

## **CHAPTER 5**

**Synthesis and characterization of barium zirconate (BaZrO<sub>3</sub>) and its application in biodiesel production from waste vegetable oil (WVO) and *Pongamia Pinnata* (Karanja) oil**

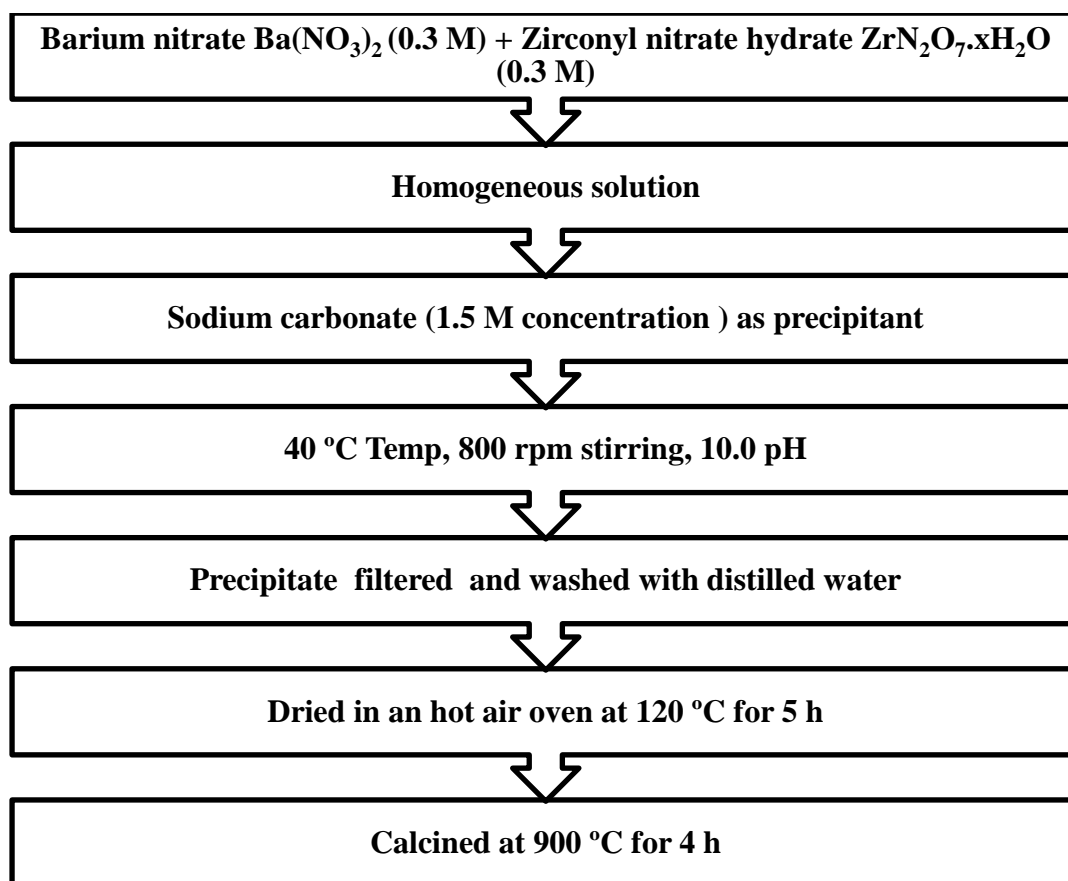


## 5.1 Introduction

In this chapter, synthesis, characterization of a heterogeneous catalyst, barium zirconate ( $\text{BaZrO}_3$ ) has been discussed. The catalyst was synthesized by co-precipitation method and was characterized 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 then utilized for transesterification of waste vegetable oil (WVO) and (*Pongamia pinnata*) Karanja oil for biodiesel production. Optimization of several reaction parameters such as catalyst concentration, molar ratio, reaction temperature, reaction time, stirring speed and catalyst reusability was reported. Synthesized biodiesel was further characterized by  $^1\text{H}$  NMR and physicochemical properties of FAME derived from both feedstocks as compared to petrodiesel and summary were discussed.

