

CHAPTER 6

Synthesis and characterization of calcium aluminate ($\text{Ca}_2\text{Al}_2\text{O}_5$) and its application in biodiesel production from waste vegetable oil (WVO) and *Pongamia Pinnata* (Karanja) oil

6.1 Introduction

Present chapter contains details of synthesis of calcium aluminate, ($\text{Ca}_2\text{Al}_2\text{O}_5$) as a heterogeneous catalyst by solid state method and characterization by thermo-gravimetric analysis (TGA), X-ray diffraction (XRD), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), Brunauer-Emmett-Teller (BET) surface area analyser, Barrett-Joyner-Halenda (BJH) analysis, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), particle size analyser and basicity. This catalyst was utilized for transesterification of waste vegetable oil (WVO) and (*Pongamia pinnata*) Karanja oil for biodiesel production. Various reaction parameters such as catalyst concentration, molar ratio, reaction temperature, reaction time, stirring speed and catalyst reusability were deliberated. Synthesized biodiesel was characterized by ^1H NMR and physicochemical properties were also studied as per ASTM standards.

6.2 Synthesis of calcium aluminate ($\text{Ca}_2\text{Al}_2\text{O}_5$)

Calcium aluminate ($\text{Ca}_2\text{Al}_2\text{O}_5$) was synthesized by solid state method as shown in Figure 6.1. Alumina (Al_2O_3) and calcium carbonate (CaCO_3) were mixed in their stoichiometric ratios of 1:1 by using ball mill for 1 h in presence of acetone. Then, this mixture was calcined at 900 °C for 4 h. Resultant product was ground by mortar and pestle and was subsequently sieved to obtained fine powder and stored in desiccator.

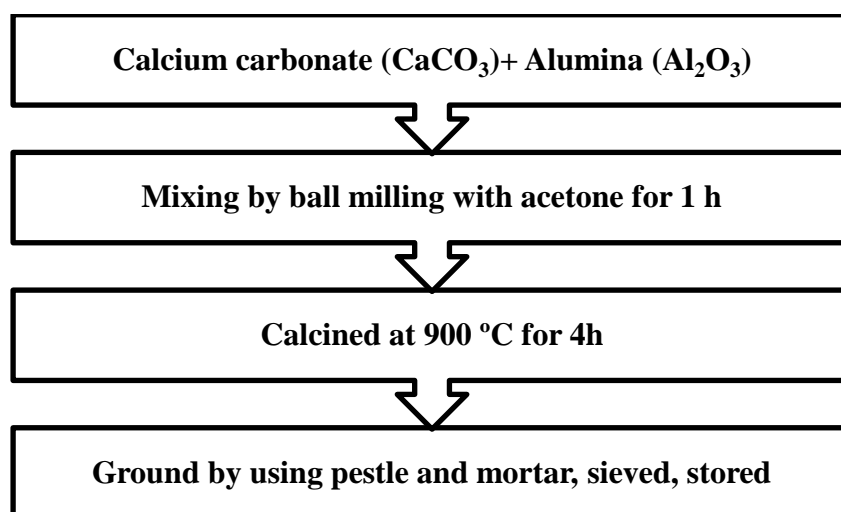


Figure 6.1 Synthesis of $\text{Ca}_2\text{Al}_2\text{O}_5$ via solid state method

6.3 Characterization of calcium aluminate ($\text{Ca}_2\text{Al}_2\text{O}_5$)

6.3.1 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) of uncalcined sample was conducted to study the decomposition of sample. Weight loss of uncalcined sample has been shown in Figure 6.2 with respect to temperature. The thermogram displays that total weight loss of 19.26% has occurred during temperature rise from 40 °C to 1000 °C at the rate of 20 °C per min in two stages. First stage of weight loss is due to evaporation of moisture content that is water of crystallization obtained from 40 °C to 200 °C and was 12.72%. However, the second weight loss was observed to be 6.54% from 200 °C to 890 °C and was attributed to carbon dioxide release from the sample. After that no weight loss was seen in the sample and hence calcination was executed at 900 °C where calcium aluminate was in stabilized phase. In transesterification, catalytic poisoning was occurred due to carbonates present on the surface of oxide [Knothe, 2006].

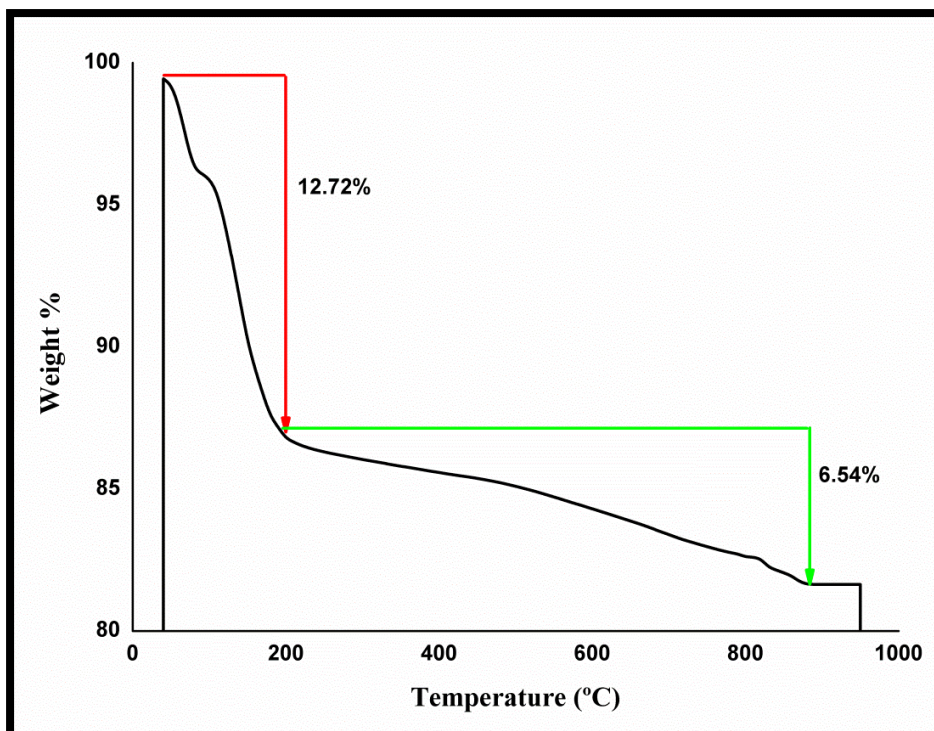


Figure 6.2 TGA curve of uncalcined $\text{Ca}_2\text{Al}_2\text{O}_5$ catalyst

6.3.2 X-ray diffraction (XRD)

In order to define the crystalline structure of synthesized sample through thermal decomposition, X-ray diffraction (XRD) analysis of the calcined catalyst was accomplished. From the Figure 6.3, it has been observed that the prominent peaks obtained were of orthorhombic calcium aluminium oxide $\text{Ca}_2\text{Al}_2\text{O}_5$ and compared with the Joint Committee on Powder Diffraction Standards (JCPDS) matches file No. 52-1722. The intense peaks at 12.01° , 18.11° , 23.65° , 26.71° , 28.45° , 34.38° , 36.50° , 42.69° , 44.58° , 52.41° , 54.34° , 62.39° , 67.39° and 72.43° were attributed to orthorhombic phase of calcium aluminium oxide $\text{Ca}_2\text{Al}_2\text{O}_5$. With this, it has been shown that some trifling peaks at 20.15° , 29.65° , 32.40° , 39.52° , 47.60° , 51.75° and 64.9° were seen due to existence of calcium oxide CaO (JCPDS file No.28-0775 and 37-1497). Solid state reaction of alumina (Al_2O_3) and calcium carbonate (CaCO_3) was responsible for calcium aluminium

