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Minor Seed Oils

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25 Minor Seed Oils

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25.1 INTRODUCTION

World energy consumption is increasing tremendously, but fossil fuel sources are limited and decreasing rapidly. Burning of fossil fuels increases the carbon dioxide (CO₂) in the atmosphere. CO₂ emissions have risen over the last 2 decades, reaching an atmospheric content of 360 ppm, estimating the world CO₂ emissions at approximately 26 billion tons/year, 80% of which comes from the combustion of fossil combustibles such as coal, petroleum, and natural gas (Muezzinoglu et al. 1992; Tuer et al. 1997).

The use of vegetable oils in energy production has almost always concentrated on its use as a substitute for diesel in cars, either directly or in the form of methyl or ethyl esters. The unrefined oils have rarely been used as combustibles in the generation of thermal energy (Lopez Sastre et al. 1998).

Biomass already provides approximately 13% of global energy, but this is largely as domestic firewood used inefficiently for cooking and heating in developing countries (Sims 2001). In developed countries, there is a growing trend toward using modern and efficient bioenergy conversion technologies using a range of biofuels that are becoming commercially competitive with fossil fuels.

25.1.1 POTENTIAL OF NONEDIBLE MINOR VEGETABLE OILS IN INDIA

Depending on the climate and soil conditions, different nations are looking into different vegetable oils for diesel fuel substitutes. Being a tropical country, India is rich in forest resources with a wide range of oil seeds. The potentials of vegetable oils in India are given in Table 25.1. From the table, it is understood that there is a huge market for vegetable oils in India. And in the near future, vegetable oils may play a vital role in the biofuel industry. The production of nonedible oils in India is given in Table 25.2.

25.1.2 DESCRIPTION OF MINOR SEED OILS

25.1.2.1 Neem (Azadirachta indica Juss)

Neem grows wild in dry forests and is adapted to all kinds of soils. It is adapted to a wide range of climatic conditions: temperatures of 0–49°C, altitudes up to 1500 m, soil pH up to 8.5, and varying soil depths. Although the tree establishes naturally, tissue culture and stem cuttings can also propagate it. The tree starts producing seeds after 5–6 years. The flowering season spreads over January to April in various parts of the country depending on the climatic conditions. The fruit yield, approximately 37–55 kg/ tree, is harvested from June to August. The kernels constitute approximately 45% of the seed and contain 40–45% oil. The oil is dark and bitter with a disagreeable odor. Small-scale laundry shop manufacturers mostly consume it, and the good-quality oil is used for other processes.

25.1.2.2 Mahua (Mahuca indica)

Mahua is a large deciduous tree with a short trunk, spreading branches, and large rounded crown. It is found in Maharashtra, Bengal, Orissa, in some South Indian forests and Ceylon. The flowering
season extends from February to April. The mature fruits fall during May to July in North India and August to September in South India. The yield of Mahua seeds depends mainly upon the size of the tree, site condition, age, etc. The yield may vary from 5 kg to approximately 200 kg/tree depending on the size and age of the tree. The average yield of sun-dried Mahua seeds is approximately 1.6 kg/tree. Mahua trees start giving seeds after 10 years, continuing up to 60 years with the yield increasing with age. Some investigations have found that at 60 years of age, the Mahua tree will yield 10 times more than the yield at 10 years of age. The kernel constitutes 70% of the seed and contains 50% oil. The oil has some medicinal value and locally is used on sore, cracked skin. The flowers are used as a vegetable and a source of alcohol. The cake from the oil seed is used as fertilizer. The leaves, flowers, and fruits are eaten by cattle.

25.1.2.3 Karanja (Pongamia pinnata)
Karanja is a native of Wetern Ghats, India. It is a hardy tree growing up to 8 m tall and is well adapted to extreme growing conditions such as temperatures of 0–50°C, altitudes up to 1200 m, rainfall of 50–2500 mm, and a soil pH up to 8. Propagation is through seed, stump-cutting, or nursery-raised plants. Seeds germinate within approximately 2 weeks. They flower from April to July and the pods ripen from February to May. Karanja starts producing 4–5 years after planting, and after 7 years it reaches its full productivity of approximately 6–9 t seed/ha per year. The seeds contain 30–40% oil by weight. The oil is nonedible and is used for illumination, lubrication, and synthesis of organic compounds, and its wood is used for firewood, cabinet work, cart wheels, and posts. Leaves of the plant are used as fodder and green manure. The oil cake is used as poultry feed and manure.

25.1.2.4 Linseed (Linum usitatissimum)
The crop is harvested when it is fully ripe and the stems are light brown throughout, the leaves shriveled or fallen, the capsules are brittle, and the seeds are brown. Linseed is grown in the
latitudes between 10° and 65°, both north and south. Its cultivation is confined to low elevations, but it can be successfully grown up to 770 m. Areas with an annual rainfall ranging from 45 to 75 cm are best suited for its cultivation. The seed crop does well under moderate cold, but the fiber crop grows best in cool moist climates. Linseed can be grown on different kinds of soils, except sandy and badly drained heavy clays or clay loams. It does well on the deep clayey black soils of central and peninsular India and on the alluvium loams of the Indo-Gangetic plains. The main season for sowing linseed is October to November, depending upon the cessation of the rains. The linseed crop starts maturing by mid-February, depending on winter spread and sowing time. Plants turn golden yellow when the crop is mature and ready for harvesting. Harvesting is done when the crop is dead ripe with a sickle or by uprooting the plants. The average yield of a pure crop varies from 210 to 450 kg/ha of seed under rain-fed cultivation. The crop in northern India generally gives a higher yield than in central and peninsular India. The irrigated crop may yield 1200–1500 kg/ha.

