RESULTS AND DISCUSSION

Kanyakumari District is located at the southern tip of peninsular India which is bordered by Thiruvananthapuram district of Kerala state at its west and Thirunelveli district of Tamil Nadu at its north and east. It lies between 77°15' and 77°36' of the eastern longitude and between 08°03' and 08°35' of the northern latitude. The district accounts for more than 95 percent of the production of natural rubber in the state of Tamil Nadu. Rubber tree (*H. brasiliensis*) whose latex forms the source of natural rubber is being cultivated mainly in the hilly areas of the Western Ghats. The seeds of this contain considerable quantity of oil which can be best used for productive purposes.

Healthy and fresh seeds required for performing the experiment were collected from the rubber plantations of Kanyakumari district between the month of August and September during the year 2007 and 2008. Rubber seed was found susceptible to biological deterioration particularly, when it was left on the ground for more than three days before being collected and these yielded poor quality oil. Fungal attack on the seed and lipase activity of the oil extracted from the affected seed increased as a function of seed's stay on the ground.

Therefore, in this study, seeds were collected soon after they fell from the tree and they were then sun dried. Normally the extraction of oil was done by two modes: i). through oil expeller and ii). through solvent extraction. The recovery of oil in the expeller mode was found to be 40.53 ± 0.73 (n = 12) percent whereas in the solvent extraction mode the same seed yielded 44.18 ± 0.45 percent (n = 8) oil. The oil expeller method was found to be relatively cheaper and therefore in the present study the oil extracted from the expeller only was used.
The oil content of the rubber seed in the present analysis (40.53 ± 0.73 %) was found to be quite higher than that of the cotton seed (15.0 - 24.0 %), soybean (17.0 - 21.0 %), safflower (25.0 - 40.0 %) and mustard (24.0 - 40.0 %) as observed by Pritchard (1991).

Moisture content and FFA of the oil are the important parameters to be determined before the production of biodiesel. Fig. 5 delineates the relationship between the FFA and moisture content of the oil. It is known that the FFA content of the oil from the freshly collected seed increased along with the increase in moisture content ($R^2 = 0.982$). It was also observed from the study that the storage of moist seeds, especially under local atmospheric conditions, resulted in mould growth which in turn caused the degradation of the oil. Rubber seed has a fat splitting enzyme, which separates the oil into glycerine and free fatty acid. This promotes rancidity and makes the oil unsuitable for industrial use. Storage of the seeds is observed to be necessary on account of its seasonal occurrence. Joseph (2004) reported that the heating of decorticated seeds at a temperature of 120 °C in an oven for an hour or at 50 °C for about 48 h would destroy the fat splitting enzyme and the seeds could then be stored with no undue increase in FFA.

![Fig. 5 Relationship between moisture and free fatty acid of rubber seed oil (n = 10).](image-url)
Colour of the oil was an index of the level of FFA present in it. It was observed that the oil containing low FFA appeared to be pale yellow in colour. Similarly when the oil had high FFA content it appeared brown in colour. The change in the colour of the oil was apparently caused by the absorbance of high moisture and consequent increase in endogenous lipase which caused a steep increase in FFA (Bringi, 1987).

To have rubber seed oil with low level of FFA, following precautions were observed:

a. Removal of seeds from the field soon after they fell down from the tree.
b. Immediate decortication.
c. Drying the kernels in the sun.
d. Storing the kernel in a warm dry place.

The batch of oil which contained high FFA (25.15 ± 0.85 percent) from the fig. 5 was chosen for the production of biodiesel and for further analyses.

**Characteristics of rubber seed oil**

The physico-chemical properties of the rubber seed oil are presented in Table 3. The FFA content of the rubber seed oil was found to be 25.15 ± 0.85 percent and the acid value was 50.3 ± 1.7 mg KOH/g. The high value of FFA indicated that the oil was exceedingly acidic. The physico-chemical characteristics of Malaysian rubber (Hevea brasiliensis) seed oil were studied by Abdullah and Salimon (2009). Its FFA (as oleic) was 7.55 ± 0.02 percent and its acid value was 15.10 ± 0.04 mg KOH/g. The specific gravity of the present oil was observed to be 0.91 ± 0.01 g/cm³ at 30 °C. The specific gravity of the oil was however closer to that of groundnut oil (0.918 g/cm³) and less denser than neem seed (0.939 g/cm³) oil (Akpan, 1999). Peterson and Scarrah, (1984) and Ramesh (2003) were of the opinion that the
specific gravity of the oil has to be reduced by removing the glycerol from the triglycerides.

Kinematic viscosity of the rubber seed oil has been observed to be 41.11 ± 0.81 cSt at 40 °C against that of the conventional diesel whose viscosity was 2.85 cSt at 40 °C. Thus the kinematic viscosity of the rubber seed oil was around 15 times higher than that of the conventional diesel and it was due to the presence of high levels of fatty acid. Singh and Singh (1991) indicated that the high viscosity of the oils was due to their larger molecular mass and chemical structure. Higher viscosity of oil has an adverse effect on the combustion in the existing diesel engines (Bhasabutra and Sutiponpeibun, 1982; Freedman et al., 1984; Rao and Gopalakrishnan, 1991; Foidl et al., 1996; Marinkovic and Tomasevic 1998 and Knothe and Steidley 2005). The viscosities of non-edible oils ranged from 20 to 22 cSt at 40 °C while for edible oils, it was between 10 and 15 cSt (Patil and Deng, 2009).

In the present study, rubber seed oil exhibited a higher iodine value (133.20 ± 0.35 gI₂/100 g) which indicated the presence of high degree of unsaturated fatty acids. High iodine value was caused by extensive oxidation and heat treatment during oil processing (Kirk and Sawyer, 1991). Higher iodine value (142.6 gI₂/100g) was observed in chosen rubber seed oils by Ikwuagwu et al. (2000). Abdullah and Salimon (2009) compared the Malaysian rubber seed oil with other oils. Malaysian rubber seed oil had a high iodine value (135.79 ± 0.33 gI₂/100 g) whereas low iodine value was observed in certain oils such as palm oil (52 gI₂/100 g) by Onyeike and Acheru (2002), cotton seed oil (99 - 119 gI₂/100g) and corn seed oil (103 - 128 gI₂/100 g) by Gunstone et al. (1994).

The saponification values of oils such as sunflower, corn, and safflower ranged between 175 and 250 mg KOH/g (O’Brien, 2004). The saponification value of
jatropha, karanja, canola and corn oil was reported as 196, 188,122 and 130 mg KOH/g respectively (Patil and Deng, 2010). In the present study, the saponification value of rubber seed oil was observed to be 182.32 ± 0.25 mg KOH/g and this data suggested that the oil has a high potential use in the production of soap and shampoos (Agatemor, 2006; Ku and Mun, 2007 and Anyasor et al., 2009). Usually, the saponification values fall outside the range of 188 – 196 mg KOH/g for most of the oils of plant origin (Pearson, 1976). The lower saponification value in the present case indicated that the rubber seed oil had higher molecular weight than that of the common oils. This might be due to high levels of fatty acids. The lower saponification value also suggested that this oil could be best used for the production of candles and also as a chemical feed stock for lubricants.

Peroxide value is an indicator of the poor quality of the oil. The peroxide value in the present case was 2.50 ± 0.40 meq/kg against the standard value of 10 meq/kg. Values lesser than 10 meq/kg normally indicates the freshness of the oil. The lower peroxide value indicates a poor oxidation rate of the oil. Values between 20 and 40 meq/kg indicate a state of rancidity (Akubugwo and Ugbogu, 2007 and Anyasor et al., 2009). According to Demian, (1990) and Pearson, (1981) the rate of
peroxide formation in the oil was found to be lower during an induction period which varied from few weeks to several months according to the type of oil and the temperature maintained during the storage.

The calorific (heating) value was considered to be an important parameter for any fuel, which was directly related to the efficiency. The calorific value of the rubber seed oil was 39.5 ± 0.03 MJ/kg which was lesser than that of the conventional diesel. Relatively low heat content of this oil might be due to the presence of high unsaturation of hydrogen in the molecule. The calorific value of methyl ester from edible and non-edible oil was lower than that of the diesel because of their high oxygen content (Patil and Deng, 2009). The presence of oxygen in the biodiesel helps to have a complete combustion in the engine.

The carbon, hydrogen, nitrogen and sulphur content of the rubber seed oil was observed to be 77.26 ± 0.50, 12.67 ± 0.65, 0.14 ± 0.06 and 0.11 ± 0.05 percent respectively.

The analytical data obtained above indicate that the rubber seed oil is closely equivalent to few edible oils in many respects.

**Esterification process (FFA reduction studies)**

Since the rubber seed oil was having high FFA (25.15 ± 0.85%) and such high level of FFA was considered unfavourable for processing the same to produce biodiesel (Freedman et al., 1984; Canakci and Gerpen, 1999; Ma and Hanna, 1999; and Dorodo et al., 2002). Therefore, it had become necessary to minimise the FFA through esterification process using acid as catalyst.
When an oil having high level of FFA undergoes a transesterification process, invariably soap and water are formed. This water consequently promotes saponification reaction. Soap not only decreased the yield of biodiesel but also necessitates additional cost - prohibitive purification process if high quality has to be ensured in the product (Vicente et al., 2004 and Myint and EL – Halwagi, 2009).

Many researchers have worked on feed stocks having elevated FFA levels (Freedman et al., 1984; Pryde, 1984; Ziejewski et al., 1984; Schwab et al., 1988; Singh and Singh, 1991; Ma and Hanna, 1999; Srivastava and Prasad, 2000; Canakci and Gerpen, 2001; Cravotto et al., 2004; Meher et al., 2006; Marchetti et al., 2007 and Patil and Deng, 2009). In an acid esterification process, the FFA was esterified into corresponding ester in the presence of an excess alcohol and acid catalyst under high temperature (Ramadhas et al., 2005; Nebel and Mittelbach, 2006; Veljkovic et al., 2006; Issariyakul et al., 2007; Kumartiwari et al., 2007; Sahoo et al., 2007; Meng et al., 2008; Naik et al., 2008; Rashid et al., 2008). For example, the FFA content of crude jatropha oil (Jatropha curcas) was lowered to a value lesser than 1 from 14 percent upon treatment at 60 °C for 88 min using 1.43 ml of sulphuric acid with 28 percent by volume of methanol. Subsequent transesterification using 0.5 by wt of potassium hydroxide at 60 °C for 30 min with 20 percent by volume of methanol yielded 99 percent of methyl esters (Kumartiwari et al., 2007).

Following three acids as homogeneous catalysts and ferric sulphate as heterogeneous catalyst were tried for their efficiency to reduce the FFA level.

1. Sulphuric acid (Homogeneous catalyst)
2. Hydrochloric acid (Homogeneous catalyst)
3. Orthophosphoric acid (Homogeneous catalyst)
4. Ferric sulphate (Heterogeneous catalyst)
The above catalysts were tried at different temperature 40, 45, 50, 55 and 60 °C. The experiments concerned with homogeneous catalysts were carried out for duration of 30, 45, 60 and 75 min whereas it was 60, 90, 120 and 150 min for ferric sulphate. All the experiments were conducted at a methanol to oil molar ratio of 9 : 1 for homogeneous catalysts as recommended by Canakci and Gerpen (2001); Kim et al., (2004) and Ramadhas et al., (2005).

**Sulphuric acid**

In the present study, the effect of sulphuric acid was tried at various application levels such as 2, 3, 4, 5, 6 and 7 ml / l at different temperatures (40, 45, 50, 55 and 60 °C) and at different durations of reaction (30, 45, 60 and 75 min) with a molar ratio of 9 : 1.
It was observed from fig.6 that at 60 °C, 3.9 ml/l of sulphuric acid was required to maximize the reduction of FFA (72.7 %). The relationship was $y = -0.77202 \cdot x^2 + 5.6726 \cdot x + 61.214$ for the reaction duration of 30 min where $y$ was the FFA reduction and $x$ was the acid dose. Ramadhas et al. (2005) who worked on the same oil identified the reaction temperature as 45 °C at a sulphuric acid concentration of 0.5 percent with a molar ratio of 9 : 1 in 30 min. Results obtained from the experiments of Ramadhas et al. (2005) revealed that 30 min of reaction was sufficient for the completion of the esterification. But in the present study high reaction time and temperature was observed to be needed to attain a maximum reduction of FFA. This otherwise means that Ramadhas et al. (2005) used 5 ml/l of acid at a relatively low temperature (i.e., 45 °C) in a short duration. The present data indicated that at a low application of sulphuric acid we may have to increase the temperature of the reaction (60 °C).

