CHAPTER 4
RESULTS AND DISCUSSION

4.1 FATTY ACID COMPOSITION OF WASTE COOKING PALM OIL

Fatty acid composition of waste cooking palm oil was determined using gas-chromatography. Thus fatty acids are converted into more volatile methyl esters using alkaline methanolysis. The chromatogram obtained from the gas chromatographic analysis is shown in Figure 4.1.

Figure 4.1 Chromatogram obtained for waste cooking palm oil

The fatty acid composition of waste cooking palm oil determined using gas chromatography with flame ionization detector is shown in Table 4.1. Figure 4.1 and Table 4.1 shows that the major fatty acid is Linoleic acid with a mass percentage of 52.50%, followed by Oleic acid with a mass percentage of 28.04%. The results obtained from Table 4.1 were used to
determine the fatty acid composition according to degree of unsaturation, given in Table 4.2.

Table 4.1 GC Fatty acid composition of waste cooking Palm oil

<table>
<thead>
<tr>
<th>Common Name</th>
<th>C: D</th>
<th>Retention Time, (min)</th>
<th>Content, (%) (m/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lauric Acid</td>
<td>C12:0</td>
<td>4758</td>
<td>0.25</td>
</tr>
<tr>
<td>Myristic acid</td>
<td>C14:0</td>
<td>7168</td>
<td>0.38</td>
</tr>
<tr>
<td>Palmitic acid</td>
<td>C 16:0</td>
<td>184101</td>
<td>9.84</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>C18:0</td>
<td>107263</td>
<td>5.74</td>
</tr>
<tr>
<td>Oleic acid</td>
<td>C18:1</td>
<td>524447</td>
<td>28.04</td>
</tr>
<tr>
<td>Linoleic acid</td>
<td>C18:2</td>
<td>981802</td>
<td>52.50</td>
</tr>
<tr>
<td>Linolenic</td>
<td>C18:3</td>
<td>1255</td>
<td>0.07</td>
</tr>
<tr>
<td>Arachidic acid</td>
<td>C20:0</td>
<td>4271</td>
<td>0.22</td>
</tr>
</tbody>
</table>

C=Carbon atoms, D=Double bond

Table 4.2 Fatty acid composition of waste cooking Palm oil according to degree of unsaturation

<table>
<thead>
<tr>
<th>Fatty Acid Composition</th>
<th>Content, (%), m/m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturated fatty acids</td>
<td>16.43</td>
</tr>
<tr>
<td>Monounsaturated fatty acids</td>
<td>28.04</td>
</tr>
<tr>
<td>Polyunsaturated fatty acids</td>
<td>52.57</td>
</tr>
</tbody>
</table>

The results obtained for the other characteristics studied for waste cooking palm oil: iodine value, acid value, sulphur content, and water content are given in table 4.3, and discussed here.
Table 4.3 Physico-chemical characteristics of WCPO

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Determined value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iodine value, (g I₂/100g)</td>
<td>116</td>
</tr>
<tr>
<td>Acid value, (mg KOH/g)</td>
<td>4.61</td>
</tr>
<tr>
<td>Water content, (mg/kg)</td>
<td>150.2</td>
</tr>
<tr>
<td>Sulphur content, (mg/kg)</td>
<td>0.10</td>
</tr>
</tbody>
</table>

4.1.1 Iodine Value

Iodine value is expressed in grams of iodine which reacts with 100 grams of fat or oil under certain conditions, being a parameter that quantifies the degree of unsaturation of the fat/oil. The iodine value obtained for the waste cooking palm oil was 116 g iodine I₂/100 g of oil, which is its specific domain, mentioned in the literature, viz, 125-135 g I₂/100 g oil (Prankl 2002). Concerns about possible problems caused by biodiesel on engines were often assigned to high iodine values although studies have shown that biodiesel stability depends, besides the degree of unsaturation, on the content of antioxidants and the production technology used.

4.1.2 Acid Value

Acid value is pointing out the presence of free fatty acids or acids formed as a result of the oil degradation and burning (during or after processing). The acid value represents the amount of base required to neutralize the oil sample and is expressed in mg KOH/g sample. This parameter is of great interest, especially for alkaline methanolysis where the presence of free fatty acids must be limited due to soap formation which leads to the formation of emulsions. The acid value of waste cooking palm oil used
as feedstock for biodiesel production is 4.61 mg KOH/g oil, a value that indicates a high content of free fatty acids.

### 4.1.3 Water Content

Water is a minor component found in most raw materials for biodiesel production. In general, high water content causes a decrease in ester yields as undesirable reaction occurs by hydrolysis of triglycerides. The water content determined for the waste cooking palm oil used as raw material was 150.2 mg/kg, a value below the maximum value allowed for biodiesel by the European quality standard EN 14214:2010, namely 500 mg/kg.

### 4.1.4 Sulphur Content

Sulfur content of biodiesel is limited to 10 mg/kg by the EN 14214:2010 quality standard. Therefore, it is important to know the sulfur content of raw material because it can contribute to the sulfur content of resulted biodiesel. The value sulphur content of the waste cooking palm oil was 0.10 mg/kg, far below the value required by the European quality standard, EN 14214:2010.

### 4.2 CHARACTERIZATION OF HETEROGENEOUS CATALYSTS

Mg/Al-SO$_4$ and Mg/Al-NO$_3$ catalysts were used to produce biodiesel from waste cooking palm oil. Both catalysts were prepared as per the procedure given in section 3.2.1.1 and 3.2.1.2 then fired in 400°C and 500°C. In that 500°C showing catalyst was more suitable than 400°C. Further characterization was given the details below.
4.2.1 Mg/Al- SO$_4$ Hydrotalcite Catalyst

4.2.1.1 XRD Technique

Figure 4.2 shows XRD pattern of Mg/Al-SO$_4$ Hydrotalcite. In the XRD analysis the prominent 2θ peaks obtained were at 25.50, 31.75, 33.99, 37.79, and 52.4. On comparison (JCPDS card no #:24-1132, 79-0612, 71-1241) the formation of Mg/Al Hydrotalcite was understood and some other peaks were due to intermediate compounds. The basal spacing was calculated to be 0.281nm. The sharp peak (211) indicates the formation of highly crystalline materials. Indexing of the diffraction peaks was done using a standard JCPDS file. The reflections were indexed in a hexagonal lattice with an R3m rhombohedral symmetry.

The parameter of Hydrotalcite corresponding to the cation-cation distance within the brucite-like layer can be calculated as follows: $a = 2 \times d$ (110). On the other hand, the $c$ parameter is related to the thickness of the brucite-like layer and the interlayer distance and can be obtained from the equation $c = 3 \times d$ (211) (Radha et al 2004, Yang et al 2007). The values of the unit cell parameters, assuming rhombohedral symmetry, with the $c$ parameter corresponding to three times the thickness of the expanded brucite like layer, are presented in table 4.4. The $a$ and $c$ parameters decreased with increasing aluminum content, which can be explained by the substitution of larger Mg$^{2+}$ ions by smaller Al$^{3+}$ ions (Rao et al 1998, Diez et al 2003 and Anbarasan et al 2005).

<table>
<thead>
<tr>
<th>Mg/Al-SO$_4$ HT</th>
<th>20 (211)</th>
<th>d211(Å)</th>
<th>d , c and Basal spacing</th>
</tr>
</thead>
<tbody>
<tr>
<td>d(211)</td>
<td>31.75</td>
<td>2.81</td>
<td>c=8.43</td>
</tr>
<tr>
<td>d(110)</td>
<td>37.79</td>
<td>0.81</td>
<td>a = 1.62</td>
</tr>
<tr>
<td>d(211) crystal basal space</td>
<td>-</td>
<td>-</td>
<td>0.281 nm</td>
</tr>
</tbody>
</table>
Using Scherrer’s formula, one can find the size of the crystal or particle size.

\[ \tau = \frac{K\lambda}{\beta \cos \theta} \]  

(4.1)

Where \( K \) is the shape factor, \( \lambda \) is the X-ray wavelength, typically 1.54 Å, \( \beta \) is the line broadening at half the maximum intensity (FWHM) in radians, and \( \theta \) is the Bragg angle, \( \tau \) is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size. The dimensionless shape factor has a typical value of about 0.9, but varies with the actual shape of the crystallite. The Scherrer equation is limited to nano-scale particles. It is not applicable to grains larger than 0.1 μm, which precludes those observed in most metallographic and ceramographic microstructures. Using the Scherrer formula the crystal size was found to be within 4.66 nm to 21.2 nm (Rao et al 1998, Anbarasan et al 2005).

Figure 4.2 XRD pattern of Mg/Al-SO₄ Hydrotalcite
4.2.1.2 EDX Technique

Figure 4.3 shows the EDX quantitative results of base peak (778) for Mg/Al-SO$_4$ Hydrotalcite and this figure clearly indicated the peaks formed with respect to total scale counts versus kilo voltage of energy dispersion. Table 4.5 shows that detailed net counts increase with respect to the atom weight (%). In that, Mg, Al elements were composed in 1:3 ratios and Sulphur, oxygen elements formed in 1:4 ratios and remaining nearly 24% sodium present. It may be that, Sodium is not properly washed with DI water catalyst at the time of catalyst preparation procedure. Anyway, it is a base compound and gives the positive effect to the biodiesel production.

