

CHAPTER 7

Synthesis and characterization of beta-tricalcium phosphate ($\beta\text{-Ca}_3(\text{PO}_4)_2$) derived from waste guinea fowl bone and its application in biodiesel production from waste vegetable oil (WVO) and *Pongamia pinnata* (Karanja) oil

7.1 Introduction

The synthesis and characterization of waste guinea fowl bone derived heterogeneous catalyst was reported in this chapter. Synthesized catalyst was characterized by thermo-gravimetric analysis (TGA), X-ray diffraction (XRD), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), Brunauer-Emmett-Teller (BET) surface area analysis, Barrett-Joyner-Halenda (BJH) analysis, particle size analysis and basicity. The catalyst was used for biodiesel production through transesterification reaction of waste vegetable oil (WVO) and (*Pongamia pinnata*) Karanja oil. Numerous reaction parameters such as catalyst concentration, molar ratio, reaction temperature, reaction time, stirring speed and catalyst reusability were considered. Synthesized biodiesel was characterized by ^1H NMR and physicochemical properties were also reported as per ASTM standards.

7.2 Synthesis of waste guinea fowl bone derived catalyst

The guinea fowl bones collected from restaurant were initially washed with boiled water several times about 15 min to remove tissues and fats attached with the bone pieces. Then the pieces were dried in hot air oven at 110 °C for 15 h to eliminate water content and moisture present in the bone before grinding. Later on these cleaned bones were ground in ball mill for 2 h and sieved by using British Sieve Size (BSS) 50 having 310 μm mesh size to obtain fine powder. This powder material was calcined at 900 °C for 5 h in muffle furnace. Calcined catalyst was then ground by pestle and mortar and sieved to achieve fine powder form. Prepared catalyst was placed in desiccator for further application. The schematic for synthesis of catalyst has been shown in Figure 7.1.

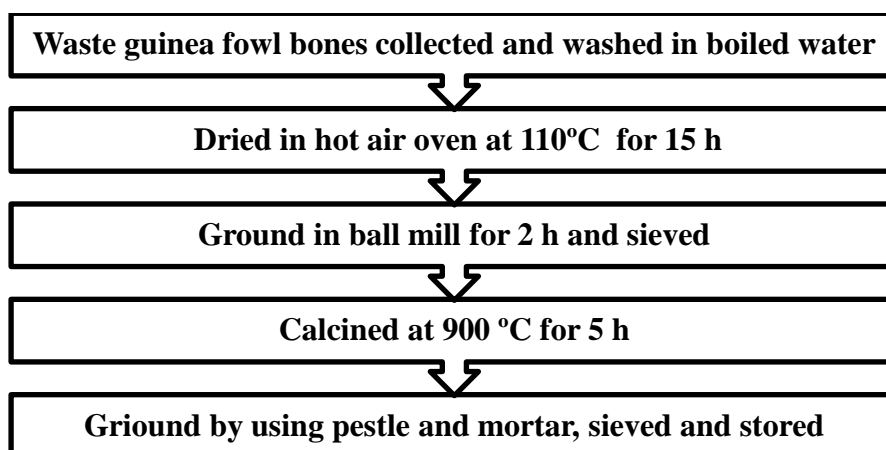


Figure 7.1 Synthesis of waste guinea fowl bone derived catalyst

7.3 Characterization of waste guinea fowl bone derived catalyst

7.3.1 Thermogravimetric analysis (TGA)

The TGA analysis of uncalcined material was performed in the range of 40 °C to 1000 °C to analyse decomposition behaviour of raw guinea fowl bones. The thermal characteristics have been studied by TGA curve as shown in Figure 7.2. Heating of the material was done at the rate of 20 °C/min. A weight loss of 53.99 wt% was observed up to 900 °C and after that it was almost constant which indicates that the decomposition temperature was attained. TGA curve shows four successive weight losses starting from 40 °C. First weight loss has been observed in the temperature ranged from 40 °C to 200 °C specifies the evaporation of adsorbed water and was 5.98 wt%. Second weight loss starting from 200 °C to 400 °C may be ascribed to exclusion of proteins and collagen which are organic moiety obtained in the sample which was 26.5 wt% [Dimovic et al., 2009]. Next peak is attributed to further elimination of organic matters which is observed

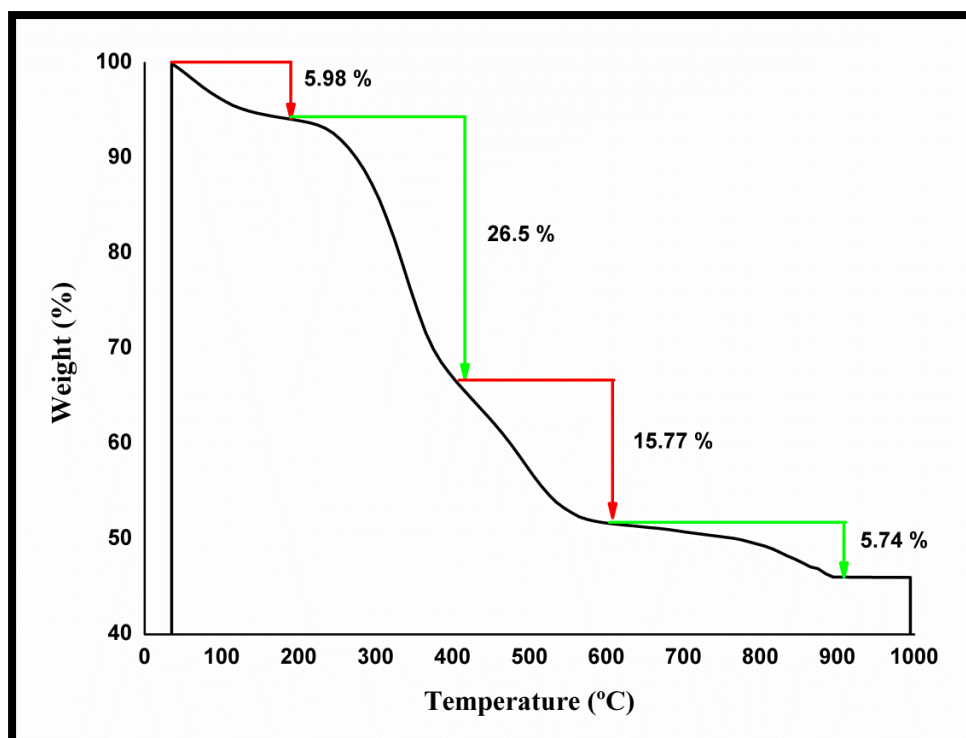


Figure 7.2 TGA curve of raw waste guinea fowl bone

in between 400 °C to 600 °C and the last weight loss has been observed in the range of 600 °C to 900 °C, was comparatively small which may be due to release of gaseous elements to form hydroxyapatite consisted inorganic residues and were 15.77 wt% and 5.73 wt% respectively [Chakraborty et al., 2011]. Calcium carbonate was converted into calcium oxide by liberation of carbon dioxide at this temperature [Deydier et al., 2005]. Further weight loss has not been observed above 900 °C and curve remains constant confirming accomplishment of decomposition process. Hence, calcination was performed at 900 °C for further reaction process. Alternatively, animal bones beyond 1000 °C calcination increases sintering effect which results into catalytic activity reduction by dropping the surface area [Resende et al., 2006].

7.3.2 X-ray diffraction (XRD)

Figure 7.3 illustrated the XRD patterns of catalyst derived from guinea fowl bone. XRD is the inimitable technique to study the crystallinity of the sample. It has been observed that intense peaks for calcined sample were associated with Joint Committee on Powder Diffraction Standards (JCPDS). The peaks at 10.94° , 21.64° , 25.94° , 32.83° , 34.74° , 39.69° , 41.93° , 46.55° , 48.00° , 49.59° , 50.40° , 52.06° , 59.81° , 62.42° , 65.08° attributed to presence of hydroxyapatite and matches with JCPDS file No. 09-0432 [Chakraborty et al., 2011; Sobczak et al., 2009]. Whereas, peaks at 27.96° , 28.97° , 31.71° and 51.18° were ascribed to presence of beta tricalcium phosphate ($\beta\text{-Ca}_3(\text{PO}_4)_2$) phase JCPDS card No. 09-0169, and thus ratifies that the alteration of beta tricalcium phosphate ($\beta\text{-Ca}_3(\text{PO}_4)_2$) from hydroxyapatite might show basic characteristic in transesterification reaction.