When the duration was extended further (45 min), maximum reduction of FFA (77.4 %) was observed at 60 °C with the sulphuric acid dose of 4.1 ml/l. The functional relationship was $y = -0.8452 \cdot x^2 + 7.9029 \cdot x + 62.552$ (Fig. 7). The highest temperature tried was 60 °C due to the limitation on account of the boiling point of 60 °C.
methanol. Even at a lower temperature (40 °C) the FFA reduction was engineered by the duration.

It is seen from fig.8 that at 60 °C, the optimum requirement of sulphuric acid was 5.2 ml/l to maximize the reduction of FFA (87.7 %) in an experimental duration of 60 min. The equation was $y = -1.1012x^2 + 11.444x + 57.624$. A combination of low methanol to oil ratio (6 :1) with 1 percent sulphuric acid at 60 °C in 60 min reduced the FFA from 20 to 2.4 percent in rice bran oil (Lin et al., 2009). This also indicated that higher temperature and increased reaction duration had greater influence than the quantity of acid used.
When the experimental duration was increased to 75 min, the FFA reduction efficiency reduced to a level of 85 percent at an acid dose of 4.97 ml/l of sulphuric acid at 60 °C. The equation obtained was \( y = -1.3036x^2 + 12.97x + 52.833 \) (Fig. 9). To trim down the FFA further, the content was once again given acid treatment for the second time. However, second treatment was not found to be advantageous. Quantity of sulphuric acid beyond the optimum level actually darkened the product and also retarded the reaction (Devi and Raj, 2009).

Haas et al. (2003) was able to reduce the FFA content of acid oil from 59.3 to 3.2 percent by treating the same with sulphuric acid at a dose of 1.5 ml/l and at a methanol to oil molar ratio of 15 : 1. This indicated that the acid dose, molar ratio and duration of experiment depended on the type of oil employed.

Freedman et al. (1984) provided extreme experimental conditions such as 30 : 1 molar ratio of methanol to soybean oil, sulphuric acid at the rate of 10 ml/l at 65 °C with an experimental duration of 69 h. However, the reduction in FFA content achieved was limited to 90 percent only. In the present experiment, with half (i.e 4.97 ml/l) of the sulphuric acid dose as referred above, 85 percent reduction in FFA content could be achieved.

<table>
<thead>
<tr>
<th>Duration (min)</th>
<th>Dose (ml/l)</th>
<th>Temperature (°C)</th>
<th>Maximum FFA reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>3.9</td>
<td>60</td>
<td>72.7</td>
</tr>
<tr>
<td>45</td>
<td>4.1</td>
<td>60</td>
<td>77.4</td>
</tr>
<tr>
<td>60</td>
<td>5.2</td>
<td>60</td>
<td>87.7</td>
</tr>
<tr>
<td>75</td>
<td>4.9</td>
<td>60</td>
<td>85.0</td>
</tr>
</tbody>
</table>

Table 4  Optimized values of sulphuric acid in reducing the FFA.

The data on the quantity of sulphuric acid derived from the fig. 6 – 9 are furnished in Table 4. In all the four trials maximum efficiency was obtained in 60 °C.
In 60 °C the sulphuric acid requirement to maximize the reduction of FFA was 3.9, 4.1, 5.2 and 4.9 ml/l for the reaction duration of 30, 45, 60 and 75 minutes respectively. The values on the duration (y) and the FFA reduction (x) were plotted in fig. 10. The functional relationship was \( y = -0.2396 x^2 + 40.952 x - 1683.2 \) and the optimum FFA reduction was 85.4 percent and the reaction duration was 66 minutes.

Wang et al. (2007) and Sharma et al. (2008) reported that the higher temperature and higher concentration of sulphuric acid as catalyst might char the oil which would then cause lower yield of biodiesel products when compared to that of the heterogeneous catalyst.

**Hydrochloric acid**

The effect of various doses of hydrochloric acid in reducing the FFA of oil at various process temperatures (40, 45, 50, 55 and 60 °C) for different experimental duration (30, 45, 60 and 75 min) was studied. The molar ratio of methanol to oil maintained was 9 : 1. The pattern of FFA reduction in 30 minutes is given in fig.11.
The highest reduction of FFA (y) was observed to be 69.5 percent at a dose (x) of 4.4 ml/l of hydrochloric acid. This relationship was given as \( y = -0.8929x^2 + 7.8929x + 52 \).

The results of identical trial made in an experimental duration of 45 min are presented in fig.12. The functional relationship was \( y = -0.8036x^2 + 6.9464x + 56 \) for the FFA reduction at 60 °C. The maximum FFA reduction (x) achieved was 71.8 percent at a dose of 4.3 ml/l.
The relationship between FFA reduction (y) and dose of hydrochloric acid (x) at an experimental duration of 60 min at 60 °C was \( y = -1.125 x^2 + 9.6774 x + 56.681 \). Here, 77.5 percent reduction of FFA (Fig. 13) was observed at a dose of 4.3 ml/l hydrochloric acid.

![Fig. 13 Effect of hydrochloric acid in reducing FFA in 60 min (n = 5).]

When the reaction time was extended to 75 min, the FFA reduction (y) was 73.8 percent at a dose (x) of 4.5 ml/l of hydrochloric acid at 60 °C. Then the relationship was \( y = -0.9107 x^2 + 8.3107 x + 54.7 \) (fig. 14).

![Fig. 14 Effect of hydrochloric acid in reducing the FFA in 75 min (n = 5).]
The highest FFA reduction at various duration and doses derived from fig. 10 – 14 was summarized in Table 5.

<table>
<thead>
<tr>
<th>Duration (min)</th>
<th>Dose (ml/l)</th>
<th>Temperature (°C)</th>
<th>Maximum FFA reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>4.4</td>
<td>60</td>
<td>69.5</td>
</tr>
<tr>
<td>45</td>
<td>4.3</td>
<td>60</td>
<td>71.8</td>
</tr>
<tr>
<td>60</td>
<td>4.3</td>
<td>60</td>
<td>77.5</td>
</tr>
<tr>
<td>75</td>
<td>4.5</td>
<td>60</td>
<td>73.8</td>
</tr>
</tbody>
</table>

Table 5 Optimized values of hydrochloric acid in reducing the FFA.

Overall results of the treatment using hydrochloric acid showed that the maximum reduction of FFA was observed at a temperature of 60 °C in all the experiments. For a wide variation in the durations of experiments, a narrow change in the dose of hydrochloric acid was observed. From the fig. 15, it was known that the optimum time required was 69 min in which a maximum of 75 percent FFA reduction could be possible. The functional relationship was \( y = -1.3594x^2 + 204.17x - 7596.6 \).
Thus the FFA reduction was largely governed by the duration of the experiment and not on the change in dose. Ting et al., (2008) who worked on soybean oil also reported that the highest reduction was achieved in one hour.

**Orthophosphoric acid**

The effect of orthophosphoric acid on the reduction of FFA was also examined at different temperatures (40, 45, 50, 55 and 60 °C) and durations (30, 45, 60 and 75 min) with 9 : 1 molar ratio of methanol to oil. The data obtained for an experimental duration of 30 min are shown in fig. 16. The highest reduction of FFA reduction (61.4 %) was reached in 60 °C at a dose of 4.0 ml/l. The corresponding dose (x) indicates a functional relationship of $y = -0.6607 x^2 + 5.3464 x + 50.414$ at 60 °C.
When the experiment was carried out at 60 °C for 45 min (Fig. 17) the FFA reduction (y) to the tune of 64.6 percent was observed at an acid dose (x) of 3.7 ml/l. It showed that its functional relationship was $y = -0.7143 \, x^2 + 5.4286 \, x + 54.286$.

In an experimental duration of 60 min and at 60 °C, the highest reduction (y) of FFA (73.5%) was achieved at an acid level (x) of 4.4 ml/l. The functional relationship was $y = -0.6607 \, x^2 + 5.0607 \, x + 56.7$ (Fig. 18).
Similarly, maximum reduction (y) of FFA (66.5%) was observed at a dose of 3.8 ml/l orthophosphoric acid at 60°C in an experimental duration of 75 min (Fig. 19). The functional relationship was parabolic (y = - 0.5536 x^2 + 3.6107 x + 58.243).

![Fig. 19 Effect of orthophosphoric acid in reducing FFA in 75 min (n = 5).](image)

Highest FFA reductions were obtained in four experimental durations (Fig. 16 – 19) are compared and given in Table 6. All the four data was obtained at a higher process temperature (60 °C). Orthophosphoric acid dose ranged from 3.2 to 4.0 ml/l.

<table>
<thead>
<tr>
<th>Duration (min)</th>
<th>Dose (ml/l)</th>
<th>Temperature (°C)</th>
<th>Maximum FFA reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>4.0</td>
<td>60</td>
<td>61.4</td>
</tr>
<tr>
<td>45</td>
<td>3.7</td>
<td>60</td>
<td>64.6</td>
</tr>
<tr>
<td>60</td>
<td>4.4</td>
<td>60</td>
<td>66.5</td>
</tr>
<tr>
<td>75</td>
<td>3.8</td>
<td>60</td>
<td>64.1</td>
</tr>
</tbody>
</table>

Table 6 Optimized values of orthophosphoric acid in reducing the FFA.
The data from Table 6 on the duration was plotted in Fig. 20 against the FFA reduction. It was known that the FFA reduction (x) is fairly low (64.6 %) for a duration (y) of 68.7 min. The functional relationship was $y = -3.5011 x^2 + 452.74 x - 14568$.

Maximum reduction was obtained at a temperature of 60 °C and it was same for all the experiments tried. The optimum dose of orthophosphoric acid was 3.43 ml/l whose FFA reduction was 64.6 percent.

**Ferric sulphate**

The effect of ferric sulphate as a catalyst in reducing the FFA of oil was studied at an experimental duration of 60, 90, 120 and 150 min at various temperatures (40, 45, 50, 55 and 60 °C) with different doses of the catalyst (1.5, 2.0, 2.5, 3.0 and 3.5 g/l) with 12 : 1 molar ratio of methanol to oil. When the experiment was carried out for duration of 60 min, the maximum reduction in FFA (y) attained was 74.8 percent at a dose(x) of 2.2 g/l of ferric sulphate at 60 °C. The functional relationship was $y = -4.2143 x^2 + 18.945 x + 53.281$ (Fig.21).
When the experiment was extended to 90 min under same experimental condition, the highest reduction in FFA achieved was 77.9 percent. However, the dose and temperature remain the same (Fig. 22). The functional relationship of it was 

$$y = -4.4524x^2 + 20.207x + 54.71.$$
When the duration was increased to 120 min the highest reduction was obtained at 60 °C. In that set, the FFA reduction(x) was 90.5 percent with a slight increase in the dose (y) of 2.5 g/l (Fig.23). The equation was \( y = -5.119x^2 + 25.874x + 57.71 \) (Fig. 23). Patil et al. (2010) reported that the maximum biodiesel yield from waste cooking oil was obtained while using 2 percent ferric sulphate and 96 percent of reduction was achieved at a reaction period of 2 h at 100 °C. The molar ratio of methanol to oil for the maximum yield was 9:1. But in the present experiment, the reduction of FFA was found to be lower. High temperature applied in the experiments of Patil et al. (2010) could be the reason for the enhanced efficiency.

Further increase in duration (150 min) did not cause any impact on the FFA reduction (y) though the dose (x) of 2.5 g/l did not change. The highest reduction attained was at 60 °C. The relationship was \( y = -4.4524x^2 + 23.045x + 58.157 \) (Fig.24).
The overall maximum reduction of FFA observed from the fig. 21 - 24 based on the concentration, temperature and time are shown in Table 7.

<table>
<thead>
<tr>
<th>Duration (min)</th>
<th>Dose (g/l)</th>
<th>Temperature (°C)</th>
<th>Maximum FFA reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>2.2</td>
<td>60</td>
<td>74.8</td>
</tr>
<tr>
<td>90</td>
<td>2.2</td>
<td>60</td>
<td>77.9</td>
</tr>
<tr>
<td>120</td>
<td>2.5</td>
<td>60</td>
<td>90.5</td>
</tr>
<tr>
<td>150</td>
<td>2.5</td>
<td>60</td>
<td>88.0</td>
</tr>
</tbody>
</table>

The duration of the experiment (y) regressed against FFA reduction (x) are shown in fig. 25. It clearly showed that the maximum reduction (x) in FFA (89.3%) was achieved in an experimental duration (y) of 135 min. The relationship was 

\[ y = -0.3992x^2 + 70.32x - 2961.9. \]
As inferred from the Table 7, the maximum reduction of FFA did not show any remarkable change with respect to dose. As ferric sulphate was insoluble in oil, it was centrifuged from the liquid after acid esterification and reused for the next batch.