Live Time: 100.0 sec. Acc.Voltage: 10.0 kV Take Off Angle: 34.6 deg.

Figure 4.3 EDX Diagram of Mg/Al-SO$_4$ Hydrotalcite
Table 4.5 EDX Quantitative results of Mg/Al-SO$_4$ Hydrotalcite

<table>
<thead>
<tr>
<th>Element</th>
<th>Net Counts</th>
<th>Weight %</th>
<th>Atom %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>16134</td>
<td>37.85</td>
<td>49.69</td>
</tr>
<tr>
<td>Na</td>
<td>19798</td>
<td>25.97</td>
<td>23.73</td>
</tr>
<tr>
<td>Mg</td>
<td>515</td>
<td>0.52</td>
<td>0.45</td>
</tr>
<tr>
<td>Al</td>
<td>21341</td>
<td>22.41</td>
<td>17.45</td>
</tr>
<tr>
<td>S</td>
<td>8327</td>
<td>13.26</td>
<td>8.69</td>
</tr>
<tr>
<td>Total</td>
<td>-</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>

4.2.1.3 SEM Technique

![SEM Image of Mg/Al-SO$_4$ Hydrotalcite](image)

The Hydrotalcite formation was confirmed by SEM analysis. Figure 4.4 show two kinds of materials obtained in SEM analysis. White fine powder indicates the MgO particles and grey colour fine powder indicates the Al$_2$O$_3$ particles. So, Mg/Al SO$_4$ HT catalyst is conformed and particles are indentified in 5μm and 10μm images. 10μm image indicates well mixed position and 5μm image indicates particles well closure position of the particles. The surface area of the catalyst is 346.32 m$^2$/kg.
4.2.1.4 FTIR Technique

Figure 4.5 shows the FTIR spectrum of Mg/Al-SO₄ Hydrotalcite. The spectrum was characterized with asymmetric and symmetric stretching vibrations of carboxyl group at 2959.9 and 2504.6 cm⁻¹, along with the O-H stretching of the hydroxyl group and deformation vibration of H₂O at 3461.9 cm⁻¹. The spectrum is skewed on the right hand side and the net small peak at 2927.5 cm⁻¹ is due to the hydrogen bonding of H₂O and interlayer of SO₄²⁻ anions. In the lower frequencies, the peak at 1457.8 cm⁻¹ in all the samples can be attributed to the bending mode of the interlayer water. The main absorption band of the sulphate anions was observed at 1370 cm⁻¹. In the low energy ranges of the spectra 704-637 cm⁻¹, peaks around 469 cm⁻¹ are attributed to the presence of Mg-O and Al-O bond. (Obadiash et al 2012).

![Figure 4.5 FTIR Spectrum of Mg/Al-SO₄ Hydrotalcite](image-url)
4.2.1.5 TGA Technique

TGA curve weight losses change with respect to temperature as shown in figure 4.6. In that, TGA curve evaluates weight changes with respect to the temperature. First region, up to 171.12°C there is an endothermic peak which relates to the dehydration of the sample to upto 7.921% weight loss. The second region 369.98°C ranging from corresponds to the weight loss due to the dehydroxylation and de-carbonation reactions, which resulted in a mass loss of 4.602%. The third endothermic region, ranging from 646.63°C to 743.95°C, resulted in a weight loss of 14.84% and remaining 56.17% is a solid materials content upto 980°C. The weight loss corresponds to the decomposition of interlayer anion present in the brucite layer and the dehydroxylation of vicinal OH groups in the hydrotalcite (Kim et al 2004, Yang et al 2007 and Obadiah et al 2012).

Figure 4.6 TGA Curve of Mg/Al-SO₄ Hydrotalcite
4.2.2 Mg/Al- NO$_3$ Hydrotalcite Catalyst

4.2.2.1 XRD Technique

Figure 4.7 shows XRD pattern of Mg/Al-NO$_3$ Hydrotalcite. In the XRD analysis the prominent 2θ peaks obtained were at 29.24, 32.24, 38.92, 42.84 and 62.23. On comparison (JCPDS card no #:36-1474, 79-0612, 71-1241) the formation of Mg-Al Hydrotalcite was understood and some other peaks were due to intermediate compounds. The basal spacing was calculated to be 0.303nm. The sharp peak (104) indicates the formation of highly crystalline materials. Indexing of the diffraction peaks was done using a standard JCPDS file. The reflections were indexed in a hexagonal lattice with an R3m rhombohedral symmetry. The parameter of Hydrotalcite corresponding to the cation-cation distance within the brucite-like layer can be calculated as follows: $a = 2 \times d\, (222)$. On the other hand, the $c$ parameter is related to the thickness of the brucite-like layer and the interlayer distance and can be obtained from the equation $c = 3 \times d\, (104)$ (Radha et al 2004 and Yang et al 2009). The values of the unit cell parameters, assuming rhombohedral symmetry, with the $c$ parameter corresponding to three times the thickness of the expanded brucite like layer, are presented in table 4.6. The $a$ and $c$ parameters decreased with increasing aluminum content, which can be explained by the substitution of larger Mg$^{2+}$ ions by smaller Al$^{3+}$ ions (Anbarasan et al 2005, Diez et al 2003, Rao et al 1998).

<table>
<thead>
<tr>
<th>Mg/Al-NO$_3$ HT</th>
<th>2θ (211)</th>
<th>d211(Å)</th>
<th>d , c and Basal spacing</th>
</tr>
</thead>
<tbody>
<tr>
<td>d(104)</td>
<td>29.36</td>
<td>3.04</td>
<td>C = 9.12</td>
</tr>
<tr>
<td>d(222)</td>
<td>62.23</td>
<td>1.49</td>
<td>a = 2.98</td>
</tr>
<tr>
<td>d(104) crystal basal space</td>
<td>-</td>
<td>-</td>
<td>0.303 nm</td>
</tr>
</tbody>
</table>

Table 4.6 XRD calculation of interlayer distance of Mg/Al- NO$_3$ HT
Using Scherrer formula, one can find the size of the crystal or particle size.

\[ \tau = \frac{K\lambda}{\beta \cos \theta} \]  

(4.2)

Where \( K \) is the shape factor, \( \lambda \) is the X-ray wavelength, typically 1.54 Å, \( \beta \) is the line broadening at half the maximum intensity (FWHM) in radians, and \( \theta \) is the Bragg angle; \( \tau \) is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size. The dimensionless shape factor has a typical value of about 0.9, but varies with the actual shape of the crystallite. The Scherrer equation is limited to nano-scale particles. It is not applicable to grains larger than 0.1 \( \mu \)m, which precludes those observed in most metallographic and ceramographic microstructures. Using the Scherrer formula the crystal size was found to be within 4.66 nm to 21.2 nm (Rao et al 1998, Anbarasan et al 2005).

![Figure 4.7 XRD pattern of Mg/Al-NO\textsubscript{3} Hydrotalcite](image)

**Figure 4.7** XRD pattern of Mg/Al-NO\textsubscript{3} Hydrotalcite
4.2.2.2 EDX Technique

Figure 4.8 shows the EDX quantitative results of base peak (781) for Mg/Al-NO$_3$ Hydrotalcite and this figure clearly identified peaks formed with respect to total scale counts versus kilo voltage of energy dispersion. Table 4.7 shows detailed net counts increases with respect to the atom weight (%). In that, Mg, Al elements were composed in 5:1 ratios and nitrogen, oxygen elements were formed in 5:1 ratios and remaining nearly 24.01% sodium present and also obtained 25.03% of oxygen combined carbon. It might be that, Sodium is not properly washed with DI water catalyst at the time of catalyst preparation procedure. Anyway, it is a base compound and gives the positive effect to the biodiesel production.

Live Time: 100.0 sec. Acc.Voltage: 10.0 kV Take Off Angle: 34.6 deg.

Figure 4.8 EDX Diagram of Mg/Al-NO$_3$ Hydrotalcite
Table 4.7 EDX Quantitative results of Mg/Al-NO\textsubscript{3} Hydrotalcite

<table>
<thead>
<tr>
<th>Element</th>
<th>Net Counts</th>
<th>Weight %</th>
<th>Atom %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>2625</td>
<td>18.54</td>
<td>25.53</td>
</tr>
<tr>
<td>N</td>
<td>1072</td>
<td>6.52</td>
<td>7.69</td>
</tr>
<tr>
<td>O</td>
<td>20758</td>
<td>41.07</td>
<td>42.45</td>
</tr>
<tr>
<td>Na</td>
<td>31544</td>
<td>33.37</td>
<td>24.01</td>
</tr>
<tr>
<td>Mg</td>
<td>96</td>
<td>0.08</td>
<td>0.05</td>
</tr>
<tr>
<td>Al</td>
<td>500</td>
<td>0.43</td>
<td>0.26</td>
</tr>
<tr>
<td>Total</td>
<td>-</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>

4.2.2.3 SEM Technique

Figure 4.9 SEM Image of Mg/Al-NO\textsubscript{3} Hydrotalcite

The Hydrotalcite formation was confirmed by SEM analysis. Figure 4.9 shows two kinds of materials obtained. White fine powder may describe the MgO particles and grey colour fine powder describes the Al\textsubscript{2}O\textsubscript{3} particles. So, Mg/Al-NO\textsubscript{3} HT catalyst is conformed and particles are indentified in 5µm and 10µm. 10µm image particles shows well mixed
position and 5µm image shows well closure position of the particles. The surface area of the catalyst is 363.24 m$^2$/kg.

