CHAPTER 2

LITERATURE REVIEW

2.1 GENERAL

In this chapter, earlier research work associated with the use of vegetable oils in diesel engines and their problems are described. Several reports on biodiesel production process and fuel properties are also reviewed. Many research work on the effect of biodiesel composition on fuel properties are also discussed. In addition the literatures reported about the combustion, performance and emissions characteristics of biodiesel in diesel engines are discussed.

2.2 VEGETABLE OILS AS DIESEL SUBSTITUTE AND THEIR PROBLEMS

Humke et al (1981) reported that injection nozzle deposits with vegetable oils and vegetable oil blends with diesel fuel caused engine performance to decrease and emissions to increase as a function of test time. During 25 hours testing at 2200 rpm, thermal efficiency losses ranged from about 1 to 6 percent and emissions increased by an average of 2 g/kWh to 14 g/kWh. Scraping the carbon deposit from the nozzle tip exterior resulted in regaining the original performance and emissions values.
Vegetable oil densities were higher than #2 diesel fuel that resulted in greater fuel mass flow to the engine because the fuel injection pump controlled volume delivery. Since viscosities were 8-10 times higher, the internal pump leakage was reduced which also contributed to increased fuel flow. At maximum fuel delivery conditions with unaltered injection pump calibration, fuel mass flows were up to 20 percent higher, energy delivery was 10 percent higher and engine power was up to 6 percent higher for vegetable oils.

The other problems when using vegetable oil are lubricating oil thickening, abnormal engine wear, and piston ring sticking. These problems again lead to fuel dilution in crankcase, lower NO\textsubscript{X}, lower thermal efficiency and higher CO, PM, and HC.

Ryan et al (1993) reported that significant chemical changes occur in the oils during injection process. The major change is the formation of low molecular weight compounds from the C18:2 and C18:3 fatty acids. One possible explanation for this phenomenon is the occurrence of chemical reactions during the injection of the oils at high temperature. These chemical reactions result in the formation of low molecular weight gases and a very dense inner core of high molecular weight liquids. Rapid gasification of the oils in the fringes of the spray could account for the rapid spread of the jet and the increase in cone angle. Polymerization of the oil in the liquid core of the spray could account for a contraction of the visible core and a decrease in the penetration rate.

Tadashi Murayama et al (1984) concluded that while using either rapeseed oil or palm oil as a diesel fuel substitute very satisfactory results (engine performance and emission levels) were obtained but only for a short duration of operation, after which they caused carbon deposit build ups and sticking of piston rings after extended operation. The practical solutions
suggested were increasing fuel temperature to over 200 degrees Celsius, blending 25 % volume diesel fuel in vegetable oil and blending 20 % volume ethanol in the fuel or converting the vegetable oils into methyl esters.

Ryan et al (1984) reported that nitrogen is most probably carried over in the oil extraction process in the form of protein. Nitrogen compounds act to inhibit the combustion process by radical trapping or some other processes and oils with more double bonds results in the aggravation of lubricating oil dilution and nozzle coking problems.

De Almeida et al (2002) concluded that the use of pure palm oil in a diesel engine resulted in poor atomization due to high viscosity of palm oil, large carbon deposits, clogging of fuel lines and starting difficulties at low temperature. When heated to 100 degree Celsius, palm oil presented lower viscosity, better combustion characteristics and less deposit of unburnt carbon particles. The suggestions given are increasing the fuel injection pressure and the use a turbocharger to increase temperature and pressure in the cylinder.

2.3 BIODIESEL PRODUCTION PROCESS AND FUEL PROPERTEIS

Anjana Srivastava et al (2000) explained the most important variables that influence transesterification reaction time and conversion as follows:

- reaction temperature;
- ratio of alcohol to oil;
- catalyst type and concentration;
- mixing intensity;
- purity of reactants.
The maximum yield of esters occurs at temperatures ranging from 60 to 80 °C at a molar ratio (alcohol to oil) of 6:1. A further increase in temperature was reported to have a negative effect on the conversion. The stoichiometry of the transesterification reaction required 3 mol of alcohol per mole of triglyceride to yield 3 mol of fatty esters and 1 mol of glycerol. To shift the transesterification reaction to the right, it was necessary to use either a large excess of alcohol or to remove one of the products from the reaction mixture. The second option was preferred wherever feasible. When 100 % excess methanol was used, the reaction rate was at its highest. A molar ratio of 6:1 was normally used to obtain methyl ester yield higher than 98 % by weight.

Transmethylations occur approximately 4000 times faster in the presence of an alkaline catalyst than those catalysed by the same amount of acid catalyst. The alkaline catalyst concentration in the range of 0.5 to 1 % by weight yields 94 to 99 % conversion of vegetable oil into esters. Further, increase in catalyst concentration did not increase the conversion and it adds to extra costs.

Transesterification reaction is diffusion-controlled and poor diffusion between the phases resulted in a slow reaction rate. As methyl esters are formed, they act as a mutual solvent for the reactants and a single-phase system was formed. The mixing effect was most significant during the slow rate region of the reaction. Impurities present in the oil also affect the conversion levels.

Kirschenbauer (1960) 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. But autoxidation of olefinic chains (oleic acid) by atmospheric oxygen gave
hyperoxide. It was generally believed that not the double bonds but a methylene group adjacent to a double bond adds molecular oxygen to yield a hyperoxide as given below:

\[ \text{CH}_2\text{CH} = \text{CH}^- + \text{O}_2 \rightarrow \text{CH.CH}=\text{CH}^ - \downarrow \text{O.OH} \]

It was believed that iodine value was not reduced in proportion to the amount of oxygen absorbed by the unsaturated ester. It was observed that the mechanism of hydroperoxide formation represents a chain reaction involving formation of free radicals. The hydroperoxides are found to be quite unstable, and their decomposition products appear to combine readily with unsaturated centers and reactive groups.