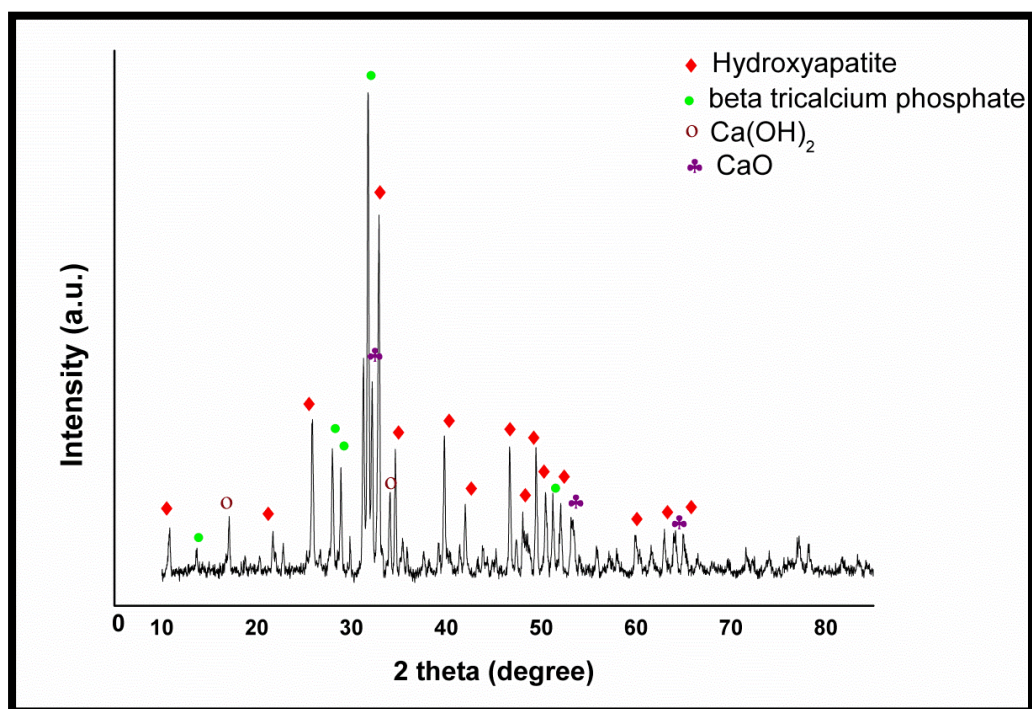


Figure 7.3 XRD pattern of the calcined waste guinea fowl bone

Intensification of XRD peaks were observed in case of calcined sample ascribed to crystalline structure of beta tricalcium phosphate ($\beta\text{-Ca}_3(\text{PO}_4)_2$) as compared with uncalcined sample [Rajesh et al., 2012]. The peaks at 17.28° and 34.10° confirmed the presence of $\text{Ca}(\text{OH})_2$ phase (JCPDS card No. 00-004-0733). The characteristic peak for CaO has been confirmed by observing peaks at 32.19° , 53.12° and 64.55° (JCPDS 00-037-1497) [Chen et al., 2014]. There was no diffraction peak observed for CaCO_3 (JCPDS card No. 00-047-1743) in calcined sample as CaCO_3 has negative impact on transesterification reaction hence can be proved to be active catalyst [Xu et al., 2001].

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

Attenuated total reflectance Fourier transform infrared spectra (ATR-FTIR) of the calcined guinea fowl bone catalyst has been carried out for assimilation of numerous phases. FTIR spectra shown in Figure 7.4 depict presence of constituents in the guinea

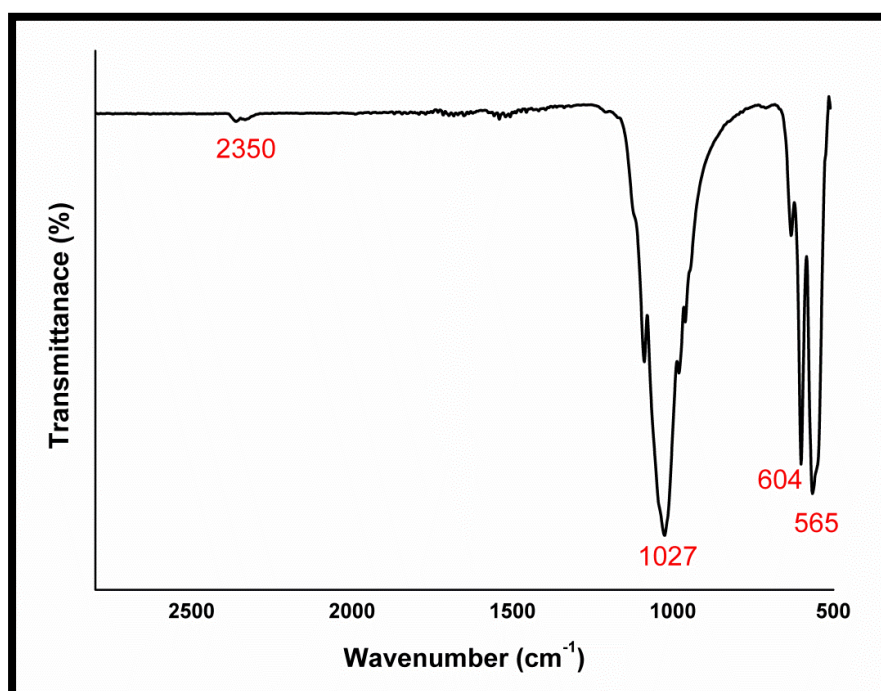


Figure 7.4 ATR-FTIR spectra of calcined waste guinea fowl bone

fowl bone which were obtained after calcination. FTIR analysis of calcined guinea fowl bone was accomplished in Figure 7.4. The absorption bands obtained at 565, 604, 1027 cm^{-1} were due to the presence of different vibrations of PO_4^{3-} group [Sobczak et al., 2009]. Small peak observed around 2350 cm^{-1} was because of presence of atmospheric carbon dioxide [Boschini et al., 2009].

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

Brunauer–Emmett–Teller (BET) surface area of guinea fowl bone derived catalyst was performed to determine surface area, pore volume and pore size. BET surface area was observed to be 23.48 m^2/g and Langmuir Surface Area was obtained as 61.08 m^2/g . BJH adsorption and desorption cumulative surface area of pores were 21.326 m^2/g and 22.199 m^2/g respectively. Pore volume obtained at single point adsorption was 0.0297 cm^3/g as well as BJH adsorption and desorption cumulative pore volumes were 0.0257 cm^3/g and 0.0261 cm^3/g respectively. Adsorption average pore width (4V/A by BET) was 50.5683 Å. BJH adsorption and desorption pore size was perceived as 48.122 Å and 47.017 Å.

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

Scanning electron microscope (SEM) analysis was accompanied to assimilate the surface morphology of calcined guinea fowl bone derived catalyst. SEM photomicrograph of catalyst was shown in Figure 7.5. SEM studies on the powder morphology of the synthesized guinea fowl bone catalyst showed that calcined powder particles are irregular in shape by forming aggregates and hence its surface area was higher [Viriyā-Empikul et al., 2012]. The tiny particles in calcined sample were merged together and formed large agglomerates due to oxide formation as shown in Figure 7.5.