### 4.2.2.4 FTIR Technique

Figure 4.10 shows the FTIR spectrum of Mg/Al-NO$_3$ Hydrotalcite. The spectrum was characterized with asymmetric and symmetric stretching vibrations of carboxyl group at 2990.5 cm$^{-1}$, along with the O-H stretching of the hydroxyl group and deformation vibration of H$_2$O at 3452.9 cm$^{-1}$. The spectrum is skewed on the right hand side and the net small peak at 2990.5 cm$^{-1}$ is due to the hydrogen bonding of H$_2$O and interlayer of NO$_3^-$ anions at 1636.4 cm$^{-1}$ and in this lower frequency, the samples can be attributed to the bending mode of the interlayer water. The main absorption band of the NO$_3^-$ anions was observed at 1384.7 cm$^{-1}$. In the low energy ranges of the spectra 704-637 cm$^{-1}$, peaks around 469 cm$^{-1}$ are attributed to the presence of Mg-O and Al-O bond. (Obadiah et al 2012).

![Figure 4.10 FTIR Spectrum of Mg/Al-NO$_3$ Hydrotalcite](image-url)
4.2.2.5 TGA Technique

TGA curve weight losses change with respect to temperature as shown in Figure 4.11. In that, TGA curve evaluates weight changes with respect to the temperature. First region up to 228.59°C there is endothermic peak which relates to the dehydration of the sample up to 2.637% weight loss. The second region 377.66°C corresponds to weight loss due to the dehydroxylation and de-carbonation reactions, resulted in mass loss of 1.877% and remaining is 90.26% is a solid materials content up to 980°C. The weight loss corresponds to the decomposition of interlayer anion present in the brucite layer and the dehydroxylation of vicinal OH groups in the hydrotalcite (Kim et al 2004, Yang et al 2007 and Obadiah et al 2012).

![Figure 4.11 TGA Curve of Mg/Al-NO₃ Hydrotalcite](image)

**Figure 4.11 TGA Curve of Mg/Al-NO₃ Hydrotalcite**
4.3 CHARACTERIZATION AND OPTIMIZATION OF BIODIESEL BY HOMOGENEOUS CATALYSTS

The various process variables were employed i.e., methanol to oil molar ratio (3:1-9:1), catalyst type (KOH, NaOH, CH₃OK, and CH₃ONa), catalyst concentration (0.5, 1.0 and 1.5wt %), temperature (50, 60, and 70°C), reaction time (30, 60, 90 and 120 min) and alcohol type (CH₃OH, C₂H₅OH, and C₃H₇OH) used to carry out the experiments.

4.3.1 Effect of Free Fatty Acid

Free fatty acids (FFAs) content after acid esterification should be minimal or otherwise less than 2% FFAs. These FFAs react with the alkaline catalyst to produce soaps instead of esters. It depicts the effect of FFAs on the yield of methyl ester during alkali catalyzed transesterification. There is a significant drop in the ester conversion when the free fatty acids are beyond 2% (Naik et al 2007). In spite of its insensibility to the free fatty acids from the raw materials, it was ignored, especially due to its low reaction rate (Al-Zuhair 2007). From table 4.3, acid value is 4.61mgKOH/gm and also the FFA value was 2.30 mg KOH/g. The molecular weight is 833g/mol and this can be calculated using this saponification value (198.34mgKOH/gm) of the waste cooking palm oil. Due to High FFA, if this oil was used directly with base catalysts it would have given only lower Biodiesel yield (74%) and this can be proved with a trial of 6:1 molar ratio of alcohol to oil with the addition of 1 wt % of each catalyst for 1 hour reaction timings where fresh palm oil is catalyzed with KOH and thus the results were shown in figure 4.12.

Also, Figure 4.12 show that, KOH is showing high biodiesel conversion when compared with other catalyst used for waste cooking palm oil and also this catalyst showing is highest catalytic activity than other catalysts used. Always, the fresh palm oil is shows higher biodiesel
conversion when compared with waste cooking palm oil. After the pretreatment esterification yield was 85% and then followed both catalysts transesterification.

![Biodiesel yield with different catalyst (unesterified condition)](image)

**Figure 4.12** Biodiesel yield with different catalyst (unesterified condition)

### 4.3.2 Effect of Alcohols

Alcohols are primary and secondary monohydric aliphatic alcohols having 1±8 carbon atoms (Sprules and Price, 1950). Among these alcohols, methanol, ethanol, propanol, butanol and amyl alcohol were used in transesterification process. Methanol and ethanol are most frequently used, especially methanol because of its low cost and its physical and chemical advantages (polar and shortest chain alcohol). This methanol can quickly
react with triglycerides and NaOH is easily dissolved in it. To complete a transesterification reaction requires stoichiometrically a 3:1 molar ratio of alcohol to triglycerides. In practice, the ratio needs to be higher to drive the equilibrium to a maximum ester yield. So, the solubility of the alcohol is the main criteria to produce biodiesel from various oil sources. In this study, 1 wt % of KOH was used with three alcohols and these alcohols act as a solvent. First take three alcohols in each beaker then add the KOH catalyst into the alcohol containers and precede the solubility process with the help of magnetic stirrer. In that, methanol shows more solubility than other two alcohols used.

Figure 4.13 shows solubility of the catalyst with respect to addition of the alcohols into the reaction vessel and according to literature methanol is more soluble than the other two alcohols because the increase in carbon content then solubility automatically will decrease. Now, in the second step these alkoxides are added into the WCPO and FPO oil containers then mixed them 1 hour thoroughly and then kept overnight for separation of biodiesel and glycerol layers. Based on the results, biodiesel yield observed on methanol was higher than other alcohols used in this experiment.

Nye et al (1983) described about the amounts of biodiesel produced by using different types of alcohol decreased in the following order: Methanol > Ethanol > Butanol and this result obtained was slightly different with the finding by them (Hossain et al 2010). They reported that methanol was the alcohol that can give the highest biodiesel yield, followed by butanol and then ethanol. According to Meher et al (2006) the production of biodiesel by using ethanol in alkali-catalyzed transesterification is more difficult than that by using methanol. This is due to the formation of stable emulsion during ethanolysis. For methanolysis, the emulsions formed would break down easily to form a lower glycerol rich layer and upper methyl ester rich layer. While in
ethanolysis, the emulsions formed are more stable due to the presence of larger non-polar group in ethanol, making the separation and purification of biodiesel more difficult (Zhou et al 2003). This explained why the biodiesel yield from ethanolysis was lower than methanolysis in this study. So, finally methanol is alcohol source used for this entire process.

![Figure 4.13 Biodiesel yield with catalyst solubility](image)

**Figure 4.13 Biodiesel yield with catalyst solubility**

### 4.3.3 Effect of molar ratio

Generally, the stoichiometry of the reaction requires 3 moles of methanol per mole of triglycerides to yield 3 moles of biodiesel and 1 mole of glycerol. Methanol is a commonly used alcohol for transesterification because of its low price and highly reactive nature (Lang et al 2001). For example, the molar ratio of 1:6 moles of soybean oil to methanol has been found to be the most suitable in the case of alkali-catalyzed transesterification because an
excess of alcohol is required to drive the reaction (Freedman et al 1986). For acid-catalyzed transesterification, a 1:30 vegetable oil to alcohol ratio is generally used (Freedman et al 1984). In this experiment, waste cooking palm oil (WCPO) was used with varying molar ratios of methanol and oil (3:1, 6:1 and 9:1) and 1.0 wt% KOH at 60°C as represented in figure 4.14. As mentioned, the transesterification activity also depends on the molar concentrations of methanol to oil and also associated with the type of catalyst used. If increased from 3:1 to 6:1, methyl esters content increased, then from 6:1 to 9:1, methyl esters content decreased much. Excess of methanol is required to shift the equilibrium favorably during transesterification for better yields of biodiesel.

Therefore, 6:1 molar ratio gives a better result than other molar ratios and also repeated same procedure done for Fresh palm oil used with varying molar ratios of methanol and oil (3:1, 6:1 and 9:1) and 1.0 wt % KOH used at 60°C were described by Figure 4.15. Figure 4.15 also indicates that 6:1 molar ratio of alcohol to oil gives better biodiesel yield with Fresh Palm Oil. The higher alcohol molar ratio interferes with the separation of glycerol because there is an increase of solubility. In addition, an excess of alcohol was able increase the conversion of di-monoglycerides, but there is possibility of recombination of esters and glycerol to form monoglycerides because their concentration and also increasing during the course of the reaction, in other words the reactions conducted with low molar ratios. Many researchers have reported an alcohol to oil molar ratio of 6:1 to be the optimal ratio, while Leung and Guo (2006) reported that the maximum biodiesel production was obtained at a molar ratio of 7:1 in transesterification of used frying oil. In base catalysis, this effect can be observed quickly because the reaction is fast, whereas in acid catalysis requires with high concentration of the reaction. These results are similar that where obtained in the ethanolysis of peanut oil (Feuge and Gros 1949), and Freedman et al (1986) and Schwad et al (1987)
described about the ethanolsysis of sunflower oil. In general, an acid catalyst requires a higher molar ratio of methanol/oil than basic catalysts (Ma et al 1999). In consequence, the alcohol/oil molar ratio is one of the most important variables affecting the esters yield and although the stoichiometry ratio for transesterification required 3 moles of alcohol and 1 mole of triglyceride, excess of alcohol was used in practice. Hence, the alcohol molar/oil ratio is an important factor that must be always optimized (Allen 1998).