Oil content of the seed is 35–45%. Crude linseed oil has a dark amber color and a strong, characteristic odor. Linseed oil is exclusively used as nonedible oil, principally in the manufacture of paints and varnishes, linoleum, oilcloth, and printing ink. India is the third-largest producer of linseed in the world. Indian linseed is mainly cultivated as a rabi seasonal crop with October through November being the main sowing season. February through April is the main harvesting season.

The oil cake left after the oil is pressed out is a most valuable feeding cake, perhaps the most favorite cattle feed. It is good in taste and contains 36% protein, 85% of which is digestible. It is fed to fattening animals. It is also used as organic manure. It contains approximately 5% nitrogen, 1.4% phosphorus, and 1.8% potash. Straw from seed varieties are used in the manufacturer of upholstery, insulating material, rugs, twine, and paper. India accounts for approximately 1.9 million ha, with a seed production of 0.498 million t, and is third among linseed-producing countries. India averages 255 kg/ha.

25.1.2.5 Rubberseed Oil (Hevea brasiliensis Muell Arg)
The botanical name of the rubber tree is Hevea brasiliensis (Euphorbiaceae). The tree is medium sized, up to 18 m in height, drought-resistant, tolerant of salinity, grows fast, and matures after 4–7 years. In India it is widely grown in the southern states of Kerala, Tamil Nadu, and Karnataka. Rubber seed kernels (50–60% of seed) contain 40–50% of the brown-colored oil. The estimated availability of rubber seeds in India is approximately 30,000 t/year, which can yield approximately 5000 t of rubber seed oil. Rubber trees yield a three-seeded ellipsoidal capsule, each capsule with one seed. Rubber seeds are ellipsoidal, approximately 2.5–3 cm long, mottled brown, lustrous, and weigh 2–4 g each. Fresh oil is pale yellow, but commercial oil is dark in color. It is a semidrying oil used in surface coatings for making alkyl resins. It is a partial substitute for linseed oil in paints and varnishes. It is effective against house flies and lice and is used up to 30% in soap making. Commercial oil contains fatty acids. The rubber seed production in India is approximately 150 kg/ha per year. The estimated availability of rubber seed is approximately 30,000 Mt/year. At present, rubber seed oil has not found any major application and hence the natural production of seeds remains underutilized.

25.2 BIODIESEL PREPARATION
Transesterification is a process of producing a reaction in a triglyceride and alcohol in the presence of a catalyst to produce glycerol and ester. The molecular weight of a typical ester molecule is roughly one-third that of a typical oil molecule and, therefore, it has a much lower viscosity. A catalyst is used to increase the reaction rate and yield. Because the reaction is reversible, excess alcohol is used to shift the equilibrium to the product side. Alcohols are primary and secondary monohydric aliphatic alcohols having one to eight carbon atoms. Among the alcohols that can be used in the transesterification process, methanol and ethanol are more common. Methanol is used extensively because of its low cost and its physicochemical advantages such as polarity and easy solubility.
for sodium hydroxide (NaOH) (Fanguri and Hanna 1999). To complete a transesterification stoichiometrically, a 3:1 molar ratio of alcohol to triglycerides is needed. The reaction can be catalyzed by alkalis, acids, or enzymes. The alkali include NaOH, potassium hydroxide (KOH), carbonates, and the corresponding sodium methoxide, sodium ethoxide, sodium peroxide, and sodium butoxide. Sulfuric acid, sulfonic acids, and hydrochloric acid are usually used as acid catalysis. Lipase can be used as biocatalysts. Alkali-catalyzed transesterification is much faster than acid-catalyzed transesterification and is most often used commercially (Nelson et al. 1996).

According to the quality of the parent oil, the selection of a transesterification process can be made as shown in Figure 25.1 and it can be explained as follows:

- If the free fatty acid (FFA) content and moisture content of parent vegetable oils are less than 0.5%, a single-stage transesterification process can be chosen.
- When the FFA content is less than 0.5% but the moisture content is greater than 0.5%, the moisture content can be removed by heating the oil at 110°C for approximately 1 h with stirring. Then, the biodiesel can be produced from single-stage transesterification.

**FIGURE 25.1** Flow chart for the selection of transesterification process.
• When the FFA content is greater than 0.5% and the moisture content is less than 0.5%, then a two-stage transesterification process can be selected. If the FFA content and moisture content are greater than 0.5%, then a three-stage transesterification process is selected.

In the work presented here, biodiesel fuels were produced by a single-stage transesterification process.

25.3 STRATEGIES AND METHODOLOGIES

25.3.1 BIODIESEL PROPERTIES AND QUALITY

Biodiesel is a mono-alkyl ester that is derived from vegetable oils or animal fats through transesterification. The purpose of transesterification is to reduce the viscosity of vegetable oils. The transesterification process parameters such as alcohol/oil ratio (6:1 molar ratio), catalyst quantity (NaOH, 0.5 wt %), reaction temperature (65°C), and reaction time (2 h) were optimized for a single oil and then subsequently adjusted for other oils. An alkali catalyst was used because of its low cost and because it is easily miscible with methanol. Methanol was used because of its low cost. The biodiesels produced from different oils were washed and dried. Different biodiesels were then blended to vary the percentage of unsaturation. The biodiesels produced were checked for quality. The important fuel properties were measured as per standard methods and compared with the ASTM limits. The fuel properties were determined following the methods specified in ASTM standards as given in Table 25.3.

25.3.2 COMBUSTION PARAMETERS

25.3.2.1 Ignition Delay

Ignition delay is the time or crank angle between the start of fuel injection into the cylinder and the time of first combustion. The fuel injection is dynamic injection and the first combustion is the heat release. The ignition delay was calculated from the heat release diagram. The dynamic injection timing was calculated based on the negative heat release in the heat release diagram. Because the fuel droplet absorbs heat from the cylinder, there is a negative heat release on the diagram. The point at which the first negative heat release starts is the dynamic injection time and the start of ignition delay period. Similarly, at the point where the first positive heat release is seen on the diagram is the end of the ignition delay period.