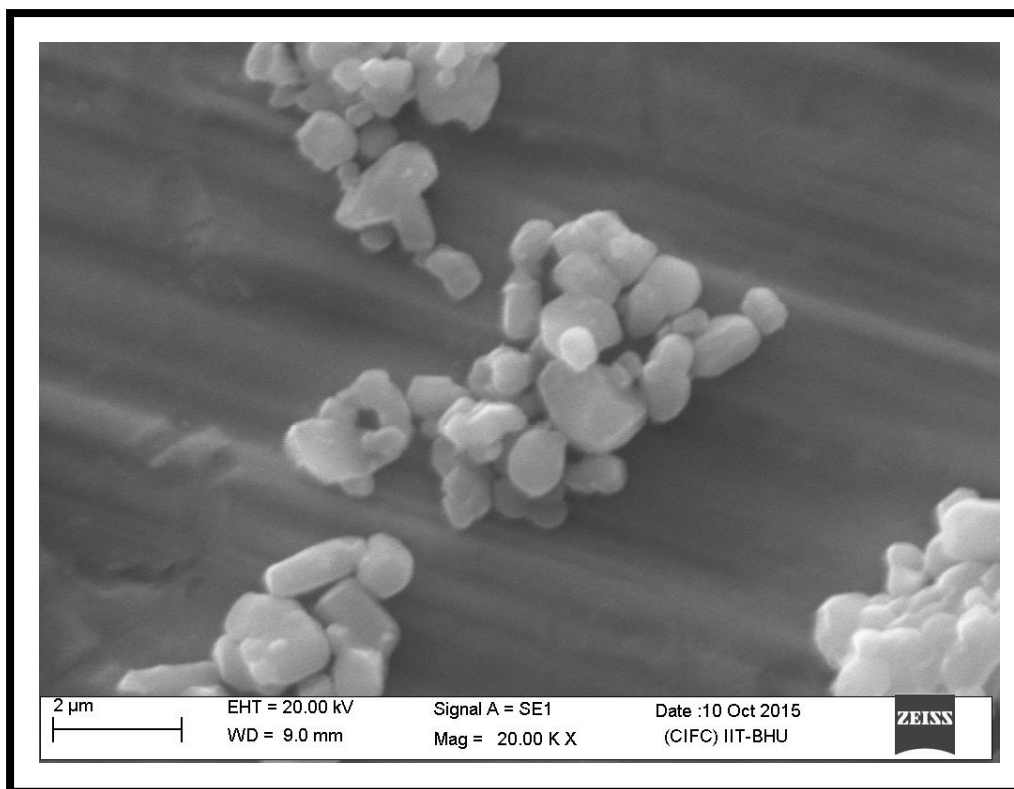


Figure 7.5 SEM image of calcined guinea fowl bone

Structural change in bone may be due to compositional changes occurred during calcination. Calcium carbonate presented in uncalcined sample was decomposed into calcium oxide during calcination by releasing carbon dioxide.

The EDS associated to the scanning electron microscope (SEM) and these two techniques were commonly used together. The EDS analysis was performed to determine the chemical composition of the guinea fowl derived catalysts and identify elements present on the surface. The compositional analysis result was epitomizing in the form of histogram of energy vs. signal strength and allied to concentration as shown in Figure 7.6. It has been observed that calcium was the major element presented in all bones derived catalysts. Other elements appeared in minor amounts.

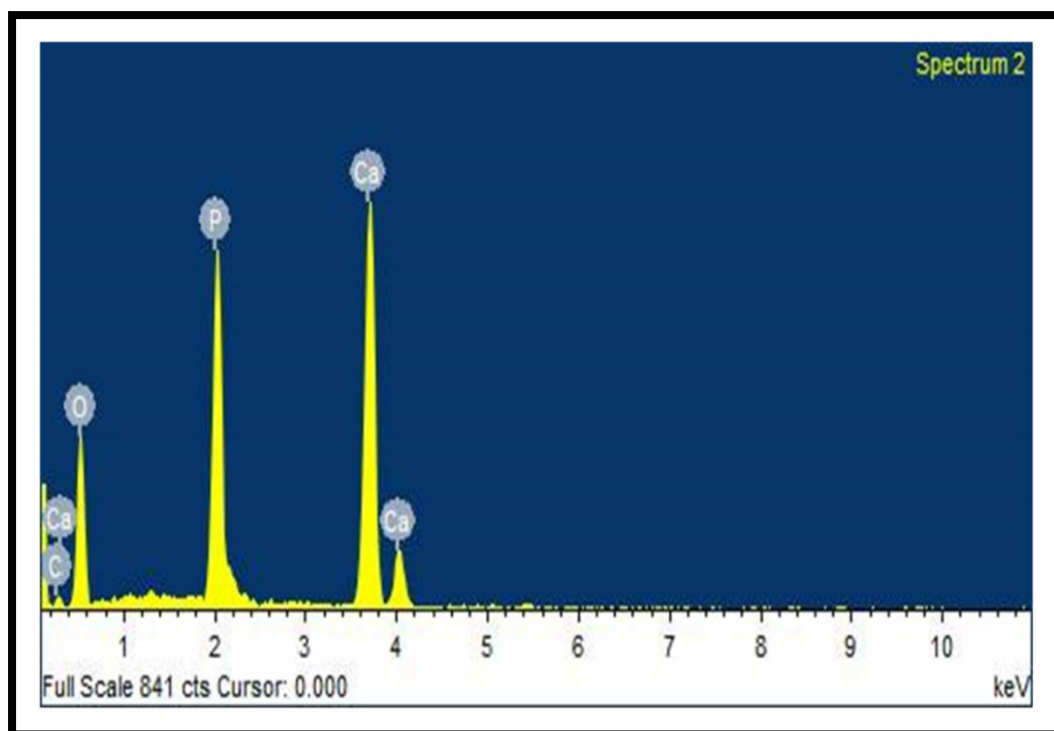


Figure 7.6 EDS image of calcined guinea fowl bone

Table 7.1 clearly shows that calcined guinea fowl bone consist of 16.70 wt % Carbon, 44.76 wt% oxygen, 13.87 wt% phosphorous and 24.67 wt% calcium confirming the formation of hydroxyapatite [Obadiah et al., 2012].

Table 7.1 Element weight % present in calcined guinea fowl bone sample

Elements	Weight (%)	Atomic (%)
C	16.70	26.47
O	44.76	53.28
P	13.87	8.52
Ca	24.67	11.72
Total	100.00	100.00

7.3.6 Particle size analysis

Figure 7.7 shows the particle size distribution of the catalyst. Particle size was calculated by using image-J software from SEM image. Graph has plotted between ‘diameters of particle vs number of particles’. From this Figure 7.7 it has been observed that maximum particle size was in the range of 0.6 μm to 0.8 μm .

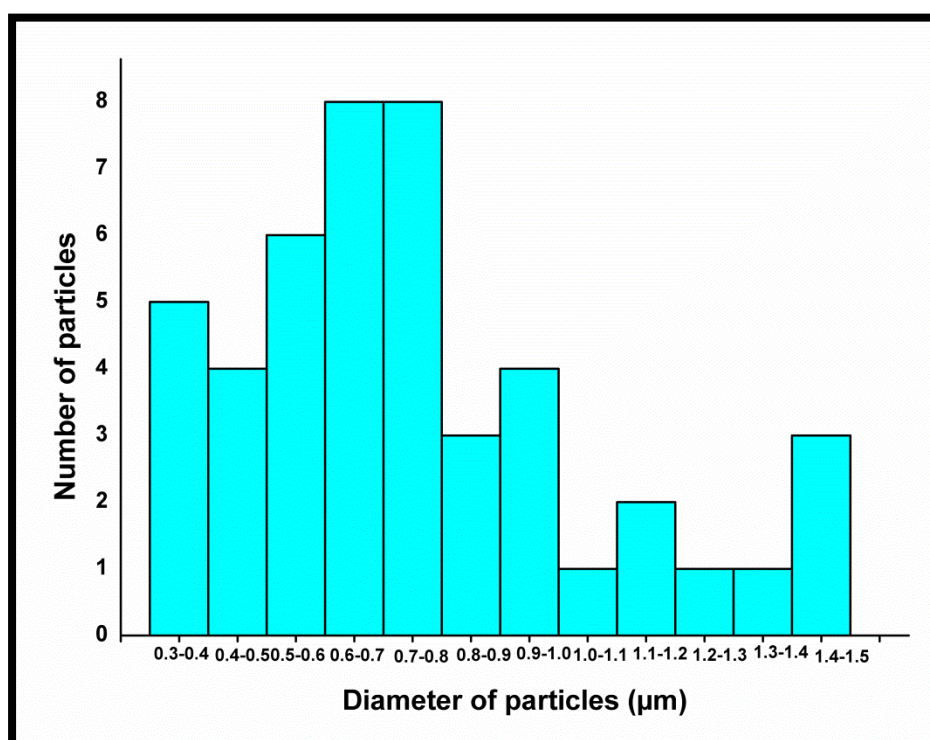


Figure 7.7 Particle size distribution of the catalyst

7.3.7 Basicity

Strength of basic sites plays consequential role in catalytic activity for transesterification reaction [Yan et al., 2009]. Presence of oxide ions was responsible for basic strength of catalyst which acts as Lewis base existing on metal oxide surface [Kaur and Ali, 2015]. Strength of basic site of guinea fowl bone derived catalyst was achieved

by Hammett indicator benzene carboxylic acid titration. Titration was conducted in presence of 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 5.2. Total basicity of guinea fowl bone derived catalyst was calculated as 2.09 mmol/g.