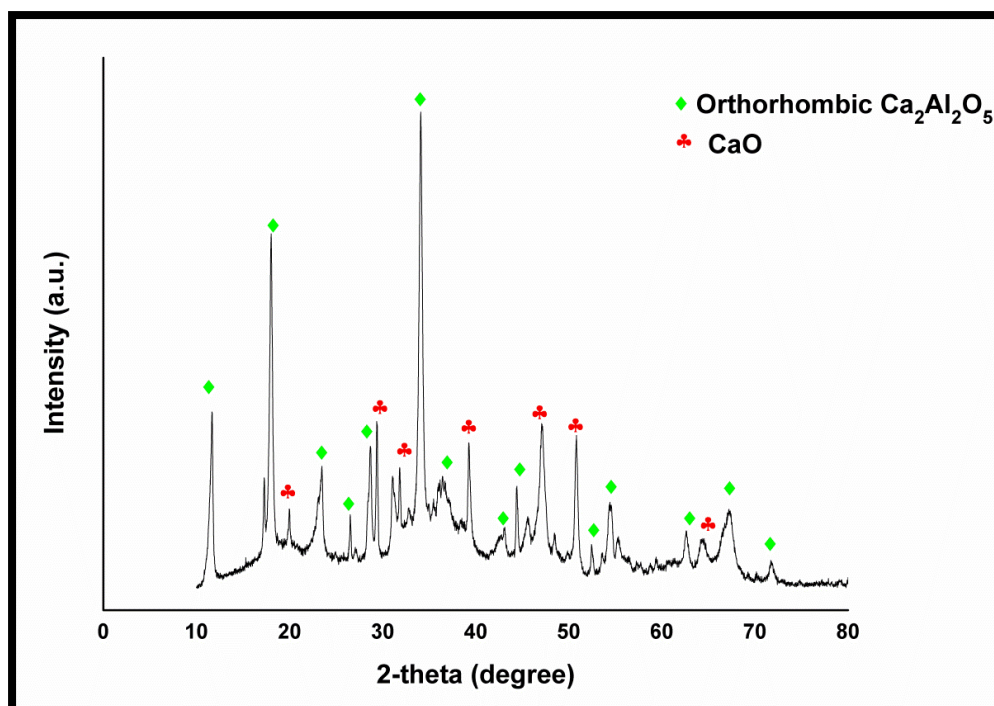


Figure 6.3 XRD pattern of the $\text{Ca}_2\text{Al}_2\text{O}_5$ catalyst synthesized via solid state method

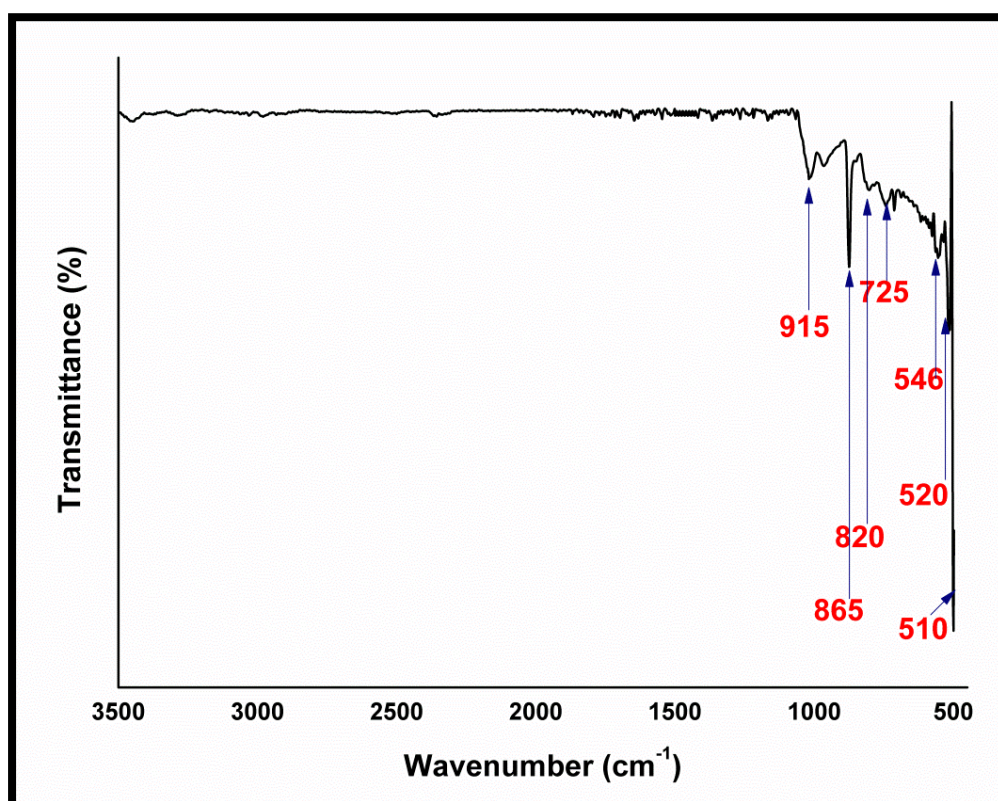


Figure 6.4 ATR-FTIR spectra of $\text{Ca}_2\text{Al}_2\text{O}_5$ catalyst

oxide $\text{Ca}_2\text{Al}_2\text{O}_5$ formation which was confirmed by XRD results $\text{Ca}_2\text{Al}_2\text{O}_5$ was utilized as heterogeneous catalyst for biodiesel production. Aluminium oxide itself was catalytically inactive to carry out transesterification reaction for biodiesel production. Our concern was towards the biodiesel production at conditions of low cost and hence basically solid state method was chosen for catalyst synthesis.

6.3.3 Attenuated total reflectance Fourier transform infrared (ATR FT-IR) spectra

Attenuated total reflectance Fourier transform infrared spectrum (ATR-FTIR) of calcium aluminium oxide $\text{Ca}_2\text{Al}_2\text{O}_5$ was illustrated in Figure 6.4. FTIR analysis is generally used to detect presence of surface species which are tough to detect by using other techniques as well as more sensitive for apperception of phases. XRD technique as mentioned earlier was not so efficient in assessment of the presence of non-crystalline phases in sample when compound present on the surface of given sample. From Figure 6.4 it has been obtained that peaks were observed between 500 cm^{-1} to 1000 cm^{-1} . Peaks at 510 cm^{-1} and 520 cm^{-1} could be due to vibrations generated from AlO_6 octahedral group, whereas peaks at $546, 725, 820, 865, 915\text{ cm}^{-1}$ could be attributed to AlO_4 tetrahedral group stretching vibrations [Nayebzadeh et al., 2016; Tarte, 1967; Saniger, 1995].

6.3.4 Brunauer-Emmett-Teller (BET) surface area and BJH analysis

BET surface area and Langmuir surface area were observed to be $18.03\text{ m}^2/\text{g}$ and $31.27\text{ m}^2/\text{g}$ respectively. Single point adsorption total pore volume of pores less than 1761.858 \AA width at P/P_0 0.9889 was $0.0386\text{ cm}^3/\text{g}$. BJH Adsorption cumulative volume of pores between 17.000 \AA and 3000.000 \AA width was $0.0359\text{ cm}^3/\text{g}$. In addition to this BJH desorption cumulative volume of pores between 17.000 \AA and 3000.000 \AA width was $0.0366\text{ cm}^3/\text{g}$. Pore size adsorption average pore width ($4V/A$ by BET) was 85.603

Å. BJH Adsorption and desorption average pore width (4V/A) were 63.151 Å and 59.083 Å respectively. BJH adsorption cumulative surface area of pores between 17.000 Å and 3000.000 Å width was 22.789 m²/g. However, BJH desorption cumulative surface area of pores between 17.000 Å and 3000.000 Å width was 24.775 m²/g.

6.3.5 Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS)

Morphology of synthesized catalytic surface has been studied by using scanning electron microscopy (SEM) and EDS. Microstructural properties of calcium aluminate were deliberated by using SEM image and shown in Figure 6.5. From the SEM image, it has been observed that diffusion of calcium and alumina occurred as a result of calcination. Interaction between support and guest molecule were responsible for high catalytic activity. Irregular and non-uniform shaped particles were obtained from solid state method. It has been concluded that solid state reaction between surface and guest molecules used for activation is auspicious for high activation of catalytic surface [Xie and Li, 2006].

EDS is equipped with scanning electron microscope (SEM) and two techniques are usually used together. This provides the signal in form of histograms of energy vs. signal strength and linked to relative concentrations. Compositional analysis of EDS proposed that the compound obtained from the solid state method consisted of calcium and aluminium oxide and has been shown in Figure 6.6. Table 6.1 clearly designates calcined calcium aluminium oxide (Ca₂Al₂O₅) consist of 30.13 wt% O, 5.38 wt% Ca and 64.49 wt% Al.