25.3.2.2 Heat Release Rate

The heat release rates were determined from the cylinder pressure history. The apparent heat release rate was calculated based on the first law of thermodynamics as given in equation (25.1).

<table>
<thead>
<tr>
<th>TABLE 25.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM Methods for Determination of Fuel Properties</td>
</tr>
<tr>
<td>Property</td>
</tr>
<tr>
<td>Fatty acid composition</td>
</tr>
<tr>
<td>Density at 15°C</td>
</tr>
<tr>
<td>Cetane number</td>
</tr>
<tr>
<td>Heating value</td>
</tr>
<tr>
<td>Iodine value</td>
</tr>
</tbody>
</table>
\[
\frac{dQ_n}{d\theta} = \frac{\gamma}{\gamma-1}p\frac{dv}{d\theta} + \frac{1}{\gamma-1}v\frac{dp}{d\theta},
\]

where \(g = \frac{C_p}{C_v}\) is the ratio of specific heat, \(dQ_n/d\theta\) is the apparent net heat release rate, \(dv/d\theta\) is the rate of volume, and \(dp/d\theta\) is the rate of pressure.

### 25.3.3 Combustion Parameters

A single cylinder air-cooled direct injection compression ignition engine developing a power output of 4.4 kW at the rated speed of 1500 rpm was used for experimental studies. The engine was coupled to an electrical dynamometer. The engine was fitted with all accessories to measure the fuel consumption, air consumption, inlet air temperature, and exhaust gas temperature. The engine was started with neat diesel fuel and warmed up. It was allowed to run for 10 min with biodiesel to attain a steady condition at its rated speed of 1500 rpm. The engine was gradually loaded to full load by switching on the load mains. The different biodiesel fuels were tested in a random order. The speed of the engine was maintained at 1500 rpm, and the time taken for 10 cm³ of fuel consumption was measured using a stopwatch. The tests were repeated 5 times, and the average value of the five readings was taken to eliminate uncertainty.

#### 25.3.3.1 Combustion Pressure Measurement

**Instrument used**

A Kistler piezoelectric transducer with a range of 0–250 bar was used.

**Method**

- The piezoelectric transducer was mounted on the cylinder head and connected to a charge amplifier for measuring the pressure inside of the engine cylinder.
- By circulating the cooling water through the inlet opening, the transducer was cooled. The central opening was used for sending signal to the amplifier.
- The TDC (top dead center) position signal was fed into the computer through the data acquisition card. In this system, the analogue signal was converted into digital impulses at fixed crank angles using an analogue-to-digital converter (ADC).
- The digital signal was then transmitted to the computer where it was stored. It was immediately processed as soon as all of the data for one or any number of cycles had been completed.
- The processing would be in the form of a pressure-crank angle diagram or a pressure-volume diagram.

The photographic view of the test engine is shown in Figure 25.2 whereas Figure 25.3 depicts the pressure setup. The schematic of the experimental setup is illustrated in Figure 25.4.

The entire experimental work was performed in the laboratory at room temperature (32°C) and an atmospheric pressure of 1.01325 bar.

### 25.4 Outputs and Impacts

#### 25.4.1 Fuel Properties

Fuel properties are of foremost importance to the validation of the combustion, performance, and emissions of a fuel in compression ignition engine. Fuel properties affect the engine combustion chemistry in many ways; hence, it is essential to study the indispensable properties to realize the combustion chemistry. Biodiesel fuel combustion chemistry is more complex than that of diesel fuel because of its complex structure and oxygen content. Biodiesel is composed of several fatty acid
The fatty acid ester profile of biodiesel affects the fuel properties.

The important fuel properties discussed in this section are density, heating value, cetane number, iodine value, fatty acid ester composition, and percentage of unsaturated fatty acids. The results of fuel tests on different biodiesel fuels are summarized in Table 25.4. The fatty acid methyl ester composition of various test fuels is shown in Table 25.5.

A correlation analysis was made to find out the degree of linear association between different biodiesel properties and percentage of unsaturation. The Pearson product moment correlation coefficient between different properties and the percentage of unsaturation is shown in Table 25.6.

The formula used to calculate the Pearson correlation coefficient ($r$) is shown in equation (25.1):

$$r = \frac{\Sigma(X - \bar{X})(Y - \bar{Y})}{\sqrt{(X - \bar{X})^2(Y - \bar{Y})^2}},$$

(25.2)

where $r$ is the Pearson correlation coefficient, $X$ is the percentage of unsaturation, and $Y$ represents properties.
25.4.1.1 Density

The density of a fuel shows how close the molecules are packed in the structure. A higher-density fuel has a more closely packed structure than a lower-density fuel. Fuel density is commonly expressed in kilograms per cubic meter. The greater the fuel density, the greater the mass of fuel that can be stored in a given tank and the greater the mass of fuel than can be pumped for a given pump.

The density of a fuel affects dynamic injection timing, ignition delay, and thereby NOx emissions. However, these properties are uncertain indications of fuel quality unless correlated with
other properties. From Table 25.4, it can be observed that the density of different biodiesels is not the same and that the maximum is observed for ROME (885 kg/m³) and minimum for MOME (875 kg/m³). It was observed from the literature (Shigley et al. 1995) that the density decreases with an increase in chain length, carbon number, or molecular weight and increases with degree of unsaturation. Density decreases from C8:0 to C18:0 and increases from C18:1 to C18:3. Because ROME is dominated by unsaturated linoleic ester (C18:2), the density of which is higher compared with lower saturated carbon chain esters, it exhibits a higher density compared with other biodiesel fuels. In the case of ROME, the unsaturation (the double bond) and when it deforms the linearity when it is introduced in a structure and forms a bend structure. This is only in the case of the cis-structure in which two hydrogen atoms are on the same side of the carbon atom and they repel each other, thereby giving a bend structure. On the other hand MOME, which is equally dominated by both unsaturated and saturated esters (C12:0), shows a lower density compared with other biodiesel fuels. From Table 25.6, it can be observed that a high positive correlation exists between the unsaturation percentage and density.