Reaction temperature was also one of the factors that influenced the esterification rate and conversion (Liu et al., 2008; Buasri et al., 2009 and Mengyu et al., 2009). The reaction rate (conversion) could be rapidly speeded up by raising the temperature. The maximum conversion was obtained at a temperature of 60 °C. Experiments beyond 60 °C were not conducted as there could be loss of methanol (in an open end reaction), since the boiling point of methanol was found to be 65 °C.

Buasri et al. (2009) produced biodiesel from crude palm oil with 2 percent ferric sulphate with an ethanol to oil molar ratio of 10 :1 at a reaction temperature of 95 °C for 1 h in a closed reactor where the evaporated methanol was allowed to condense and recycle. Patil et al. (2010) reported that the ferric sulphate catalyst shows good catalytic activity in the methanolysis of FFA of waste cooking oil.
As high as 97.2 percent FFA reduction in the waste cooking oil was obtained when it was treated with ferric sulphate at the rate of 2 g/l with a molar ratio 20 : 1 of methanol to oil at 95 °C in 4 h (Wang et al., 2007).

**Comparison of various catalysts in FFA reduction**

In the present study, three homogeneous catalysts (sulphuric acid, hydrochloric acid and orthophosphoric acid) and one heterogeneous (ferric sulphate) catalyst were investigated for their ability to reduce the FFA of the oil. The data obtained are consolidated and are presented in the Table 8. The performance of heterogeneous catalyst (ferric sulphate) was higher than the homogeneous catalyst. The dose, duration and the FFA reduction of all the acid catalysts tried in the study were presented in Table 8.

<table>
<thead>
<tr>
<th>Acids</th>
<th>Dose (ml/l)</th>
<th>Maximum FFA reduction (%)</th>
<th>Duration (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphuric acid</td>
<td>4.9</td>
<td>85.4</td>
<td>66.0</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>4.3</td>
<td>75.0</td>
<td>69.0</td>
</tr>
<tr>
<td>Orthophosphoric acid</td>
<td>3.4</td>
<td>64.6</td>
<td>68.7</td>
</tr>
<tr>
<td>Ferric sulphate</td>
<td>2.5</td>
<td>89.3</td>
<td>135.0</td>
</tr>
</tbody>
</table>

Table 8 Comparison of the efficiency of catalysts in reducing the FFA at 60 °C.

Among the three homogeneous acids tried, sulphuric acid showed the highest catalytic activity in esterifying the oil. This was due to its relatively higher acid strength *i.e.*, more H⁺ would have been released to protonate the carboxylic moiety of the fatty acid. This in turn increases the electrophilicity of the carbonyl carbon atom and facilitates the nucleophilic attack of the alcohol thus forming a tetrahedral intermediate. It includes proton migration and breakdown of the intermediate (Kocsisova et al., 2005; Lotero et al., 2005 and Aranda et al., 2008).
Saifuddin et al. (2009) compared the effectiveness of acid catalysts (sulphuric, hydrochloric, nitric, acetic, and phosphoric acids) at 5 percent level (v/v) in esterifying the waste cooking oil with an methanol to oil molar ratio of 20 : 1 at 50 °C for 1 h. Results showed that the strong acids (sulphuric, hydrochloric and nitric acid) exhibited higher catalytic activity when compared to that of the weak acids (phosphoric and acetic acid).

Highest reduction of FFA according to Dean, 1985; Ting et al., 2008 and Saifuddin et al., 2009 was obtained in the presence of sulphuric acid which dips down from 75 to 12 percent. The acid dissociation indexes (pKa) for hydrochloric, sulphuric, nitric, phosphoric, and acetic acids were 6.1, 3.1, 3.8, 2.1 and 4.8 respectively. However, the results of their study indicated that the pKa is not the only criterion to identify an acid as an effective catalyst for esterification.

Goff et al. (2004) studied the catalytic ability of various acids in the transesterification of soybean oil and reported that the superiority of the sulphuric acid. Sulphuric acid offers another advantage of being converted into insoluble salt when neutralized with alkali.

**Recovery of catalyst**

Out of the two (sulphuric acid and ferric sulphate) favourable catalysts, sulphuric acid is homogeneous and therefore it cannot be recoverable. But ferric sulphate being heterogeneous can be reused. In the present case, ferric sulphate was reused for 5 times (1- original and 4 – replicates). After each run, the whole reaction mixture was centrifuged and separated. The efficiency slowly declined with the reuse of every passing batch of recovered ferric sulphate (Fig. 26). The catalyst showed a marked loss of activity after four cycles. The functional relationship was $y = -0.3429 x^2 + 0.7371 x + 85.08$. 
Effect of molar ratio on heterogeneous esterification process

Application of excess methanol was found to be favourable in esterifying the FFA since it speed up the forward reaction (Titipong et al., 2007). Variables such as the amount of the catalyst (2.5 g/l), temperature (60 °C) and duration (135 min) were kept constant in accordance with the optimized results. The experiments on molar ratio of methanol to oil were performed at 3 :1, 5 :1, 7 :1, 9 :1, 12 :1 and 15 :1 (Fig. 27). An excess of methanol was necessary for the esterification of FFA because it increases the methanolysis.
The optimized results of molar ratio of methanol to oil indicated that a ratio of 9.5:1 was required to obtain the maximum reduction of FFA (89.3%) using ferric sulphate at the rate of 2.5 g/l at 60 °C in 135 min. The functional relationship was 
\[ y = -0.3003x^2 + 5.7086x + 61.988. \]

Overall results of acid catalysts tried, showed that the maximum reduction of FFA was observed while using a heterogeneous acid catalyst (ferric sulphate). Though this type of heterogeneous catalyst requires longer duration of time than homogeneous catalyst for transesterification, it is considered as a candidate due to its reusability. Therefore, the acid esterified oil using ferric sulphate was taken for transesterification process.

**Transesterification process**

The acid esterified oil which was prepared using ferric sulphate with methanol was taken for the analysis of free fatty acid content present in it. The calculated value of FFA content in the acid esterified oil was

\[
\text{FFA level} = \frac{100 - \text{FFA reduction} \times \text{FFA in oil}}{100} 
\]

\[
\text{FFA level} = \frac{100 - 89.3 \times 25.15}{100} = 2.6 \%
\]

As the FFA level of the acid esterified oil was found below 3 percent, the transesterification process was proceeded making use of the product obtained with the use of ferric sulphate as catalyst. A total of 4 agents were tested. They were:
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Sodium hydroxide (Homogeneous catalyst)
Potassium hydroxide (Homogeneous catalyst)
Sodium methoxide (Homogeneous catalyst)
Calcium oxide (Heterogeneous catalyst)

The above alkaline catalysts were investigated at different temperatures (40 - 60 °C) and different durations. As far as the homogeneous catalysts were concerned the experimental durations tried were 30, 45, 60 and 75 min. With reference to heterogeneous catalyst it was 60, 90, 120 and 150 min. Regression analysis was carried out for all the experimental results.

**Sodium hydroxide**

Zhang et al. (2003) reported that the alkali catalysed process was sensitive to water. Presence of water in the feedstock or the catalyst contributes to saponification reaction. When a base catalyst such as sodium hydroxide or potassium hydroxide was used it was first mixed with methanol and water and the product was

\[
\text{NaOH} + \text{H}_3\text{C} - \text{OH} \leftrightarrow \text{H}_3\text{CO}^-\text{Na}^+ + \text{H}^+\text{OH}^- 
\]

The presence of OH\(^-\) ion from water promoted the reaction of Na with triglyceride, allowing soap to be formed.

The study examined the effect of sodium hydroxide concentration in transesterifying the acid esterified oil with its concentration varying from 2 to 6 g/l at different temperatures (40, 45, 50, 55 and 60 °C) and time (30, 45, 60 and 75 min). Molar ratio of methanol to oil was 6 : 1 as recommended by Freedman et al.,(1984); Krishnangkura and Simamaharnnop (1992); Canakci and Gerpen (1999); Ma and
Studies on biodiesel production and quality analysis, 2010.


Results of fig. 28 showed the changes in ester yield in accordance with varied catalyst concentration. Experimental results (Fig. 28) showed that the changes in the ester yield against varied catalyst concentration followed a parabolic curve. Insufficient amount of catalyst resulted in incomplete formation of an ester. The ester formation reached high when the sodium hydroxide was increased to a certain level beyond which ester level decreased. Methyl ester formation was 74 percent when the catalyst concentrations was 3.6 g/l in 30 min duration at 60 °C with a functional relationship of $y = -3.7619x^2 + 27.629x + 23.133$.

When the above experiment was carried out for a longer duration (45 min) the yield increased to 78.4 percent with no conspicuous change in the dose of sodium hydroxide in the graph. The relationship between yield ($y$) and sodium hydroxide dose ($x$) at 60 °C was $y = -4.381x^2 + 33.048x + 15.8$ (Fig. 29).
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The reaction temperature and the process duration positively affected the production of ester. It could be seen that the best conversion were obtained at the highest temperature, which corroborates the fact that alkaline-catalyzed alcoholysis of vegetable oils was normally high near the boiling point of the alcohol (Freedman et al., 1984; Alcantara et al., 2000) and De Oliveira et al., (2005).

Further improvement in the yield was obtained (Fig. 30) when the duration was increased to 60 min at a process temperature of 60°C. The maximum yield (y) of methyl ester (83.7%) was attained while using 3.7 ml/l of sodium hydroxide (x). The equation was $y = -4.5714x^2 + 34.238x + 19.267$. 

![Fig. 29](image1.png) Yield of methyl ester at different doses of sodium hydroxide in 45 min (n = 5).

![Fig. 30](image2.png) Yield of methyl ester at different doses of sodium hydroxide in 60 min (n = 5).
When the duration was increased to 75 min the yield did not increase indicating that the optimum duration was within 75 min. The dose of the catalyst also did not change. The yield was 81.4 percent. The functional relationship was 
\[ y = -4.5952x^2 + 34.395x + 17.133 \] (Fig. 31).

![Graph showing yield of methyl ester at different doses of sodium hydroxide in 75 min (n = 5).](image)

The optimized results on methyl ester yield (y) on applying sodium hydroxide dose (x) at different duration of time was presented in Table 9 and the results showed that maximum yield of ester (83.7%) was obtained at a dose of 3.7 g/l of sodium hydroxide at 60 °C in 60 min.

<table>
<thead>
<tr>
<th>Duration (min)</th>
<th>Dose (g/l)</th>
<th>Temp. (°C)</th>
<th>Yield of ester (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>3.6</td>
<td>60</td>
<td>74.0</td>
</tr>
<tr>
<td>45</td>
<td>3.7</td>
<td>60</td>
<td>78.4</td>
</tr>
<tr>
<td>60</td>
<td>3.7</td>
<td>60</td>
<td>83.7</td>
</tr>
<tr>
<td>75</td>
<td>3.7</td>
<td>60</td>
<td>81.4</td>
</tr>
</tbody>
</table>

Table 9 Influence of sodium hydroxide at different duration of time with respect to their methyl ester yield at 60 °C.
The information in Table 9 indicated that the experimental duration has greater influence in the yield of ester than the dose of sodium hydroxide. The experimental duration ($y$) and the methyl ester yield ($x$) was plotted (Fig. 32) and the maximum yield of ester (83.8 %) was obtained at a duration of 65 min. The functional relationship was $y = -0.3823x^2 + 64.115x - 2623.2$.

Larger quantities of soap were formed during the experiment especially when excess sodium hydroxide was used. Consequently the yield diminished in such cases. This was because the addition of excess quantity of alkaline catalyst caused more triglycerides to participate in the saponification reaction which resulted in the generation of soap, thereby reducing the ester yield.

Sharma and Singh (2008) transesterified the karanja oil using sodium and potassium hydroxides. Out of which sodium hydroxide was found to be a better choice than potassium hydroxide. Sarin et al. (2007) prepared biodiesel from edible oils such as sunflower, soybean and palm and from non-edible oils such as jatropha
and karanja. The catalyst used was either sodium hydroxide or potassium hydroxide with 1 percent weight of the oil.

Leung and Guo (2006) tried three different homogeneous catalysts (sodium hydroxide, potassium hydroxide, and sodium methoxide) on frying oil. The optimum requirements of the catalyst were 1.1, 1.3 and 1.5 percent by weight of sodium hydroxide, sodium methoxide and potassium hydroxide respectively for the production of maximum quantity of ester. The amount of sodium hydroxide required was lesser than that of sodium methoxide and potassium hydroxide for the production of the same quantity of methyl ester as sodium hydroxide has lower molar mass (40 g/mol), compared to sodium methoxide (54g/mol) and potassium hydroxide (56 g/mol).