Table 7.2 Basicity of calcined guinea fowl bone

S. No.	Indicators	Basicity (mmol/g of catalyst)
1	Neutral red $pK_{BH^+} = 6.8$	0.14
2	Bromothymol blue $pK_{BH^+} = 7.2$	0.29
3	Phenolphthalein $pK_{BH^+} = 9.3$	0.4
4	Nile blue $pK_{BH^+} = 10.1$	0.58
5	Trapeolin $pK_{BH^+} = 11.1$	0.46
6	2,4- Dinitroaniline $pK_{BH^+} = 15.0$	0.22
	Total basicity	2.09

7.4 Biodiesel production via transesterification and its analysis

Waste vegetable oil (WVO) was filtered to remove suspended materials and dried for 2 h at 105 °C in hot air oven to exclude moisture from oil. Acid value was estimated as per ASTM standards and found to be 2.36 mg KOH/g and was below 4 mg KOH/g and hence direct transesterification was conducted for biodiesel production. On the other hand, 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 performed in 250 ml three neck round bottom flask fitted out with mechanical stirrer, condenser and

thermometer in hot water bath. Methanol and catalyst (varied from 1.0 wt% to 5.0 wt% of oil) was heated in water bath at 45 °C for 30 min through continuous stirring for catalyst activation. After that, oil was added to this mixture and refluxed at 65 °C for 180 min with continuous stirring of 700 rpm. Mixture was transferred in separating funnel for overnight; three separate phases of methyl ester (top), glycerol (middle) and catalyst (bottom) layers were attained. Catalyst was separated and reused for further experiments after its activation. Excess methanol and moisture present in methyl ester was removed by using rotary evaporator [Birla et al., 2012] and by passing through anhydrous Na₂SO₄ [Sharma and Singh, 2009] respectively. Ester conversion in waste vegetable oil methyl ester and Karanja oil methyl ester was calculated by ¹H NMR (Equation 3.1).

In present study, optimization has been performed with varying oil: methanol molar ratio from 1:6 to 1:24 by taking 1.0 wt% to 5.0 wt% of catalyst. The reaction time varied from 30 min to 210 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 considered up to seven runs. All the experiments were performed thrice and uncertainties were studied. Physicochemical properties of waste cooking oil methyl ester as well as Karanja oil methyl ester were reported.

¹H NMR spectrum of WVO and Karanja oil derived FAME at optimum reaction condition was represented in Figure 7.8 and 7.9 correspondingly. The FAME conversion of WVO and Karanja oil was calculated by considering integrated values of signal at 3.664 ppm (methoxy group of FAME i.e. A_{ME}) and 2.286 ppm (methylene group i.e. A_{CH₂}). Conversion was calculated as follows:

$$\text{FAME conversion of WVO(\%)} = (2 \times 3.00 / 3 \times 2.15) \times 100 = 93.02\% \quad \dots \text{(Equation 7.1)}$$

$$\text{FAME conversion Karanja oil(\%)} = (2 \times 3.03 / 3 \times 2.13) \times 100 = 94.84\% \quad \dots \text{(Equation 7.2)}$$

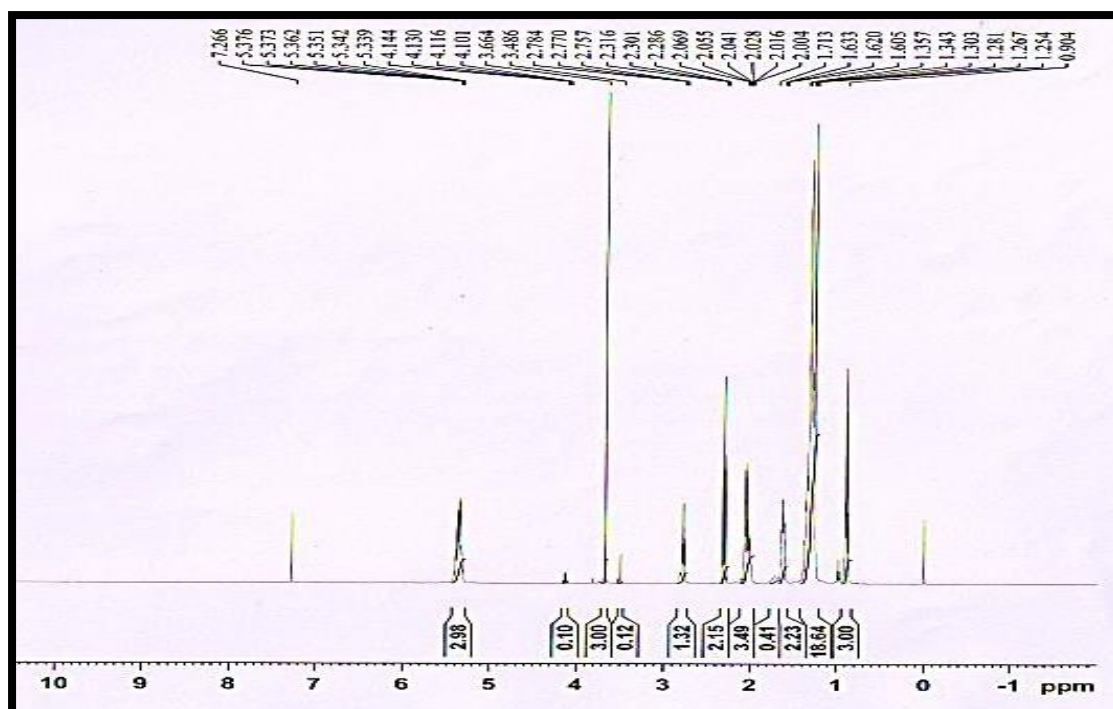


Figure 7.8 ^1H NMR spectrum of WVO FAME obtained at 4.0 wt% ($\beta\text{-Ca}_3(\text{PO}_4)_2$), 1:21 oil: methanol, 180 min reaction time at 65 °C temperature, 700 rpm stirring speed

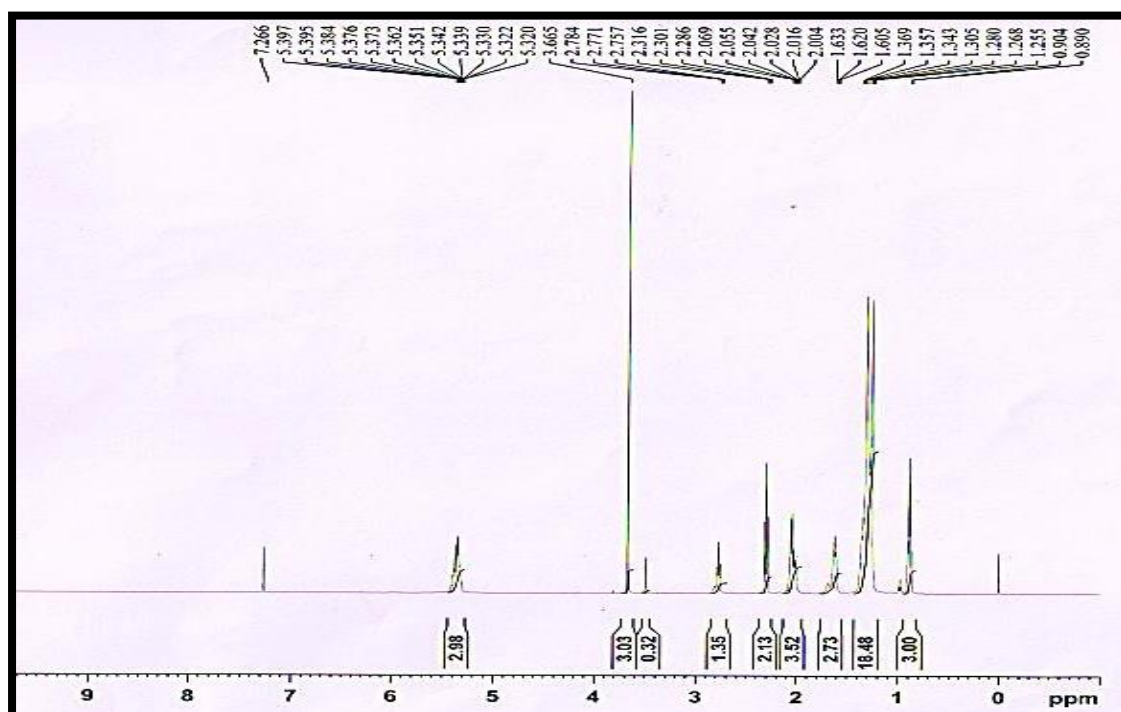


Figure 7.9 ^1H NMR spectrum of Karanja oil FAME obtained at 4.0 wt% ($\beta\text{-Ca}_3(\text{PO}_4)_2$), 1:18 oil: methanol, 180 min reaction time at 65 °C temperature, 700 rpm stirring speed

and was observed to be 93.02% for WVO methyl ester and 94.84% for Karanja oil methyl ester. These two peaks were used for conformation of existence of methyl ester in FAME.