Figure 4.14 Biodiesel yield with varying molar ratios used for WCPO.
4.3.4 Effect of catalyst

In this case, the experiments were carried out at 6:1 molar ratio of alcohol to oil used 1 wt% of KOH, NaOH, CH₃OK, and CH₃ONa with varying temperature ranges at 30, 60, 90 and 120 min for both waste cooking Palm Oil and Fresh Palm Oil. Figure 4.16 shows the biodiesel yield with catalysts used with varying time in the molar ratio of 6:1 at 60°C for WCPO and figure 4.17 shows similar conditions applied for that effect catalyst used to Fresh Palm Oil. Figure 4.16 and 4.17 show that KOH catalyst was the better biodiesel yield behavior than other catalysts used here (i.e., NaOH, CH₃OK, and CH₃ONa) and also higher time of mixing had proved higher biodiesel yield and the figure also indicates that hydroxides gave rise to higher percentages than the corresponding methoxides. These results are very similar to those found in the literature in transesterification processes of used
frying oil with methanol and other alcohols that also concluded that potassium hydroxide was the best catalyst (Tomasevic et al 2003, Xiaohu Fan et al 2009). The reaction can be catalyzed by alkalis, acids, or enzymes. The alkalis include NaOH, KOH, carbonates and corresponding sodium and potassium alkoxides, such as, sodium methoxide, sodium ethoxide, sodium propoxide and sodium butoxide. Acid catalysts are usually sulfuric acid; sulfonic acids and hydrochloric acid. Lipases also can be used as biocatalysts. Alkali-catalyzed transesterification is much faster than acid-catalyzed transesterification and is more often used commercially (Connemann et al 1998).

Several researchers found that alkali-catalyzed transesterification proceeds much faster than acid catalyzed transesterification (Meher et al 2006). Based on the above results KOH was the best catalyst compared with other base catalyst and also studied with 0.5, 1.0 and 1.5 wt % of KOH catalyst for both WCPO and FPO at 60°C with 6:1 molar ratio of alcohol to oil. Figure 4.18 shows that 1.0 wt % showed the higher yield than 0.5 wt % and 1.5 wt % of KOH used. Similarly, figure 4.19 also show that 1.0 wt % showed the higher yield than 0.5 wt % and 1.5 wt % of KOH used. In general, as the catalyst concentration increased, the conversion of triglycerides also increased. This is because an insufficient amount of catalyst results in an incomplete conversion of triglycerides into fatty acid esters (Nye et al 1983). In basic catalyst, a slight decrease in ester content was observed in the experiments with 1.5 wt % of catalyst with regard to the experiments with 1 wt %. This is because the addition of excess alkaline catalysts caused more triglycerides participation in the saponification reaction, resulting in increased production of soap and mentioned reduction of the esters yield (Krishnangura et al 1992). So, any increase in concentration of catalyst beyond the neutralization limit results in decrease in biodiesel conversion.
Figure 4.16 Biodiesel yield with catalyst used for WCPO
Figure 4.17 Biodiesel yield with catalyst used for FPO
Figure 4.18  Biodiesel yield with varying concentration of catalyst used for WCPO
Figure 4.19  Biodiesel yield with varying concentration of catalyst used for FPO
4.3.5 Effect of Temperature

In this process, the temperature ranges were used from 50, 60 and 70°C and in order to optimize the suitable yield of methyl esters production. For all temperatures, alcohols to oil molar ratio was 6:1 with KOH concentration of 1 wt % for waste cooking palm oil and fresh palm oil. The reaction temperature can influence the rate of reaction and biodiesel yield. Figure 4.20 shows for Waste Cooking Palm Oil the percentages of alkyl esters at 60°C showing higher yield than other temperatures 50 and 70°C for 20 min reaction time. After 20 min, the esters present in the temperatures 50, 60 and 70°C runs were 54, 57 and 51 wt % respectively. After 120 min, the percentages were 85, 91, and 79 wt % of methyl esters obtained for the temperature 50, 60 and 70°C, which indicated that the reaction was very fast with respect to increase in time intervals. Therefore, the optimum temperature for Waste Cooking Palm Oil process was 60°C.

Similarly, Figure 4.21 shows for Fresh Palm Oil the percentages of alkyl esters at 60°C showing higher yield than other temperatures 50 and 70°C for 20 min reaction time. After 20 min, the esters present in the temperature 50, 60 and 70°C runs were 75, 82 and 73 wt % respectively. After 120 min, the percentages were 95, 97, and 91 wt % of methyl esters obtained for the temperature 50, 60 and 70°C. Therefore the optimum temperature of fresh palm oil was 60°C. Based on the WCPO and Fresh Palm Oil results, the optimum temperature of transesterification process was 60°C and biodiesel yield of fresh palm oil is higher than waste cooking palm oil because the FFA content of waste cooking palm oil is higher than that of fresh palm oil. The primary advantage of higher temperatures influences to shorter reaction time. However, higher reaction temperatures causes methanol to vaporize resulting in decreased yield (because the boiling point of methanol is 65°C). When the temperature was decreased, the rate of reaction was also decreased. Therefore,
the equilibrium concentration was strongly conditioned by the temperature and favored for the same; that is, the equilibrium concentration increased as the temperature increased. Encinar et al (2007) explained three temperatures like 35, 60, 78°C for used frying oil in 12:1 molar ratio of methanol-oil condition with 1 wt. %. But in that 60, 78°C temperatures show almost same curve, whereas in the present case three temperatures show different curve with 6:1 ratio and 1 wt % of KOH used. Encinar et al (2010) explained about castor oil with temperatures (25, 35, 45, 55, 65°C) and methanol/oil ratio (3:1, 6:1, 9:1, 12:1) with different catalyst concentrations. Prafulla et al (2009) explained about waste cooking, Jatropha curcus and camelina oils with up to maximum temperature 140°C and in that, maximum biodiesel obtained at 100°C because it contained high FFA value compared with this process waste cooking palm oil (Allen 1998).

![Figure 4.20 Biodiesel yield with 1.0 wt %, KOH used for 6:1 molar of WCPO](image-url)
Figure 4.21  Biodiesel yield with 1.0 wt %, KOH used for 6:1 molar of FPO

4.3.6  Effect of Reaction Time

According to many researchers, the biodiesel yields are directly proportional to the reaction times used. Based on the results, Figure 4.20 and 4.21 show that effect longer mixing gives higher yield than using shorter time. So, 120 min of reaction time gave a good result than other reaction times used here. In other words, the biodiesel yields increase with increasing the reaction timing. However, based on the results, it shows that the biodiesel yields were higher when reaction time of 120 min was used. This undesirable result may be due to the higher soap formation when longer reaction time was used. Thus, the rate of soap formation was also increased. The experiment was conducted from 30-120 min of reaction timings with 50-70°C of reaction temperature for 1 wt % of catalyst used in 6:1 molar ratio of WCPO and FPO.
4.4 CHARACTERIZATION AND OPTIMIZATION OF BIODIESEL BY HETEROGENEOUS CATALYSTS

The following process variables are employed i.e., methanol to oil molar ratio (3:1-12:1), catalyst type (Mg/Al-SO₄ and Mg/Al-NO₃), catalyst concentration (0.5, 1.0 1.5 and 2.0 wt %), temperature range (50, 60, 70 and 80°C), reaction time (3, 4, 5 and 6 hours) and methanol (best choice of alcohol) to carry out all the experiments.

4.4.1 Effect of Molar ratio

The molar ratio of methanol to waste cooking palm oil is the most important variables that affect biodiesel production from its sources. Usually alcohol to oil ratio increases and the biodiesel yield also increase upto the exact molar ratio. Based on the literature, the stoichiometry molar ratio of alcohol to oil is 3.0. But when mass transfer is limited due to problems of mixing, the mass transfer rate seems to be much slower than the reaction rate, so the conversion can be elevated by introducing an extra amount of the reactant alcohol to shift the equilibrium to the right-hand side.

Figure 4.22 show parameters used like the molar ratio of methanol and oil ratio (3:1, 6:1, 9:1 and 12:1) with 1.0 wt% of Mg/Al-SO₄ and Mg/Al-NO₃ catalysts, 60°C reaction temperature and 4 hour reaction time throughout the reaction. First, 3:1 molar ratio the biodiesel yield was 68% for Mg/Al-NO₃, 62% for Mg/Al-SO₄ and again increased the molar ratio from 6:1 to 9:1, the biodiesel yield was 95% obtained for Mg/Al-NO₃, 90% for Mg/Al-SO₄. If further, molar ratio increased to 9:1 to 12:1 molar increased, the result of biodiesel conversion decreased because of the negative of the molar ratio shift the reaction towards the left side of the equation. The biodiesel yield was 84% for Mg/Al-NO₃, 71% for Mg/Al-SO₄. It is evident that the optimum molar ratio of methanol to oil is 9.0. Beyond the molar ratio of 9.0, does not have
significant ester conversion. In addition, the conversion increased sharply with reaction time, then reached a plateau value representative of a nearly equilibrium conversion after 4 h reaction and maximum conversion of 94.5% for nitrate catalyst whereas sulphate was 89%. Also, the figure 4.22 show, Mg/Al-NO$_3$ HT higher biodiesel yield than Mg/Al-SO$_4$ HT.