**Potassium hydroxide**

Potassium hydroxide was also studied at various doses (2 – 6 g/l) and the yield of methyl ester was examined at different temperatures (40, 45, 50, 55 and 60) and reaction durations of 30, 45, 60 and 75 min. The molar ratio of methanol to oil was 6 : 1. The results of the experiments carried out at 30 min are presented in fig. 33. Maximum yield (y) of ester (68.7%) was obtained at a dose(x) of potassium hydroxide (4.1g/l) with an equation of y = - 6x² + 49.8x - 34.267 at 60 °C.
When the same experiment was carried out for 45 min at 60 °C, the ester recovery was slightly increased (72.6 %) at a dose of 4.1 ml/l of potassium hydroxide (Fig. 34). The equation was \( y = -6.4286 x^2 + 52.962 x - 36.8 \) where \( y \) and \( x \) refers to the yield of ester and the amount of potassium hydroxide required.

![Fig. 34 Yield of methyl ester at different doses of potassium hydroxide in 45 min (n = 5).](image)

Higher yield of methyl ester was observed (81%) when the experimental duration was extended to 60 min. The ideal dose of potassium hydroxide was 4.1 g/l at 60 °C. The relationship established was \( y = -6.5714 x^2 + 54.371 x - 32.133 \) (Fig. 35). It was observed that the amount of ester increases as the catalyst dose increases at a lower range of dosing. When catalyst dose was increased soap was formed which retarded the yield of methyl ester.

![Fig. 35 Yield of methyl ester at different doses of potassium hydroxide in 60 min (n = 5).](image)
Jeong et al. (2004) showed the effect of potassium hydroxide dose on the basis of oil weight at 60 °C with a molar ratio of 6 : 1 methanol to oil. The ester yield increased rapidly at a higher dose of potassium hydroxide within 5 min and declined slowly after 10 min. At a low dose (0.1%), the yield was low. According to Fillieres et al. (1995) 1 percent potassium hydroxide was found to be optimum for transesterification of rapeseed oil.

When the experimental duration was increased to 75 min the yield declined but the dose did not change (Fig. 36). In 60 °C the maximum yield was 78 percent. The equation obtained was $y = -6.4048x^2 + 52.871x - 31.133$.

The optimum values obtained in fig. 33 – 36 are consolidated and presented in Table 10. It was observed that doses remain the same. The only deciding factor was the duration.
Table 10 Influence of potassium hydroxide at different duration of time with respect to methyl ester yield at 60 °C.

<table>
<thead>
<tr>
<th>Duration (min)</th>
<th>Dose (g/l)</th>
<th>Temperature (°C)</th>
<th>Yield of ester (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>4.1</td>
<td>60</td>
<td>68.7</td>
</tr>
<tr>
<td>45</td>
<td>4.1</td>
<td>60</td>
<td>72.6</td>
</tr>
<tr>
<td>60</td>
<td>4.1</td>
<td>60</td>
<td>81.0</td>
</tr>
<tr>
<td>75</td>
<td>4.1</td>
<td>60</td>
<td>78.0</td>
</tr>
</tbody>
</table>

Results showed that maximum yield of esters (68.7, 72.6, 81.0 and 78.0 percent) were observed at a dose of 4.1 g/l of potassium hydroxide for the various reaction durations (30, 45, 60 and 75 min) at 60 °C. However in the present case, yield of ester changes with duration although the calculated doses and temperature was found to be same for all the experiments. The data from Table 8 on the duration (y) and the yield of methyl ester (x) were plotted (Fig. 39) whose relationship was \[ y = -0.4083x^2 + 64.138x - 2451.9 \]. The graph indicated a maximum yield of ester (78.5 %) at a duration of 68 min.
Separation of ester from the glycerol layer using potassium hydroxide as catalyst was observed to be more convenient and simpler than using sodium hydroxide or sodium methoxide as a catalyst. Due to this reason, potassium hydroxide is commonly used for producing biodiesel from waste oils.

Sahoo et al. (2007) used an alkaline transesterification process after reducing the free fatty acid content of polanga seed oil from 22 to 2 percent using acid catalyst. According to them, 1.5 percent by weight of potassium hydroxide was needed to maximise the yield of ester. Karmee and Chadha (2005) who worked on karanja oil obtained a conversion of 92 percent with 10 : 1 molar ratio (methanol : oil) at 333 K and 1.0 percent potassium hydroxide by weight.

**Sodium methoxide**

In an effort to investigate the effect of sodium methoxide on the ester yield, a series of experiments were carried out using different doses of sodium methoxide (2, 2.5, 3, 3.5 and 4 g/l) at different temperatures (40, 45, 50, 55 and 60 °C) and durations (30, 45, 60 and 75 min). The molar ratio of methanol to oil was 6 : 1.

In an experimental duration of 30 min at 60 °C the maximum yield of ester (y) achieved was 66.7 percent at a dose (x) of 3 g/l. The equation obtained was $y = -23.429x^2 + 144.17x - 155.08$ (Fig. 38).
When the experimental duration was extended, the yield marginally increased (71.9%) though the dose of catalyst does not change (Fig. 39). The relationship was

\[ y = - 25.714 x^2 + 157.62 x - 170.3. \]

The ester yield further increased to 77.8 percent when the duration of the process was extended to 60 min at 60 °C. However there was no shift in the concentration of catalyst. The functional relationship was

\[ y = - 26.762 x^2 + 163.44 x - 171.88 \] (Fig. 40).
At higher duration (75 min) the yield of ester declined from that of 60 min (Fig. 41). The experimental equation was $y = -27.238 x^2 + 165.7 x - 177.12$.

It was observed from fig. 38 - 41 that if sodium methoxide concentration decreased below the optimum level, the yield of ester was not satisfactory. There could be increase in glycerol and emulsion due to the presence of excess free fatty acid in oil. On the contrary, if the dose of sodium methoxide was increased beyond the optimum, the yield of ester declined. This was in accordance with the observation of Encinar et al. (1999) and Dorado et al. (2004). If the catalyst quantity was more than its requirement, soap was formed which promotes viscosity causing the depression in the yield.

Freedman et al. (1986) contended that sodium methoxide was a most effective catalyst formulation than sodium hydroxide and almost equal oil conversion was observed at 6:1 alcohol to oil molar ratio in soybean oil. Ma et al. (1998) opined that sodium hydroxide was a better catalyst than sodium methoxide in the transesterification of beef tallow. According to Vicente et al. (2004) higher yields were obtained when methoxide catalysts was used. But the rate of reaction was highest in
sodium hydroxide and lowest in potassium methoxide at 65 °C at a methanol to soybean oil molar ratio of 6 :1 and at a catalyst concentration of 1 percent weight.

The results obtained from fig 38 – 41 on the maximum yield of the ester and the corresponding dose of sodium methoxide, temperature and duration are presented in Table 11.

<table>
<thead>
<tr>
<th>Duration (min)</th>
<th>Dose (ml/l)</th>
<th>Temperature (°C)</th>
<th>Yield of ester (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>3.0</td>
<td>60</td>
<td>66.7</td>
</tr>
<tr>
<td>45</td>
<td>3.0</td>
<td>60</td>
<td>71.9</td>
</tr>
<tr>
<td>60</td>
<td>3.0</td>
<td>60</td>
<td>77.8</td>
</tr>
<tr>
<td>75</td>
<td>3.0</td>
<td>60</td>
<td>75.0</td>
</tr>
</tbody>
</table>

Table 11 Influence of sodium methoxide at different duration of time with respect to methyl ester yield at 60 °C.

Whatever change in the duration there was no change on the dose or temperature. This table makes us to understand that the duration was the single overruling factor and therefore it was regressed against that ester yield. Results of Table 9 were taken to plot the fig. 44 where y is the yield of methyl ester and x is the duration required for the completion of the reaction. The relationship was 

\[ y = -0.2966 x^2 + 46.176 x - 1732.2 \]

The regressed value indicated a maximum yield of 77.8 percent at a process duration of 65 min.
Calcium oxide

Comparative study of calcium oxide as a catalyst was made in different temperatures (40 – 60 °C) at an experimental duration of 60, 90, 120 and 150 min. The catalyst concentration chosen ranged from 1.5 – 3.5 g/l in methanol to oil molar ratio of 6:1. Fig. 43 indicates the effect of calcium oxide catalyst at various application levels. It was known that 2.3 g/l of calcium oxide was needed to maximize the yield of methyl ester (71 %) at 60 °C. The equation obtained was $y = -13.238x^2 + 61.057x + 0.6476$.

![Fig. 43 Yield of methyl ester at different doses of calcium oxide in 60 min (n = 5).](image)

Higher percentage of methyl ester (75%) could be reached at an application of 2.2 g/l for 90 min at 60 °C and the equation is $y = -14.667x^2 + 65.733x + 1.2667$. The results indicated that the biodiesel yield significantly improved with the increase in calcium oxide (Fig. 44). Further increase in the amount of catalyst was not found to be advisable as it shows reduction in the yield of biodiesel.
Calcium oxide at a dose of 2.2 g/l gave a higher efficiency of methyl ester (82 %) in 120 min at 60 °C. The regression equation obtained was \( y = -16.667x^2 + 76.067x - 4.9333 \). Increasing the amount of calcium oxide up to 2.5 g/l showed a remarkable yield of ester and drastic decline was observed after the dose of 2.5 g/l. Similarly, increase in temperature resulted in increase in the ester yield (Fig. 45).
Rapid changes were noticed when treatment duration was increased beyond 120 min at a rate of 2.3 g/l. Calcium oxide gave a highest turnover of methyl ester (78.1%) at 60 °C in 150 min. The equation thus obtained from fig. 46 was 

$$y = -15.429x^2 + 71.143x - 3.581.$$ 

The optimized results of methyl ester yield on the application of calcium oxide at different duration of time was analysed and furnished in Table 12.

<table>
<thead>
<tr>
<th>Duration (min)</th>
<th>Dose (g/l)</th>
<th>Temperature (°C)</th>
<th>Yield of ester (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>2.3</td>
<td>60</td>
<td>71.0</td>
</tr>
<tr>
<td>90</td>
<td>2.2</td>
<td>60</td>
<td>75.0</td>
</tr>
<tr>
<td>120</td>
<td>2.2</td>
<td>60</td>
<td>82.0</td>
</tr>
<tr>
<td>150</td>
<td>2.3</td>
<td>60</td>
<td>78.1</td>
</tr>
</tbody>
</table>

Table 12 Influence of calcium oxide at different duration of time with respect to methyl ester yield at 60 °C.
Results showed that maximum yield of ester were obtained at a temperature of 60 °C for all the experiments conducted. It was also observed from Table 12 that there was no change in dose but the changes were observed in the reaction duration. Therefore, the data from the Table 12 were used to plot the fig. 47. Maximum yield of ester (79.5 %) were obtained at a duration of 132 min. The functional relationship was $y = -1.0577x^2 + 168.31x - 6564$.

Comparison of the yield of methyl ester

A comparison was made on the quantum of the yield due to various catalysts at their optimum doses and duration of the experiments (Table 11). It was noticed that sodium hydroxide showed significantly better catalytic activity with respect to the yield of methyl ester than potassium hydroxide, sodium methoxide and calcium oxide. Calcium oxide due to its weak solubility in the reaction medium was found to be less active than sodium hydroxide.
Studies on biodiesel production and quality analysis, 2010.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Dose (g/l)</th>
<th>Yield (%)</th>
<th>Duration (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium hydroxide</td>
<td>3.7</td>
<td>83.8</td>
<td>65</td>
</tr>
<tr>
<td>Potassium hydroxide</td>
<td>4.1</td>
<td>78.5</td>
<td>68</td>
</tr>
<tr>
<td>Sodium methoxide</td>
<td>3.0</td>
<td>77.8</td>
<td>65</td>
</tr>
<tr>
<td>Calcium oxide</td>
<td>2.2</td>
<td>79.5</td>
<td>132</td>
</tr>
</tbody>
</table>

Table 13  Comparison of the efficiency of catalysts with respect to their yield at 60 °C.

It was known from Table 13 that the highest percentage of yield (83.8%) was obtained while using sodium hydroxide as an alkaline catalyst in a shorter duration of time than the other type of catalysts. Therefore, further study on the molar ratio was made by keeping the dose of sodium hydroxide as 3.7 g/l at a temperature of 60 °C for 65 min. Different molar ratio of methanol to oil (3:1, 6:1, 9:1, 12:1 and 15:1) were tested.