7.5 Effect of various reaction parameters on transesterification

The guinea fowl bone derived catalyst was observed to be capable and used for optimization of several reaction parameters for its better catalytic activity by using waste vegetable oil (WVO) and Karanja oil as feedstock. Transesterification reaction was carried out in existence of guinea fowl bone derived catalyst in order to achieve the reaction conditions for optimization of reaction parameters and reusability of catalyst was also evaluated.

7.5.1 Effect of catalyst concentration (wt%)

Influences of catalyst amount on FAME conversion were scrutinized in the range of 1.0 wt% to 5.0 wt% by using molar ratio of 1:21 oil:methanol for WVO and 1:18 oil:methanol for Karanja oil at 65 °C for 180 min, 700 rpm stirring speed (Figure 7.10). Results clearly designated that FAME conversion was increased as catalyst concentration increased from 1.0 wt% to 4.0 wt% and the maximum conversion was achieved at 4.0 wt%. This proposes that increment in catalytic active sites is responsible for increase in FAME conversion in transesterification reaction. At 1.0, 2.0, 3.0, 4.0 and 5.0 wt% catalyst amount FAME conversion for WVO were $61\pm 0.55\%$, $76\pm 0.39\%$, $84.77\pm 0.1\%$, $93.02\pm 0.6\%$, $90.21\pm 0.41\%$, whereas Karanja oil displays FAME conversion of $62.56\pm 0.49\%$, $76.84\pm 0.61\%$, $85.99\pm 0.22\%$, $94.84\pm 0.51\%$ and $91\pm 0.33\%$ respectively. Henceforward, WVO and Karanja oil both show maximum conversion ($93.02\pm 0.6\%$ and $94.84\pm 0.51\%$) at 4.0 wt% catalytic concentration respectively. Chemical component distinctions in feedstock were liable for this difference in FAME conversion. Catalytic

concentration of 4.0 wt% was chosen for optimization purpose since FAME conversion declined with increase in catalytic concentration caused by soap formation which increases viscosity of reactant [Sharma and Singh, 2010]. At high catalytic amount, viscosity of reaction mixture rises as well as unused catalyst causes resistance during mass transfer, which decreases FAME conversion. Subsequently 4.0 wt% of catalyst was opted for optimization purpose.

7.5.2 Effect of molar ratio

As transesterification is reversible reaction, additional methanol is obligatory to increase reaction rate and favours forward transesterification reaction. Consequence of methanol on FAME conversion was studied in the range of 1:6 to 1:24 molar ratio of oil: methanol at 65 °C, 700 rpm for 180 min and 4.0 wt% of catalyst. As shown in Figure 7.11, FAME conversion was increased as molar ratio rises since high amount of methanol promotes methoxy species formation on surface of catalyst. Therefore, equilibrium shifts towards forward direction and FAME conversion was increased [Wang et al., 2011]. Thus, there was rise in conversion from 1:6 to 1:24 molar ratio as 54.22±0.2%, 60.21±0.25%, 68±0.65%, 79.99±0.57%, 87.57±0.3%, 93.02±0.6%, 88.07±0.38% for WVO whereas, Karanja oil shows FAME conversion of 60.89±0.49%, 70.06±0.67%, 78.35±0.5%, 87.8±0.36%, 94.84±0.51%, 91±0.23%, 85.4±0.42% for 1:6, 1:9, 1:12, 1:15, 1:18, 1:21 and 1:24 respectively. Hence, in case of WVO maximum conversion (93.02±0.6%) was accomplished at 1:21 molar ratio and 94.84±0.51% of FAME was observed at 1:18 molar ratio in Karanja oil. Further increase in molar ratio after this optimized reaction condition; FAME conversion decreases as glycerol formed in product dissolves in excess of methanol and inhibits in the transesterification reaction along with this glycerol separation becomes problematic which causes equilibrium shift towards

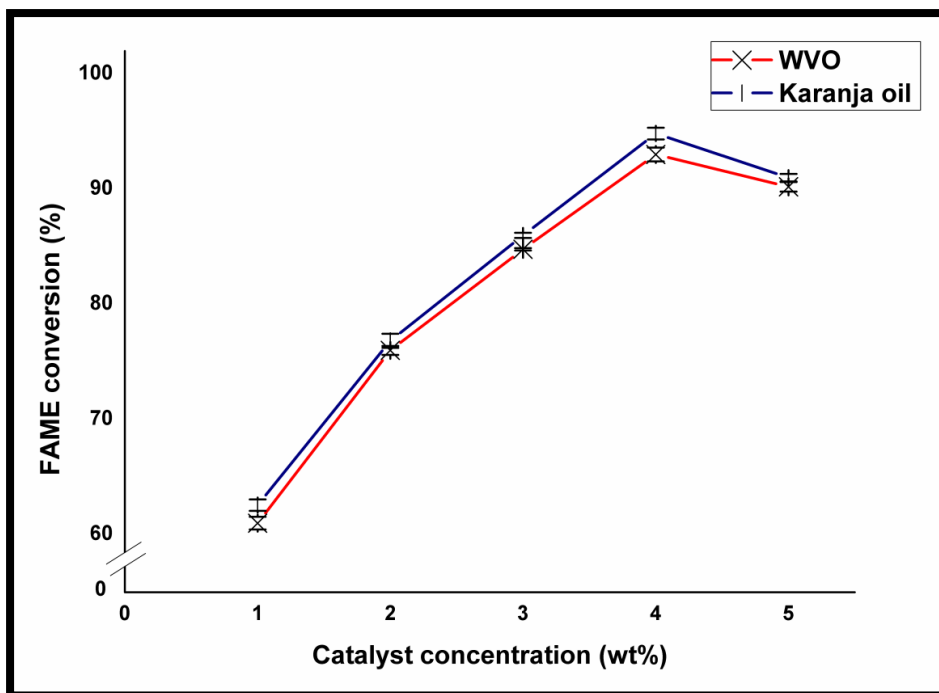


Figure 7.10 Effect of catalyst concentration on FAME conversion (%) of WVO and Karanja oil [temperature 65 °C; time 180 min; stirring speed 700 rpm; molar ratio 1:21 for WVO and 1:18 for Karanja oil]

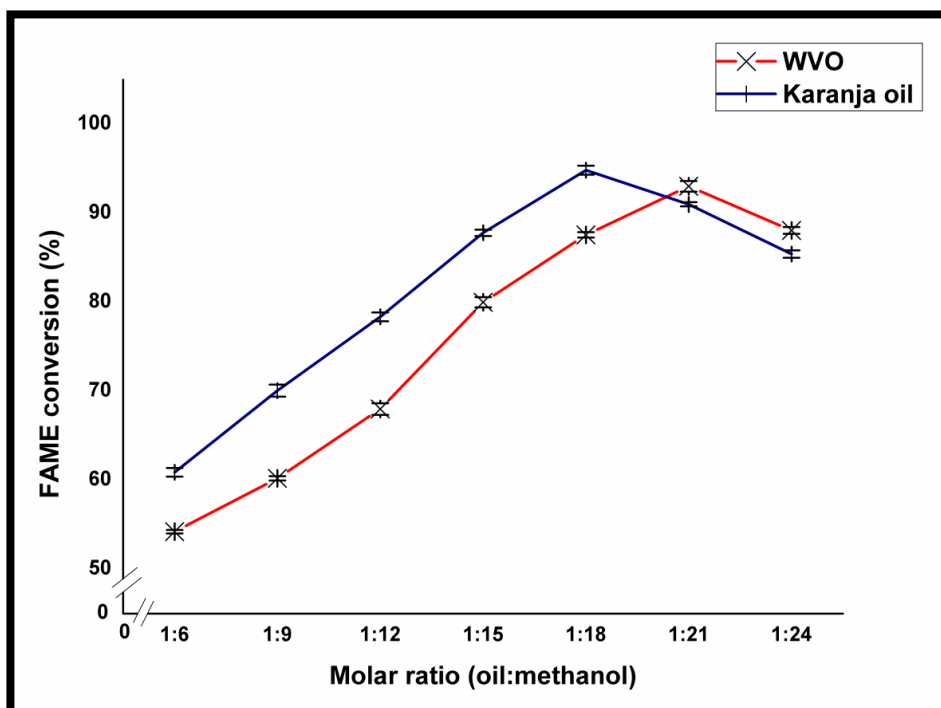


Figure 7.11 Effect of oil:methanol molar ratio on FAME conversion (%) of WVO and Karanja oil [temperature 65 °C; time 180 min; stirring speed 700 rpm; catalyst concentration of 4.0 wt%]

backward direction and FAME conversion drops [Lim et al., 2009]. From this 1:21 molar ratio for WVO and 1:18 molar ratio for karanja oil was used for optimization purpose.