![Figure 4.22 Biodiesel yield versus molar ratio of alcohol to oil](image)

Deng et al (2011) have given 4:1 molar ratio as the best optimum value for jatropha to methanol. Higher molar ratio over the stoichiometric value resulted in a high rate of esters formation and ensures complete reaction (Leung et al 2006) and Volodymyr Brei et al (2011) described rapeseed oil used with methanol in ratio of 29:1with 1.6 hours reaction time. Obadiah et al (2012) describes that 6:1 molar ratio was better for pongamia oil with 90.85% of biodiesel yield. When increasing the amount of catalyst, the slurry (mixture of catalyst and reactants) becomes too viscous giving rise to a problem of mixing and a demand of higher power consumption for adequate stirring. On the other hand, when the catalyst amount is not sufficient,
maximum conversion cannot be reached. In most cases, sodium hydroxide or potassium hydroxide had been used in the process of alkaline methanolysis. But 1 wt. % of catalyst has been used here for both catalyst.

4.4.2 Effect of Temperature

The effect of reaction temperature studied at temperature ranges of 50, 60, 70 and 80°C for both NO$_3$ and SO$_4$ HT catalysts. Figure 4.23 show ester conversion with respect to the reaction temperature of both catalysts. At 50°C, transesterification reaction proceeded slowly and the conversion was 65% of Mg/Al-NO$_3$ HT and 53% of Mg/Al-SO$_3$ HT for 3h reaction. If lower the temperatures resulted in a drop of the ester conversion because only a small amount of molecules were able to get over the required energy barrier. For Mg/Al-NO$_3$ HT the biodiesel yield was increased up to 95.5% in 5h reaction by increasing the reaction temperature to 60°C whereas SO$_4$ HT is 91.20 % (for Mg/Al-NO$_3$ HT: 80°C was 81% and 70°C was 85% and Mg/Al-SO$_4$: 80°C was 69% and 70°C was 74%). Thus, the optimum temperature was found 60°C. Probably the molar ratio of methanol to oil decreased when the methanol may be volatilized into gas phase above 65°C (boiling point of pure methanol). Therefore the optimum reaction temperature was 60°C with the optimum biodiesel yield were 95% and 92% for Mg/Al-NO$_3$ HT and Mg/Al-SO$_4$ HT respectively. In this experiment also show, Mg/Al-NO$_3$ HT gave higher biodiesel then Mg/Al-SO$_4$.

Wenlei Xie et al (2006) studied at 60°C was the optimum temperature for soybean oil with 67% biodiesel yield. Oguzhan Ilgen et al (2007) studied for canola oil at 60°C was the optimum temperature for soybean oil with 71.9% biodiesel yield. Xing Deng et al (2011) studied for canola oil at 45°C was the optimum temperature for soybean oil with 95.2 % biodiesel yield for two stage operation.
4.4.3 Effect of Catalyst

Figure 4.24 show the catalytic study of the concentration range from 0.5-2.0 wt. % Mg/Al-HT catalysts. First, 0.5 wt% catalyst taken with 9:1 molar ratio of alcohol to oil, at 60°C in 4 hour reaction time and the maximum ester conversion was 66% of Mg/Al-NO$_3$ HT and 61% of Mg/Al-SO$_4$ HT respectively. Therefore, lower concentration of catalysts gave lesser biodiesel yield compared higher amount of catalyst used. Mixing is very important for the transesterification of waste cooking oil; generally, a more vigorous stirring speed causes better contact among the reactants and solid catalyst, resulting in the increase of the reaction rate. Further, the catalyst concentration increased to 1.0 wt% and then biodiesel yield will be 79% of Mg/Al-NO$_3$ HT and 75% of Mg/Al-SO$_4$ HT respectively. Again, the catalyst concentration increased to 1.5 wt%, biodiesel yield will be 94% of Mg/Al-NO$_3$ HT and 88% of Mg/Al-SO$_4$ HT respectively. If further, catalyst concentration increase, biodiesel yield gets the negative results. i.e., beyond
the transesterification limits, the biodiesel yield will be decreased. For 0.5 % catalyst had only lesser biodiesel yield of NO$_3$ HT (66%) and SO$_4$ HT (61%). The optimum catalysts concentrations were 1.5 % for both NO$_3$ HT and SO$_4$ HT.

Obadiah et al (2012) described about the Mg/Al based catalyst concentration were 1.5 wt% used with 1:6 molar ratio of the alcohol to oil with 65°C and obtained 90.8%. Xing Deng et al (2011) described about the Mg/Al HT catalyst used 1.0 wt% of jatropha oil with 4:1 molar ratio of alcohol to oil at 45°C in the presence of 210W Ultrasonic Power supplied and obtained 95.2% of biodiesel yield. Wan Omar et al (2011) described with transesterification of biodiesel from waste cooking palm oil used Sr/ZrO$_2$ 2.7 wt% catalyst with 29:1 molar ratio of alcohol to oil at the temperature of 120°C and obtained 79.7% of biodiesel yield. Therefore, higher concentration of catalyst added mean biodiesel yield will be lesser and generally it is based on the condition of the catalyst i.e., basicity of the catalyst used because of the base components only increase the biodiesel yield when compared with acid catalysts.
4.4.4 Recycle of Catalyst

Generally, recycling is a difficult one to recovery anything. But homogeneous catalyst can’t be separate it from the glycerol waste mixture because of the excess oil converted into soap. So, it is not easy to separate it. But heterogeneous catalysts are generally the solubility nature less in alcohols than homogeneous catalysts. Therefore, excess catalysts are available in the final stream of the biodiesel waste products and it contains excess alcohol and unconverted catalyst and glycerol.

From the figure 4.25 shows the catalysts yield get increased with respect to no. of times of recycling. This is mainly due to basicity of catalyst concentration increases then the activity of the catalyst gets increased. Therefore, once increase the pH value of the catalyst automatically catalyst yield will be increased. Mg/Al-NO₃ catalysts are basic nature when compared with sulphate based catalysts used. First time, the catalyst concentrations get
increased up to 43% for Mg/Al-NO₃ and 37% for Mg/Al-SO₄ respectively for 1 hour centrifugation process. Similarly, reaction mixing time increases and then concentration of the catalyst gets increased to 55% for Mg/Al-NO₃ and 45% for Mg/Al-SO₄ for 2 hour mixing time used. So, the fifth stage, catalyst concentration gets increased to 93% for Mg/Al-NO₃ and 88% for Mg/Al-SO₄ respectively.

4.4.5 Effect of Reaction Time

Figure 4.26 shows that, 9:1 molar ratio of alcohol to oil used with 70°C with both heterogeneous catalysts and taken 3-6 hours reaction time because the heterogeneous catalyst less solubility than homogeneous one. So, prolonged time required to get reacted the oil with alcohol in the presence of heterogeneous catalyst. In that, for 3 hour reaction time show biodiesel yield was 61% for Mg/Al-NO₃ and 53% for Mg/Al-SO₄ respectively. Further the reaction increased to 5 hours, and then biodiesel yield will be 89% for Mg/Al-NO₃ and 84% for Mg/Al-SO₄ respectively. If further reaction time increased
biodiesel yield was decreased. Therefore the optimum reaction time was 5 hours for both type catalysts used here. Obadiah et al (2012) described about adding solid catalyst to the reactants while stirring facilitated the chemical reaction, and the reaction started quickly. It quickly established a very stable emulsion of oil, MeOH and catalyst. The ester conversion increased rapidly with an increase of stirring speeds from 100 to 500 rpm. When the stirring speed was over 300 rpm, there was no significant enhancement in the conversions (above 90.2%).

Bao-Xiang Peng et al (2008) described about transesterification of waste cooking palm oil and methanol with the presence of SO4^2-/TiO_2-SiO_2 (3.0 wt%) used for 6 hours reaction time and obtained 98% biodiesel yield. Nezahat Boz et al (2009) described about transesterification of biodiesel from canola oil used KF/Al_2O_3 (3.0 wt%) catalyst in the proportion of 15:1 molar ratio of alcohol to oil to produce 99.6% biodiesel yield required 8 hour reaction time.

**Figure 4.26 Biodiesel yield versus reaction temperature**

Bao-Xiang Peng et al (2008) described about transesterification of waste cooking palm oil and methanol with the presence of SO4^2-/TiO_2-SiO_2 (3.0 wt%) used for 6 hours reaction time and obtained 98% biodiesel yield. Nezahat Boz et al (2009) described about transesterification of biodiesel from canola oil used KF/Al_2O_3 (3.0 wt%) catalyst in the proportion of 15:1 molar ratio of alcohol to oil to produce 99.6% biodiesel yield required 8 hour reaction time.
4.5 BIODIESEL CONFIRMATION TEST

Biodiesel confirmation was done by using GC analysis, FTIR technique.