**Effect of methanol to oil molar ratio for transesterification**

The amount of methanol required for the transesterification process was assessed in terms of the methanol to oil molar ratio. The effect of methanol to oil molar ratio on the yield of methyl ester and was shown in fig. 48. The stoichiometric molar ratio of methanol to oil required for a complete transesterification was 3:1. But, in practice this is not sufficient to complete the transesterification reaction. Percentage conversion increases linearly with the increase in molar ratio till the optimum is reached beyond which there was negative effect. The molar ratio does not have any adverse effect on acid, peroxide, saponification and iodine values of methyl ester (Tomasevic and Marinkovic, 2003 and Lin et al., 2008). The conversion efficiency at different molar ratio was shown in Fig. 48.

All the experiments concerned with the molar ratio of methanol to oil were carried out at 60 °C at an optimized dose (3.7g/l) of sodium hydroxide as the results
of the alkaline catalysts concentration exhibited maximum conversion of triglycerides into esters in 60 min. It showed proportional response when the amount of methanol was increased especially at lower ratio. However, when the molar ratio was increased beyond 6 : 1, the conversion efficiency reduced slowly but steadily (Fig. 48). The optimum molar ratio of methanol to oil molar ratio was said to be 6.1 : 1. The functional relationship was found to be \( y = -0.5429x^2 + 6.7143x + 62.903 \).

It was known that, higher molar ratio of alcohol to vegetable oil normally interfered with the separation of glycerine because there appeared to be an increase in solubility. When glycerine remained in the reactor, it drives the equilibrium back to the left side of the reaction, resulting in a lower yield of ester (Meher et al., 2006). This was due to the fact that methanol, with a polar hydroxyl group can work as an emulsifier which enhances emulsion (Leung and Guo, 2006 and Rashid and Anwar, 2008). Therefore, increasing the molar ratio of methanol : oil beyond 6 : 1 did not increase the yield of the product. Further it was observed that the methanol to oil has the potentiality to complicate the ester recovery process and raise the cost for methanol recovery. The results showed that the molar ratio of alcohol to oil was a
major factor in affecting the biodiesel yield and purity apart from the issue of catalyst concentration, reaction time and temperature.

Therefore, biodiesel produced from the rubber seed oil using ferric sulphate as an acid catalyst with methanol followed by sodium hydroxide as a base catalyst with methanol was taken for the further analysis.

**FTIR studies of biodiesel**

The infrared spectrum of biodiesel showed the presence of pronounced functional groups, which indicated the presence of alkanes and poly-aromatic groups with an absence of phosphorus and sulfur. The typical FT - IR spectrum of the transesterified rubber seed oil showed that it contained significant amount of esters. The comparative frequency ranges of the spectra, their corresponding functional groups and indicated compounds have been presented in fig. 49.

Different bonds were present in biodiesel (C-C, C=C, C-O, C=O, O -H, N -H etc.) have different vibrational frequencies. The presence of these bonds in biodiesel could be detected by identifying characteristic frequencies as absorption bands in the infrared spectrum. Functional group vibrations were made for most of the dominant peaks. The carbonyl band in FTIR was sensitive to substituent effects and to the structure of the molecule. From the spectrum, it was observed that the peak of C=O vibration band (in the range 1750 – 1735 cm$^{-1}$) of methoxy carbonyl group changed from 1743 cm$^{-1}$ in oil to 1740 cm$^{-1}$ in biodiesel. Biodiesel could be elucidated from the absorption peak at 1743 cm$^{-1}$ corresponding to C=O stretching and hence the resultant product was confirmed as biodiesel. The ester carboxyl band at 1740 cm$^{-1}$ indicates the formation of compounds containing other C=O groups. The broad band appeared at 3400 cm$^{-1}$ was attributable to the –N-H- stretch. Hydroperoxides formed during oxidative process would have given rise to characteristic –O-O-H stretching
vibration at approximately 3531 cm\(^{-1}\). The peak at 3006 cm\(^{-1}\) was attributed to \(\text{–HC = CH–}\) stretching of methyl ester.

The vibrational peak appeared at 2925 cm\(^{-1}\) of the biodiesel was corresponded to asymmetric CH\(_3\) stretching of weaker band. The asymmetric CH\(_3\) deformation near 1455 cm\(^{-1}\) and the symmetric CH\(_3\) deformation near 1375 cm\(^{-1}\) were observed.

The vibrational peak at 3002 cm\(^{-1}\) was assigned to O - CH\(_2\) asymmetric stretching of methyl ester. C-O-C stretching at 874 cm\(^{-1}\) and isophthaletes at 730 cm\(^{-1}\) were present in the biodiesel. Actually esters were characterized by the strong absorption due to C=O stretching frequency near 1740 cm\(^{-1}\) and by the strong absorption involving the stretching of C- O near 1240 cm\(^{-1}\).

![Fig. 49 FTIR studies of biodiesel.](image-url)
From the above analysis the compound produced was confirmed as methyl ester. The higher percentages of esters, alkanes and absence of phosphorus and sulfur make this transesterified rubber seed oil as the future candidate for alternative environment – friendly diesel fuel.

**Fuel properties**

Biodiesel was prepared in bulk quantity using ferric sulphate as an acid catalyst and sodium hydroxide as an alkaline catalyst which exhibited better efficiency than the biodiesel prepared using other alkaline catalysts. It was then analysed for the fuel properties.

**pH**

The pH of the biodiesel was assessed soon after it was prepared. The pH was observed to be $7 \pm 0.04$.

**Acid value and FFA**

Acid value is a direct measure of FFA content of the biodiesel. It is also an index of aging of the fuel. The acid value may become a serious issue when oil having high FFA content is processed to produce biodiesel. The standard acid value for biodiesel according to ASTM D 6751 is less than 0.5 mg KOH/g. Biodiesel thus produced in this study has an acid value of $0.10 \pm 0.008$ mg KOH/g and FFA of $0.05 \pm 0.004$ percent (Table 14). Hence the biodiesel produced in the study met the requirement of an acid value specified in ASTM D 6751 standard.

It was reported by Felizardo *et al.* (2006) that the acid value showed the degradation of biodiesel due to thermal effects. High acid value (above 0.5 mg KOH/g) could damage the injector and also would cause deposits in fuel injection
system thus seriously impairing the performance of the pumps and filters. Also it causes corrosion and often indicates the presence of moisture in the fuel.

FFA might be present in biodiesel that was prepared from a feedstock containing high FFA content or it may be formed during hydrolysis (Moser, 2009). The higher content of FFA in biodiesel might impact other important fuel properties such as low temperature performance, oxidative stability, kinematic viscosity and lubricity. In addition to these issues, FFA was known to act as a pro-oxidant (Miyashita and Takagi, 1986 and Frankel, 2005) thus has a negative impact on oxidative stability. The presence of high FFA promoted corrosion in fuel injection systems and in their metallic components.

**Specific gravity (SG)**

Biodiesel has higher specific gravity than conventional diesel (Canakci and Gerpen, 1999). The specific gravity of biodiesel produced must satisfy the requirement (0.87 – 0.90 g/cm³) of ASTM D 6751 specifications. The specific gravity of the biodiesel observed in this study was 0.87 ± 0.0005 g/cm³ (Table 14). After the transesterification process, in the study the specific gravity of biodiesel (0.874 ± 0.0005 g/cm³) was lower than that of the oil (0.91 ± 0.01 g/cm³) due to the removal of glycerol from triglycerides.

The specific gravity of conventional diesel was reported to be 0.85 g/cm³ (Rashid and Anwar, 2008). Lower value of the specific gravity of biodiesel was an indication of the completion of reaction and the removal of heavy glycerine. Higher value of the specific gravity of biodiesel would result in the delivery of a slightly greater mass of fuel (Demirbas, 2008). It was known that the specific gravity of biodiesel depended on its alkyl ester content (Kulkarni and Dalai (2006); Encinar et al., 2007 and Predojevic (2008). Hence this property is primarily influenced by the
choice of vegetable oil (Mittelbach, 1996). The effect of molar ratio of methanol to oil, temperature and catalyst amount variations in relation to the specific gravity of the biodiesel was studied by Miao and Wu (2006). Increase in the molar ratio of methanol to oil decreases the specific gravity of the ester. This was due to a decrease in residual triglycerides (Canakci and Gerpen, 1999). This property is important mainly in airless combustion systems because it influences the efficiency of atomization of the fuel (Ryan et al., 1984 and Felizardo et al., 2006).

**Kinematic viscosity (KV)**

One of the most important properties of biodiesel and conventional diesel is viscosity, which is also an important property of lubricants (Knothe and Steidly, 2005). According to ASTM D 6751 standard, the viscosity of fatty acid alkyl ester must be 3 – 6 cSt at 40 °C. In the present case, the viscosity of rubber seed oil was 41.11± 0.81 cSt (Table 3) but after transesterification process it came down to 5.80 ± 0.004 cSt at 40 °C (Table 14). The viscosity of biodiesel was found to meet the fuel specification requirement. Kinematic viscosity of biodiesel was closer to that of ordinary diesel. The rate of change of viscosities of methyl ester and conventional diesel decreased with increase in temperature and are presented in fig. 50. Thus, it was clearly understood that kinematic viscosity is inversely proportional to the temperature. The functional relationship between the temperature (x) and kinematic viscosity (y) for biodiesel was $y = 0.0004 x^2 - 0.107 x + 9.4731$. Similarly, the functional relationship between the temperature (x) and kinematic viscosity (y) for conventional diesel was $y = 0.0009x^2 - 0.1399 x + 6.2431$. 


It was discussed by Kulkarni et al. (2007) that the methyl and ethyl esters of canola oil had kinematic viscosities of 3.9 and 4.4 cSt respectively. This indicated that the methyl ester has a lesser viscosity than the ethyl ester.

De Filippis et al. (1995) and Felizardo et al. (2006) reported that the different viscosities are due to the incomplete reaction of the oils or inefficient biodiesel purification leaving conjugated or free glycerine in the methyl ester phase. In fact, the presence of glycerides changed the apparent viscosity of the methyl esters, revealing the extent of the transesterification reaction and methyl ester phase purity.

Results of Knothe, (2005) and Enweremadu and Mbarawa, (2009) discussed that higher viscosity affects the behaviour of fuel injection and led to larger droplet size, poorer atomization and satisfactory in-cylinder penetration of the fuel spray. These conditions are likely to lead engine deposit formation, poor combustion, higher emissions and increase in engine oil dilution. The dependence of viscosity of biodiesel on temperature must be taken into account for solving the tasks of practical application of biodiesel because at temperature lower than 273 K, the viscosity of biodiesel is highly influenced by temperature. Fig. 50 shows the comparison of kinematic viscosities of biodiesel and diesel in relation to temperature.
biodiesel increased significantly and the reason was the crystallization of saturated methyl esters.

Viscosities of biodiesel from fats and greases appeared to be higher when compared to those from vegetable oils since their saturation level was higher (Ali et al., 1995; Graboski and Mc. Cormick, 1998 and Canakci and Gerpen, 2001). Viscosity of any fuel is related to its chemical structure. Viscosity increased with increase in chain length and decreased with increase in the number of double bonds (Georing et al., 1982; Graboski and Mc. Cormick, 1998; Demirbas, 2003 and Knothe, 2005).

Reyes and Sepulveda (2006) reduced the kinematic viscosity of the salmon – oil biodiesel from 4.96 cSt to 3.46 cSt at 70 °C by removing some components at higher boiling points, which suggested that the kinematic viscosity of the mixed marine fish – oil biodiesel could be decreased if the biodiesel undergoes a similar treatment process.

**Iodine value (IV)**

When iodine was introduced in the oil, the iodine attached itself over a double bond so as to form a single bond. Thus iodine number referred to the amount of iodine required to convert unsaturated oil into saturated oil. It does not refer to the amount of iodine in the oil but to the presence of unsaturated fatty acids present in the oil (Ramadhas, 2006). It was used to check the chemical stability of different biodiesel against oxidation. However there was no specification available for iodine value in ASTM D 6751 standards. The biodiesel now prepared from rubber seed oil had an iodine value of 123.0 ± 0.70 gI₂/100 g (Table14).
Issariyakul et al. (2007) have reported that the type of parent oil used was a major parameter largely affecting the iodine value. During the frying process, oil was continuously or repeatedly subjected to high temperature in the presence of air and moisture. Under these conditions, a variety of degradation reactions occur such as auto oxidation, thermal polymerization, thermal oxidation, isomer cyclization and hydrolysis (Supple et al., 2002, Kulkarni and Dalai, 2006 and Cayh and Kusefoğlu, 2008). These reactions normally raised the iodine value of oil and hence several samples of biodiesel revealed iodine values close to oil (Felizardo et al., 2006 and Predojevic, 2008).