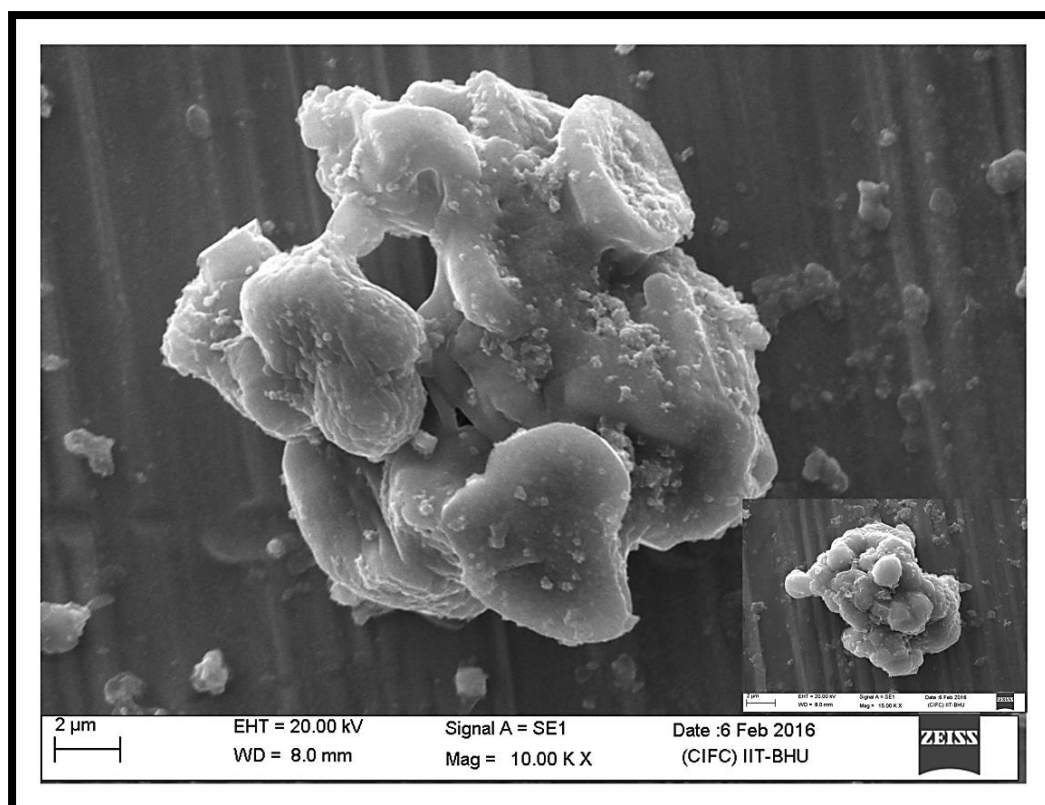


Figure 6.5 SEM image of the $\text{Ca}_2\text{Al}_2\text{O}_5$ synthesized catalyst

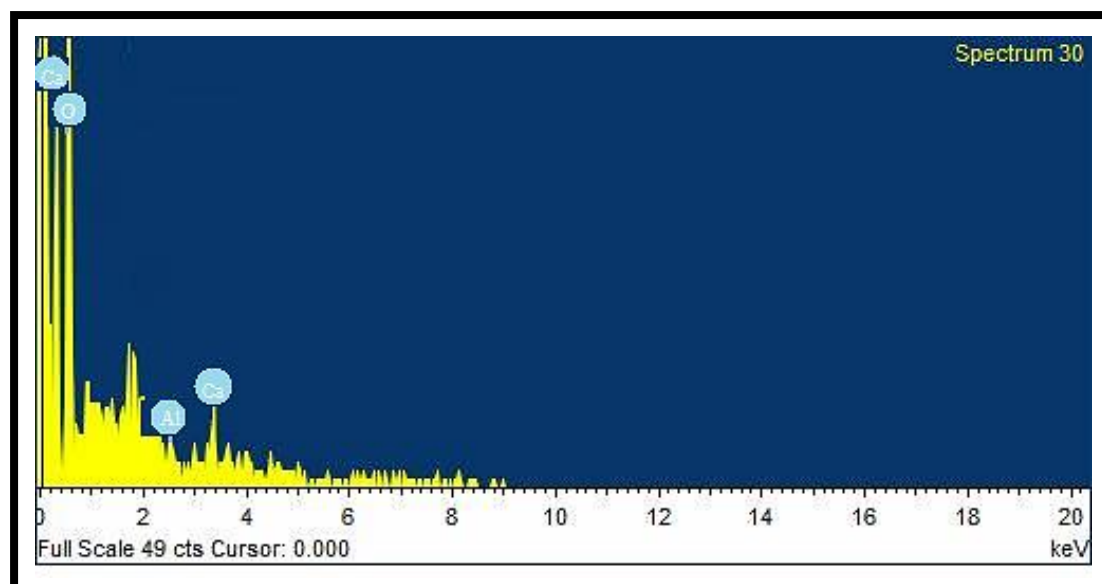


Figure 6.6 EDS image of the $\text{Ca}_2\text{Al}_2\text{O}_5$ synthesized catalyst

Table 6.1 Element weight % present in $\text{Ca}_2\text{Al}_2\text{O}_5$ sample

Elements	Weight (%)	Atomic (%)
O	30.13	70.96
Ca	5.38	7.30
Al	64.49	21.74
Total	100.00	100.00

6.3.6 Particle size analysis

The diameter of the particles was dignified with the help of particle size analyser on the principle of dynamic light scattering (DLS). Figure 6.7[A, B, C, D] shows the intensity size distribution, volume distribution, number distribution and natural logarithmic graph respectively. Photon correlation spectroscopy was used to measure intensity size distribution as shown in Figure 6.7 in form of histogram. Results based on intensity relied on scattering angle, however were independent in case of volume distribution. Volume distribution histogram shows the relative volume of particles in given sample for every single size. Volume percentage divided by cubed diameter of particles in sample was represented in form of number distribution histogram. All the analyses were performed at 25 °C temperature by using water as diluent. However polydispersity index was 0.311, diffusion constant (D) was 1.285e-008 (cm²/sec). Refractive index was 1.3328, whereas, viscosity was found to be 0.8878 cP and 10640 cps of scattering intensity. According to intensity distribution, average diameter of particles was 0.75 μm and standard deviation of 0.76 μm .

