injection duration increased with density increase. To precisely correlate spray characteristics and the fuel properties, it can be said that the penetration length greatly influenced by fuel density and the diameter of the fuel droplets significantly affected by the fuel viscosity.

Zubik et al. (1984) have investigated the combustion behavior of sunflower oil methyl ester and compared with diesel No. 2 fuel. The results exhibited that the rate of pressure rise and peak in-cylinder pressure of sunflower were higher compared to diesel fuel. Hamasaki et al. (2001) have studied the combustion characteristics of waste vegetable oil methyl ester and found that the exhaust gas emissions from the waste vegetable oil methyl ester were in agreement with and smoke emission was lower than that of the JIS No. 2 diesel fuel.

Kinoshita et al. (2003) have investigated the usefulness of palm oil methyl ester in a diesel engine. The authors have exhibited that the ignition quality of palm biodiesel was better than that of JIS No.2 diesel fuel. They
also found that the NO\textsubscript{X} and smoke emissions from palm biodiesel were lower than those of JIS No.2 diesel fuel. Yamane et al. (2001) have investigated the dependence of injection and spray characteristics on the physical properties of biodiesel fuels. The authors have found that the biodiesel fuels showed earlier injection timing compared to petro-diesel fuel. The earlier injection timing in the case of biodiesel fuels is attributed to their higher bulk modulus when compared to diesel fuel. In regard to spray characteristics, biodiesel fuel showed a shorter penetration length compared to diesel. The correlation between penetration length and spray cone angle is inverse.

Schonborn et al. (2009) have investigated the effect of molecular structure of various fatty acid alkyl esters on their combustion characteristics. For the study, eight different fatty acid alkyl esters and four biodiesel fuels produced from jatropha, palm, tallow, and rapeseed oils were used as fuels and experimented in a diesel engine. The results showed that both the formation and concentrations of NO\textsubscript{X} and PM emissions were significantly affected by and better correlated with the number of double bonds in the fuels.

Zhang et al. (2009) have carried out experiments to study the premixed ignition characteristics of four types of fatty acid esters namely methyl nonanoate, methyl 2-nonenoate, methyl 3-nonenoate, and ethyl nonanoate. The tests were conducted at different compression ratios and the exhaust gas was analyzed to investigate the low temperature oxidation of fatty acid ester compounds. The authors found from the analysis that the low-temperature heat release was in the order of methyl 3-nonenoate < methyl 2-nonenoate < methyl nonanoate < ethyl nonanoate. The authors have elucidated that the poorer oxidation reaction in the case of olefinic methyl esters was due to the reduced amount 6- or 7- membered transition-state rings that formed during the oxidation of unsaturated esters (due to the double bonds presence in the chain). The position of double bonds can also influence
the low-temperature oxidation. The reticence effect of the low-temperature oxidation was more articulated when the double bonds moved toward the centre position of the fatty acid ester chain.

Puhan et al. (2010) carried out experiments in a direct injection diesel engine fuelled with three biodiesel fuels having different degree of unsaturation and molecular weight. The biodiesel were produced from coconut oil (highly saturated), linseed oil (highly unsaturated), and jatropha oil (moderately unsaturated). The authors have investigated the effects of molecular structure on the combustion and emission characteristics and found that the biodiesels with high unsaturation showed earlier injection, longer ignition delay, higher peak heat release rate, and higher exhaust gas temperature. The emissions such as NO$_X$, hydrocarbons (HC), carbon monoxide (CO), and smoke were also increased with increase in degree of unsaturation. Similarly, biodiesels with high unsaturation exhibited a lower brake thermal efficiency.

Peterson et al. (1992) have investigated the performance characteristics of ethyl and methyl esters of rapeseed oil fuelled in a diesel engine. The results showed that the performance of biodiesel fuels was as good as diesel fuel. The esters have reported higher brake specific fuel consumption and lower power output when compared to diesel fuel; however the difference was very marginal. When comparing the power output of methyl and ethyl esters, the former showed more power output than the latter one.

McCormick et al. (2001) have carried out experiments in a diesel engine fuelled with around 20 biodiesel fuels obtained from different raw material sources and with various pure FAMEs. The authors have investigated the effects of the number and length of the double bonds of the FAME chain on NO$_X$ and particulate matter (PM) emissions. The number of double bonds
was quantified as iodine value and a significant increasing correlation was found with NO$_X$ emissions, whereas the effect on PM emissions was marginal. For the saturated fatty acids ranging from lauric (C12:0), palmitic (C16:0), and stearic (C18:0), the NO$_X$ emissions were increased with a decrease in chain length, whilst PM emissions were practically remained same.

Tat et al. (2007) have tested and compared two types of soybean biodiesel, one with high content of monounsaturated fatty acid (high-oleic) and another with high content of polyunsaturated fatty acids in a direct injection diesel engine. The authors found that the NO$_X$ emissions were significantly reduced when using high-oleic based soybean biodiesel compared to the polyunsaturated based soybean biodiesel. There were no major differences found in the case of smoke and unburned hydrocarbon emissions using both the soybean biodiesel types.

Lapuerta et al. (2009) have conducted experiments in a direct injection diesel engine to investigate the effect of degree of unsaturation of biodiesel fuels on PM and NO$_X$ emissions. Biodiesels derived from four different feedstocks were used for the study. To quantify the degree of unsaturation, iodine values were measured. The iodine values of these biodiesels were ranging from 90 to 125. It was found from results that the NO$_X$ and PM emissions had been significantly affected by the degree of unsaturation. Whilst, the NO$_X$ emissions were increased, the PM emissions were decreased with increase in unsaturation.