A high content of unsaturated fatty acids in the ester (indicated by high iodine number) increased the polymerization in the engine oil. The presence of unsaturated fatty acid component in methyl esters was found to be necessary as it restricted the methyl esters from solidification. However, with higher degree of unsaturation, methyl esters were not suitable for biodiesel. This might cause the formation of deposits or deterioration in lubricating oil. This effect increases with the number of double bonds in the fatty acid chain. Therefore, it is better to limit the content of higher unsaturated fatty acids like linolenic acid, than to limit the degree of unsaturation with the iodine value (Encinar et al., 2007).

**Saponification Value (SV)**

Saponification value is also important because it helps us to ensure that the final soap is not caustic hot and not overly super fatted. There is no specification for saponification value in ASTM D 6751 standards. Saponification value of biodiesel was found to be 184 mg KOH/g (Table 14). Akbar et al., (2009) studied the characteristics and composition of *Jatropha curcas* oil seed from Malaysia which was considered as one of the potential feedstock for biodiesel. The saponification value of the studied oil was 193.55 mg KOH/g. Higher saponification value indicated that oils
have normal triglycerides and are very useful in the production of liquid soap and shampoo industries. The saponification value is related to the average molecular weight of the sample (Encinar et al., 2007).

**Peroxide value (PV)**

Peroxidation studies of biodiesel were observed to be 8.0 ± 0.005 (meq/kg). Higher peroxide value in the methyl ester of the high eurcic *B. carinata* oil was probably due to a higher amount of oxygen absorbed during the vegetable oil storage, which, in any case, provided evidence of the oxidation problem with the use of high unsaturated vegetable oils (Vicente et al., 2006). Liu and White (1992) observed that the peroxide value increased more substantially when the oil was heated to higher temperature. It was observed by Lin and Li, (2009) that the rate of peroxide value of biodiesel increased when the oil contained high unsaturated fatty acids. There is no specification for saponification value in ASTM D 6751 standards.

**Calorific (Heating) value (CV)**

Calorific value is a measure of the energy produced when the fuel is burnt completely. It determines the suitability of biodiesel as an alternative diesel fuels. There is no limit specified for calorific value in ASTM D 6751 specifications. Calorific value of the produced biodiesel in this study was 35.44 ± 0.08 MJ/kg (Table 14). Biodiesel consists of esters of fatty acids with a different degree of saturation. Lower degrees of saturation of fatty acid esters determine the lower calorific value (Gerpen et al., 2004a and Lebedevas and Vaicekauskas, 2006). The density of biodiesel was higher than diesel fuel and this compensates lower calorific value.
It has been reported that generally biodiesel have approximately 10 percent less energy when compared to that of the conventional diesel. This indicated that around 10 percent by volume of biodiesel would be additionally required to make a travel of the same distance normally covered through diesel (Agarwal, 2007; Encinar et al., 2007; Issariyakul et al. 2007 and Phan and Phan, 2008). It was due to the presence of oxygen as an extra component in the biodiesel causing lower calorific value in the fuel properties (Ramadhas et al., 2005). However, the presence of oxygen in the biodiesel helps to have a complete combustion of the fuel in the engine (Ramadhas et al., 2005).

Similarly, the calorific value of biodiesel was slightly lower than that of the raw oil due to the chemical changes that occur during the transesterification process. It was reported by Demirbas (1997) that there was high regression between viscosity and higher heating values (HHVs) of vegetable oil and biodiesel. The HHVs of a fuel increased with the increase in carbon number in fuel molecules. Also the heating value was directly related to the ratio of carbon and hydrogen to oxygen and nitrogen.

There are several works available on the heating value of biodiesel which are largely the function of its physical properties (Georing et al., 1982; Pryor, 1982 and Krisnangkura, 1991). Calorific value of vegetable oils and biodiesel increased with viscosity. The higher heating values (HHVs) of vegetable oils and their corresponding biodiesels were measured and these were correlated using linear least square regression analysis by Demirbas, (2008). Equations were developed by correlating the higher heating value (HHVs) of vegetable oils and biodiesel from the viscosity (VS), density (DN) and flash point (FP). The equations between viscosity and heat values are predicted by Demirbas (2008).
For vegetable oils (HHV) = 0.0317 VS + 38.053
For biodiesels (HHV) = 0.4625 VS + 39.450

**Sulphated ash (SA)**

ASTM D 874 was the standard test method for determining sulfated ash in lubricating oils and additives. The ASTM D 874 standard specifies that the samples could have a maximum of 0.02 percent sulfated ash. It could be seen from Table 14 that biodiesel produced exhibited a sulphated ash of 0.01 ± 0.004 percent by weight. The sample had the sulfated ash less than 0.02 percent by weight and the reason lying behind was that the biodiesel thus produced in the study does not have any inorganic contaminants.

The primary purpose of determining sulphated ash in biodiesel was to ensure whether it contained less contamination from the alkaline catalysts being used during the transesterification process. This test was also an indicator of the quality of residual metals present in the fuel which comes from the catalyst being used in the esterification process (Gerpen et al., 2004b and Fernando et al., 2007). Soluble metallic soap, unremoved catalysts and other solids are the possible sources of sulphated ash in the fuel (Rashid and Anwar, 2008). Excessive levels of sodium hydroxide and potassium hydroxide usage during the production of biodiesel led to engine deposits and other harmful consequences (Felizardo et al., 2006).

**Elemental analysis**

Elemental analyses of biodiesel produced from the rubber seed oil are given in Table 14. Carbon and hydrogen are the major constituents of biodiesel, but appreciable quantity of nitrogen was also present. Nitrogen content of biodiesel was not yet regulated by the ASTM D 6751 standards (Canoira et al., 2008). The
presence of nitrogen indicates the quality of biodiesel and it was an index of incomplete washing of the alkali by water.

Presence of high amount of oxygen in biodiesel would result in a more comprehensive chemical reaction during combustion and consequently less carbon residue was produced. It also reduces the emission of non-combusted products (carbon monoxide, hydrocarbon and soot) but at the same time it increased the emission of the oxides of nitrogen which is one of the most toxic gases.

**Water and sediments (WS)**

The water content of the biodiesel should not exceed 0.05 percent (Canakci and Gerpen, 1999). ASTM D 2709 in ASTM D 6751 prescribes the use of a centrifugal method to identify the water and sediments present in the sample. The water and sediment of the biodiesels prepared from rubber seed oil was 0.01 ± 0.0008 percent (Table 14) which was within specification.

Water and sediment if present in the biodiesel reduce the effectiveness of the catalyst resulting in lower efficiency (Kusdiana and Saka, 2004 and Rashid and Anwar, 2008). Water is also formed as a by product during the saponification and esterification of FFA.

There is a chance for microbial growth if water is present in biodiesel. Further it will promote the corrosion of the fuel tank. There is a risk of the formation of emulsion along with hydrolysis of the triglyceride. Sediment reduces the flow of oil from the tank to the combustion chamber (Knothe, 2006 and Rashid and Anwar, 2008). Sediments are of major concern since it may plug the fuel filters and also adversely affect the performance of fuel injectors. Huge quantity of water and sediment in the biodiesel disrupt the flow of fuel.
Copper corrosion (CC)

ASTM D 130 is used to measure the level of corrosion that may occur if biodiesel is used in any application where metals such as copper are present (Gerpen et al., 2004b). The value (Table 14) of the copper strip corrosion test in the present case is observed to be 1a. The strip was observed to be light orange in colour when tested in biodiesel which was almost the same as freshly polished strip. The result shows that the copper corrosion was within the limits of ASTM D 6751 specifications.

The presence of FFA in biodiesel beyond the limit aggravated the copper corrosiveness of the fuel (Knothe, 2006). Since copper compounds are particularly susceptible to this type of corrosion, copper was used as an indicator of the tendency of the fuel to cause corrosion. Copper and its compounds are susceptible to chemical attack and the corrosivity of a fuel has an implication on storage.

Vacuum distillation

Distillation is a recommended process to purify the biodiesel. Distillation depends on the determination of the range of boiling points for the fuel and it is used to characterize the fuel in terms of the boiling temperatures of its components. The distillation characteristics of biodiesel are quite different from that of the diesel. Biodiesel does not contain any highly volatile components as the fuel evaporates only at a relatively higher temperature. Usually, the methyl esters present in the biodiesel have molecular chains of 16 – 18 carbons. Boiling point of biodiesel generally ranged from 330 to 357 °C. If the boiling point was exceeded above 360 °C its purity was suspected. Since diesel consists of different compounds, a distillation curve may be
useful to know the constituents. Biodiesel usually contains 4 to 5 major compounds and all of them boil at the same temperature.

The distillate of the biodiesel produced with respect to different temperature was presented in fig. 51. The distillate of biodiesel at 90 % was observed to be 345.5 °C. It was also observed that the distillate of biodiesel increased with increase in temperature. The functional relationship of the distillate was $y = 0.2376x + 325.85$.

Similarly, the distillate of conventional diesel ($x$) against temperature ($y$) was presented in fig. 52. The distillate of conventional diesel at 90 percent was observed to be 343.5 °C. The equation obtained for the relationship was $y = 2.0139x + 166.62$. 

![Fig. 51 Boiling temperature of biodiesel with respect to distillate.](image)

![Fig. 52 Boiling temperature of diesel with respect to distillate.](image)
It was observed by Saravanan et al. (2008) that when the FFA was high, the volatility of the fuel was observed to be low. A high distillation temperature may shorten the ignition delay of fuel and decreased the probability of the occurrence of knocking in diesel engines (Zheng and Hanna, 1996 and Lin and Li, 2009).

**Carbon residue (CR)**

Carbon residue of the biodiesel is an indicator of any deposits of carbon which remains after combustion. This test is more relevant to biodiesel than to diesel because it shows a positive correlation with FFA, glycerides, polymers, unsaturated fatty acids, inorganic impurities and even on the additives used for pour point depression.

The quantities of carbon residue that were left after burning the biodiesel are presented in Table 14. The maximum limit of carbon residue specified in ASTM D 6751 is 0.05 percent. A lower value for carbon residue (0.021± 0.0005 %) was observed in the present case.

Phan and Phan (2008) reported that carbon residue increased exponentially when biodiesel was blended with conventional diesel. According to this report, the level of carbon residue increased when biodiesel was blended with diesel at a rate higher than 20 percent. This was one of the major disadvantages of biodiesel blend.

The presence of impurities such as ash and additives in biodiesel may affect the quantity of carbon residue after the fuel was burnt. In addition to the above, the presence of a larger proportion of aromatic compounds in biodiesel generally produced more carbon residue. A higher level of oxygen present in fuel normally results in complete combustion and thus in turn less carbon residue is produced after burning (Lin et al., 2006). Lin and Li (2009) demonstrated that the excess amount of
carbon residue in biodiesel would showed an excessive level of total glycerine. It correlates with the amount of carbonaceous deposits in the combustion chamber. Greater the carbon deposits, higher the residue.

**Flash point (FP)**

Flash point is the temperature at which the fuel will ignite when exposed to a flame or spark. Usually, the flash point of conventional diesel ranged from 50 to 80 °C but in the present case, the flash point of biodiesel was found to be 134.8 ± 0.44 °C (Table 14). The minimum limit of flash point for biodiesel specified in ASTM D 6751 is 130 °C. It is observed that the flash point of biodiesel is higher than conventional diesel. This feature provides an advantage of biodiesel over conventional diesel since decreases the risk due to fire and safer for transport purpose. The flash point of biodiesel increased with a smaller addition of diesel. Hence, it is safer to store biodiesel – diesel blends when compared to diesel alone. It also prevent auto ignition and fire hazards at high temperature during transportation and storage (Lin and Li, 2009). Flash point could reduce drastically if the alcohol used during the biodiesel production was not removed properly which is harmful to fuel pump, seals, elastomers etc., It also reduces the combustion quality. Works of Felizardo et al. (2006) indicated that the biodiesel containing less than 0.1 percent of methanol had a flash point ranged from 160 to 170 °C. However, when the biodiesel contain 0.05 percent methanol, the flash point (98 – 110 °C) was below the minimum acceptable value.

**Pour point (PP)**

Pour point is the temperature at which the fuel stops to flow. A longer chain of fatty acid and a higher degree of saturation influence the level of pour point. Pour point of biodiesel was found to be - 8.8 ± 0.44 °C (Table 14).
The key flow properties of biodiesel are cloud and pour point. Cold flow properties of biodiesel are the important indicators of the commercial applicability of the fuel. According to ASTM D 6751 specifications, there is no limit specified for cloud and pour point. The reason is that the climatic conditions in the world vary considerably, thus affecting the use of biodiesel in a specific region.