The studies of pure compounds indicate that the reaction rate for methyl linoleate is about 12 times as great as that of methyl oleate, whereas that of methyl linolenate is 24 times that of methyl oleate.

Saran and Narula (1995) reported that the specific heat of fats and oils increases with temperature and with degree of unsaturation. As chain length or carbon number of fatty acid increases, the specific heat decreases. The latent heat of vaporization of fatty acids decreases with chain length and increases with degree of unsaturation. Surface tension increases with increase in length of the fatty acid chain.

Polymerization of unsaturated acids takes place through a “Diels-Alder” type of consideration reaction akin to the addition of maleic anhydride to the unsaturated conjugated chain. This type of reaction is limited to the conjugated unsaturated fatty acids. This reaction is influenced both by the
reaction temperature and the catalysts employed, and is responsible for the production of numerous useful fatty acids derivatives.

Ayan Demirbas (1998) has investigated and compared the fuel properties of vegetable oils, and related the combustion heats to their chemistry. The author has derived a relationship between saponification value, iodine value and higher heating value of vegetable oils. It was stated that the heating value of vegetable oils increases with increasing chain length and decreases with increase in number of double bonds. The increase in heat content was attributed to the increase in number of carbon and hydrogen, as well as increase in the ratio of these elements relative to oxygen. The possible cause for the decrease in heat content may be deficiency of hydrogen atoms (greater unsaturation).

The author has also stated that the saponification value of vegetable oils decreases with increase in its molecular weight. The increase in iodine value i.e. carbon-carbon double bond (C = C), results in a decrease in the heat content of an oil. A regression model shown in equation (2.1) was developed to estimate the higher heating value of vegetable oils using their iodine and saponification value.

\[
HHV = 49.43 - [0.041(SV) + (0.015(IV)]
\]

where, \( SV \) = Saponification Value and \( IV \) = Iodine Value and \( HHV \) = Higher Heating Value of Vegetable oils. The regression model yielded the correlation coefficient as 0.9999 and mean difference as 0.0067 %. The maximum percentage difference between the calculated and determined HHV was reported as 6.389 % (lower prediction error). Using equation (2.1), HHV of twenty different vegetable oils were calculated from their IV and SV and compared with experimentally determined HHV.
However, the extent of using equation (2.1) for biodiesel fuels was not cited in the literature.

Allen et al (1999) have presented a method for predicting the dynamic viscosity of mixtures of fatty acid esters. The carbon number ranges from 8:0 to 18:0. It was cited that dynamic viscosity of pure fatty acid methyl esters (FAMEs) at 40°C increased with carbon number in a curvilinear (second order polynomial) trend for saturated esters. 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 became 18:1. A completely different curve was observed as the degree of unsaturation progressed from 18:1 to 18:3. As the number of double bonds increased, a non-linear (second order polynomial) 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. The trend curve of viscosity of methyl esters is shown in Figure 2.1.

**Figure 2.1** Viscosity trend lines for methyl esters at 40°C
A logarithmic equation shown in equation (2.2) was used to predict the dynamic viscosity of biodiesel/fatty ester mixtures from the viscosities of the individual components.

\[ \ln \mu_m = \sum y_i \ln \mu_i, \quad i = 1 \text{ to } n. \]  

(2.2)

where, \( \mu_m \) is the mean viscosity of mixture (Pa s), \( \mu_i \) and \( y_i \) are the viscosity (Pa s) and mass fraction of the pure \( i^{th} \) components. The average prediction error was reported as 3 % of the measured value.

Shigley et al (1954) reported that the densities of any one series of esters decrease with increase in molecular weight up to a certain temperature and above that temperature the densities increase with increasing molecular weight. Viscosity increases with molecular weight.

Ejim et al (2007) have performed an analytical comparison of atomization characteristics of D2 (No.2 diesel) at 80°C with seven pure biodiesels and 14 biodiesel-D2 blends. From the reported values, it is observed that the density of FAMEs generally increases with degree of unsaturation. In other words, the density of FAMEs increases with increase in the number of double bonds. The data points and trend curve of density of methyl esters are shown in Figure 2.2.

The authors have performed the analytical study of the effect of viscosity, density and surface tension at 80°C on atomization characteristics for seven biodiesels in a diesel engine. It was reported that coconut biodiesel has the smallest (20.1 µm) and rapeseed biodiesel has the largest (28.9 µm) Sauter Mean Diameter (SMD). Coconut biodiesel is not significantly different from that of No.2 diesel. The reason for the smallest and largest SMD in the case of coconut and rapeseed biodiesel is that the coconut biodiesel has the
lowest density, viscosity and surface tension, where as the rapeseed biodiesel has the highest values. No significant difference in drop size was observed for all B5 blends, B20 blends and B100 biodiesels of palm, soybean, cottonseed and canola.

![Figure 2.2 Density trend lines for methyl esters at 80°C](image)

The most influencing physical property of the fuels on atomization showed that viscosity is the largest contributor, about 90%, to the change in SMD, whereas the density contributions were the least, causing only less than 2% change. Hence to achieve improved fuel atomization the viscosity should be the first choice of a fuel’s physical properties to be reduced.

Freedman et al (1990) have calculated the cetane number of n-alcohols and saturated methyl esters from their properties. The cetane number of n-alcohols was predicted from their boiling point, melting point, carbon number, heat of combustion, refractive index and density. While the cetane number of saturated fatty methyl esters was predicted from their boiling point, viscosity, heat of vaporisation, carbon number, surface tension,
melting point, refractive index and density. The regression models shown in equations (2.3) to (2.11) were developed to predict cetane numbers (Y) of saturated fatty methyl esters from the physical properties (X).