7.5.3 Effect of reaction temperature

Diffusion resistance due to phase difference in case of heterogeneous catalyst can be overcome by setting proper reaction temperature for maximum FAME conversion. Effect of reaction temperature on FAME conversion was studied from 35 °C to 75 °C by interval of 10 °C and other variables constant. As shown in Figure 7.12 result displays that FAME conversion increases as reaction temperature rises from 35 °C to 65 °C. Wide increment in FAME conversion was observed at 35 °C, 45 °C, 55 °C and 65 °C as $54.56\pm 0.65\%$, $66.91\pm 0.43\%$, $79.33\pm 0.23\%$, $93.02\pm 0.6\%$ for WVO while $55.87\pm 0.36\%$,

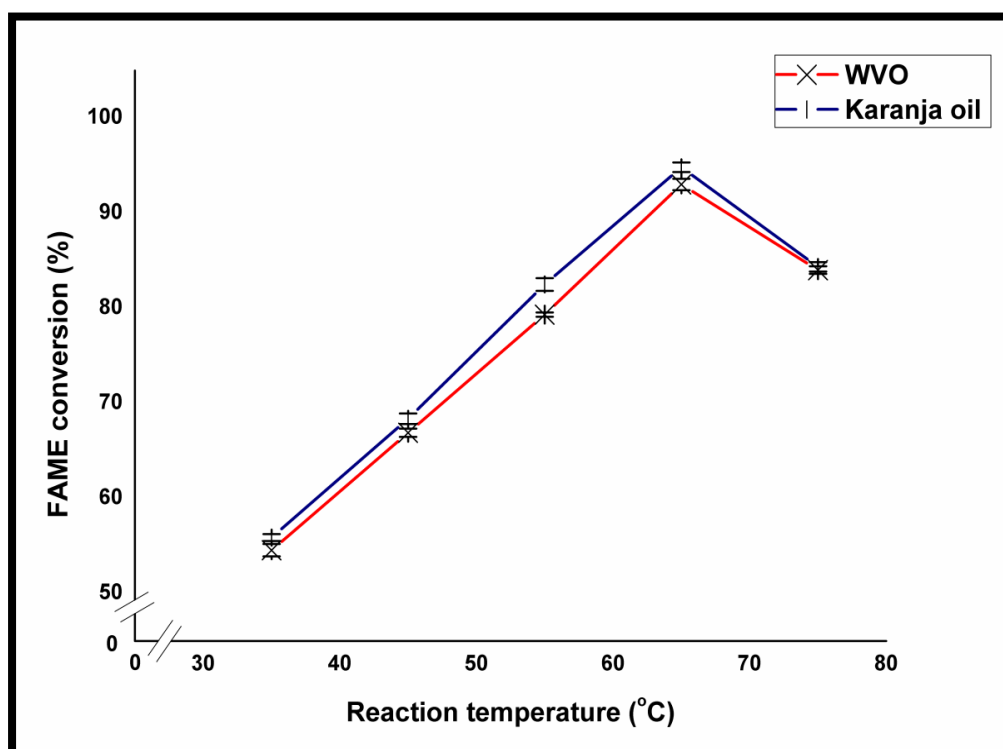


Figure 7.12 Effect of reaction temperature on FAME conversion (%) of WVO and Karanja oil [time 180 min; stirring speed 700 rpm; catalyst concentration of 4.0 wt%, 1:21 oil: methanol molar ratio for WVO and 1:18 oil: methanol molar ratio for Karanja oil]

68.39±0.56%, 82.51±0.66% and 94.84±0.51% for Karanja oil. Transesterification reactions were significantly influenced by change in temperature [Brennan and Owende, 2010]. The contribution of solvent's chemical properties in transesterification reaction is favoured nearer to boiling point of methanol [Yuan et al., 2005] and beyond the boiling point conversion was decreased because of evaporation of methanol. This effect of transesterification reaction due to temperature can be caused by endothermic reaction [Samart et al., 2009]. The maximum FAME conversion of 93.02±0.6% and 94.84±0.51% was attained at 65 °C reaction temperature for WVO and Karanja oil respectively. After this optimum temperature, when temperature increases to 75 °C, FAME conversion drops to 84.01±0.4% in WVO and 84.58±0.5% in Karanja oil, since at high temperature, methanol was quickly vaporizes after its boiling temperature to form bubbles hence impedes the reaction by creating interface of two phase [Chai et al., 2007]. At high temperature polarity of methanol decreases hence lowers the amount of methoxide ions in present reaction mixture. Selection of low temperature is preferred to save the energy need and hence optimum reaction temperature accomplished for FAME conversion was 65 °C.

7.5.4 Effect of reaction time

Influence of reaction time on FAME conversion was investigated by carrying out reaction for various time ranging from 30 min to 210 min and keeping other reaction parameters constant, as illustrated in Figure 7.11. From this Figure, it has been observed that as reaction time increases from 30 min to 180 min, FAME conversion was also increased. At 30, 60, 90, 120, 150 and 180 min FAME conversion was 55.71±0.27%, 66.92±0.32%, 75.8±0.54%, 80.2±0.46%, 87.25±0.51%, 93.02±0.6% for WVO whereas

57±0.19%, 67.54±0.44%, 78.6±0.39%, 82.28±0.41, 89.5±0.67% and 94.84±0.51% for Karanja oil respectively.

Maximum FAME conversion was accomplished at optimized reaction parameters with time 180 min. Further rise in reaction time for 210 min does not affect FAME conversion which virtually remains constant as 93±0.5% for WVO and 94.85±0.23% for Karanja oil shown in Figure 7.13. Consequent increase in time after optimization did not change the FAME conversion, since transesterification is reversible reaction plus equilibrium was achieved at that time and no additional time was obligatory in that process.

7.5.5 Effect of stirring speed

In case of heterogeneous catalyst for transesterification oil, alcohol and heterogeneous catalyst form immiscible phases, thus to increase exchange between the active sites of catalyst and reactant; stirring plays a significant role by eliminating mass transfer effect on FAME conversion. As shown in Figure 7.14. there is progressively increase in FAME conversion with respect to stirring speed starting from 200 rpm to 700 rpm at the interval of 100 rpm as 57.31±0.69%, 63.47±0.38%, 70.04±0.5%, 77±0.68%, 87.16±0.16%, 93.02±0.6% for WVO however 59.03±0.57%, 65.9±0.63%, 71.53±0.5%, 79.16±0.46%, 88.74±0.4% and 94.84±0.51% for Karanja oil this displays that reaction rate was controlled by external mass diffusion. Above 700 rpm stirring speed, no substantial increment in reaction rate and FAME conversion was observed as 93±0.35% and 94.58±0.48% for WVO and Karanja oil, hence all experiments were performed at 700 rpm to exclude mass transfer limitation and chosen for optimization purpose.