The relationship between the fatty acid methyl ester composition and density of biodiesel fuels was investigated, revealing that the higher density of ROME may be more due to the contribution of unsaturated fatty acids in ROME than that of the other biodiesels. Similarly, the lower density of MOME is believed to be due to the lesser contribution of unsaturated fatty acids in MOME. The scatter plot between the density and percentage of unsaturation with the fitted trend line equation is shown in Figure 25.5. The figure provides a clear picture that a highly positive correlation exists between density and percentage of unsaturation. Therefore, it may be stated that the density of biodiesel fuels increases with an increase in the percentage of unsaturation or in the number of double bonds.

By differentiating the fitted line equation $y = 0.268x + 860.47$ with respect to $x$ (i.e., percentage of unsaturation) the gradient between density and percentage of unsaturation can be found as 0.268. This means, for every 1% increase in unsaturation, it may result in 0.268 units (kg/m³) increase in density, where, $r^2$ denotes the coefficient of determination.

### Table 25.5
**Fatty Acid Methyl Ester Composition of Biodiesel Fuels**

<table>
<thead>
<tr>
<th>Biodiesel</th>
<th>Percentage of United States</th>
<th>Lauric C12:0</th>
<th>Myristic C14:0</th>
<th>Palmitic C16:0</th>
<th>Stearic C18:0</th>
<th>Oleic C18:1</th>
<th>Linoleic C18:2</th>
<th>Linolenic C18:3</th>
</tr>
</thead>
<tbody>
<tr>
<td>ROME</td>
<td>88.00</td>
<td>Trace</td>
<td>0.10</td>
<td>6.00</td>
<td>5.90</td>
<td>16.00</td>
<td>71.40</td>
<td>0.60</td>
</tr>
<tr>
<td>LOME</td>
<td>78.87</td>
<td>Trace</td>
<td>0.24</td>
<td>12.46</td>
<td>8.32</td>
<td>27.78</td>
<td>37.65</td>
<td>13.44</td>
</tr>
<tr>
<td>KOME</td>
<td>72.32</td>
<td>Trace</td>
<td>0.05</td>
<td>9.94</td>
<td>7.83</td>
<td>53.19</td>
<td>19.09</td>
<td>0.04</td>
</tr>
<tr>
<td>NOME</td>
<td>60.40</td>
<td>Trace</td>
<td>0.47</td>
<td>18.20</td>
<td>20.10</td>
<td>43.70</td>
<td>16.40</td>
<td>0.30</td>
</tr>
<tr>
<td>MOME</td>
<td>50.00</td>
<td>Trace</td>
<td>0.00</td>
<td>24.20</td>
<td>25.80</td>
<td>37.20</td>
<td>12.80</td>
<td>0.00</td>
</tr>
</tbody>
</table>

### Table 25.6
**Pearson Correlation Coefficient**

<table>
<thead>
<tr>
<th>$x$ Variable</th>
<th>$y$ Variable</th>
<th>Correlation Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percentage of unsaturation</td>
<td>Density</td>
<td>0.955</td>
</tr>
<tr>
<td></td>
<td>Heating value</td>
<td>-0.869</td>
</tr>
<tr>
<td></td>
<td>Cetane number</td>
<td>-0.989</td>
</tr>
<tr>
<td></td>
<td>Iodine value</td>
<td>0.956</td>
</tr>
</tbody>
</table>
Heating value, or the energy content or heat of combustion, is a measure of the energy available in a fuel. It is a critical property of fuel intended for use in weight-limited vehicles. The energy content of various biodiesel fuels can be observed from Table 25.5.

From the literature (Demirbas et al. 1998; Knothe 2005), it was observed that the heating value, cetane number, and viscosity increase with an increase in carbon number and decrease with the degree of unsaturation.

- The molecular weight of fatty acids increases with chain length.
- The heating value increases with chain length (molecular weight) and decreases with increase in the number of double bonds.

The increase in heat content may be due to the increase in the number of carbons and hydrogens. The possible cause for decrease in heat content may be the deficiency of hydrogen atoms (greater unsaturation). From Table 25.5, it can be noticed that LOME has the lower energy content and MOME has the higher energy content. Because MOME is dominated by a higher carbon chain (16 to 18), it exhibits a higher energy content, whereas LOME, which is dominated by a lower carbon chain, exhibits lower energy content as compared with other biodiesel fuels. The scatterplot between the heating value and percentage of unsaturation with a fitted trend line equation is illustrated in Figure 25.6.
From the fitted line equation $y = -0.027x + 41.63$, the projected decrease in heating value for every 1% increase in unsaturation is 0.027 units (MJ/kg).

25.4.1.3 Cetane Number

Cetane number (CN) indicates the ignition quality of a fuel, i.e., how fast a fuel takes part in combustion. In other words, it quantifies the activation energy to start the reaction. Higher CN implies lower activation energy and therefore quick reaction. Hence, the time required for a fuel to start the combustion reduces, which is the ignition delay period. Therefore, higher CN indicates a shorter ignition delay period. Delay period is the time interval between the start of fuel injection and the start of combustion. When the delay period is reduced, the fuel accumulated during the delay period also reduces and therefore a small amount of fuel can take part in combustion. In contrast, lower CN fuel has a higher activation energy and longer ignition delay period. A longer ignition delay period accumulates more fuel and higher premixed combustion, which in turn produces more oxides of nitrogen.