4.5.1 GC analysis

The biodiesel obtained by KOH and Mg/Al-NO$_3$ catalysts transesterification of waste cooking palm oil was analyzed by specific methods to determine physico-chemical characteristics that indicate its quality compared to quality specifications required by the European Standard for biodiesel, i.e., EN 14214:2010. The GC-MS result of biodiesel formation for both KOH and Mg/Al-NO$_3$ were shown in figure 4.27 and 4.28. The following physico-chemical characteristics were determined: ester content, density at 15°C, viscosity at 40°C, flash point, sulphur content, water content, acid value, iodine value, methanol content, mono-, di-, triglycerides content, free and total glycerol content, and calorific power. The values obtained are given in Table 4.8. These characteristics are detailed below, showing their direct influence on engine parameters.

4.5.1.1 Ester content

Ester content is a measure of completion of transesterification reaction. A higher conversion of triglycerides into methyl esters leads to a better engine performance. Ester content of biodiesel can vary greatly depending on the different technologies used and the raw materials available. European biodiesel standard, EN 14214:2010, sets a limit for the ester content of at least 96.5% while the American standard for biodiesel, ASTM D 6751 does not specify a minimum for the ester content (ASTM, 2002). The ester content of the biodiesel obtained by KOH and Mg/Al-NO$_3$ catalysts transesterification of waste cooking palm oil was determined by gas chromatography; with methyl heptadecanoate as internal standard and the
The chromatogram obtained is shown in Figure 4.27 and 4.28. The resulted data were processed, yielding a value of 95.23 and 94.54\% ester content of KOH and Mg/Al-NO\textsubscript{3} catalysts, indicating an almost complete conversion of triglycerides into methyl esters.

### 4.5.1.2 Density at 15 °C

The European standard for biodiesel, EN 14214:2010, specifies an allowable domain for density at 15°C ranging from 860-900 kg/m\textsuperscript{3}. The American standard for biodiesel, ASTM D 6751, does not set a limit on density, and stipulates that biodiesel density falls between 860 and 900 kg/m\textsuperscript{3} (typical values between 880 and 890 kg/m\textsuperscript{3}) when other quality specifications are met. Density value for the biodiesel produced by KOH and Mg/Al-NO\textsubscript{3} catalysts were 891 and 887 kg/m\textsuperscript{3}, thus meeting the quality specified by EN 14214:2010 standards.

![Figure 4.27 The chromatogram obtained for the fatty acid analysis of KOH catalyzed biodiesel](image)
4.5.1.3 Viscosity at 40ºC

Viscosity determines the fuel flow through pipes, nozzles and injection holes as well as the temperature range for the proper functioning of the burning fuel. A high viscosity can cause problems for the spray effect of the injector which can cause excessive coking and oil dilution. These problems are associated with reduced engine life. The quality standards also specify a minimum limit for viscosity to prevent wear of the friction produced by the fuel injection system, which would reduce engine power. A value of viscosity between the limits imposed by the quality standards ensures proper lubrication and corresponding pumping characteristics. The European biodiesel standard, EN 14214:2010, specifies a viscosity domain between 3.5-5 mm²/s. The American standard for biodiesel, ASTM D 6751 specifies a
viscosity domain between 1.9-6 mm²/s. The biodiesel produced by KOH and Mg/Al-NO₃ catalysts from waste cooking palm oil has a viscosity of 4.89 and 5.15 mm²/s, meeting the quality specification imposed by both EN 14214:2010 and ASTM 6751, respectively.

### 4.5.1.4 Flash point

The flash point determines the flammability of the material. In general, the flash point value specified by the quality standards is relatively high, for safety reasons regarding storage and transport and also to ensure that the alcohol is removed from the finished product. Low flash points may indicate alcohol residue in biodiesel. European biodiesel standard, EN 14214:2010, sets a minimum limit for the flash point of 120°C while the American standard for biodiesel, ASTM D 6751, sets a minimum limit for the flash point of 130°C. The flash point for the biodiesel obtained by KOH and Mg/Al-NO₃ catalysts from waste cooking palm oil were 145 and 152°C which corresponds to quality requirements imposed by the quality standard, EN 14214:2010 and ASTM D 6751.

### 4.5.1.5 Sulphur content

The engine combustion of fuels that contain sulphur leads to the formation of sulphur dioxide emissions and particulate matter. Sulphur limits are generally imposed for environmental reasons. European biodiesel standard, EN 14214:2010, sets a maximum limit of sulphur content of 10 mg/kg while the American standard for biodiesel, ASTM D 6751 sets a maximum limit on the sulphur content of 50 mg/kg. For the biodiesel obtained by KOH and Mg/Al-NO₃ catalysts from waste cooking oil, the sulphur content were 0.14 and 0.16 mg/kg, a very low value compared with the maximum value imposed by the quality standards. The immediate consequence is a decrease in sulphur dioxide emissions.
Table 4.8 Biodiesel Fuel specification

<table>
<thead>
<tr>
<th>Biodiesel parameters</th>
<th>KOH Catalyst</th>
<th>Mg/Al-NO₃ HT</th>
<th>Standard EN14214</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>min</td>
</tr>
<tr>
<td>Methyl Ester, (w/w %)</td>
<td>95.23</td>
<td>94.54</td>
<td>96.5</td>
</tr>
<tr>
<td>Density at 15 °C, (kg/m³)</td>
<td>891</td>
<td>887</td>
<td>860</td>
</tr>
<tr>
<td>Viscosity at 40°C, (cSt)</td>
<td>4.89</td>
<td>5.15</td>
<td>3.50</td>
</tr>
<tr>
<td>Flash point, (°C)</td>
<td>145</td>
<td>152</td>
<td>120</td>
</tr>
<tr>
<td>Sulphur content, mg/kg</td>
<td>0.14</td>
<td>0.16</td>
<td>-</td>
</tr>
<tr>
<td>Water content, (mg/kg)</td>
<td>400</td>
<td>350</td>
<td>-</td>
</tr>
<tr>
<td>Acid value, (mg KOH/gm)</td>
<td>0.48</td>
<td>0.42</td>
<td>0.5</td>
</tr>
<tr>
<td>Iodine value, (gm I₂/100gm)</td>
<td>95</td>
<td>109</td>
<td>120</td>
</tr>
<tr>
<td>Monoglyceride content, %</td>
<td>0.16</td>
<td>0.13</td>
<td>-</td>
</tr>
<tr>
<td>Diglyceride content, %</td>
<td>0.03</td>
<td>0.06</td>
<td>-</td>
</tr>
<tr>
<td>Triglyceride content, %</td>
<td>0.05</td>
<td>0.04</td>
<td>-</td>
</tr>
<tr>
<td>Free glycerol, %</td>
<td>0.00</td>
<td>0.00</td>
<td>-</td>
</tr>
<tr>
<td>Total glycerol, %</td>
<td>0.27</td>
<td>0.23</td>
<td>-</td>
</tr>
<tr>
<td>Calorific power, (MJ/Kg)</td>
<td>37.34</td>
<td>36.54</td>
<td>-</td>
</tr>
</tbody>
</table>
4.5.1.6 Water content

The European biodiesel standard, EN 14214:2010 together with the American standard for biodiesel, ASTM D 6751, sets a maximum limit for water content of 500 mg/kg. The water content determined for the biodiesel obtained by KOH and Mg/Al-NO₃ catalysts from waste cooking palm oil were 400 and 350 mg/kg, a value that corresponds to the quality requirements imposed by the quality standards.

4.5.1.7 Acid value

Acid value is a pointer of the presence of free fatty acids or acids formed as a result of the degradation and burning of oil (during or after processing). European biodiesel standard, EN 14214:2010, sets a maximum limit for acid value of 0.5 mg KOH/g. The American standard for biodiesel, ASTM D 6751, sets a maximum limit for the acid value of 0.80 mg KOH/g. For the biodiesel obtained by KOH and Mg/Al-NO₃ catalysts from waste cooking palm oil acid values of 0.48 and 0.42 mg KOH/g, below the maximum limit required by the quality standards.

4.5.1.8 Iodine value

For the biodiesel obtained by KOH and Mg/Al-NO₃ catalysts from waste cooking palm oil iodine values of 95 and 109 gm I₂/100g was obtained, exceeding the maximum limit imposed by the standard EN 14214:2010. If the European biodiesel standard, EN 14214:2010, sets a maximum limit for iodine value of 120 g I₂/100g, the American standard for biodiesel, ASTM D 6751, does not set a limit for iodine value. Iodine value required by the European standard for biodiesel quality, limits the raw material that can be used for biodiesel production. The presence of this parameter in certain quality standards can actually be a political tactic to limit imports of certain raw materials for this purpose.
4.5.1.9 Glycerides content

The content of mono-, di-, triglycerides, free and total glycerol was determined by mass spectrophotometer-gas chromatography using Methyl heptanoate. The chromatogram obtained after the GC analysis is given in Figure 4.27 and 4.28. Figure 4.27 shows for the biodiesel obtained by KOH catalytic transesterification of waste cooking oil, the content of mono-, di- and triglycerides, is within the limits of the quality standards, with values of 0.16%, 0.03% and 0.05%, respectively. The European biodiesel standard, EN 14214:2010, sets a limit for the maximum content of 0.8% for monoglycerides, a maximum content of 0.2% for diglycerides and triglyceride content up to 0.2%. The American standard for biodiesel, ASTM D 6751, does not set a limit for the content of mono-, di-, and triglycerides. The free glycerol content for biodiesel obtained by KOH catalytic transesterification of waste cooking oil 0.05% under the maximum limit imposed by the European biodiesel standard, EN 14214:2010 and the American standards for biodiesel, ASTM D 6751, 0.02%. The total glycerol content of KOH Catalytic biodiesel was 0.27%, close to the maximum limit imposed by the quality standards for biodiesel. Thus, the European biodiesel standard, EN 14214:2010, sets a limit on total glycerol content up to 0.25% while the limit imposed by the ASTM D 6751 standard is 0.24%.