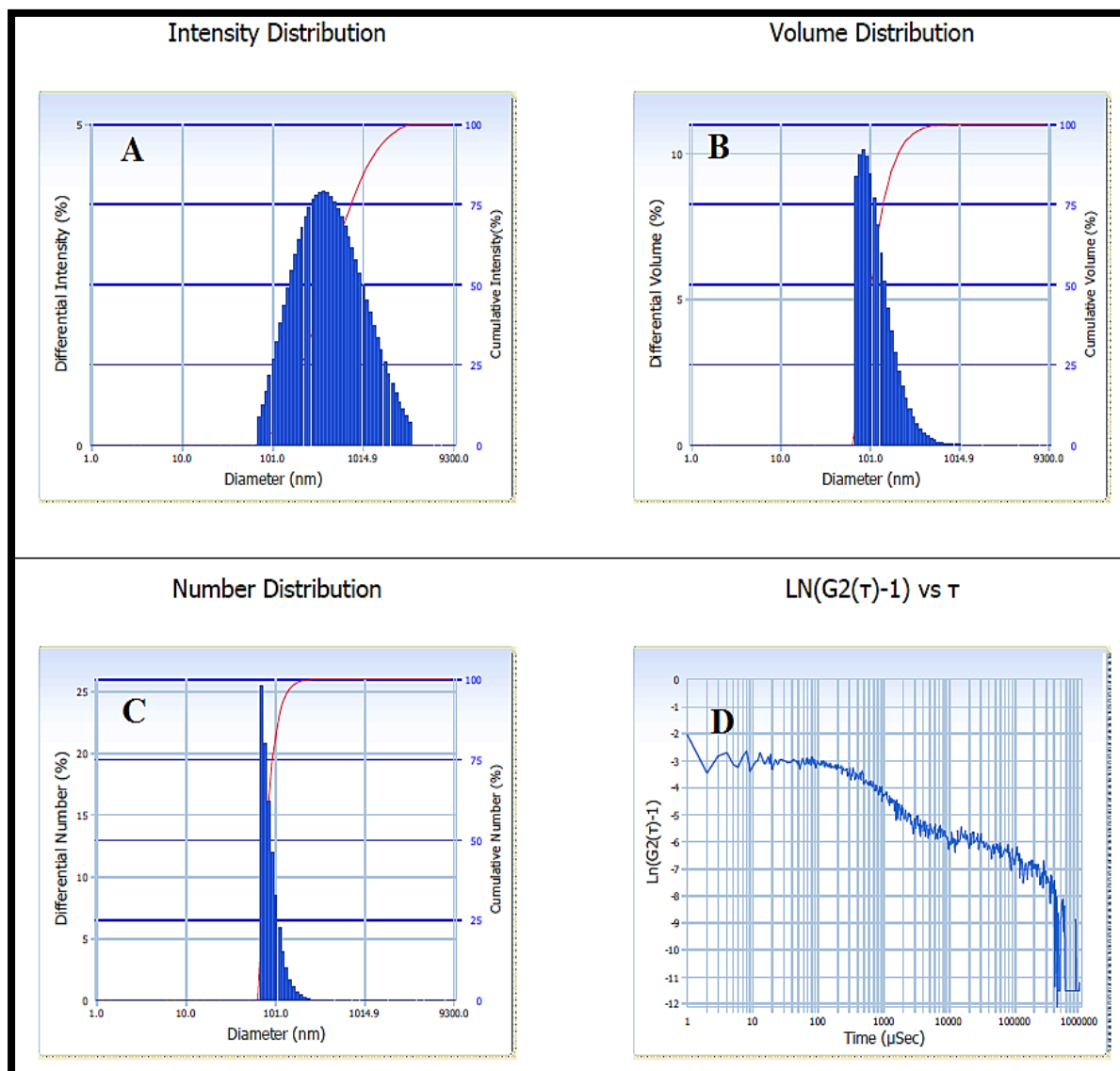


Figure 6.7 Particle size distribution (A) Diameter with respect to differential intensity (B) Diameter with respect to differential volume (C) Diameter with respect to differential number (D) Natural logarithmic graph in between $\ln(G2(t)-1)$ Plot and decay time

Volume distribution illustrates the average diameter of particles as $0.13 \mu\text{m}$ and standard deviation of $0.08 \mu\text{m}$, whereas, in number distribution graph average particle diameter was found to be $0.09 \mu\text{m}$ and standard deviation of $0.02 \mu\text{m}$ was observed.

6.3.7 Basicity

Basicity of calcium aluminate was calculated as per Hammett indicator benzene carboxylic acid titration. Titration was performed by using indicators having pK_{BH^+} in between 6.8-15.0 (Neutral red, Bromothymol blue, Phenolphthalein, Nile blue, Trapeolin and 2,4-dinitroaniline) was presented in Table 6.2. The total basicity of calcium aluminate was attained as 1.89 mmol/g. This basic strength was due to Lewis base existence in the form of oxide ion. [Yan et al., 2009]. Basic site strength plays vital role for activity of catalyst in transesterification reaction [Kaur and Ali, 2015].

Table 5.2 Basicity of $Ca_2Al_2O_5$

S. No.	Indicators	Basicity (mmol/g of catalyst)
1	Neutral red $pK_{BH^+} = 6.8$	0.1
2	Bromothymol blue $pK_{BH^+} = 7.2$	0.21
3	Phenolphthalein $pK_{BH^+} = 9.3$	0.39
4	Nile blue $pK_{BH^+} = 10.1$	0.51
5	Trapeolin $pK_{BH^+} = 11.1$	0.43
6	2,4- Dinitroaniline $pK_{BH^+} = 15.0$	0.25
	Total basicity	1.89

6.4 Biodiesel production via transesterification and its analysis

Suspended stuff and moisture content in waste vegetable oil (WVO) was removed by filtration and by drying in hot air oven respectively. As the acid value of WVO was low (2.36 mg KOH/g), therefore, its direct transesterification was performed to obtain

biodiesel. However, in case of Karanja oil, acid value was high (5.60 mg /KOH) and was lowered by acid esterification reaction (0.52 mg KOH/g). Transesterification was accomplished in 250 ml three neck round bottom flask equipped with mechanical stirrer, condenser and thermometer in hot water bath. Methanol and calcium aluminate (varied from 0.5 wt% to 3.5 wt% of oil) was heated in water bath at 45 °C for 30 min through continuous stirring intended for catalyst activation. After activation, oil was added to the above mixture and refluxed for 150 min at 65 °C under constant stirring. Reaction mixture was transferred to separating funnel for overnight and three separate phases of methyl ester (top), glycerol (middle) and catalyst (bottom) were obtained. Catalyst was collected and recovered for further experiments after its activation. Methanol remaining in FAME was recovered by rotary evaporator; and hot water washing was carried out to remove impurities from FAME and traces of water was removed by passing through anhydrous Na₂SO₄ [Sharma and Singh, 2009]. Ester content in final biodiesel obtained from waste vegetable oil and Karanja oil was calculated by using Equation 3.1.

In present study, optimization has been done by carrying out reaction with varying oil: methanol molar ratio from 1:6 to 1:24 by taking 0.5 wt% to 3.5 wt% of catalyst. The reaction time varied from 30 min to 180 min and temperature from 35 °C to 75 °C with stirring speed of 200 rpm to 800 rpm. In addition to this, reusability of catalyst was also deliberated up to seven runs. All experiments were performed thrice to study uncertainties. Physico-chemical properties of synthesized methyl ester from WVO and Karanja oil were studied as per ASTM standards.

¹H NMR spectrum of WVO and Karanja oil derived FAME at optimum reaction condition was represented in Figure 6.8 and 6.9 correspondingly. The FAME conversion of WVO and Karanja oil was calculated by considering integrated values of signal at

3.665 ppm (methoxy group of FAME i.e. A_{ME}) and 2.286 ppm (methylene group i.e. A_{CH_2}). Conversion was calculated as follows:

$$\text{FAME conversion of WVO}(\%) = (2 \times 3.10 / 3 \times 2.17) \times 100 = 95.24\% \quad \dots (\text{Equation 6.1})$$

$$\text{FAME conversion Karanja oil}(\%) = (2 \times 3.13 / 3 \times 2.15) \times 100 = 97.05\% \quad \dots (\text{Equation 6.2})$$

and was observed to be 95.24% for WVO methyl ester and 97.05% for Karanja oil methyl ester. These two peaks were used for conformation of existence of methyl ester in FAME.