<table>
<thead>
<tr>
<th>X</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling point</td>
<td>[ Y = (-41.30) + 0.2785X + 0.001209X^2 + 3E-06X^3 ] ( R^2 = 0.9999, S = 0.1 ) (2.3)</td>
</tr>
<tr>
<td>Viscosity</td>
<td>[ Y = (-23.48) + 61.6828X + (-12.7738X^2) + 0.87697X^3 ] ( R^2 = 0.9985, S = 1.4 ) (2.4)</td>
</tr>
<tr>
<td>Heat of vaporisation</td>
<td>[ Y = (-1054.90) + 32.324X + (-0.23097X^2) ] ( R^2 = 0.9930, S = 1.4 ) (2.5)</td>
</tr>
<tr>
<td>Heat of combustion</td>
<td>[ Y = (-62.96) + 0.09700X + (-1.69E-05X^2) ] ( R^2 = 0.9921, S = 2.6 ) (2.6)</td>
</tr>
<tr>
<td>Carbon number</td>
<td>[ Y = (-57.26) + 14.892X + (-0.4149X^2) ] ( R^2 = 0.9919, S = 2.6 ) (2.7)</td>
</tr>
<tr>
<td>Surface tension</td>
<td>[ Y = (-1500.58) + 104.656X + (-1.7330X^2) ] ( R^2 = 0.9893, S = 3.0 ) (2.8)</td>
</tr>
<tr>
<td>Melting point</td>
<td>[ Y = 58.22 + 0.556X ] ( R^2 = 0.9822, S = 3.4 ) (2.9)</td>
</tr>
<tr>
<td>Refractive index</td>
<td>[ Y = (-2107.38) + 1522.21X ] ( R^2 = 0.9805, S = 3.5 ) (2.10)</td>
</tr>
<tr>
<td>Density</td>
<td>[ Y = 7206.14 + (-8648.96X) ] ( R^2 = 0.9799, S = 3.6 ) (2.11)</td>
</tr>
</tbody>
</table>

where, \( X = \) Properties, \( Y = \) Cetane number, \( R^2 = \) Coefficient of determination, \( S = \) Standard error of Y estimate. Figure 2.3 depicts the variation of cetane number with boiling point for methyl esters.
From the trend of Figure 2.3, it can be observed that the cetane number of saturated fatty methyl esters increases with increase in boiling point. It was concluded that the boiling point was precisely correlated with cetane number than other properties. The above conclusion was based upon $R^2$ value and the average percentage of error. The maximum prediction error was reported as 0.2 % from boiling point, 2.0 % from viscosity, 1.9 % from heat of vaporisation, 4.8 % from heat of combustion, 4.9 % from carbon number, and 5.4 % from surface tension, 6.9 % from melting point, 7.5 % from refractive index and 9.4 % from density.

Goodrum et al (1996) have reported that the mixture of analogous compounds, such as triglycerides, might be assumed to behave as ideal solutions. It was stated that based on the above assumption the density of a mixture is equal to the summation of density of each pure component. Equation (2.11) was used to calculate the density of a mixture from its pure component.
\[ \rho_{\text{mix}} = \sum x_i \rho_i, \quad i = 1 \text{ to } n. \]  

(2.11)

\[ \rho_i \text{ and } x_i \text{ are the density and mole fraction of the pure } i^{\text{th}} \text{ components.} \]

It was stated that the heat capacity of triglycerides increases with increasing molecular weight. It was also reported that the surface tension, which is the measure of surface energy, decreases moderately with increasing temperature. A linear regression model was developed to determine the relation between surface tension and temperature (\(R^2 = 0.997\)). Linear regressions were also developed to establish the relation between density versus temperature and viscosity versus temperature.

Kanit Krisnangkura (1986) has provided a simple method of estimating the cetane indexes of vegetable oil methyl esters from their saponification and iodine numbers. Equation (2.12) was formed to quantitatively relate the cetane index of vegetable oil methyl esters to their saponification and iodine numbers and then compared with equation (2.13), which was already developed by Klopfenstein to estimate the cetane index.

\[
\text{Cetane Index} = 46.3 + (5458/x) - 0.225y 
\]  

(2.12)

where, \(x\) and \(y\) are the saponification and iodine numbers of vegetable oils.

\[
\text{Cetane Index} = \quad 58.1 + 2.8 \left(\frac{(n - 8)}{2}\right) \\
- \left[15.9 \times \text{number of double bonds}\right] 
\]  

(2.13)

The author states that the triglycerides and fatty acid methyl esters have almost the same saponification and iodine numbers, but cetane indexes of the parent oil are much lower than those of methyl ester derivatives. It was stated that when individual fatty acid methyl esters from \(C_8\) to \(C_{24}\) were tested, a parallel straight line three units higher than that of Klopfenstein’s
was obtained. The comparison of cetane index calculated by equation (2.12) and (2.13) is shown in Figure 2.4.

![Cetane Index Graph](image)

**Figure 2.4  Cetane indexes of fatty acid methyl esters calculated by equations (2.12) and (2.13)**

Yuan et al (2005) have predicted the temperature dependent vapour pressure of methyl esters of fourteen fatty acids those are commonly present in biodiesel fuels by the Antoine equation and a group contribution method. Antoine equation constants were calculated for each of these esters. The predicted boiling points of these esters up to a pressure of 100 mm Hg were within $\pm 1.0 \%$ of reported data for these two methods. Normal boiling points were determined from both the predicted vapour pressure and a correlation equation and the prediction errors were less than 5 K compared to available published data. The vapour pressure of nineteen biodiesel fuels were predicted by weighing the vapour pressure of each component in the mixture with the percentage composition of each component in the ester blends. The normal boiling points of the 19 biodiesel fuels were calculated from the predicted vapour pressure. It was cited that the normal boiling points for
alkenes are usually marginally lower than those for alkanes with same carbon number and the normal boiling points were nearly independent of the degree of unsaturation.