Figure 4.28 shows for the biodiesel obtained by Mg/Al-NO₃ catalytic transesterification of waste cooking oil, the content of mono-, di- and triglycerides, is within the limits of the quality standards, with values of 0.13%, 0.06% and 0.04%, respectively. The European biodiesel standard, EN 14214:2010, sets a limit for the maximum content of 0.8% for monoglycerides, a maximum content of 0.2% for diglycerides and triglyceride content up to 0.2%. The American standard for biodiesel, ASTM D 6751, does not set a limit for the content of mono-, di-, and triglycerides. The free glycerol content for biodiesel obtained by Mg/Al-NO₃ catalytic
transesterification of waste cooking oil 0.03% under the maximum limit imposed by the European biodiesel standard, EN 14214:2010 and the American standards for biodiesel, ASTM D 6751, 0.02%. The total glycerol content of Mg/Al-NO$_3$ Catalytic biodiesel was 0.23%, close to the maximum limit imposed by the quality standards for biodiesel. Thus, the European biodiesel standard, EN 14214:2010, sets a limit on total glycerol content up to 0.25% while the limit imposed by the ASTM D 6751 standard is 0.24%.

4.5.1.10 Energy content (Calorific power)

For the biodiesel obtained by KOH and Mg/Al-NO$_3$ catalysts from waste cooking oil, an energy value of 37.34MJ/kg and 36.54 MJ/kg were obtained, a value that corresponds to data reported in the literature (Bajpai et al 2006). Although the presence of oxygen lowers the energy value of biodiesel comparatively to that of diesel (an average of 37.2 MJ/kg compared with 43.8 MJ/kg for diesel), the energy value of biodiesel is much less variable, and depends especially on the feedstock used and not on the production process.

4.5.2 FTIR Technique

In this study, FTIR technique is used to identify the frequency peaks are formed with respect to the % transmittance. A detailed description was given for waste cooking palm oil with biodiesel peaks result of KOH and Mg/Al-NO$_3$ catalysts.

Figure 4.29 shows the FTIR spectrum of waste cooking palm oil. The spectrum was characterized with asymmetric and symmetric strong stretching vibrations of carboxyl group at 2675.6 cm$^{-1}$, along with the O-H stretching of the hydroxyl bonded with alcohol at 3461.3 cm$^{-1}$ and Aldehyde, Ketones(C=O) group along with carboxylic group at 1747.2 cm$^{-1}$. C-O group
combined with carboxylic group at 1238.9, 1165.4 cm\(^{-1}\). Finally Alkanes groups strongly stretched at 2905.5, 2854.8 and 1458.2 cm\(^{-1}\).

Figure 4.29 FTIR Spectrums for Waste Cooking Palm Oil
Figure 4.30 FTIR Spectrums of biodiesel for KOH Catalyst

Figure 4.30 shows the FTIR spectrum of biodiesel for Mg/Al-SO$_4$ Catalyst. The spectrum was characterized with asymmetric and symmetric strong stretching vibrations of carboxyl group at 3000-2500 cm$^{-1}$, along with the O-H stretching of the hydroxyl bonded with alcohol at 3600-3200 cm$^{-1}$ (broad) with Alcohols, Phenols groups. Aldehyde, Ketones (C=O) group along with carboxylic group, Ester group strongly stretched found at 1744.2 cm$^{-1}$ (1470-1670 cm$^{-1}$). C-O group combined with carboxylic group, Ester group strongly stretched at 1169.9 cm$^{-1}$ (1260-1000 cm$^{-1}$). Finally, Alkanes(C-H) groups strongly stretched at 1458-1377.7 cm$^{-1}$. 
Figure 4.31 FTIR Spectrum of biodiesel for Mg/Al-NO$_3$ Catalyst

Figure 4.31 shows the FTIR spectrum of biodiesel for Mg/Al-NO$_3$ Catalyst. The spectrum was characterized with asymmetric and symmetric strong stretching vibrations of carboxyl group at 3000-2500 cm$^{-1}$, along with the O-H stretching of the hydroxyl bonded with alcohol at 3473.9 cm$^{-1}$ (strong, broad) with Alcohols, Phenols groups. Aldehyde, Ketones (C=O) group along with carboxylic group, Ester group strongly stretched found at 1747.4 cm$^{-1}$ (1760-1670 cm$^{-1}$). C-O group combined with alcohols, carboxylic acids, Ester group strongly stretched at 1169.9 cm$^{-1}$ (1260-1000 cm$^{-1}$). Finally, Alkanes(C-H) groups strongly stretched at 3005.4, 2922.7, 14627 and 7225 cm$^{-1}$. 
4.6 KINETIC STUDY OF WASTE COOKING PALM OIL

The kinetic study of waste cooking palm oil describes about order of reaction, rate constant of forward and backward reaction and also describes about activation energy of conversion of TG-DG, DG-MG, and MG-GL which describe on which conversion lowest activation energy is required.

4.6.1 Effect of Molar Ratios

This experiment was carried out with 4:1 molar ratio of methanol to oil. Generally, biodiesel process requires only 3:1 molar ratio of alcohol to oil to form 3:1 molar ratio of methyl ester and glycerol. The FFA value of this palm oil is contains only 0.65% and the process required small amount of catalyst to perform the transesterification reaction. So, it was decided to use 4:1 molar ratio of alcohol to oil for biodiesel kinetic study. Further increase of molar ratio (5:1 to 9:1) leads to decrease in the methyl ester value, increase in the cost of methanol also observed the effect of molar ratio of ester yield of both because of the variation in the molar ratio reported as necessary by various investigators and no correlation has been found for the system variation in molar ratio with ester yield. At the same time, the change in concentrations of tri, di and monoglycerides were also monitored. The result obtained from menthanolysis of waste cooking palm oil is shown in figure 4.32. Anusan et al (2011) described the experimental investigation that was carried out with pure palm oil and methanol at molar ratio of 46:1, temperatures between 150 to 200°C and pressure around 140 to 190 atmospheres in a 400 ml batch reactor. Encinar et al (2007) studied molar ratios of alcohol to oil as 3:1 to 12:1 and it depicts that as molar ratio increases it led to decrease in the methyl ester content. Also, transesterification reaction carried out with 4:1 molar ratio of alcohol to oil gave more than 95% of the methyl ester.
Figure 4.32 Rate of reaction time with Triglycerides fall rate concentration
4.6.2 Optimization of Reaction Parameters

Classical optimization technique was used to optimize the reaction parameters such as, catalyst quantity, methanol to oil ratio and temperature. 0.45 weight % catalysts were taken as the optimum amount as further increase in catalyst concentration shows significant improvement in the reaction. Transesterification reaction was carried out with methanol to oil ratio from 4:1 to 9:1. An increase in transesterification was observed till a ratio of 6:1, beyond which no substantial increase in transesterification rate was observed. Temperature studies were done in the range of 50 to 65°C. The optimum value was found at 60°C, because at a temperature greater than 60°C, methanol is lost from the reaction medium in spite of using a condenser. If further increase in temperature leads to formation of methyl ester, it will be less due to alcohol volatility.

4.6.3 Effect of Concentration of Glycerides

Figure 4.33 shows the progress of the transesterification reaction for waste cooking palm oil in every 20 min of reaction time, when the temperatures of 50, 55, 60 and 65°C were used. The conversion of methyl ester was obtained at 95% and the glycerol concentration was increased with the maximum limitation of 3.5%. In the initial stages of the reaction, triglycerides were first converted into diglycerides, diglycerides were converted into monoglycerides and finally monoglycerides were converted into methyl ester with glycerol. If increased, the effect of concentration of triglycerides leads to formation of fat or oil, whereas, diglycerides and monoglycerides lead to formation of triglycerides. For transesterification process, methaoxide was added into the heated palm oil reactor and the reaction led to the formation of tri-di, di-mono and mono-glycerol. As the rate of reaction proceeds, concentration of glycerides contents diminished and
finally reached equilibrium time at the 240 min as shown in Figure 4.32. Concentration of tri, and diglycerides decreased slowly with reaction time and monoglycerides decreased gradually with the reaction time. After 200 min, all three glycerides coincided and after 240 min, all the three glycerides attained equilibrium (that is, all three glycerides were converted into glycerol and formed 100% methyl ester). The increase in methyl ester (ME) concentration was followed by an increase in glycerol concentration as it was liberated from TG molecules. However, the relative proportion of glycerol produced is not always the same as that of the esters produced.