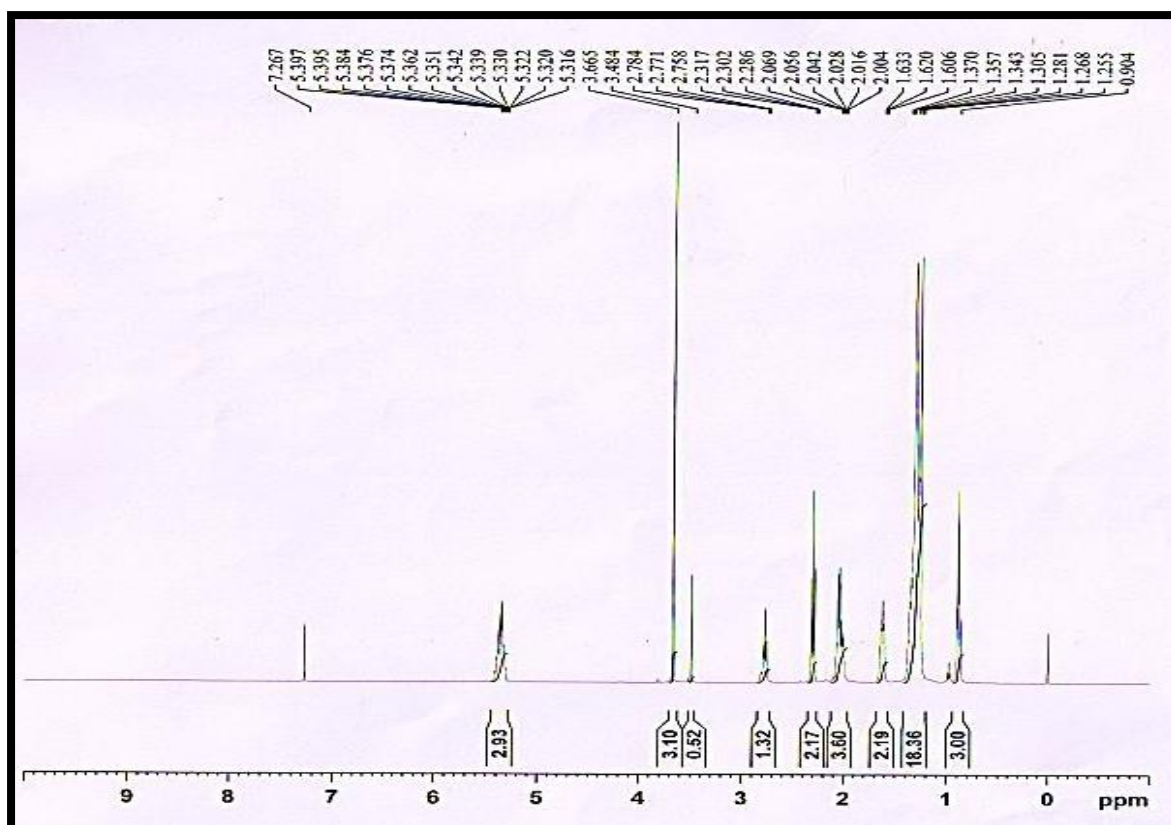


Figure 6.8 ^1H NMR spectrum of WVO FAME obtained at 3.0 wt% $\text{Ca}_2\text{Al}_2\text{O}_5$, 1:21 oil: methanol, 150 min reaction time at 65 °C temperature, 700 rpm stirring speed

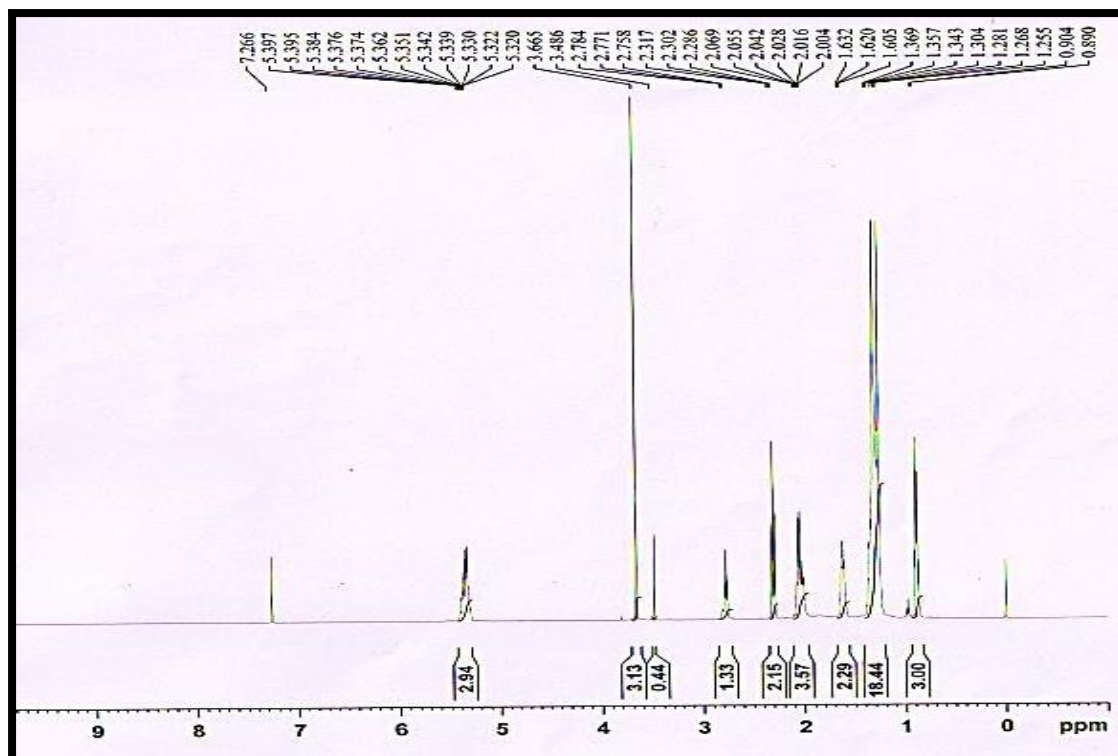


Figure 6.9 ^1H NMR spectrum of Karanja oil FAME obtained at 2.5 wt% $\text{Ca}_2\text{Al}_2\text{O}_5$, 1:18 oil: methanol, 150 min reaction time at 65 °C temperature, 700 rpm stirring speed

6.5 Effect of various reaction parameters on transesterification

The catalyst calcium aluminium oxide ($\text{Ca}_2\text{Al}_2\text{O}_5$) was observed to be effective and was employed for optimization of various reaction parameters for its improved catalytic activity by using waste vegetable oil (WVO) and Karanja oil as feedstock. Systems of transesterification process were carried out in existence of calcium aluminium oxide $\text{Ca}_2\text{Al}_2\text{O}_5$ in order to accomplish the reaction conditions for optimization and reusability of catalyst was also assessed.

6.5.1 Effect of catalyst concentration (wt%)

The influence of catalyst concentration on FAME conversion was explained from 0.5 wt% to 3.5 wt% of oil using 1:21 oil: methanol molar ratio for waste vegetable oil and

1:18 oil: methanol molar ratio for Karanja oil at 65 °C for 150 min at 700 rpm stirring speed (Figure 6.10). The result displays that FAME conversion increases as the concentration of catalyst increases from 0.5 wt% to 3.5 wt%. At 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 and 3.5 wt% catalyst concentration FAME conversion for WVO were $62\pm 0.15\%$, $70.5\pm 0.29\%$, $78.78\pm 0.01\%$, $84.53\pm 0.55\%$, $90.21\pm 0.21\%$, $95.24\pm 0.1\%$, $92.22\pm 0.5\%$ whereas Karanja oil shows FAME conversion of $65.57\pm 0.44\%$, $72.24\pm 0.39\%$, $83.99\pm 0.22\%$, $89.98\pm 0.23\%$, $97.05\pm 0.21\%$, $93.08\pm 0.46\%$ and $90.12\pm 0.03\%$ respectively. Hence, in case of WVO maximum conversion ($95.24\pm 0.1\%$) was achieved at 3.0 wt% concentration and $97.05\pm 0.21\%$ of FAME was accomplished at 2.5 wt% catalytic concentration in Karanja oil. This is caused by rise in active sites of catalyst for transesterification reaction [Mutreja et al., 2014]. Chemical constituent variations obtained in feedstock were responsible for this dissimilarity in optimum FAME conversion. Catalytic concentration of 3.0 wt% for WVO and 2.5 wt% for Karanja oil were chosen for optimization purpose, since afterwards FAME conversion decreased with catalytic concentration due to soap formation which enriches the viscosity of reactant [Sharma and Singh, 2010]. At high catalytic concentration, viscosity of reaction mixture increases and in addition to this, some catalyst remains unexploited caused by resistance during mass transfer, which reduces FAME conversion [Xie and Zhao, 2014].

6.5.2 Effect of molar ratio

The molar ratio of oil: methanol considerably affects both the FAME conversion as well as cost of the FAME production. The effect of oil: methanol molar ratio was studied from 1:6 to 1:24 by keeping other reaction variables constant (Figure 6.11). Excess of methanol is obligatory since it's contributes on the rate of methanolysis. Excess of methanol endorses the formation of methoxide species which leads to shift in equilibrium