Heinrich Prankl (2002) stated that standards are of importance for the producers, suppliers and users of biodiesel. Authorities need approved standards for the evaluation of safety risks and environmental pollution. Some important biodiesel fuel properties are discussed. At very low temperature there is a big difference between diesel and biodiesel viscosity. Therefore fuel injection manufacturer claimed: If the cold filter plugging point (CFPP) of biodiesel is \(< -20 \, ^\circ\text{C}\), the viscosity at \(–20 \, ^\circ\text{C}\) shall not exceed 48 \(\text{mm}^2/\text{s}\).

The oxidation stability determined by EN14112 (Rancimat) at 110 \(^\circ\text{C}\) is 6 h in EN 14214 and 4 h in EN14213. Iodine value limit was set at 120 in EN 14214 and 135 in EN 14213.

High content of unsaturated acids in the esters increases the risk of polymerization in the engine oil. The limit was set at 12 % for linolenic and 1 % for fatty acids with \(> = 4\) double bonds. The problem is that there is no method to determine fatty acids \(> = 4\) double bonds.

### 2.4 EFFECT OF BIODIESEL COMPOSITION ON FUEL PROPERTIES

Gerhard Knothe (2005) has studied the influence of the structure of fatty esters on ignition quality, heat of combustion, cold flow, oxidative stability, viscosity and lubricity of biodiesel fuels. The author has reported that the cetane number decreases with increasing unsaturation and increases with increasing chain length.
It was also stated that the viscosity of fatty ester mixtures/biodiesel increases with chain length (number of carbon atoms) and with increasing degree of saturation. The configuration of double bond influence viscosity (cis double bond configuration offers lower viscosity than trans) while double bond position dose not affect the viscosity. Branching in the ester moiety, however, has little or no influence on viscosity. The author has also reported that the heat of combustion of neat fatty compounds increases with increasing chain length and decreases with increasing unsaturation.

Gerhard Knothe et al (2003) have determined the cetane numbers of 29 samples of straight-chain and branched C$_1$-C$_4$ esters as well as 2-ethylhexyl esters of various common esters. The cetane numbers were determined in an Ignition Quality Tester (IQT), which was a newly developed, automated rapid method using only a small amount of materials. It was reported that the effect of increasing unsaturation (oleic and linoleic esters) results in reduced cetane numbers and increasing chain length leads to increased cetane numbers. It was also reported that the esters of fatty compounds obtained from branched alcohols have improved low-temperature properties compared to those derived from straight-chain alcohols.

Klopfenstein (1985) has reported the cetane numbers of a series of methyl esters of the saturated fatty acid esters from 8 to 18 carbons and the effect of fatty acid chain length on cetane numbers. The author has mentioned that the cetane number increases in a nonlinear manner with increase in chain length of fatty acid for methyl esters. It was also reported that the cetane number increases with increase in molecular weight for esters of normal alcohols when 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.
Equation (2.14) was derived to calculate the cetane number of individual fatty esters using their fatty acid chain length. It was stated that the equation in ASTM standard D-976, using boiling point and density for the calculation of cetane index of petroleum products, is inaccurate for vegetable oils and fatty acid esters. The reported trend line of cetane number of individual methyl esters is shown in Figure 2.5.

\[ y = 24.48 + 8.431x - 0.1299x^2 \]  \hspace{1cm} (2.14)

where, \( y \) = fitted cetane number, and \( x \) = chain length of the fatty acid.

![Figure 2.5 Cetane number trend lines for methyl esters](image)

Yuan et al (2003) have presented methods for predicting key properties including; vapour pressure, latent heat of vapourisation, density, surface tension and liquid viscosity of biodiesel those can be used for combustion modeling. The properties of soybean oil-based methyl ester biodiesel were estimated by two widely used methods: Joback modification of Lydersen’s method, and Ambrose’s method. The influence of composition on
the fuel properties was also studied. It was reported that highly unsaturated fatty acid methyl esters contribute most to critical temperature and cause the highest latent heat of vapourisation, but the lowest vapour pressure and the least liquid density. Long-chain unsaturated and less saturated fatty acid methyl esters contribute most to surface tension and liquid viscosity.

Szybist et al (2005) stated that bulk modulus, which can be thought of as a resistance to compression, is dependent on the amount of free space available between molecules. Thus, rather than compressing the molecules themselves, the reduction in liquid volume under pressure is achieved through a reduction in free space between molecules. As pressure is increased further, less free space is available and the resistance to compression increases, thus compressibility decreases with increasing pressure.

For hydrocarbon fuels compressibility decreases as the rigidity of the molecular structure increases. Thus aromatics have a much lower compressibility than n-alkanes. Rigid molecule such as aromatic packs together more tightly than less rigid ones.

In addition to the structure rigidity, intermolecular force largely dictate the free space between molecules. Hydrocarbon intermolecular interactions are dominated by London- forces, a week type of hydrogen bonding which relies on induced dipole moments, such as oxygenates and halogenates, exhibit much stronger hydrogen bonding and have a greater affinity for one another. Thus a strong attraction between molecules with permanent dipole moments decreases the free space between molecules.