In diesel engines, solids and crystals rapidly grow and agglomerate, clogging fuel lines and filters resulting into major operation problems. Saturated fatty compounds have significantly higher melting points and in a mixture they crystallize at higher temperature than the unsaturated fatty acid compounds. Since biodiesel derived from fats or oils might contain significant amounts of saturated fatty compounds, it may have higher cloud and pour points.

The use of branched esters such as isopropyl, isobutyl and 2-butyl esters instead of methyl ester was another way of improving the low-temperature properties of biodiesel (Lee et al., 1995, Foglia et al., 1997 and Yori et al., 2006). Branched esters have lower melting points, but in terms of economics they are more expensive than methyl esters.

**Cloud point (CP)**

Cloud point refers to the temperature at which a cloud or haze of crystals appear in the fuel under test conditions and thus becomes important for low temperature operations. This is the most conservative measurement of cold flow properties. Biodiesel has higher cloud point than conventional diesel. The cloud point of biodiesel was 4.8 ± 0.44 °C (Table 14). The cloud point depends upon the feedstock used and thus the selection of feedstock must be taken into consideration such that it could be suitable for cold environments (Gerpen et al., 2004b and Ferando et al., 2007). Since the saturated methyl esters are the first to precipitate,
the amount of these esters namely methyl palmitate and methyl stearate determined the cloud point.

All biodiesel fuels regardless of its source have higher cloud and pour points than that of diesel fuel. This poor cold flow property was one of the most critical obstacles against the widespread use of biodiesel. The fatty acid compositions of biodiesel greatly influenced its cold flow properties. The freezing point of biodiesel increased with the increase in carbon atoms in the carbon chain and also increases with the increase in double bonds (Georing et al., 1982; Graboski and Mc. Cormick, 1998; Demirbas, 2003; Knothe, 2005 and Canakci and Sanli, 2008). Biodiesel from feed stocks with large amounts of saturated fatty acids have higher cloud and pour points.

Biodiesel produced from vegetable oil have lower cloud and pour point than that of the biodiesel from fats and greases. The saturation level of the cloud point of biodiesel produced from animal fat was found to be higher. Moreover, branched chain alcohols could improve the cold flow quality, but their reactions resulted in smaller amount of impurities such as monoglycerides, diglyceride and triglycerides showing the incompleteness of the transesterification. This was due to the low reactivities of these alcohols (Lee et al., 1995 and Lang et al., 2001). This impurity could cause problems during the engine operation (Knothe, 2006). Further more, branched chain alcohols required higher molar ratio of alcohol to oil (70 : 1) and their molecular weights are higher. This makes the production cost from bad to worst and lower yields might be obtained by their usage.

**Cetane number (CN)**

Cetane number is the ability of fuel to ignite quickly after being injected. Cetane number of biodiesel now produced was 48.73 ± 0.016. The variations in
cetane number might be due to the variations in carbon chain length. This parameter guarantees good control of increase in the performance of combustion and thereby improves the cold starts, which gives rise to less exhaust gases (Reed et al., 1992). A longer chain and higher saturation of fatty acids provides higher cetane number.

Higher the value, better the ignition quality of the fuel (Azam et al., 2005). Long ignition delay is not accepted since it causes diesel knock. The cetane number was generally between 46 and 60 depending on the oil used to make the biodiesel. Biodiesel has higher cetane number than conventional diesel and consequently its ignition delay time was shorter compared to that of diesel fuel because of its higher oxygen content (Demirbas, 2005 and 2008). Cetane number affects the engine performance parameters such as combustion, stability, white smoke, noise and emissions of carbon monoxide and hydrocarbon.

If the cetane number of a diesel was too high, then fuel would ignite in a short distance to the injector and cause excessive heating. Coked fuel particles inside the injector might plug the injector nozzle. Because of this, cetane number of a diesel fuel should not be higher than 65 (Demirbas, 2005 and 2008).

Graboski and Mc. Cormick (1998) observed that the cetane number of biodiesel produced from soybean oil was between 45.7 and 56.4. The cetane number of biodiesel produced from marine fish oil was 50.9 which were higher than the cetane number of the commercial biodiesel from waste cooking oil (48.1). This was due to the biodiesel from marine fish oil contained as high as 37.06 percent saturated fatty acids, whereas the commercial biodiesel from waste cooking oil contained only 19.77 percent saturated fatty acids. Hence, the cetane number of the biodiesel increases with the proportion of saturated fatty acids. This difference did not significantly affect the combustion process (Canakci and Gerpen, 2003).
As the chain lengths, branching and unsaturation of fatty acids increases, the cetane number also increased (Georing et al., 1982; Graboski and Mc. Cormick, 1998; Demirbas, 2003; Knothe, 2005 and Canakci and Sanli, 2008). Since the chemical structures increase the heating value, there was a tendency for the cetane number to increase with viscosity and heating value (Demirbas, 2003).

**Total glycerol (TGL)**

Glycerol is insoluble in biodiesel. Glycerol has a higher density than biodiesel and hence the glycerol was removed by settling. Glycerol could be either free or bonded. Total glycerol was the sum of free and bonded glycerol. Bonded glycerol was the glycerol portion of the mono, di and triglyceride molecules. Elevated total glycerol was the indicator of incomplete esterification reactions and causes excessive carbon deposits in the engine.

The maximum limit of total glycerol prescribed in ASTM D 6751 was 0.24 percent. It was inferred from Table 14 that the biodiesel had lower total glycerol content (0.21 ± 0.005%). Lower level of total glycerol in biodiesel ensured a high conversion rate of triglyceride into fatty acid methyl esters.

Presence of glycerol in the fuel contributes deposit formation during combustion (Knothe et al., 2005). Bound glycerol present in biodiesel resulted from incomplete conversion of triglyceride into fatty acid alkyl esters during the transesterification might cause carbon deposits on fuel injector tips and piston rings of diesel engines during combustion (Knothe et al., 2005). The presence of bound glycerol in biodiesel might also influence low-temperature operability, kinematic viscosity and lubricity.
Free glycerol (FGL)

Free glycerol is present as molecules of glycerol in the fuel. Free glycerol can also be a source of carbon deposits in the engine because of incomplete combustion. It resulted from the incomplete separation of ester and glycerol products after the transesterification and imperfect water washing or other approaches that do not completely separate the glycerol from biodiesel.

The limit of free glycerol as per ASTM D 6751 is 0.02 percent. The value for the present work was 0.01± 0.0008 percent which shows that it is in agreement with ASTM D 6751 specifications (Table 14). This confirmed that there were no incomplete reactions that occurred during the transesterification process as the level of free glycerols was observed to be low.

Excessive free glycerol in biodiesel created viscous mixture that blocked the fuel filters and create combustion problems in the engine so the suspended or dissolved free glycerol in biodiesel were removed by washing with water.

The present study suggested that the properties of biodiesel produced from rubber seed oil showed better fuel properties and found to meet the requirements of ASTM D 6751 standard.
### Table 14  Fuel properties of biodiesel produced from rubber seed oil (n = 5).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Units</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>-</td>
<td>7 ± 0.04</td>
</tr>
<tr>
<td>FFA</td>
<td>(%)</td>
<td>0.05 ± 0.004</td>
</tr>
<tr>
<td>Acid value</td>
<td>(mg KOH/g)</td>
<td>0.10 ± 0.008</td>
</tr>
<tr>
<td>Specific gravity @ 30 °C</td>
<td>(g/cm³)</td>
<td>0.874 ± 0.0005</td>
</tr>
<tr>
<td>Viscosity @ 40°C</td>
<td>(cSt)</td>
<td>5.80 ± 0.004</td>
</tr>
<tr>
<td>Iodine value</td>
<td>(gI₂/100g)</td>
<td>123.0 ± 0.70</td>
</tr>
<tr>
<td>Saponification value</td>
<td>(mg KOH/g)</td>
<td>184.0 ± 0.14</td>
</tr>
<tr>
<td>Peroxide value</td>
<td>(meq/kg)</td>
<td>0.8 ± 0.005</td>
</tr>
<tr>
<td>Calorific value</td>
<td>(MJ/kg)</td>
<td>35.44 ± 0.08</td>
</tr>
<tr>
<td>Sulphated ash</td>
<td>(%)</td>
<td>0.01 ± 0.004</td>
</tr>
<tr>
<td>Carbon</td>
<td>(%)</td>
<td>76.61</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>(%)</td>
<td>12.16</td>
</tr>
<tr>
<td>Oxygen</td>
<td>(%)</td>
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</tr>
<tr>
<td>Sulphur</td>
<td>(%)</td>
<td>0.02</td>
</tr>
<tr>
<td>Water &amp; sediments</td>
<td>(%)</td>
<td>0.01 ± 0.0008</td>
</tr>
<tr>
<td>Copper corrosion</td>
<td>-</td>
<td>1a</td>
</tr>
<tr>
<td>Vacuum distillation @ 90%</td>
<td>(°C)</td>
<td>345.50 ± 0.22</td>
</tr>
<tr>
<td>Carbon residue</td>
<td>(%)</td>
<td>0.021 ± 0.005</td>
</tr>
<tr>
<td>Flash point</td>
<td>(°C)</td>
<td>134.8 ± 0.44</td>
</tr>
<tr>
<td>Pour point</td>
<td>(°C)</td>
<td>-8.8 ± 0.44</td>
</tr>
<tr>
<td>Cloud point</td>
<td>(°C)</td>
<td>4.8 ± 0.44</td>
</tr>
<tr>
<td>Cetane number</td>
<td>-</td>
<td>48.73 ± 0.016</td>
</tr>
<tr>
<td>Total glycerol</td>
<td>(%)</td>
<td>0.21 ± 0.005</td>
</tr>
<tr>
<td>Free glycerol</td>
<td>(%)</td>
<td>0.01 ± 0.0008</td>
</tr>
</tbody>
</table>

**Shelf life of biodiesel produced**

Biodiesel produced using ferric sulphate as an acid catalyst and sodium hydroxide as an alkaline catalyst possesses better efficiency and adequate fuel properties. Therefore, biodiesel produced from sodium hydroxide were selected for the stability studies.

Biodiesel has a good bio-degradability. It degrades by 98 percent biologically within three weeks whereas conventional diesel will degrade only by 50 percent within the same period of time (Williamson and Badr, 1998). The presence of saturated fatty acid level in biodiesel proves to be advantageous in terms of storage.
stability as compared to the more unsaturated vegetable oil based fuels. Biodiesel prepared from polyunsaturated vegetable oil was more susceptible to chemical deterioration (e.g. auto oxidation and polymerization) under certain conditions of storage temperature, moisture, ultraviolet radiation and packaging materials used (Wu et al., 1998 and Ferrari et al., 2005).

Industrial experts recommended that biodiesel could be best used within six months of its manufacture to ensure that the quality of the fuel was maintained. Due to the fact that vegetable oils possess a significant amount of fatty acids with double bond, oxidative stability was of great concern especially when storing biodiesel over an extended period of time.

The stability of fuel is characterized by three parameters namely thermal, oxidation and long storage. The nature and the length of fatty acid chains govern its oxidative stability. Generally, factors such as contact with air or elevated temperatures or the presence of metals facilitate oxidation. The chemical changes in biodiesel caused by the oxidation produce hydroperoxides as a primary product which are very unstable. Hydroperoxides then cleaves so as to form secondary products such as short chain fatty acid, aldehydes, ketones, hydrocarbons and alcohol.

The fatty acid alkyl ester would get hydrolysed to form alcohol and acid in the presence of air. Conversion of ester into alcohol would cause the reduction in the freezing point whereas conversion of ester into acid would increase the total acid number. This makes the biodiesel unstable on storage (Sarin et al., 2007 and Sharma et al., 2008).

The stability of biodiesel depends upon the feedstock used for the production of biodiesel. The feedstock with large proportion of saturated fatty acids is more
stable than those having larger proportion of unsaturated fatty acids. But again, higher portion of saturated fatty acid lowered the lower temperature property such as cloud and pour points. Hence, a major drawback of biodiesel lies in its trade off between the level of saturation of biodiesel and its cold flow properties (Sarin et al., 2007 and Canakci, 2007).

Oxidative stability is an important issue that biodiesel research must address since oxidized product may impair fuel quality and subsequently affect the engine performance (Bouaid et al., 2007). Generally, in the biodiesel feed stocks, the fatty acid chains contain 16 or 18 carbon atoms and with zero to three double bonds. The relative oxidation rates for these C18 esters are linolenic > linoleic > oleic (Cosgrove et al., 1987). This ranking occurs because the di and tri unsaturated fatty acid chains contained the most reactive sites for initiation of the auto oxidation chain reaction sequence (Mc Cormick et al., 2007).