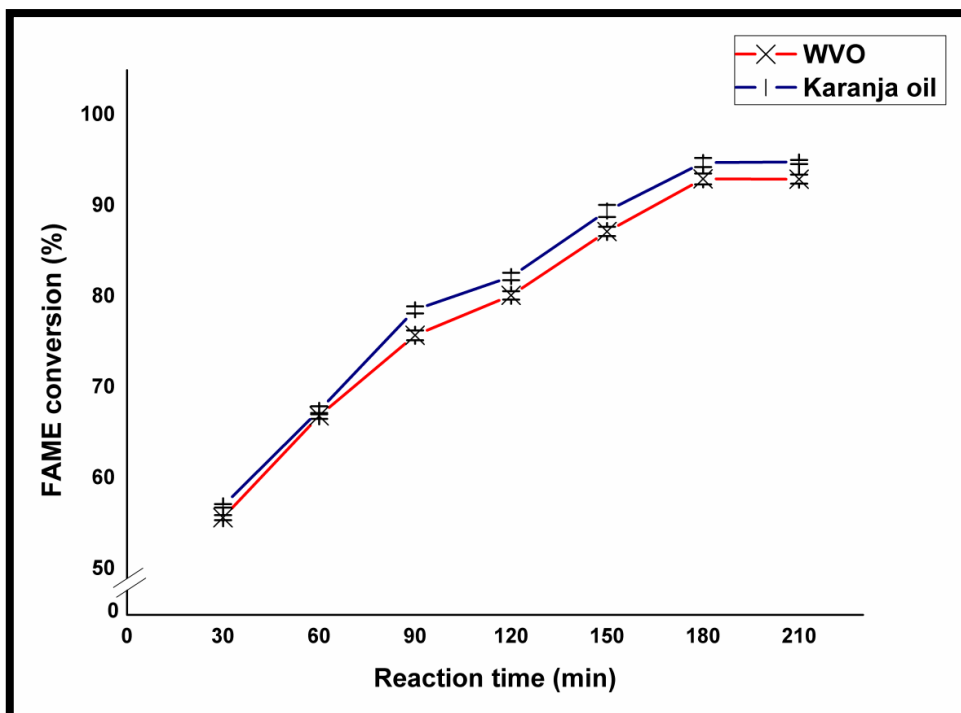


Figure 7.13 Effect of reaction time on FAME conversion (%) of WVO and Karanja oil [temperature 65 °C; stirring speed 700 rpm; catalyst concentration of 4.0 wt%, 1:21 oil: methanol molar ratio for WVO and 1:18 oil: methanol molar ratio for Karanja oil]

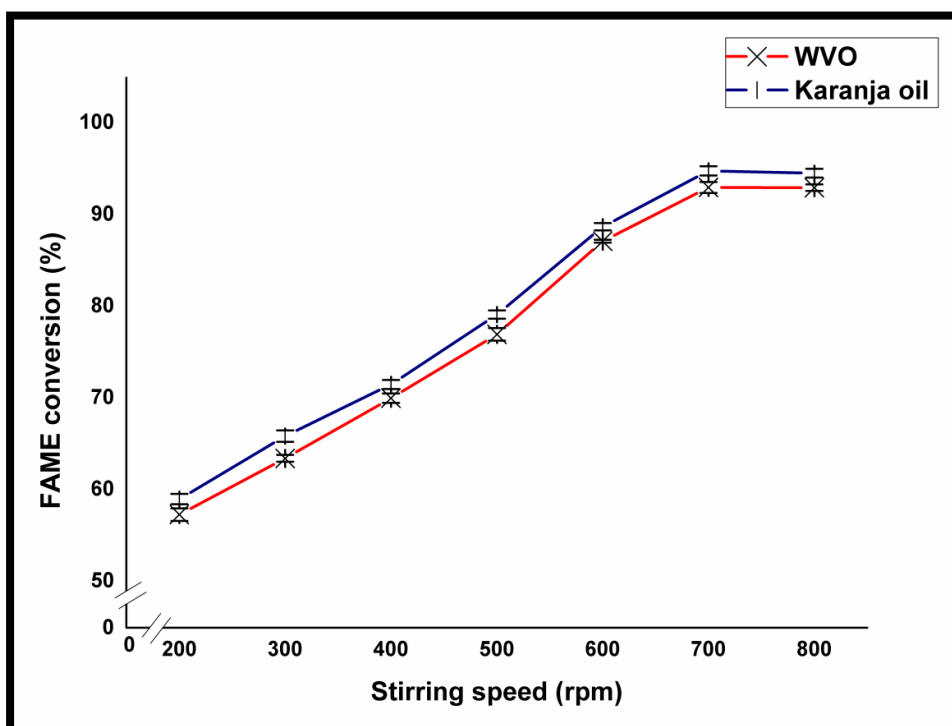


Figure 7.14 Effect of stirring speed on FAME conversion (%) of WVO and Karanja oil [time 180 min; temperature 65 °C; catalyst concentration of 4.0 wt%, 1:21 oil: methanol molar ratio for WVO and 1:18 oil: methanol molar ratio for Karanja oil]

7.5.6 Catalyst reusability

Homogeneous catalyst cannot be reused due to limitation in separation; on the other hand, heterogeneous catalyst can be reused several times. Reusability of synthesized catalyst for transesterification reaction was studied under optimum condition of parameters 1:21 molar ratio of WVO while 1:18 molar ratio of Karanja oil (oil: methanol), 4.0 wt% catalyst concentration, 65 °C reaction temperature and 700 rpm stirring speed for 180 min of reaction time (Figure 7.15). After each effective runs catalyst was washed through hot methanol to eliminate organic impurities remaining on the catalytic surface. Afterward dried in hot air oven for 3-4 h at 120 °C followed by calcination at 600 °C for 2 h. Reusability of catalyst in transesterification reaction has been illustrated in Figure 7.15. It was observed that catalytic activity continuously

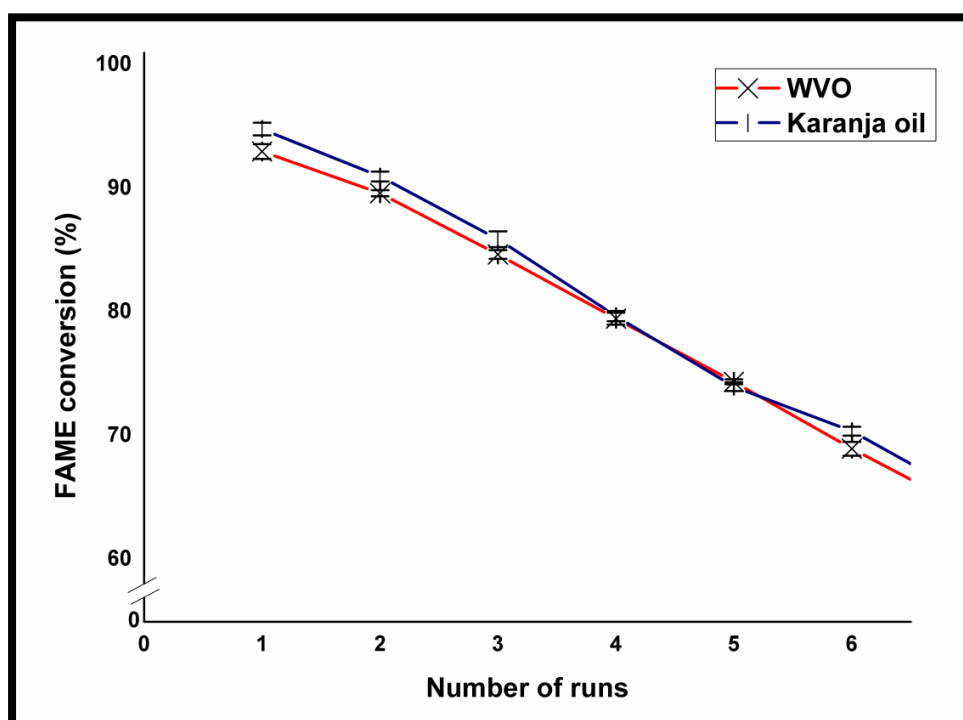
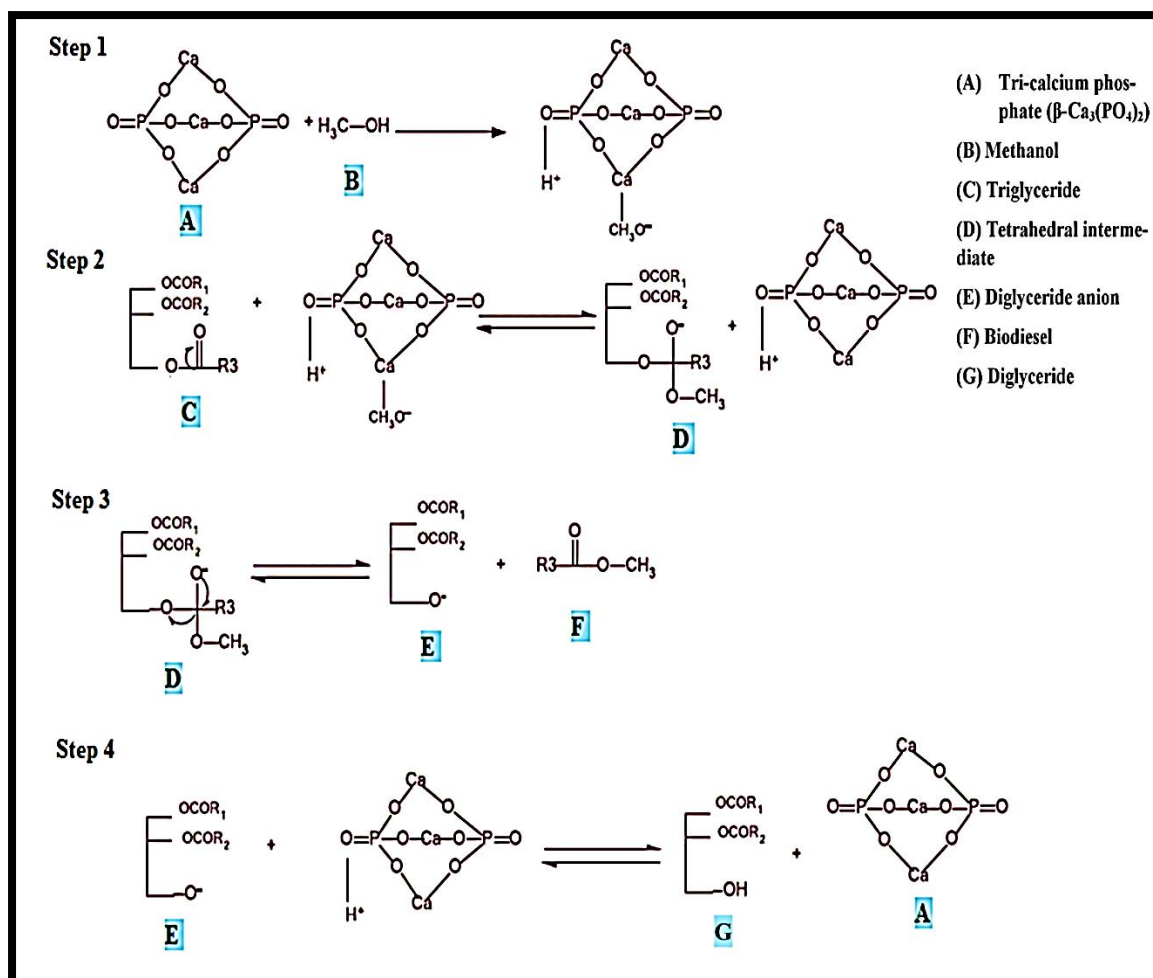