McCormick et al (2001) studied to understand the impact of biodiesel chemical structure, specifically, fatty acid chain length and number of double bonds, on emissions of NOx and particulate matter (PM). A group
of seven biodiesel fuels produced from real world feed stocks and 14 produced from pure fatty acids were tested in a heavy duty truck engine. It was concluded that the molecular structure of biodiesel has substantial impact on the performance and emissions. It was observed that the density, cetane number, and iodine number were highly correlated with one another. The cetane number was highly negatively correlated with iodine number and density. The correlation coefficient between cetane number and iodine number was reported as \((-0.896\) and between cetane number and density as \((-0.897\).

The increase in iodine number and density of biodiesel fuels were proposed as factors for increase in NO\(_X\) emissions. The cetane number decreases with increase in iodine number, thus, excessive ignition delay and poor combustion performance may also be proposed as a cause of higher NO\(_X\). Increasing density may increase NO\(_X\) because the fuel injectors inject a constant volume, but larger mass of more dense fuels. Since a larger mass of fuel is burned, more NO\(_X\) is produced. The authors mentioned 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\(_X\) to increase. The authors have stated that the speed of sound and isentropic modulus are 3\% and 1\% higher, respectively, in methyl soy ester than in certification diesel. They also made a mention that this could advance injection timing by as much as 1° CA. The authors concluded that the most fundamental way to alter the emissions performance of a fuel is to alter the molecular structure.

Graboski et al (1998) have made an extensive review of the utilization of biodiesel fuels in compression ignition engines. The status of fat and oil derived biodiesel fuels with respect to fuel properties, engine performance and emissions were reviewed. It was reported that the saturated
acids exhibit higher freezing points than the unsaturated acids. The structural properties of biodiesel that affect freezing point are degree of unsaturation, chain length, and degree of branching. The boiling points of the acids are dependent on the length of the carbon chain but nearly independent of the degree of unsaturation of the fatty acid. It was stated that the cetane number increases with chain length, decreases with number of double bonds and decreases as double bonds and carbonyl groups move toward the center of the chain. It was also reported that the iodine value of biodiesels increases with increase in unsaturation.

The authors have affirmed that the fuel spray properties, specifically the droplet size and sauter mean diameter, are influenced by fuel surface tension and viscosity. Sauter mean diameter has been shown to increase with increasing surface tension and viscosity. It was proposed that the relatively higher boiling point of the biodiesel fuels might increase the NO$_X$ emissions. This is because higher boiling point fuels may require longer to be heated to boil and to vaporise. This effect may reduce the rate of evaporation.

Hess et al (2007) attempted to reduce NO$_X$ emission by modifying the “cis” bonds in the soy oil methyl to trans isomers. The two configurations of a double bond are not found in equal proportions in biologically produced lipids. Rather, the cis configuration predominates in the living world. Vegetable oils, and biodiesel fuels produced from them, can be considered to contain exclusively cis unsaturation. It was postulated that differences might exist in the NO$_X$ emissions of biodiesel based on their proportions of cis and trans double bonds.

The modified methyl oleate, which underwent a more complete isomerization of its cis double bonds, elevated NO$_X$ production. It was stated
that as the fatty acid chains are isomerized from cis to trans geometry, the molecules become more linear. The more linear structure of a trans bonded system would be expected to allow the molecules to pack closer together, and the London forces to thus be more effective, drawing the molecules into closer proximity and eradicating free space. This could increase compressibility and lead to early injection, followed by NO\textsubscript{X} elevation.

## 2.5 BIODIESEL COMBUSTION, PERFORMANCE AND EMISSIONS CHARACTERISTICS

Robert Bosch GmbH (2004) stated that the volume of the fuel on the high-pressure side of the fuel-injection system for an individual nozzle, which is called as detrimental volume is pressurized and depressurized every time. As a result, compression losses occur and a fuel injection lag is produced. The dynamic process generated by the pressure waves compresses the fuel volume inside the pipes.

Burman Paul et al (1962) reported that since fuel is compressible there is an injection lag between the beginning of the delivery by the pump and the beginning of discharge from the nozzle, and the rate of delivery from the pump is not identical with the rate of discharge from the nozzle.

The compressibility of a liquid is the reciprocal of the modulus of elasticity or bulk modulus. The modulus of elasticity for liquids can be expressed in the same way as that for solids:

\[
K = \frac{\text{Change in stress}}{\text{Change in strain}} = \frac{\text{Increase in pressure}}{\text{Decrease in specific volume}}
\]

where K= Modulus of elasticity
The pressure build causes the pressure wave up by the plunger in compressing the fuel in the pump, while accelerating the fuel column towards the nozzle. These waves not only travel from the pump to the nozzle, but they are also reflected back towards the pump from the nozzle. The pressure wave alters the designed rates of injection and pressures.

The authors also explained the effect of viscosity, surface tension, density and operating conditions like injection pressure, discharge quantity and speed on the spray characteristics, which are given in Table 2.1.

Table 2.1 Effect of various factors on spray characteristics

<table>
<thead>
<tr>
<th>Change in parameters</th>
<th>Effect</th>
<th>Effect</th>
<th>Effect</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Break up distance</td>
<td>Penetration</td>
<td>Dispersion</td>
<td>Droplet size</td>
</tr>
<tr>
<td>Increase in Injection pressure</td>
<td>Decreases</td>
<td>Increases</td>
<td>Increases</td>
<td>Decreases</td>
</tr>
<tr>
<td>Increase in Discharge quantity</td>
<td>Decreases</td>
<td>Increases</td>
<td>Increases</td>
<td>Decreases</td>
</tr>
<tr>
<td>Increase in Speed</td>
<td>Decreases</td>
<td>Increases</td>
<td>Increases</td>
<td>Decreases</td>
</tr>
<tr>
<td>Increase in Viscosity</td>
<td>Increases</td>
<td>Increases</td>
<td>Decreases</td>
<td>Increases</td>
</tr>
<tr>
<td>Increase in Surface Tension</td>
<td>Increases</td>
<td>Increases</td>
<td>Decreases</td>
<td>Increases</td>
</tr>
<tr>
<td>Increase in Density</td>
<td>Increases</td>
<td>Increases</td>
<td>Decreases</td>
<td>Increases</td>
</tr>
</tbody>
</table>

After the fuel is injected into the engine combustion chamber, the fuel has to undergo several physical and chemical processes before ignition. The physical and chemical processes are called as physical and chemical delay, which need not occur one after another but may overlap also. After or even overlapping the physical delay is the period required by preflame reactions to reach flame conditions. The ignition of hydrocarbon fuels is not one of simple oxidation but proceeds in stages involving chain reactions with
aldehydes, peroxides, and hydrocarbon free radicals being formed as intermediate products.