From the Figure 4.32, this is due to intermediate products such as DG, MG and TG concentrations that decreased as the reaction proceeded after particular time interval and TG concentration was only 0.16% with the highest concentration of DG and MG observed in the first minutes of their levels of each 20 min intervals. The concentration of the decrease of the three triglycerides conversion into biodiesel is described in Figure 4.30. Theerayut et al (2004) had discussed 6:1 ratio of methanol and oil used for transesterification reaction of palm using 1 weight % of the catalyst whereas, the work used only 0.45 weight % for effective transesterification reaction from vegetable waste cooking oil. In this work, the molar ratio of methanol and oil used only 4:1, but, Noureddini et al (1997) described about 6:1 molar ratio of the mixture used. American Society of testing and materials (ASTM) does not have a standard limit for triglycerides, diglycerides and monoglycerides content in the final product. However, European biodiesel standard (EN14214) recommends that the triglycerides, diglyceride and monoglyceride contents should not exceed 0.8 and 0.2, 0.2 wt. % respectively.
4.6.4 Effect of Temperature

To determine the effect of temperature on methyl esters formation, transesterification reactions of waste cooking palm oil were carried out with molar ratio of methanol to oil 4:1, the best condition found in Figure 4.34, at the various temperatures such as, 50, 55, 60 and 65°C. Generally, oil is semisolid at room temperature but the minimum temperature will give optimum value to the process; the minimum temperature of 50°C was used. Below 50°C, the high viscosity of the oil caused problems in pumping and stirring and storage temperature of oil was about 50 to 55°C to maintain its liquidity. The maximum temperature was studied at 65°C because the boiling point of methanol is 68°C (boiling point of methanol is 65°C). Temperature had noticeable effect with methyl ester on the transesterification reaction as shown in Figure 4.34. At 50°C, conversion of TG to ME was 85% and the same at 60°C conversion of TG to ME was 94%, and further increase in temperature that is almost 95% of the conversions of methyl ester were found at 65°C. Therefore, increase in temperature up to particular point of methyl
ester conversion would be high beyond that limiting period again conversion would be negative effect of the process due to the increase in methanol and catalyst requirement with respect to methyl ester production, optimum temperature was 60°C. The typical glycerides results with temperature increments are shown in Figure 4.35.

Initially from 50 to 60°C, the glycerides concentrations slowly decrease with respect to temperature increase and after 60°C glycerol concentration only increases and other three glycerides concentration got decreased. So, optimum temperature for waste cooking palm oil is 60°C. Owing to the semisolid nature of palm oil at room temperature discussed by Darnoko et al (2000) studied the effect of temperature on palm oil transesterification at 50°C and a catalyst (KOH) concentration of 1% with 6:1 molar ratio of methanol/oil gives 83% methyl ester. Freedman et al (1984) also reported rapid formation of ME during transesterification of soybean oil and sunflower oil and after 1 min, 80% of TG was converted to ME and after 1 h, ME concentration was 93 to 98% of the reaction mixture. At 60°C, this study gave 95% of methyl ester conversion for 4:1 molar ratio of methanol to oil with 0.45 wt. % of catalyst used.
Figure 4.34 Rate of Methyl Ester conversion with Temperatures

Figure 4.35 Rate of Concentration of Triglycerides with Temperatures
4.6.5 Reaction Kinetics

The feasibility of a reaction is determined from the thermodynamic parameters. Arrhenius equation was used to study the influence of temperature on specific reaction rate. The best kinetic model for the data appears to be a second order model kinetics. To test this hypothesis, a model was developed based on the kinetics of TG, methanolysis (Darnoko et al 2000). The second order reaction rate for TG in equation (4.3) would be as follows (Smith, 1981):

$$\frac{d[TG]}{dt} = k_{TG} [TG]^2$$  \hspace{1cm} (4.3)

Integration of equation (4.3) yields:

$$-k_{TG}.t = \frac{1}{[TG]} - \frac{1}{[TG_0]}$$  \hspace{1cm} (4.4)

Similarly, the same procedure was applied to equation (4.5) and (4.6) resulting in:

$$-k_{DG}.t = \frac{1}{[DG]} - \frac{1}{[DG_0]}$$  \hspace{1cm} (4.5)

$$-k_{MG}.t = \frac{1}{[MG]} - \frac{1}{[MG_0]}$$  \hspace{1cm} (4.6)

Where k is the overall second order rate constant, t is the reaction time, TG0 is the initial highest triglyceride concentration, DG0 is the initial highest diglycerides concentration, MG0 is the initial highest monoglycerides concentration, TG is final concentration of triglycerides, DG is the final concentration of diglycerides, MG is the final concentration of monoglycerides and k_{TG}, k_{DG}, k_{MG} are rate constant for tri, di and monoglycerides of oil.
For methanolysis of TG a plot of reaction time versus $1/ [\text{TG}]$ will be straight line if the model is valid. A second order rate equation (4.3) was applied to find the rate constant. Figure 4.36 shows rate constant values calculated by plotting concentration of different glycerides at different temperatures (50, 55, 60 and 65°C) with respect to time variation. From Figure 4.36 select various points of concentration with respect to temperature with applying scatter model graph and found the rate constant, correlation coefficient ($R^2$). From the plot, the slope is called rate constant $k_{\text{TG}}$ (wt % min$^{-1}$). Rate constant values for triglycerides can be calculated by using equation (4.4).

From the Figure 4.36 values of rate constant, correlation coefficient ($R^2$) can be tabulated and obtained in Table 4.9. For TG-DG plot, at 50°C, the rate constant value was 0.0180 (wt % min$^{-1}$) and correlation coefficient ($R^2$) was 0.9157 and at 65°C, the k value was 0.0244 (wt % min$^{-1}$) and correlation coefficient was 0.8608. There is an increase in k at higher temperature and the order of magnitude also increases. Similarly, straight lines were obtained for DG and MG methanolysis by applying the equations (4.5) and (4.6). These data were used to determine the energy of activation ($E_a$) from a plot of the rate constant ($k$) versus the reciprocal of absolute temperature ($T$), according to the equation (4.7):

$$\log_{10} k = (-E_a/2.303 R)/T+C \quad (4.7)$$

Where $E_a$ is the energy of activation, $R$ is the Gas constant, $k$ is rate constant and $C$ is a constant.

The Figure 4.37 shows activation energy values calculated, similar from rate constant procedure and plotted values can be obtained in Table 4.10. Based on the plot of Arrhenius, values of $E_a$ with respect to TG – DG was 2.53 (Kcal/mol), DG – MG was 1.93 (Kcal/mol) and MG - GL was 1.29
(Kcal/mol). Also, observed activation energy of these three triglycerides reaction had only less energy required exhibiting the conversion of triglycerides. The activation energy is defined as the energy that must be overcome in order for a chemical reaction to occur. Activation energy may also be defined as the minimum energy required to starting chemical reaction. Table 4.10 show good results and compatibility to precede the reaction easily. Also, compared with other process from waste cooking oil kinetics highlights higher values of activation energy and may promotes the reaction effectively.

![Figure 4.36 Rate constant Plot for Glycerides at different temperatures](image)

Figure 4.36 Rate constant Plot for Glycerides at different temperatures
Figure 4.37 Arrhenius plot of Reaction Rate vs. Reciprocal Temperature

Table 4.9 Reaction Rate Constant $k$ (wt% min$^{-1}$) for Triglycerides (TG), Diglycerides (DG), and Monoglycerides (MG) Hydrolysis at different temperatures

<table>
<thead>
<tr>
<th>Glycerides</th>
<th>Temperature ($^\circ$C)</th>
<th>Reaction Rate Constant (Wt. % min$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TG → DG</td>
<td>50</td>
<td>0.0180</td>
<td>0.9157</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>0.0188</td>
<td>0.9176</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.0208</td>
<td>0.8861</td>
</tr>
<tr>
<td></td>
<td>65</td>
<td>0.0244</td>
<td>0.8608</td>
</tr>
<tr>
<td>DG → MG</td>
<td>50</td>
<td>0.0360</td>
<td>0.8514</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>0.0420</td>
<td>0.8454</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.0610</td>
<td>0.8348</td>
</tr>
<tr>
<td></td>
<td>65</td>
<td>0.0801</td>
<td>0.8114</td>
</tr>
<tr>
<td>MG → GL</td>
<td>50</td>
<td>0.1012</td>
<td>0.8101</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>0.1431</td>
<td>0.7981</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.1528</td>
<td>0.7856</td>
</tr>
<tr>
<td></td>
<td>65</td>
<td>0.1682</td>
<td>0.7813</td>
</tr>
</tbody>
</table>
Table 4.10  Activation Energy for Hydrolysis of TG, DG, and MG during transesterification of waste cooking oil

<table>
<thead>
<tr>
<th>Glycerides</th>
<th>Ea (Kcal/mol)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>TG → DG</td>
<td>2.53</td>
<td>0.7772</td>
</tr>
<tr>
<td>DG → MG</td>
<td>1.93</td>
<td>0.2904</td>
</tr>
<tr>
<td>MG → GL</td>
<td>1.29</td>
<td>0.2904</td>
</tr>
</tbody>
</table>