CN is a derived property that is influenced by several other physical and chemical properties. In the case of biodiesel, CN is influenced by chain length, alcohol moiety, degree of unsaturation, position of double bond, and cis or trans structure (Knothe 2005). CN increases with chain length and decreases with degree of saturation (Knothe 2005). Gerhard Knothe states that

- CN increases with chain length and decreases with the number of double bonds or unsaturation.
- CN of fatty esters generally increases with the number of methylene groups (CH$_2$) in the chain of the fatty compound, the number of CH$_2$ groups in the ester moiety, and the increasing saturation of the fatty compound.
- For the methyl esters, the CN were found to increase in a nonlinear relationship with molecular weight (chain length).

From Table 25.5, it can be observed that MOME has a higher cetane number compared with other biodiesel fuels. The higher CN of MOME can be attributed to the higher carbon number, i.e., stearic ester (C18:0). On the other hand, the ROME has a lower CN than that of other biodiesel fuels. This is because the CN decreases as the number of double bonds (unsaturation) increases. The influence of unsaturation on CN is depicted in Figure 25.7.

From the fitted line equation $y = -0.027x + 41.63$, the projected decrease in heating value for every 1% increase in unsaturation is 0.027 units (MJ/kg).

25.4.1.4 Iodine Value

Iodine value (IV) that can be considered as a direct measure of unsaturation may be defined as the amount of iodine (in grams) necessary to saturate a 100-g oil sample. IV is included in the European biodiesel standards. It purportedly addresses the issue of oxidation stability because the IV is a measure of total unsaturation of fatty materials measured in grams of iodine per 100 g of a sample when formally added to the double bonds. Another idea behind the use of the IV is that it indicates the propensity of the oil or fat to polymerize and form engine deposits (Graboski et al. 1998). The engine manufacturers have always been aware of the iodine number which expresses the number of double bonds. The limit was set at 120 in EN14214 and 135 in EN14213 (Prankl 2002). From Table 25.5, it can be noticed that ROME has an IV of 160 and MOME has a value of 65.

From Table 25.5, it can be observed that MOME has a higher cetane number compared with other biodiesel fuels. The higher CN of MOME can be attributed to the higher carbon number, i.e., stearic ester (C18:0). On the other hand, the ROME has a lower CN than that of other biodiesel fuels. This is because the CN decreases as the number of double bonds (unsaturation) increases. The influence of unsaturation on CN is depicted in Figure 25.7.

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From the fitted line equation $y = -0.027x + 41.63$, the projected decrease in heating value for every 1% increase in unsaturation is 0.027 units (MJ/kg).

25.4.1.4 Iodine Value

Iodine value (IV) that can be considered as a direct measure of unsaturation may be defined as the amount of iodine (in grams) necessary to saturate a 100-g oil sample. IV is included in the European biodiesel standards. It purportedly addresses the issue of oxidation stability because the IV is a measure of total unsaturation of fatty materials measured in grams of iodine per 100 g of a sample when formally added to the double bonds. Another idea behind the use of the IV is that it indicates the propensity of the oil or fat to polymerize and form engine deposits (Graboski et al. 1998). The engine manufacturers have always been aware of the iodine number which expresses the number of double bonds. The limit was set at 120 in EN14214 and 135 in EN14213 (Prankl 2002). From Table 25.5, it can be noticed that ROME has an IV of 160 and MOME has a value of 65.

From Table 25.5, it can be observed that MOME has a higher cetane number compared with other biodiesel fuels. The higher CN of MOME can be attributed to the higher carbon number, i.e., stearic ester (C18:0). On the other hand, the ROME has a lower CN than that of other biodiesel fuels. This is because the CN decreases as the number of double bonds (unsaturation) increases. The influence of unsaturation on CN is depicted in Figure 25.7.

From the fitted line equation $y = -0.027x + 41.63$, the projected decrease in heating value for every 1% increase in unsaturation is 0.027 units (MJ/kg).

From Table 25.5, it can be observed that MOME has a higher cetane number compared with other biodiesel fuels. The higher CN of MOME can be attributed to the higher carbon number, i.e., stearic ester (C18:0). On the other hand, the ROME has a lower CN than that of other biodiesel fuels. This is because the CN decreases as the number of double bonds (unsaturation) increases. The influence of unsaturation on CN is depicted in Figure 25.7.

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From the fitted line equation $y = -0.027x + 41.63$, the projected decrease in heating value for every 1% increase in unsaturation is 0.027 units (MJ/kg).
The gradient between different properties and percentage of unsaturation was based only upon the slope of the fitted lines. It may not be true for all cases. Because a large sample size would be taken for investigation, the gradient of the aforesaid parameters may vary.

25.4.2 Combustion Parameters

The influences of biodiesel properties on different combustion parameters are discussed. The following parameters were considered for the investigation:

- Dynamic injection timing
- Ignition delay
- Peak heat release rate
- Peak cylinder pressure

The experimental values of all of the above parameters at full load for various biodiesel fuels are listed in Table 25.7.

25.4.2.1 Dynamic Injection Timing

Dynamic injection timing is the crank angle point at which the fuel jet actually enters into the engine combustion chamber. Dynamic injection timing is one of the most important parameters because it can have a significant effect on the engine performance and emissions. The advancement of injection
Timing will increase NOx emissions (Szybist et al. 2005a). For a given engine at the same operating conditions, the dynamic injection may not be the same for different fuels; that is, dynamic injection timing can greatly be affected by fuel properties. The fuel injection timing can be influenced by the bulk modulus, i.e., the compressibility of the fuel. The bulk modulus or compressibility is a measure of how easily a unit of fluid volume can be decreased when increasing the pressure working on it. A higher bulk modulus indicates that the fluid is relatively incompressible.