In this context the authors stated that the most important factor in reducing this period is the cetane number of the fuel. It does not mean that cetane number has no effect on physical delay but the extent it affects the chemical delay is not the same as physical delay, which is shown in Figure 2.6. The physical delay can be reduced by finer atomization of the fuel and high relative velocity between the air and fuel to effect more rapid heat transfer to the droplets, and by increasing air density and temperature.

![Figure 2.6 Effect of cetane number on ignition delay](image)

**Figure 2.6 Effect of cetane number on ignition delay**

Szybist et al. (2005) reported that the fundamental principle of the bulk modulus measurement as developed by O’Brien is that under high pressure, a reduction in liquid volume occurs. The bulk modulus is calculated using the equation:

\[
B = (P - P_0)\frac{V_o}{(V_o - V)}
\]

(2.15)
where \( B \) = Bulk Modulus  
\( P \) = Applied pressure  
\( P_o \) = Ambient pressure  
\( V \) = Volume of sample at pressure  
\( V_o \) = Volume of sample at atmospheric pressure

It was observed that there is an advance in fuel injection timing of 1.0 – 1.2 CA deg, for B100 compared to diesel and an advance of 0.1 – 0.3 CA deg, for the B20 blends, but there is no difference between the three B20 fuel blends.

Yamane et al (2001) made two studies. One was on the effects of biodiesel fuel physical properties on injection characteristics and spray behavior. The second one was on the effects of the constituents of biodiesel fuel on combustion and exhaust emission characteristics in a retrofitted compression ignition engine, as well as combustion under high injection pressure. A critical difference between the gas oil and biodiesel fuel properties is the dependence of the bulk modulus on pressure and temperature. Computation results show that at lower fuel temperatures, the injection timing of biodiesel is effectively advanced relative to that of gas oil. This is because at lower liquid temperature the bulk modulus of biodiesel is higher than that of gas oil; then the rate of liquid pressure rise goes up and the injection timing is advanced.

At higher fuel temperatures, there is no difference in the injection timing and the injection pressure between biodiesel fuel and gas oil. It was observed that the spray penetration for biodiesel was shorter than gas oil. Thus the air- fuel mixing process was relatively poor for the biodiesel fuel. This resulted in fuel- rich mixture formation at the center of the combustion
chamber, and a portion of this mixture that failed to burn was emitted as SOF. In general it is known that fuel with a higher density shows shorter penetration and a greater spray cone angle than fuel with a lower density.

Needham et al (1985) measured the ignition delay using ASTM D613 method which describes three different techniques as follows:

a) Start of pressure rise  
b) Start of optical combustion  
c) Start of measured heat release

They reported that with optical transducer, the ignition delay was 0.5 - 1.0 degree CA longer compared to the delay with start of pressure rise. But when measured by the start of heat release, the delay was approximately 1 degree CA shorter.

The author also correlated the shape of the heat release diagram to fuel consumption and the factors which relate to the shape of heat release diagram, such as premixed combustion fraction and the peak rates of premixed and diffusion burning, should correlate with fuel economy. Peak rate of heat release correlated well with NOX emissions, since it was influenced by both ignition delay and volatility. Finally it was concluded that ignition delay is not the single controlling factor in determining overall performance. Ignition delay does, however influence cold start, noise and CO emissions in both DI and IDI engines, and light load HC in the DI engine.

Senatore et al (2000) tested a DI turbocharged diesel engine with rapeseed oil methyl ester and found that heat release always takes place in advance with respect to TDC (between 3 and 5 deg. CA) compared to diesel
fuel. It was stated that the mean combustion temperature attained peak value at the same crank angle, which correlated to NO\textsubscript{X} production.

Klopfenstein et al (1983) tested a single cylinder DI engine with saturated methyl esters from carbon number 12 to 18 and unsaturated esters of carbon number 18. The authors observed the following:

1. Among the saturated series, the heat of combustion per kg increased with chain length, reflecting their higher proportion of reduced carbon. For the same reason esters of unsaturated acids had somewhat lower heats of combustion than the corresponding saturates.

2. For the series of saturated esters, the volumetric fuel consumption is seen to increase with chain length. This might be expected in view of the inverse relationship, which exists between density and chain length for the fatty acid esters at near room temperature. Similarly the decreased volumetric consumption observed for methyl oleate and linoleate are partially accounted for the increase in density with increased unsaturation.

3. Although the energy content of the esters increases with chain length, the increased specific fuel consumption with increasing chain length produces a marked linear decrease in thermal efficiency.
The test results are given in Table 2.2.