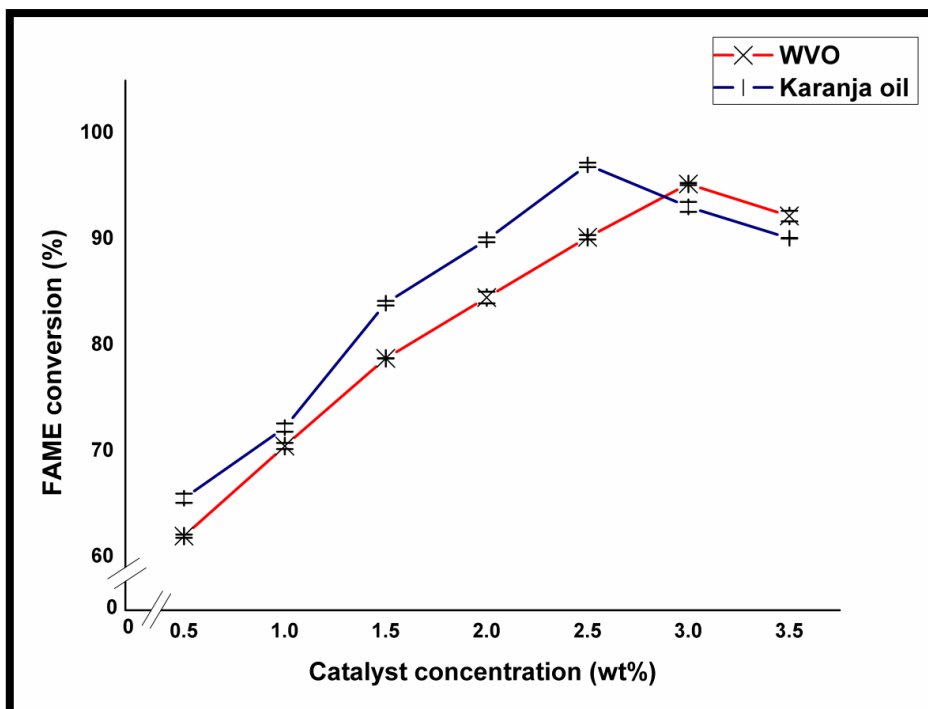


Figure 6.10 Effect of catalyst concentration on FAME conversion (%) of WVO and Karanja oil [temperature 65 °C; time 150 min; stirring speed 700 rpm; molar ratio 1:21 oil: methanol for WVO and 1:18 for Karanja oil]

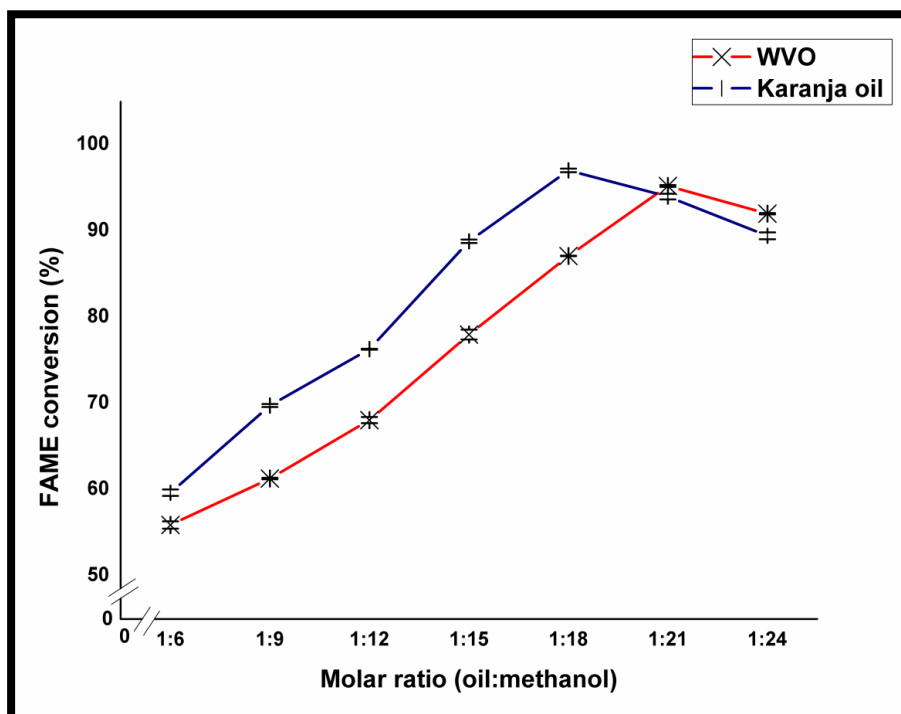


Figure 6.11 Effect of oil: methanol molar ratio on FAME conversion (%) of WVO and Karanja oil [temperature 65 °C; time 150 min; stirring speed 700 rpm; catalyst concentration of 3.0 wt% for WVO and 2.5 wt% for Karanja oil]

in forward direction. Hence, an increase in conversion from 1:6 to 1:24 molar ratio was observed as $55.91\pm 0.42\%$, $61.31\pm 0.09\%$, $68.08\pm 0.36\%$, $77.99\pm 0.57\%$, $87.12\pm 0.03\%$, $95.24\pm 0.1\%$, $92.01\pm 0.08\%$ for WVO, on the other hand Karanja oil shows FAME conversion of $59.66\pm 0.38\%$, $69.77\pm 0.17\%$, $76.31\pm 0.05\%$, $88.82\pm 0.2\%$, $97.05\pm 0.21\%$, $94\pm 0.33\%$, $89.46\pm 0.4\%$ for 1:6, 1:9, 1:12, 1:15, 1:18, 1:21 and 1:24, respectively. Therefore, in case of WVO maximum conversion ($95.24\pm 0.1\%$) was achieved at 1:21 molar ratio and $97.05\pm 0.21\%$ of FAME was accomplished at 1:18 molar ratio in Karanja oil. Upon further increment in molar ratio after optimized reaction condition, FAME conversion starts decreasing because glycerol formed in the product dissolves in the excessive methanol and interferes in the transesterification reaction. In addition to this, glycerol separation becomes difficult; hence equilibrium shift towards backward direction, eventually FAME conversion declines [Xie and Zhao, 2014]. From this 1:21 molar ratio for WVO and 1:18 molar ratio for Karanja oil was chosen for optimization purpose.

6.5.3 Effect of reaction temperature

Transesterification reactions were considerably affected by change in the temperature of reaction mixture [Brennan and Owende, 2010]. Though, involvement of chemical properties of solvent in transesterification, reaction is preferred closer to boiling point of methanol [Yuan et al., 2005] and above the boiling point, yield was reduced due to evaporation of methanol. The influence of reaction temperature was studied from 35 °C to 75 °C at the interval of 10 °C by other constant reaction variables condition as shown in Figure 6.12. Extensive increment in FAME conversion observed at 35 °C, 45 °C, 55 °C and 65 °C as $54.56\pm 0.61\%$, $66.91\pm 0.34\%$, $79.33\pm 0.13\%$, $95.24\pm 0.1\%$ for WVO while $56.88\pm 0.6\%$, $68\pm 0.26\%$, $82.1\pm 0.17\%$ and $97.05\pm 0.21\%$ for Karanja oil. This result of

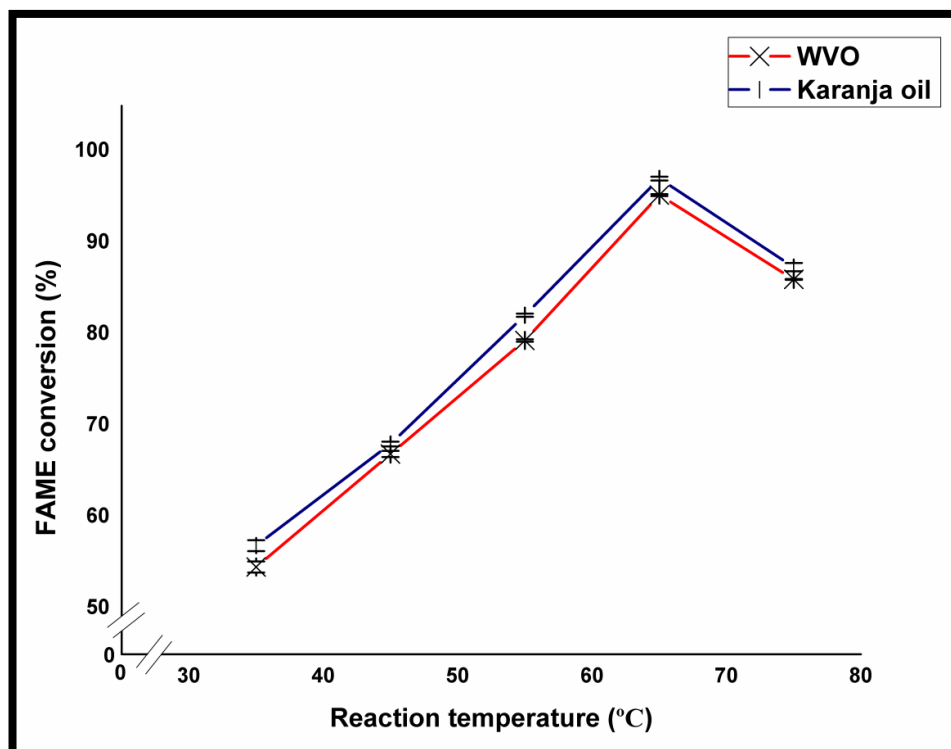


Figure 6.12 Effect of reaction temperature on FAME conversion (%) of WVO and Karanja oil [time 150 min; stirring speed 700 rpm; 1:21 oil: methanol molar ratio, catalyst concentration of 3.0 wt% for WVO and 1:18 oil: methanol molar ratio, 2.5 wt% catalyst for Karanja oil]