Figure 7.15 Waste guinea fowl bone derived catalyst reusability analysis up to seven runs [1:21 M ratio of oil: methanol, 4.0 wt% of catalyst at 65 °C for 180 min and 700 rpm stirring speed for WVO and 1:18 M ratio of oil: methanol, 4.0 wt% of catalyst at 65 °C for 180 min and 700 rpm stirring speed for Karanja oil]

decreases as shown in the Figure and catalyst can be reused up to seven times with FAME conversion of >64%. For first, second, third, fourth, fifth, sixth and seventh cycles we obtained FAME conversion of $93.02 \pm 0.6\%$, $89.65 \pm 0.25\%$, $84.7 \pm 0.35\%$, $79.51 \pm 0.48\%$, $74.4 \pm 0.2\%$, $68.99 \pm 0.55\%$, $64 \pm 0.6\%$, for WVO whereas $94.84 \pm 0.51\%$, $91 \pm 0.4\%$, $85.93 \pm 0.64\%$, $79.71 \pm 0.41\%$, $74.01 \pm 0.35\%$, $70.41 \pm 0.36\%$, $65.11 \pm 0.5\%$ in Karanja oil. Decrease in FAME conversion for each run ascribed to deposition of biodiesel, unreacted oil and glycerol on the catalytic surface which is responsible for decrement in active sites [Kaur and Ali, 2015]. Catalytic activity drops after surface of catalyst was surrounded by product which eventually diminishes the contact of catalytic surface and reactant [Sun et al., 2010]. Therefore, catalyst derived from guinea fowl bone can be reused in transesterification reaction for seven runs due to its good activity.

7.6 Active component in waste guinea fowl bone synthesized catalyst

From XRD data it has been observed that major peak is attributed to tri-calcium phosphate ($\beta\text{-Ca}_3(\text{PO}_4)_2$). This proposed that tri-calcium phosphate ($\beta\text{-Ca}_3(\text{PO}_4)_2$) is one of the active components present in catalyst is responsible for transesterification reaction in biodiesel production. Usually, strongest basicity of catalyst is not essential to be the best for biodiesel production, as we have calculated as 2.09 mmol/g in basicity section, ideal active basic site strength is required for transesterification process. Hence, displays better performance of transesterification from WVO and Karanja oil. The detailed mechanism of tri-calcium phosphate ($\beta\text{-Ca}_3(\text{PO}_4)_2$) for transesterification reaction were shown in Scheme 7.1 [Farooq and Ramli, 2015].



Scheme 7.1 Transesterification reaction mechanism in the presence of beta-tricalcium phosphate ($\beta\text{-Ca}_3(\text{PO}_4)_2$) [Source: Farooq and Ramli, 2015]

7.7 Characteristics of FAME synthesized from WVO and Karanja oil

FAME synthesized from WVO and Karanja oil was characterized for physicochemical properties as per American Society for Testing and Materials (ASTM) D6751 as shown in Table 7.3. Fuel properties of FAME at optimum condition have been observed to be obeying with ASTM standards. Acid value of FAME was found to be 0.85 mg of KOH/g and 0.50 mg of KOH/g for WVO methyl ester and Karanja oil methyl ester respectively as per ASTM standards. Density is directly related to viscosity, moreover transesterification reaction reduces viscosity and was found to be 0.863 g/cm^3 and 4.52

Table 7.3 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	0.85	0.50
Density (40 °C, g cm ⁻³)	D1448-1972	0.863	0.860
Kinematic viscosity (cSt at 40 °C)	D445	4.52	3.98
Cetane number	D613	48	49
Calorific value (MJ/Kg)	D6751/ DIN51900	38.85	39
Flash point (°C)	D93	140	138
Fire point (°C)	D93	152	149
Cloud point (°C)	D2500	4	3
Pour point (°C)	D97-05	7	6
Ash content (%)	D482	0.02	0.02

cSt for WVO methyl ester and 0.860 g/cm³ and 3.98 cSt for Karanja oil methyl ester respectively were within ASTM range for biodiesel. Cetane number and calorific value of FAME were found to be 48, 38.85 MJ/kg for WVO methyl ester and 49, 39 MJ/kg for Karanja oil methyl ester respectively. Flash point, fire point, cloud point and pour point were observed to be 140 °C; 152 °C; 4 °C; 7 °C for WVO methyl ester while 138 °C; 149 °C; 3 °C; 6 °C respectively for Karanja oil methyl ester, which was within safe limit for transportation and storage purpose. Ash content was 0.02% for both WVO methyl ester as well as Karanja oil methyl ester which was within ASTM limit. Biodiesel produced from WVO and Karanja oil fulfilled with biodiesel standards. This confirms that catalyst used in present study has potential for large scale biodiesel production.

7.8 Conclusion

Guinea fowl bone derived catalyst was efficaciously developed and applied as active heterogeneous catalyst for biodiesel production from waste vegetable oil and Karanja oil with methanol by transesterification reaction. This catalyst was characterized by TGA, XRD, ATR-FTIR, SEM, EDS, BET surface area, BJH analysis, particle size and basicity techniques. Reaction parameters molar ratio (oil:methanol), catalyst concentration, reaction time, temperature, stirring speed and catalyst reusability were studied to achieve optimized reaction conditions. Under optimized conditions of transesterification reaction for WVO was molar ratio of 1:21 oil: methanol, 4.0 wt% catalytic concentration, 65 °C reaction temperature, 180 min time of reaction and 700 rpm of stirring speed FAME conversion was $93.02 \pm 0.6\%$, however, Karanja oil shows FAME conversion of $94.84 \pm 0.51\%$ at 1:18 oil: methanol molar ratio, 4.0 wt% catalyst, 65 °C reaction temperature, 180 min time of reaction and 700 rpm of stirring speed. The catalyst used was derived from waste guinea fowl bone has been recovered and recycled up to seven runs with $>64\%$ of FAME conversion in seventh run. Physicochemical properties of WVO methyl ester and Karanja oil methyl ester have been studied and obtained within ASTM standards limit. From these studies, it has been confirmed that waste guinea fowl bone derived catalyst could be attractive catalyst for economically viable biodiesel production. To reduce overall production cost for biodiesel production, WVO and Karanja oil as feedstock whereas waste guinea fowl bone were utilized for biodiesel production hence entire reaction is eco-friendly and economically viable.