The most common type of diesel injector is the pump-line-nozzle injector. In this configuration, the pressure is applied to the fuel upstream of the injector nozzle. The pressure increases 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. Fuels with higher compressibility require a longer time to reach the nozzle opening pressure, which results in late injection. The presence of oxygen and double bonds in biodiesel fuels can increase the bulk modulus, thereby advancing the injection timing (McCormick et al. 2005). The actual start of injection (SOI) was not experimentally determined in this investigation. It was calculated based on the dip in the heat release rate diagram.

The bulk modulus of unsaturated biodiesel is higher than that of saturated biodiesel because of the introduction of double bond carbons. A carbon-carbon double bond introduces a bend in the structure and thereby distorts the linearity of a carbon–carbon single bond. This bend configuration may foster intra- or intermolecular interactions in the fuel that reduce compressibility, leading to earlier injection. It was reported (Szybist et al. 2005b) that the bulk modulus of diesel was 2% lower than B20 soybean, yielding a shift in the fuel injection timing by 0.1–0.3 crank angles.

When biodiesel is injected, the pressure rise produced by the pump is quicker as a consequence of its lower compressibility (higher bulk modulus). It also propagates quicker toward the injectors as a consequence of its higher sound velocity. In addition, higher viscosity reduces leakages in the pump, leading to an increase in the injection line pressure. Therefore, a quicker and earlier needle opening is realized with respect to the case of more unsaturated biodiesel fuel. It can therefore be stated that higher density fuels can have a higher value of bulk modulus because of an increase in unsaturation.

From the above statements, it can be concluded that the injection timing is advanced for higher unsaturated and hence higher density fuels. It can be observed from Table 25.7 that high unsaturated content biodiesel (ROME), which has a higher density, advances the injection timing by approximately 2° crank angle (CA) compared with relatively low unsaturated biodiesel (MOME). A correlation analysis was done to find out the relationship between dynamic injection timing, density, and percentage of unsaturation using equation (25.2). The correlation coefficients are shown in Table 25.8.

<table>
<thead>
<tr>
<th>Biodiesel</th>
<th>Dynamic Injection Timing (°CA bTDC)</th>
<th>Ignition Delay (°CA)</th>
<th>Peak HRR (J/°CA)</th>
<th>Location of Peak HRR (°CA)</th>
<th>Peak Pressure (bar)</th>
<th>Location of Peak Pressure (°CA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ROME</td>
<td>14</td>
<td>346–353</td>
<td>7</td>
<td>63</td>
<td>356</td>
<td>63</td>
</tr>
<tr>
<td>LOME</td>
<td>14</td>
<td>346–353</td>
<td>7</td>
<td>66</td>
<td>357</td>
<td>65</td>
</tr>
<tr>
<td>KOME</td>
<td>13</td>
<td>347–353</td>
<td>6</td>
<td>67</td>
<td>358</td>
<td>66</td>
</tr>
<tr>
<td>NOME</td>
<td>13</td>
<td>347–353</td>
<td>6</td>
<td>71</td>
<td>359</td>
<td>67</td>
</tr>
<tr>
<td>MOME</td>
<td>12</td>
<td>348–354</td>
<td>6</td>
<td>73</td>
<td>360</td>
<td>68</td>
</tr>
</tbody>
</table>

It can be observed from the table that the dynamic injection timing is highly positively correlated with percentage of unsaturation and the density of biodiesel fuels. Figure 25.9 illustrates the variation of dynamic injection timing with percentage of unsaturation. A good r2 value of 0.879 can be observed from Figure 25.10 between the percentage of unsaturation and dynamic injection timing.
The positive correlation indicates that the dynamic injection advances with increase in percentage of unsaturation. It can also be proposed that a unit increase in percentage of unsaturation can advance the dynamic injection timing by $0.052^\circ$ CA.

### 25.4.2.2 Ignition Delay

The ignition delay can be defined as the time (in seconds or degrees crank angle) interval between the points at which the fuel jet actually enters into the combustion chamber and the start of combustion.
Understanding the physical and chemical processes is important to thoroughly describing the ignition delay.

Hydrocarbon combustion occurs only in the gas phase. Thus, for a liquid fuel, the first step toward ignition involves transitioning from a liquid to a gas phase. The time required for this transition is the “physical delay” in ignition and includes the amount of time required for a droplet of fuel to heat, vaporize, and mix with hot air in the cylinder.

The physical delay is influenced by the density and temperature of air in the cylinder; velocity and turbulence of the air; atomization; penetration; shape of the spray; and the properties of the fuel, including density, viscosity, surface tension, specific heat, enthalpy of vaporization, and vapor pressure.

Combustion is a sequence of chemical reactions in which the gas-phase fuel reacts with oxygen. These reactions proceed stepwise through a mechanism involving free radicals. For ignition to occur, the fuel must be heated to a temperature sufficient for some of the weaker bonds to break and form radicals. The finite rate of these radical-forming oxidation reactions is responsible for the chemical delay in compression ignition. Once a sufficient concentration of free radicals is reached, rapid oxidation occurs (ignition). The heat-release pattern can be considerably influenced by ignition delay, which in turn affects fuel economy and pollutant emissions. The start of injection is usually taken as the time when the injector lifts from its seat (determined by a needle lift indicator).

The correlation coefficients among ignition delay, fuel CN, density, percentage of unsaturation, and start of injection were found and shown in Table 25.9.

From the table, it can be observed that the ignition delay is negatively correlated with CN and positively correlated with fuel density, percentage of unsaturation, and dynamic injection timing. Apart from CN, the reason behind relating ignition delay with density, percentage of unsaturation, and dynamic injection timing can be explained as follows:

- CN has a greater influence on chemical delay whereas fuel density, viscosity, and surface tension can have a significant influence on physical delay (Burman and Deluca 1962).
- The density and CN were found to be highly correlated with one another (McCormick et al. 2005).
- The ignitability of an ester fuel depends not only upon the CN but also upon the fatty acid ester composition (Kinoshita et al. 2006).
- If the injection timing is advanced, the fuel is injected to the combustion chamber at a lower temperature and pressure. If the prevailing temperature and pressure are lower, it is obvious that there would be a longer ignition delay.