transesterification reaction with temperature can be described due to endothermic reaction [Samart et al., 2009]. The maximum FAME conversion of $95.24 \pm 0.1\%$ and $97.05 \pm 0.21\%$ was obtained at $65\text{ }^{\circ}\text{C}$ reaction temperature for both WVO and Karanja oil respectively. After this optimum temperature, as reaction temperature rises to $75\text{ }^{\circ}\text{C}$ the conversion of FAME drops to $86.01 \pm 0.04\%$ in WVO and $87.35 \pm 0.45\%$ in Karanja oil, this was due to at high temperature, methanol was rapidly evaporated after its boiling temperature to form bubbles hence obstructs the reaction by making interface of two phase [Chai et al., 2007]. Low temperature selection is desired to save the energy necessity and thus optimum reaction temperature achieved for FAME conversion was $65\text{ }^{\circ}\text{C}$.

6.5.4 Effect of reaction time

The effect of reaction time on FAME conversion was studied as illustrated in Figure 6.13. As reaction time increased from 30 min to 180 min, FAME conversion was also increased. FAME conversion of $55.71\pm 0.26\%$, $62.69\pm 0.47\%$, $77.89\pm 0.47\%$, $87.28\pm 0.41\%$, $95.24\pm 0.1\%$, $95.3\pm 0.15\%$ for WVO, whereas $57.18\pm 0.12\%$, $63.11\pm 0.54\%$, $79.69\pm 0.38\%$, $89.28\pm 0.21\%$, $97.05\pm 0.21\%$ and $97\pm 0.26\%$ for Karanja oil for 30, 60, 90, 120, 150 and 180 min, respectively. Maximum conversion of FAME was attained at optimized reaction parameters with time 150 min. Further increase in reaction time for 180 min does not affect the conversion and it almost remains stable (Figure 6.13). Subsequent rise in time longer than 150 min did not change the FAME conversion, as the transesterification is reversible reaction and equilibrium was attained at that time. Hence, 150 min of reaction time was chosen for optimization purpose.

6.5.5 Effect of stirring speed

Alcohol, oil and heterogeneous catalyst, these are immiscible phases therefore to improve exchange between the catalytic active site and reactant, stirring plays a substantial role by excluding mass transfer influence on FAME conversion. As shown in Figure 6.14, steady rise in FAME conversion with increase in stirring speed starting from 200 rpm to 700 rpm at the interval of 100 rpm as $56.33\pm 0.71\%$, $59.44\pm 0.4\%$, $66.14\pm 0.39\%$, $78.05\pm 0.54\%$, $89.69\pm 0.1\%$, $95.24\pm 0.1\%$ for WVO however $57.04\pm 0.45\%$, $59.99\pm 0.26\%$, $68.56\pm 0.57\%$, $80.01\pm 0.17\%$, $90.98\pm 0.24\%$ and $97.05\pm 0.21\%$ for Karanja oil this shows that reaction rate was regulated by external mass diffusion. Above 700 rpm, no significant increase in rate of reaction and FAME conversion was obtained. The conversions were $95\pm 0.2\%$ and $96.59\pm 0.38\%$ for WVO and Karanja oil at 800 rpm. All experiments were performed at optimum 700 rpm to eliminate mass transfer limitation.

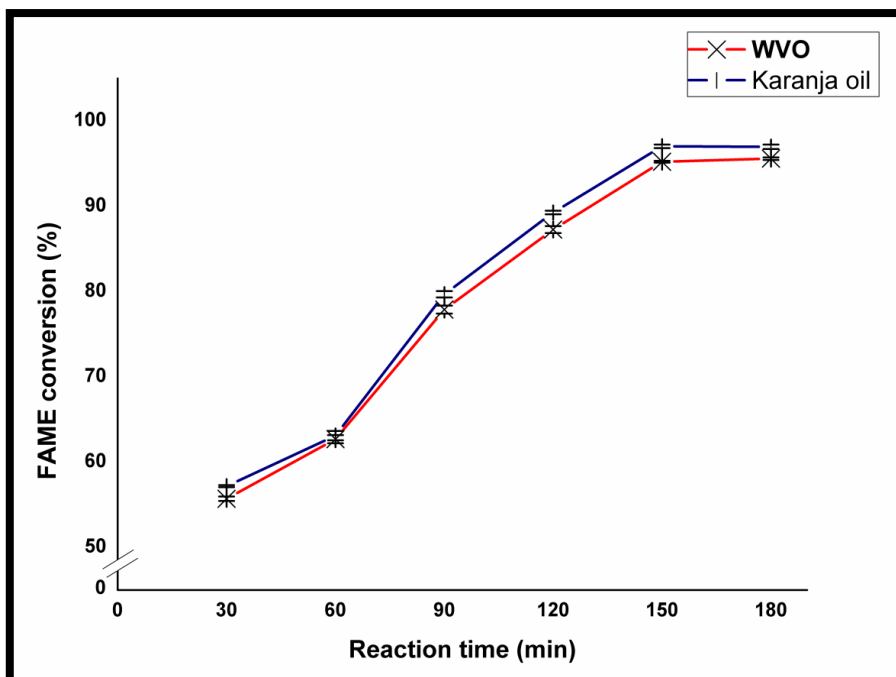


Figure 6.13 Effect of reaction time on FAME conversion (%) of WVO and Karanja oil [temperature 65 °C; stirring speed 700 rpm; 1:21 oil:methanol molar ratio, catalyst concentration of 3.0 wt% for WVO and 1:18 oil:methanol molar ratio, 2.5 wt% for Karanja oil]

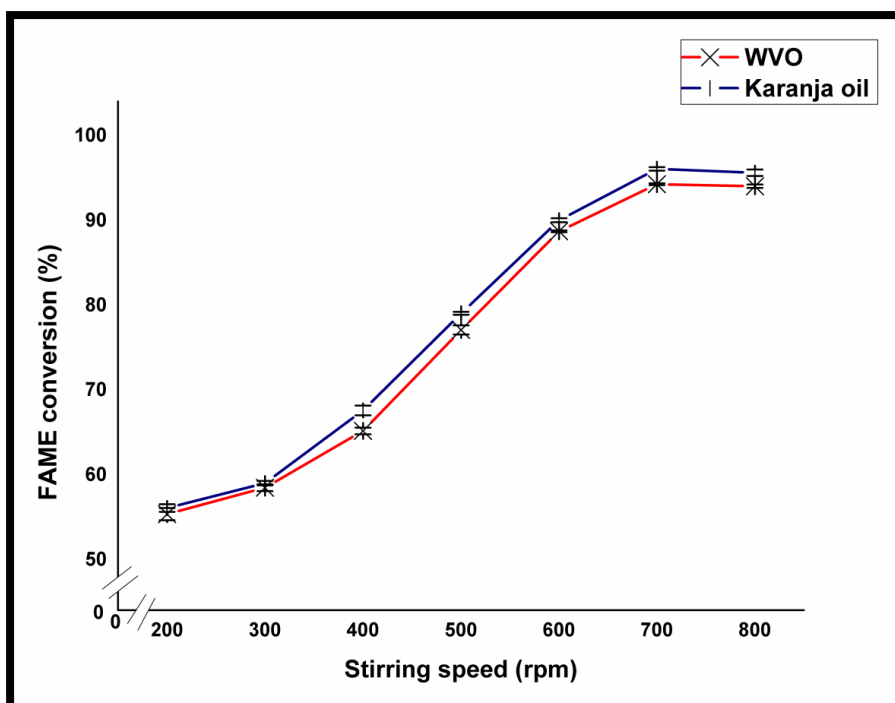


Figure 6.14 Effect of stirring speed on FAME conversion (%) of WVO and Karanja oil [time 150 min; temperature 65 °C; 1:21 oil:methanol molar ratio, catalyst concentration of 3.0 wt% for WVO and 1:18 oil:methanol molar ratio, catalyst concentration of 2.5 wt% for Karanja oil]

6.5.6 Effect of catalyst reusability

Separation limitation of homogeneous catalyst responsible for its ineffectual reuse, however, heterogeneous catalyst can be reused several times. Catalytic activity declines when catalytic surface was surrounded by the product which ultimately reduces the contact of catalytic surface and reactant [Sun et al., 2010]. Catalyst reusability was tested for seven runs by using 3.0 wt% catalyst for WVO and 2.5 wt% of catalyst for Karanja oil at optimized reaction parameters of molar ratio, reaction temperature, time and stirring speed at each step as shown in Figure 6.15. After each successful run, calcium aluminate was washed by using hot methanol to remove organic impurities remaining on the catalytic surface. After that, it was dried in hot air oven at 120 °C for 3-4 h followed by calcination at 600 °C for 2 h.