### Table 2.2 Engine test results

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Fuel consumption (g/hp h)</th>
<th>Thermal efficiency (%)</th>
<th>Heating value (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#2 Diesel</td>
<td>280</td>
<td>21.7</td>
<td>36.579</td>
</tr>
<tr>
<td>ME 12:0</td>
<td>298</td>
<td>24.4</td>
<td>36.579</td>
</tr>
<tr>
<td>ME 14:0</td>
<td>302</td>
<td>23.3</td>
<td>37.899</td>
</tr>
<tr>
<td>ME 16:0</td>
<td>321</td>
<td>21.1</td>
<td>39.098</td>
</tr>
<tr>
<td>ME 18:0</td>
<td>322</td>
<td>20.8</td>
<td>39.777</td>
</tr>
<tr>
<td>ME 18:1</td>
<td>281</td>
<td>23.3</td>
<td>38.453</td>
</tr>
<tr>
<td>ME 18:2</td>
<td>299</td>
<td>23.2</td>
<td>38.283</td>
</tr>
<tr>
<td>ME 18:3</td>
<td>298</td>
<td>22.7</td>
<td>39.425</td>
</tr>
</tbody>
</table>

Grimaldi et al (2000) reported the effect of fuel viscosity and density on spray characteristics and injection rate, duration and mass.

The observation was change in viscosity (2.33 to 10.39 mm$^2$/s) do not significantly affects both the injection rate and penetration length, while low viscosity causes spray near-angle to be higher in the initial part of the injection duration. Further low viscosity fuel spray was characterised by lower SMD value and higher jet dispersion. Near angle is defined as the angle that includes the spray structure from the nozzle up to 1/3 of penetration. Injection rate, duration and injected mass of all these quantities increased with fuel density. As far as spray evolution is concerned fuel viscosity affects the drop diameter, while fuel density is more important for spray penetration.

Tat et al (2000) reported that the use of biodiesel increases NO$_X$ emissions by an average of 12 % compared to petrodiesel, and 20 % biodiesel/80 % petrodiesel (referred to as B20) increases NO$_X$ emissions by 2 - 4 %. Although biodiesel has a higher cetane number than diesel and
therefore should lower the ignition delay and lower NO\textsubscript{X} emissions, but other physical properties like viscosity, surface tension and bulk modulus impact the fuel injection and combustion behaviour of the fuels. Biodiesel has a higher bulk modulus than conventional diesel, which has been shown to contribute higher NO\textsubscript{X} emissions.

The most common type of diesel injector is the pump – line – nozzle injector. In this configuration, pressure is applied to the fuel upstream of the injector nozzle, and increased until it reaches the nozzle opening pressure, whereupon injection occurs. If a fuel is less compressible, the pressure will build more quickly and the fuel will be injected into the combustion chamber earlier in the compression cycle, whereas if the fuel is more compressible more time will be required to reach the nozzle opening pressure, and the fuel will be injected into the combustion chamber later. Injection timing advance due to fuel compressibility can lead to a longer premixed burning phase and an increase in the production of NO\textsubscript{X}.

Kinoshita et al (2003) have analysed the combustion characteristics and exhaust emissions of palm oil methyl ester (PME) in a direct injection diesel engine. For the experiments, rapeseed oil methyl ester (RME) that contains 92.9 % unsaturated fatty acid esters, palm oil methyl ester which contains 50 % of unsaturated fatty acid esters and gas oil were considered as fuels. The authors have reported that the distillation temperatures of PME at 5 to 90 % recovery are lower than RME and stated that PME may have better volatility compared with RME.

It was also reported that the specific heat at constant pressure \( C_p \) and at constant volume \( C_v \), of PME are highest and lowest in the case of gas oil, but the specific heat ratio \( C_p/C_v \) of PME and RME is lower than that of gas oil. The injection timing, ignition delay and ignition timing for the three
fuels were reported at different loads. The injection occurs earlier for RME than PME, and the earlier injection of RME was believed to be due to the higher density of RME than that of PME. The reported ignition delay was observed to be shorter for PME than that of RME. It was considered that the lower amount of linoleic acid methyl ester (PME 9.1 % and RME 21.7 %) and higher amount of palmitic acid methyl ester (PME 44.1 % and RME 4.3 %) in PME as compared to RME would affect ignition delay.

The reported values of both CO and HC emissions from PME were lower than from RME. The above findings were believed to be due to the shorter ignition delay of PME as compared to RME. The authors have stated that the smoke emission from PME was found to be higher than that of RME. The authors stated that higher smoke emission from PME may be due to the higher stoichiometric AFR_{mass} of PME (12.61) than that of RME (12.57). That is PME needs more air for complete combustion than RME and therefore, the soot formation from PME may increase in the rich mixture of fuel spray and the cooler part of spray impingement on cylinder wall than that from RME. The NO_{x} from PME was found to be lower than that of RME.

Traver et al (1999) have explored the feasibility of using in-cylinder pressure-based variables to predict exhaust emission levels at steady state conditions from a Navistar T444 (7.3 L V8) direct injection diesel engine through the use of neural networks. In this work, a test matrix of 64 separate load and speed settings were chosen to provide a wide range of engine performance and emission values. When all the data had been collected and averaged for each of the 64 points, a correlation analysis was performed between exhaust emission values and in-cylinder variables. This analysis provided a way to select the most promising potential inputs to a series of neural network architectures for each gaseous emission. Absolute values above 0.5 have been considered as potential inputs.
The HC, CO, CO₂, and NOₓ emissions were predicted using the networks. To predict these emissions, ignition delay, peak combustion pressure values, location of peak pressure, indicated mean effective pressure, combustion duration, maximum burn rate, maximum burn rate location, location of 50 % of mass fraction burned, maximum torque, maximum torque angle, maximum heat release, and location of maximum heat release were given as input variables. Different combinations of input variables with different algorithms were used to predict the aforesaid exhaust emissions. The reported r² values of the networks are shown in Table 2.3.