The reason for auto oxidation was the presence of double bond in the chains of many fatty compounds. These esters undergoes auto oxidation depending on the number and position of the double bond which forms the by - product such as acids, esters, aldehydes, ketones and lactones etc., (Frankel et al., 2005; Waynick, 2005; Mc Cormick et al., 2007 and Sarin et al., 2007).

According to Du Plessis et al. (1985) methyl esters have better stability than ethyl esters. Fatty acid methyl esters form a radical next to the double bond during the oxidation process. This radical binds with the oxygen in air, which was biradical to form peroxide radical. A new radical was created from fatty acid methyl ester by this peroxide radical which binded with oxygen in air. This augments the auto oxidation cycle at an exponential rate whereby hundreds of new radicals were created quickly from one single radical resulted in the formation of a series of by-products. The fuel thus gets deteriorated as there was a formation of sediment and gum. Peroxide
formation through this route lead to obligomerization even at ambient temperature. As the deterioration of biodiesel is attributed to the formation of peroxide in the initial step, the remedy suggested was to prevent peroxide formation during the stages of biodiesel manufacture and throughout its distribution chain (McCormick et al., 2007; Sarin et al., 2007 and Sharma et al., 2008).

To check the stability of the biodiesel produced from rubber seed oil, major parameters that affect the stability was analysed every month for a period of 12 months (one year).

**Acid value (AV)**

Acid value is an indicator of the stability of the fuel and the acid value increases when the fuel is oxidized. The acid value has a direct correlation with the purity of the sample. The acid value of biodiesel sample (x) increases with the increase in storage days (y) as in fig.53. The acid value (ASTM D 6751) of the methyl esters samples was within the limits (0.5 mg KOH/g) even after 360 days. The acid value remained relatively stable for a month and then took a significant increase in storage time. Acid value increases slowly and sudden rise in acid value was observed after 210 days. The increase in the acid value was due to the fatty acid composition of the vegetable oils which was used as a raw material. The equation obtained was $y = 0.0012x + 0.0497$. 

![Fig. 53 Change in the acid value of biodiesel during storage for a period of year (n = 5).](image-url)
Higher acid value was due to the breakdown of the fatty acid methyl ester molecules during the degradation. Higher the degradation, higher will be its acidity (Leung et al., 2010 and Wang et al., 2008). Thus, the acid value provides alternative index to biodiesel degradation.

The acid value increased with an increase in peroxides as the esters were first oxidized to form peroxides, which then underwent complex reactions so as to split into more reactive aldehydes which later oxidized to form acids. Reports of Bouaid et al., (2007) suggested that the fuel stored in the daylight increase its acid value at a faster rate than the fuel stored in the dark especially when it was stored for a longer time.

Free fatty acid (FFA)

Biodiesel with a higher acid value indicates a higher FFA. Generally, freshly prepared biodiesel would have a lower acid number, since the base catalyst used in the transesterification process would remove all available fatty acids. However, upon degradation of the fuel by exposure to water and air, FFA might be regenerated. The FFA values of biodiesel during the course of study showed an initial increase with storage days (Fig. 54). The increase in FFA suggested that the experiment duration caused the formation of FFA. The storage days (x) were plotted against the FFA (y). The equation obtained for FFA of biodiesel during storage was \( y = 0.0006x + 0.0265 \).
The quality of ester and oil was assessed based on the presence of FFA. Since at higher temperature, the FFA was known to react with metals like zinc, lead, manganese, cobalt, tin etc., This could lead to quick wear and tear of the engine (Romano, 1982 and Pryde, 1984).

Sangha et al. (2004) reported that the esters have better storability compared to the oils as far as FFA increase was concerned. Also it was discussed that biolipids with a higher unsaturated fatty acid content were more prone to oxidative reaction leading to faster degradation of fuel properties. Lin and Chiu (2009) indicated that the saturated fatty acid content was likely to increase with the length of storage at a higher temperature.

**Kinematic viscosity (KV)**

Viscosity was considered as one of the major constraints in the use of vegetable based biodiesel oils as an engine fuel (Ryan et al., 1982 and Sangha et al., 2004). Therefore, study was undertaken to find out the effect of storage time on the viscosity of methyl ester. Increasing the kinematic viscosity of biodiesel (y) was known to increase the storage time (x) as in fig. 55. Increasing the storage time in the absence of an antioxidant leads to an increase in kinematic viscosity. Higher kinematic viscosity causes an inferior fuel fluidity resulting into less fuel atomization and incomplete combustion.
In this study, it was observed that the samples exhibited slight increase in kinematic viscosity during storage. However, the limit prescribed by ASTM D 6751 was (6.0 cSt) at 40 °C which is not exceeded in the present case. The variations in viscosity could be attributed to the structural variations of the ester. The functional relationship was \( y = 0.0004 \times + 5.776 \).

Abromovic and Klofutar (1998) and Demirbas (2008) discussed that the viscosity decreased linearly as the iodine value increases. The length of the fatty acid chain was shown to have a marked influence on the viscosity. The viscosity of the system was also influenced by the degree of unsaturation. Single double bond was shown to increase the viscosity, whereas two or three double bonds caused a decrease in the viscosity of the systems (Rodrigues et al., 2006 and Demirbas, 2008). The kinematic viscosity of unsaturated fatty compounds strongly depends upon the nature and number of double bonds (Knothe, 2002).

Kinematic viscosity increases with chain length and also increases along with the degree of saturation of either the fatty acid or alcohol moiety in a fatty ester or in an aliphatic hydrocarbon.

Oxidation of methyl ester begins with the build up of peroxides and the viscosity started to increase only after the peroxides have reached a certain level. During storage, the viscosity of the methyl ester increases by the formations of polar and oxidized polymeric compounds. This led to the formation of gums and sediments and resulted in clogging of the filters (Tang et al., 2008). The increase in kinematic viscosity could also be due to auto oxidation. The more the unsaturation, the more was the polymerization.

Higher FFA of biodiesel during storage has greater viscosity than the corresponding methyl or ethyl ester. It was reported by Mittelbach and Gangl (2001)
that long carbon chain saturated fatty acids with a high molecular weight and strong molecular bonding were formed during the peroxidation reaction process, particularly when the biodiesel was stored at a high temperature for a sufficient period of time. Hence, the biodiesel become more viscous when the extent of oxidative degradation increases.

**Specific gravity (SG)**

The standard for biodiesel states that the fuel should have a specific gravity between 0.860 and 0.900 g/cm$^3$. From the fig. 56, it was inferred that the specific gravity of freshly prepared biodiesel was 0.87 g/cm$^3$. The equation obtained was linear ($y = 9E - 05x + 0.8657$). During the course of the stability study, it was found that biodiesel does not show any remarkable changes up to 90 days. Some minor changes were observed after 90 days. However, the results obtained showed that the biodiesel produced had a specific gravity in the range of 0.87 – 0.90 g/cm$^3$, thus meeting the ASTM D 6751 standards.

![Fig. 56 Changes in the specific gravity of biodiesel during storage (n = 5).](image-url)
The specific gravity was correlated with the emission of particulate matter and nitrous oxide. The fuel which has a high specific gravity generally causes an increase in particulate matter and nitrous oxide emissions in diesel engine (Ali et al., 1995; Szybist et al., 2007 and Canakci and Sanli, 2008).

Graboski and Mc Cormick (1998); Lang et al. (2001) and Knothe (2005) explained that the chain length and saturation level of the fuel raise the specific gravity. Thus, biodiesel produced from feed stocks such as fats or greases have more saturated fatty acids than the biodiesel produced from vegetable oils (Ali et al., 1995 and Canakci and Gerpen, 2001).

**Iodine value (IV)**

The iodine value is a structure-related index in fatty acid chemistry which is related to the total number of double bond in a fat or oil. A major drawback of the iodine value is that it does not distinguish between the structural differences present in different fatty acid compounds.

The iodine value provides information on the unsaturation degree of the oil, which directly affected its stability with regards to oxidation. The reason for auto oxidation was the presence of double bonds in the chains of the fatty compounds. The auto oxidation of unsaturated fatty compounds proceeded with different rates depending on the number and position of double bond. The species formed during the oxidation process cause the fuel to eventually deteriorate. Smaller amount of more highly unsaturated fatty compounds have a disproportionately strong effect on iodine value (Knothe and Dunn, 2003).

Iodine value (y) decreases with the increase in storage days (x) as in fig.57. The functional relationship was $y = -0.0489 x + 124.26$. The fluctuating values may
be due to the dehydrogenation and saturation (Nkafamiya et al., 2007). The decrease in iodine value is an indication of lipid oxidation, since there is a decline in unsaturation during oxidation. Holiday and Pearson (1974) have also found similar observation for the oil from soybean.

Further, the iodine value increases during the later stages of oil degradation and especially when the oil was exposed to temperatures higher than 180 °C, due to the elimination reactions of the oxidized triglyceride molecules (Felizardo et al., 2006). Iodine value restrictions could be overcome by the use of higher esters such as ethyl or propyl, although the fatty acid profile remained unchanged (Knothe, 2002). This property greatly influences the fuel oxidation, the type of aging products and deposits formed in diesel engine injectors.

**Water and sediment (WS)**

Water and sediment is a complicating factor connected with the storage of biodiesel. Water and sediment increases (y) with the increase in storage days (x) as indicated in fig. 58. The increase in water and sediments might be due to the
characteristics of the raw material. The equation was $y = 8E - 05x + 0.007$. Sediment accumulation was shown to be significantly reduced by the addition of antioxidant (Geller et al., 2008).

![Graph showing changes in water and sediment of biodiesel during storage (n = 5).]

The maximum content of water and sediments specified by ASTM standard specification was 0.05 percent. It is inferred from fig. 58 that water and sediments did not exceed the ASTM standard of D 6751.

The presence of water in biodiesel induces hydrolysis of fatty acids leading to the formation of acids and alcohols. The peroxidation chain reaction in the biodiesel could then be accelerated further and thus enhanced the extent of oxidative stability. Fuel contaminated with water could cause engine corrosion or react with the glycerides to produce soaps and glycerine. Water content in biodiesel enhanced degradation due to hydrolysis but its effects were much lesser than that of other factors (Leung et al., 2010).
Peroxide value (PV)

It was observed that the peroxide value of the sample increases with the storage days. The changes in peroxide value with storage time in days are presented in fig. 59. The relationship between the peroxide value (y) and days (x) was $y = 0.0348x + 8.5055$. The changes in peroxide value was due to many factors, which include the initial amount of fatty acids present and the presence of metallic ions, which was one of the factors that promote or enhance oxidation after the formation of hydro peroxide (Rossell, 1984 and Nkafamiya et al., 2007). The initial increase in peroxide values up to a maximum might be due to the fact that the rate of production of peroxide out-weighs the rate of decomposition of the peroxide.

Although peroxide value is not specified in the fuel standards, this parameter is known to influences cetane number. High peroxide value enhanced the cetane number which reduced the ignition delay time (Dunn, 2006). However it had a compatibility problem with plastics and elastomers.

Higher peroxide value was observed in 330 days (Fig. 59). As the storage time increased, production of the primary oxidation products, hydro peroxides were formed. Higher peroxide value in the methyl ester was probably due to a higher amount of oxygen absorbed during the vegetable oil storage (Vicente et al., 2006).
A higher peroxide value implies that the greater formation of hydro peroxides through the peroxidation chain mechanism (Tomasevic and Marinkovic, 2003). Peroxide value is one of the significant indicators of oxidative degradation and measures the extent of lipid peroxidation.

Peroxide value of the samples tested increased as the storage time elapsed, which implies that hydrogen peroxide species were the primary product of the oxidative degradation during the storage period. A higher storage temperature also enhanced the peroxidation reaction and increases the peroxide value.

The peroxide value is an indicator of the extent of peroxidation of fatty acid in oil at its initial stage of storage (Lin et al., 2006). Liu and White (1992) found that the peroxide value of soybean oil increased from 0.1 to 45.2 meq/kg when the oil remained at a temperature of 60 °C from 0 to 15 days whereas in the current study, the peroxide value increases from 8 to 19 meq/kg at room temperature for a period of 360 days.

The peroxide value is less suitable for monitoring oxidation as it tends to increase and then decrease upon further oxidation due to the formation of secondary products (Canakci et al., 1995; Monyem et al., 2000; Bondioli, 2002 and Knothe, 2007).

The variation in the peroxide value depends on the samples. For samples, initially not too oxidized, peroxide value increases are slow. It must be noted that peroxide value is not included in the biodiesel specification table (ASTM D 6751).

The overall results of this study suggested that the biodiesel produced from rubber seed oil were relatively stable for up to one year under normal environmental conditions.