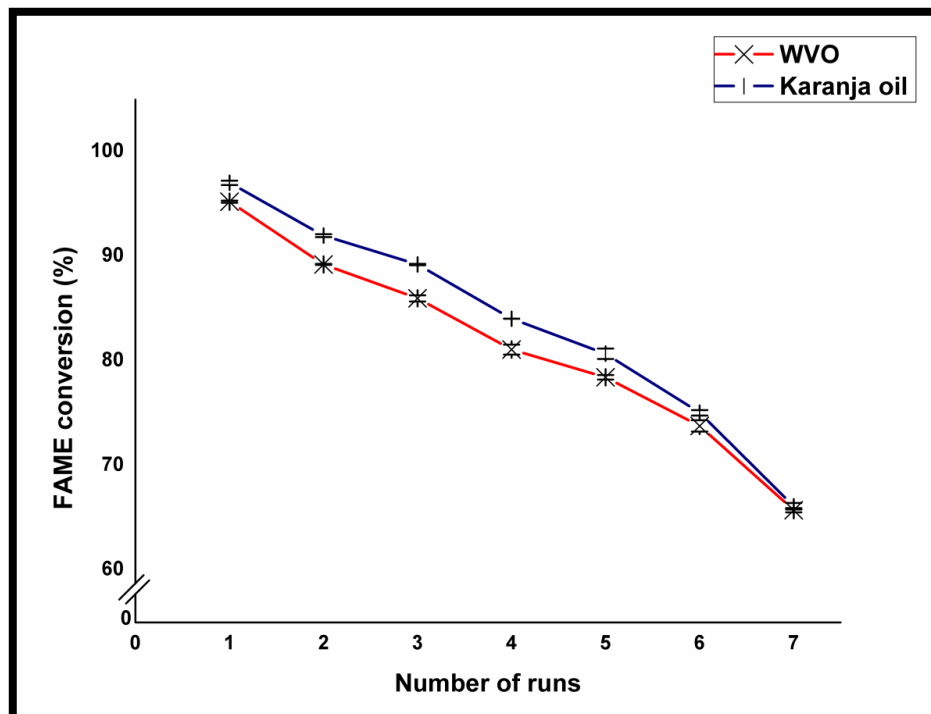


Figure 6.15 Calcium aluminate ($\text{Ca}_2\text{Al}_2\text{O}_5$) reusability analysis up to seven runs [temperature 65 °C for 150 min and 700 rpm stirring speed; 1:21 M ratio of oil:methanol at 3.0 wt% of catalyst for WVO and 1:18 M ratio of oil:methanol at 2.5 wt% catalyst for Karanja oil]

From Figure 6.15, it has been confirmed that activity of catalyst continuously decreased up to seven cycles and achieved >65% of FAME conversion. From first cycle to seven cycles as we got FAME conversion of 95.24±0.1%, 89.24±0.05%, 86±0.3%, 81.1±0.47%, 78.45±0.22%, 73.8±0.54%, 65.73±0.2%, for WVO whereas 97.05±0.21%, 92±0.14%, 89.23±0.07%, 84.05±0.01%, 80.71±0.5%, 75.05±0.26%, 66.11±0.31% in Karanja oil. Therefore, calcium aluminate can be reused in transesterification reaction for seven runs due to its better activity.

6.6 Characteristics of FAME synthesized from WVO and Karanja oil

Physicochemical properties of FAME derived from waste vegetable oil and Karanja oil were scrutinized and accomplished as per ASTM D6751 [Tariq et al., 2011] standards and are shown in Table 6.3. Fuel property of WVO methyl ester and Karanja oil methyl ester at optimized conditions has been detected from following ASTM standards.

Table 6.3 Physicochemical properties of WVO methyl ester and Karanja oil methyl ester

Parameters	ASTM test Method used	WVO methyl ester	Karanja oil methyl ester
Acid value (mg KOH/g)	D664-07	0.8	0.51
Density (40 °C, g cm ⁻³)	D1448-1972	0.864	0.849
Kinematic viscosity (cSt at 40 °C)	D445	3.78	3.31
Cetane number	D613	48	47
Calorific value (MJ/Kg)	D6751/ DIN51900	37.98	39.54
Flash point (°C)	D93	138	141
Fire point (°C)	D93	149	152
Cloud point (°C)	D2500	6	5
Pour point (°C)	D97-05	7	4
Ash content (%)	D482	0.03	0.02

The acid value of WVO methyl ester and Karanja oil methyl ester was observed to be 0.8 mg of KOH/g and 0.51 mg of KOH/g respectively and were within ASTM standards. Density is directly correlated to viscosity and in addition to this, transesterification reaction decreases its viscosity which effects on fuel injection property. The density and kinematic viscosity of WVO FAME were observed as 0.864 g cm⁻³ and 3.78 cSt at 40 °C respectively and also within ASTM range for biodiesel. On the other hand, density and kinematic viscosity of Karanja oil FAME were observed to be 0.849 g cm⁻³ and 3.31 cSt at 40 °C and within ASTM limit of biodiesel.

Cetane number of FAME was observed to be 48 and 47 for WVO and Karanja oil as per ASTM standard D613. Cetane number of the biodiesel plays an important role for fuel quality, combustion quality along with ignition delay time; thus for better engine performance, cetane number should be in good agreement. The calorific value of the FAME was observed to be 37.98 MJ/kg and 39.54 MJ/kg respectively. Flash point as well as fire point was observed to be 138 °C; 149 °C and 141 °C; 152 °C respectively for WVO methyl ester and Karanja oil methyl ester, which is within safe limit for transportation and storage. Cloud point and pour point were found to be 6 °C; 7 °C and 5 °C; 4 °C respectively. Ash content obtained for WVO methyl ester was 0.03% while, Karanja oil methyl ester displays ash content of 0.02% which was within ASTM limits. Biodiesel produced from WVO and Karanja oil absolutely satisfied with biodiesel standard. This endorses that catalyst used in the present study has significant potential on industrial scale biodiesel production.

6.7 Conclusion

Calcium aluminate ($\text{Ca}_2\text{Al}_2\text{O}_5$), as heterogeneous catalyst has been synthesized by solid state method and characterized by TGA, XRD, ATR-FTIR, SEM, EDS, BET surface area, BJH analysis, particle size and basicity techniques. Calcium aluminate ($\text{Ca}_2\text{Al}_2\text{O}_5$) was ascertained to be an efficient catalyst for transesterification of waste vegetable oil and Karanja oil as feedstock. Various reaction parameters were studied to achieve optimized reaction conditions. Under optimized conditions of transesterification WVO at molar ratio of 1:21 oil: methanol, 3.0 wt% catalytic concentration, 65 °C reaction temperature, 150 min time of reaction and 700 rpm of stirring speed FAME conversion was $95.24 \pm 0.1\%$, whereas Karanja oil shows FAME conversion of $97.05 \pm 0.21\%$ at 1:18 oil: methanol molar ratio, 2.5 wt% catalyst, 65 °C reaction temperature, 150 min time of reaction and 700 rpm of stirring speed. The catalyst used, calcium aluminate ($\text{Ca}_2\text{Al}_2\text{O}_5$) has been recovered and recycled up to seven runs with $>65\%$ of FAME conversion. Physicochemical property of WVO methyl ester and Karanja oil methyl ester have been deliberated and observed within ASTM standards range. From these studies it has been affirmed that calcium aluminate ($\text{Ca}_2\text{Al}_2\text{O}_5$) could be a fascinating substitute catalyst for production of economically viable biodiesel.