<table>
<thead>
<tr>
<th>Emission</th>
<th>Range of r² value for Testing</th>
<th>Range of r² value for Training</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC</td>
<td>0.9161 to 0.9766</td>
<td>0.9341 to 0.9892</td>
</tr>
<tr>
<td>CO</td>
<td>0.9980 to 0.9992</td>
<td>0.9980 to 0.9986</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.9982 to 0.9991</td>
<td>0.9984 to 0.9990</td>
</tr>
<tr>
<td>NOₓ</td>
<td>0.9982 to 0.9989</td>
<td>0.9966 to 0.9976</td>
</tr>
</tbody>
</table>

Eiji Kinoshita et al (2006) have determined the usefulness of coconut and palm oil biodiesels as alternative diesel fuels. The combustion characteristics and exhaust emissions of a single cylinder DI diesel engine using methyl and ethyl esters of palm, coconut, and rapeseed oils were investigated. It was reported that under the same manufacturing conditions, the ester conversion ratio of an ethyl ester is lower than that of a methyl ester fuel.

The authors have reported that the fuel injection timing is mainly influenced by the bulk modulus and viscosity of fuel (the higher the bulk
modulus and viscosity is, the faster the injection timing is). The bulk modulus of saturated FAME is lower than that of unsaturated FAME. It was stated that the dynamic injection timing of rapeseed oil methyl ester (RME) and palm oil methyl ester (PME) are earlier than that of coconut oil methyl ester (CME). This may be believed to be due to the higher content of saturated fatty acid methyl esters (FAMEs) in CME which may lower the bulk modulus and hence later the injection timing. The contribution of saturated FAMEs in CME, PME, and RME were reported as 90 %, 50 %, and 6 % respectively. It was also affirmed that CME has a shorter ignition delay than that of RME and a longer ignition delay than that of PME at all loads. The peak heat release rate of RME was found to be higher than that of CME and PME due to longer ignition delay of RME than that of the other two. The authors have mentioned that the saturated FAMEs have lower NO\textsubscript{X} emissions compared with the unsaturated FAMEs. The authors found that the CME with higher saturated FAMEs has lower NO\textsubscript{X} emissions compared with PME and RME. It was also reported that the higher oxygen content and shorter ignition delay of the ester fuels may have an effect on reducing the HC emissions.

Mc Cormick et al (2005) found that soy biodiesel produces 1° CA advance in injection timing but nearly 4° CA advance in the start of combustion.

Biodiesel produced from more saturated feedstocks (lower iodine number) such as animal fats produced lower NO\textsubscript{X} emissions. The bulk modulus of compressibility has also correlated with iodine value and to be lower for biodiesel produced from more saturated feedstocks.

The biodiesel degree of saturation and by implication bulk modulus of compressibility had a small effect on NO\textsubscript{X} for a common rail injection
system. For B20 blends no significant effect of biodiesel degree of saturation on NO\textsubscript{X} was observed.

Ming Zheng et al (2008) found the start of injection (SOI) by observing dip in the net heat release rate. It was however observed that the SOI was consistent for all the fuels.

The major finding from their investigation was the fraction of the energy released during the premixed phase was lower for high cetane number fuel. The high cetane number resulted in a shortened ignition delay period estimated from the SOI to the start of combustion (SOC). The SOC was taken as the crankangle position at which the net heat release rate became positive after the initial dip coinciding with the SOI. This was also verified by taking both the first and second derivatives of the cylinder pressure, \( \frac{dp}{d\theta} \) (bar/\(^\circ\)CA) and \( \frac{d^2p}{d\theta^2} \) (bar/(\(^\circ\)CA))\(^2\), respectively.

Scholl et al (1993) tested soybean oil methyl ester with different nozzle hole diameter and compared with diesel fuel. They calculated the instantaneous combustion rate in terms of the mass burning rate divided by the total mass burned. It was reported that diesel fuel has ignition delay marginally longer, and also has a marginally higher maximum combustion rate during the premixed stage of combustion. The observable differences in the combustion process can be mainly attributed to differences in the ignition delay between the two fuels. While ignition delay of the two fuels were comparable in magnitude, the ignition delay of soybean oil methyl ester was found to be more sensitive to changes in injection timing and nozzle diameter than diesel fuel.

CO and HC emissions were lower for soybean oil methyl ester compared to diesel fuel. NO\textsubscript{X} emissions for the two fuels are comparable and
are related to the peak rate of pressure rise, which occur during the initial portion of the combustion process. Smoke numbers for soybean oil methyl ester were lower than that of diesel fuel.

Nicos Ladommatos et al (1996) reported that a change in aromatic content of a diesel fuel can affect a number of physical and chemical properties of the fuel, which have a significant influence on the combustion process. Such fuel properties include chemical structure, cetane number, density, viscosity and boiling range.

It was reported that as cetane number increases, the NO\textsubscript{X} level generally decreases with fixed start of injection (FSOI) and fixed start of combustion (FSOC). An increase in cetane number is accompanied by a reduction in the ignition delay. In turn, decreasing ignition delay results in less mixture being involved in premixed combustion, lower gas temperature and lowers NO\textsubscript{X} formation rates. With start of injection at 13°CA, the premixed combustion period occurs largely during the last stage of the compression process, and this result in higher peak cylinder pressure, temperature and exhaust NO\textsubscript{X} level. On the other hand, with start of combustion at TDC, the premixed combustion period always occurs after TDC, when the gases are expanding. This has the effect of moderating the combustion temperature and exhaust NO\textsubscript{X} level.

From the above literature survey, it is understood that biodiesel can be a potential substitute to diesel. But the problems associated with biodiesel are correlated to the structure. No attempt was made to study the effect of percentage of unsaturation on biodiesel fuel properties and engine combustion characteristics. Hence in the present work the percentage of unsaturation effect was studied in extensively.

The chemistry of biodiesel is discussed in the next chapter.