Benjumea et al. (2011) have investigated the effects of the biodiesel chemical structure, specifically its degree of unsaturation, on engine performance, combustion characteristics, and emissions. For the study, experiments were conducted on a high-speed direct-injection automotive
diesel engine fueled with three mixtures of fatty acid methyl esters. The fuel matrix was designed in such a way that the effect of the degree of unsaturation of the tested biodiesel fuels was isolated. This allowed maximizing the effect of the cetane number, while the other properties, such as chain length, oxygen content, density, viscosity, and volatility, varied within a small range. The results showed that the effect of degree of unsaturation on engine performance and start of injection was not significant, whilst it had a noticeable influence on combustion characteristics and emissions, through its effect on the cetane number.

A longer ignition delay period and thus a more retarded start of combustion were resulted with increase in degree of unsaturation. Irrespective of engine loads, the start of injection was almost constant, whereas the premixed portion of combustion, peak heat release rate, peak in-cylinder bulk-gas-averaged temperature, and maximum pressure gradient increased with increase in degree of unsaturation. In regard to emissions, the NO\textsubscript{X}, total hydro carbon, and smoke emissions increased with increase in degree of unsaturation.

2.5 FATTY ACID PROFILE MODIFICATION TO ACHIEVE THE DESIRED PROPERTIES OF BIODIESEL

From the literature review, it is observed that the properties of various fatty acid compounds can have a significant effect on biodiesel properties and in turn on the combustion, performance, and emission characteristics of the biodiesel fuels. It is important to decide whether a biodiesel should contain a larger amount of saturated or unsaturated fatty acids esters so that it has better fuel properties, since the contribution of a particular fatty acid(s) favors some properties while it has an undesirable
effect on other properties. For example biodiesel with larger amount of saturated fatty acid esters can do well in terms of cetane number, oxidative stability, and volatility but possess poor low temperature properties. On the other hand the biodiesel with higher amount of unsaturated fatty acids exhibits better cold flow properties with a penalty in oxidative stability and ignition quality as compared to their saturated counterparts.

A number of methods are possible to resolve these issues such as using antioxidants, cetane improvers, cold flow improvers, etc. However while using these additives it is necessary to study the effect on other properties. Previous studies suggest that the low temperature properties can be improved by winterization process in which the saturated esters with higher melting points are removed by repetitive cooling cycles. But winterization will result in a reduction in oxidative stability and ignition quality.

Another approach is to modify the fatty acid profile inherently through genetic modification (Knothe 2008; Standal et al. 2007; Charles De et al. 2009). Hence it is necessary to suggest a specific fatty acid profile which will provide a biodiesel with almost all the properties are optimal. In this context, oleic acid methyl ester has been studied and suggested as a prime component of such modified biodiesel fuels (Bringe 2005; Kinney & Clemente 2005). Knothe (2008) has investigated to propose alternatives to oleic acid methyl ester, which include esters of palmitoleic acid, saturated short-chain esters, hydroxyl-containing esters, and esters other than methyl. He has suggested that the methyl palmitoleate and esters of decanoic acid are strong candidates for improving fuel properties besides methyl oleate (oleic acid methyl ester). The author (Knothe 2008) has finally concluded that the inherent genetic modification of the fatty acid profile offers the best possibility of addressing several fuel property issues simultaneously.
2.6 SUMMARY

From the literature review it was observed that most of the studies were focused in comparing combustion, performance, and emissions of biodiesel with petro-diesel. Similarly, when reviewing the studies on fatty acid composition of biodiesel, a good amount of research studies were focused only on properties. But exhaustive studies on the effect of structural parameters on properties with a wider coverage for a given set of test fuels are not available. In addition, the studies that analyze the effects of the various structural parameters on combustion, performance, and emission parameters are very much limited. A single exhaustive study, which investigates the effects of various structural parameters of biodiesel on its properties, combustion, performance, and emission characteristics in order to establish a better correlation between them could not be found. Having this as a primary motivation factor, the various structural parameters of biodiesels such as % of total saturated fatty acids (% of TSFA), % of total unsaturated fatty acids (% of TUFA), double bond equivalent (DBE), allylic position equivalent (APE), bis-allylic position equivalent (BAPE), total position equivalent (TPE), degree of unsaturation equivalent (DUSE), and average chain length (ACL) were determined and their effects on the properties, combustion, performance, and emission characteristics are studied.

Similarly from the literature review, it was found that most of the studies have investigated on the effect of individual properties of fuels on combustion, performance, and emissions parameters. But it is very important to understand the composite effects of multi-properties in order to compare different biodiesel fuels. Having this as a secondary motivation factor, a single index named as “Composite Fuel Property Index (CFPI)” was developed. This CFPI can be calculated for any given biodiesel. The ASTM D6751, EN 14214, and IS 15607 standard specifications were used as
reference values for this index. The purpose of developing this index is to have a single unit-less indicator based on which the entire engine performance can be correlated. The objectives of the present research are as follows.

1. Investigate the effects of various structural parameters of biodiesel fuels on
   - their fuel properties
   - their combustion, performance, and emission characteristics in a direct-injection diesel engine

2. Establish numerical correlations between structural parameters of biodiesels and their fuel properties, combustion, performance, and emission characteristics

3. Develop a composite fuel property index from the properties of biodiesel fuels to correlate with combustion, performance, and emission characteristics of biodiesel fuels