From Table 25.9, it can be observed that the ignition delay increases with an increase in percentage of unsaturation. The effect of unsaturation percentage on ignition delay is illustrated in Figure 25.10.

<table>
<thead>
<tr>
<th>Variable</th>
<th>y Variable</th>
<th>Correlation Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cetane number</td>
<td>Ignition delay</td>
<td>-0.771</td>
</tr>
<tr>
<td>Density</td>
<td></td>
<td>0.933</td>
</tr>
<tr>
<td>Percentage of unsaturation</td>
<td></td>
<td>0.823</td>
</tr>
<tr>
<td>Dynamic injection timing</td>
<td></td>
<td>0.873</td>
</tr>
</tbody>
</table>
It can also be proposed from the figure that a unit increase in percentage of unsaturation can increase the ignition delay by 0.03° CA.

25.4.2.3 Heat Release Rate

The details about combustion stages and events can often be determined by analyzing heat release rates (HRRs) as determined from cylinder pressure history. Before further discussion, paying attention to the following points may offer a successful understanding on investigation findings:

- Generally, a fuel that has a longer ignition delay should have a higher value of maximal HRR as compared with fuels that have a shorter ignition delay. However, the maximal HRR not only depends on ignition delay, but also upon heating value and the mass fraction burnt for a given crank angle duration.
- Sauter mean diameter (SMD) has been shown to increase with increasing surface tension, density, and viscosity.
- An increase in droplet size can reduce the fraction of fuel burned in the premixed combustion phase.
- Density increases with increase in unsaturation.

From the aforesaid points it may be concluded that a fuel with more density may lead to an increased droplet size, which in turn reduces the mass fraction burnt in the premixed combustion phase as compared with a lower density fuel. Therefore, a higher density fuel may be expected to have a lower value of maximal HRR. In addition, it was already found that the heating value decreases with increase in unsaturation. Hence, for a given value of mass fraction burnt, fuel with a lower heating value may release less heat energy as compared with the fuel with a higher heating value. From the above discussions it may be concluded that the maximal HRR tended to decrease with an increase in unsaturation. The correlation coefficient among peak HRR, density, unsaturation percentage, and heating value is listed in Table 25.10.

From the table, it can be observed that the maximal HRR is highly negatively correlated with percentage of unsaturation and density. Similarly, the peak HRR is positively correlated with heating value (however, the correlation coefficient is not so significant). From Table 25.7, it can be observed that ROME has a lower value of maximal HRR and MOME has a higher value than that of other biodiesel fuels. The table shows that the order of magnitude of peak HRR for the biodiesel fuels is matched with the reverse order of percentage of unsaturation. This is because the density increases whereas the heating value decreases with increase in percentage of unsaturation.

It can be said that the mass fraction burnt for a given angle decreases with an increase in the percentage of unsaturation and the stoichiometric air-to-fuel ratio increases with an increase in percentage of unsaturation. This can be explained as follows. For the same quantity of supplied air (and hence oxygen), the burning volume for a less unsaturated biodiesel would be more. Because it has a lesser air-to-fuel ratio, the less unsaturated biodiesel could find more oxygen at a given crank angle than that of a more unsaturated biodiesel. From the above discussion, it can be concluded that the peak HRR decreases with an increase in the percentage of unsaturation.

<table>
<thead>
<tr>
<th>TABLE 25.10</th>
<th>Correlation Coefficient among Peak HRR, Density, Percentage of Unsaturation, and Heating Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>x Variable</td>
<td>y Variable</td>
</tr>
<tr>
<td>Density</td>
<td>Peak HRR</td>
</tr>
<tr>
<td>Percentage of unsaturation</td>
<td>Peak HRR</td>
</tr>
<tr>
<td>Heating value</td>
<td></td>
</tr>
</tbody>
</table>
From Table 25.7, it can be seen that the location of peak HRR for MOME occurs at a 360° CA whereas for ROME it occurs at a 356° CA. It may be stated that the location of peak heat release is closer to top dead center (TDC) as the percentage of unsaturation increases (i.e., for more unsaturated biodiesel, the location of peak HRR is before TDC and for less unsaturated, it is away from TDC). As the percentage of unsaturation increases, the peak heat release would shift toward the left side in the HRR diagram. This may be because as the unsaturation composition increases, the dynamic injection timing advances, which in turn can effectively bring the peak heat release before TDC in the HRR diagram. The variation of HRR with percentage of unsaturation is shown in Figure 25.11.

From Figure 25.12, it can be proposed that a reduction of 0.265 units (J) in peak HRR can occur for every 1% increase in unsaturation.

25.4.2.4 Peak Cylinder Pressure

Peak cylinder pressure is the magnitude of maximum pressure developed due to the combustion of fuel by which chemical energy is converted into pressure energy. The magnitude and occurrence of peak pressure affects engine power and emissions. Table 25.11 shows the correlation coefficient between peak cylinder pressure and percentage of unsaturation. From the table, a high positive correlation between peak cylinder pressure and peak HRR can be observed. This is obvious because

![Figure 25.11](image1)

**FIGURE 25.11** Variation of peak HRR with percentage of unsaturation.

![Figure 25.12](image2)

**FIGURE 25.12** Variation of peak cylinder pressure with percentage of unsaturation.
the magnitude of peak cylinder pressure must always be proportionate with peak HRR. It could also be seen from the table that the peak cylinder pressure decreases with an increase in unsaturation percentage.

The influence of unsaturation percentage on peak cylinder pressure is shown in Figure 25.12. From the fitted line equation \( y = -0.125x + 74.54 \) shown in Figure 25.13, it can be seen that every 1% increase in unsaturation percentage may cause a reduction of 0.125 bar in peak pressure.

25.4.2.5 Brake Specific Energy Consumption

Brake specific energy consumption (BSEC) is defined as the energy required to develop a unit power in unit time. Brake specific fuel consumption (BSFC) is the quantity of fuel required for developing unit power in unit time. In the case of BSFC, the effect of fuel density alone is considered. But in BSEC, both the density and the heating value of a fuel are taken into account. When comparing different fuels with different densities and heating values, it is essential to discuss BSEC rather than BSFC.

The BSEC can be obtained by multiplying the heating value with BSFC. From Table 25.12, it can be observed that the BSEC is higher for sunflower biodiesel and lower for coconut biodiesel as compared with other biodiesel fuels. From the table, it can also be seen that the order of magnitude of BSEC is exactly matched with the order of magnitude of unsaturation percentage. From the correlation analysis, it was found that the BSEC was highly positively correlated with density and percentage of unsaturation. It can be noted that the BSFC increases with a decrease in heating value. Figure 25.13 depicts the variation of BSEC with percentage of unsaturation.

From the fitted line equation \( y = 0.012x + 12.188 \), the gradient between BSEC and percentage of unsaturation can be proposed as 0.0116. Every 1% increase in unsaturation may result in an increase of 0.0116 units (MJ/kWh) in BSEC.
25.4.2.6 Brake Thermal Efficiency

Thermal efficiency is the ratio between the power output and the energy introduced through fuel injection, the latter being the product of the injected fuel mass flow rate and the lower heating value. Thus, the inverse of thermal efficiency is often referred to as BSEC. Because it is usual to use the brake power for determining thermal efficiency in experimental engine studies, the efficiency obtained is really the brake thermal efficiency. This parameter is more appropriate than fuel consumption to compare the performance of different fuels, besides their heating value.

Brake thermal efficiency can be correlated with fuel burn angle and the generic statement is that the lower the burn angle, the higher the efficiency. But, for the same fuel burn angle, it is difficult to obtain a correlation with burn angle. Rather it can be well correlated to the shape of the heat release diagram. Brake thermal efficiency shown in Table 25.12 is higher for COME and is lower for SFOME. This shows that the order of magnitude of brake thermal efficiency for the biodiesel fuels matches exactly with the reverse order of BSEC. From the correlation analysis, it was found that the brake thermal efficiency decreases with an increase in percentage of unsaturation. This is because the BSEC increases with an increase in percentage of unsaturation. The variation of brake thermal efficiency with percentage of unsaturation is illustrated in Figure 25.14. From the fitted line equation $y = -0.026x + 29.481$, a decrease of 0.026 units (%) could be predicted for every 1% increase in unsaturation.

<table>
<thead>
<tr>
<th>Biodiesel</th>
<th>Percentage of United States</th>
<th>BSEC (MJ/kWh)</th>
<th>Brake Thermal Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SFOME</td>
<td>88.00</td>
<td>13.20</td>
<td>27.27</td>
</tr>
<tr>
<td>ROME</td>
<td>78.87</td>
<td>13.15</td>
<td>27.38</td>
</tr>
<tr>
<td>JOME</td>
<td>75.50</td>
<td>13.12</td>
<td>27.44</td>
</tr>
<tr>
<td>KOME</td>
<td>72.32</td>
<td>12.94</td>
<td>27.82</td>
</tr>
<tr>
<td>JT 80:20</td>
<td>68.18</td>
<td>12.91</td>
<td>27.89</td>
</tr>
<tr>
<td>NOME</td>
<td>60.40</td>
<td>12.88</td>
<td>27.96</td>
</tr>
<tr>
<td>JT 50:50</td>
<td>57.92</td>
<td>12.91</td>
<td>27.88</td>
</tr>
<tr>
<td>SFCt 50:50</td>
<td>52.05</td>
<td>12.87</td>
<td>27.98</td>
</tr>
<tr>
<td>MOME</td>
<td>50.00</td>
<td>12.81</td>
<td>28.11</td>
</tr>
<tr>
<td>POME</td>
<td>48.80</td>
<td>12.75</td>
<td>28.23</td>
</tr>
<tr>
<td>JCt 50:50</td>
<td>44.44</td>
<td>12.66</td>
<td>28.43</td>
</tr>
<tr>
<td>COME</td>
<td>10.00</td>
<td>12.29</td>
<td>29.28</td>
</tr>
</tbody>
</table>

25.5 CONCLUSIONS

In this study, minor seed oils such as mahua, karanja, neem, rubber seed, and linseed oil methyl esters were prepared and studied in a four-stroke, direct injection diesel engine. The availability of these seeds in India is discussed. Also, the effect of biodiesel fatty ester composition on biodiesel is studied. In addition, the effect of biodiesel composition and properties on combustion parameters is studied. The gradient between biodiesel properties, combustion parameters, and percentage of unsaturation are proposed. It was found that the biodiesel properties that include density and IV are increased with an increase in biodiesel unsaturation, whereas CN and heating value are decreased with an increase in unsaturation percentage. The investigation reveals that the dynamic injection timing advances with increase in unsaturation. The ignition delay increases with an increase in unsaturation whereas the magnitude of the peak heat release rate and the peak pressure decreased...
Minor Seed Oils

with unsaturation. The brake thermal efficiency decreases with increasing unsaturation. On the whole, it is concluded that biodiesel with more unsaturation decreases heating value and CN but increases density and iodine number.

REFERENCES


\[ y = -0.026x + 29.481 \]

\[ r^2 = 0.955 \]

FIGURE 25.14 Variation of brake thermal efficiency with percentage of unsaturation.