## 5.2 Synthesis of barium zirconate ( $\text{BaZrO}_3$ )

Barium zirconate ( $\text{BaZrO}_3$ ) was synthesized by co-precipitation method and the schematic representation was shown in Figure 5.1. In this method, precursors taken were aqueous solutions of both barium nitrate,  $\text{Ba}(\text{NO}_3)_2$  and zirconyl nitrate hydrate,  $\text{ZrN}_2\text{O}_7 \cdot x\text{H}_2\text{O}$ , having concentrations of 0.3 M with Ba/Zr molar ratio equal to 0.5. These aqueous solutions were added concomitantly and dropwise to the solution of sodium carbonate,  $\text{Na}_2\text{CO}_3$  (1.5 M) which is used as precipitant in this synthesis. The temperature was maintained at 40 °C throughout the addition with continuous stirring at 800 rpm. Addition was stopped when solution attained a pH of 10.0. Precipitate obtained was



**Figure 5.1** Synthesis of barium zirconate (BaZrO<sub>3</sub>) via co-precipitation method

placed overnight at room temperature and was separated by simple filtration by using Whatman filter paper, Grade 42 having pore size of 2.5  $\mu\text{m}$  (slow speed filter paper) and washed with distilled water. The sample was dried in a hot air oven at 120 °C for 5 h. Solid product obtained was calcined at 900 °C for 4 h. Synthesized sample was ground by mortar and pestle and sieved to obtain fine powder before it was used as a catalyst.

### 5.3 Characterization of barium zirconate (BaZrO<sub>3</sub>)

#### 5.3.1 Thermogravimetric analysis (TGA)

Figure 5.2 depicts the thermal characteristics of dried precursor with the help of TGA curve in order to explore the synthesis of BaZrO<sub>3</sub>. Thermal characterization has

been carried out by thermo gravimetric analysis (TGA) up to 1000 °C, starting from 40 °C at the heating rate of 20 °C/min. From the thermogram, TG analysis designates emission of water, carbon monoxide and carbon dioxide at the distinct decomposition temperature ranges. About 13.45 mg of sample was analysed and total 23.53% weight loss has been observed. From Figure 5.2, it has been observed that weight loss obtained from 40 °C to 275 °C is attributed to both adsorbed atmospheric as well as crystallized water respectively and was up to 9.22%. After that, the second weight loss was observed between 300 °C and 670 °C and is due to expulsion of CO<sub>2</sub> and CO at a time which represents decarboxylation process which was 3.11%. The last concluding weight loss occurred from 670 °C to 860 °C which is due to emission of second substantial CO<sub>2</sub> and was 11.20%. TGA curve shows that after 860 °C, no weight loss was observed due to completion of decomposition and hence calcination was accomplished at 900 °C. This implies that barium zirconate phase has been stabilised completely.

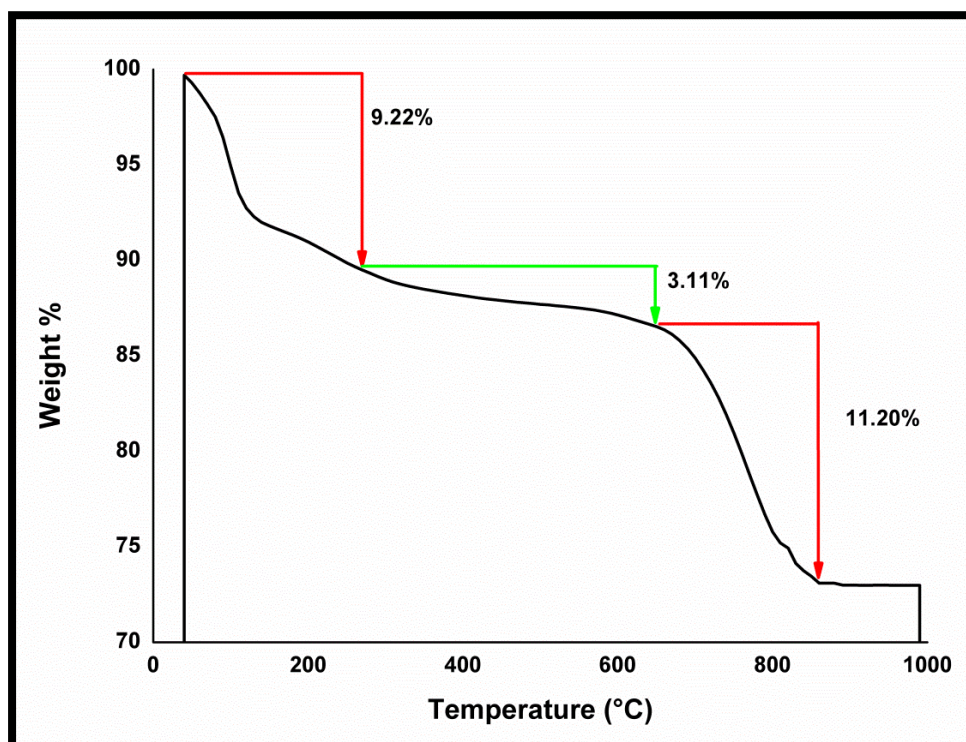


Figure 5.2 TGA curve of uncalcined BaZrO<sub>3</sub> catalyst

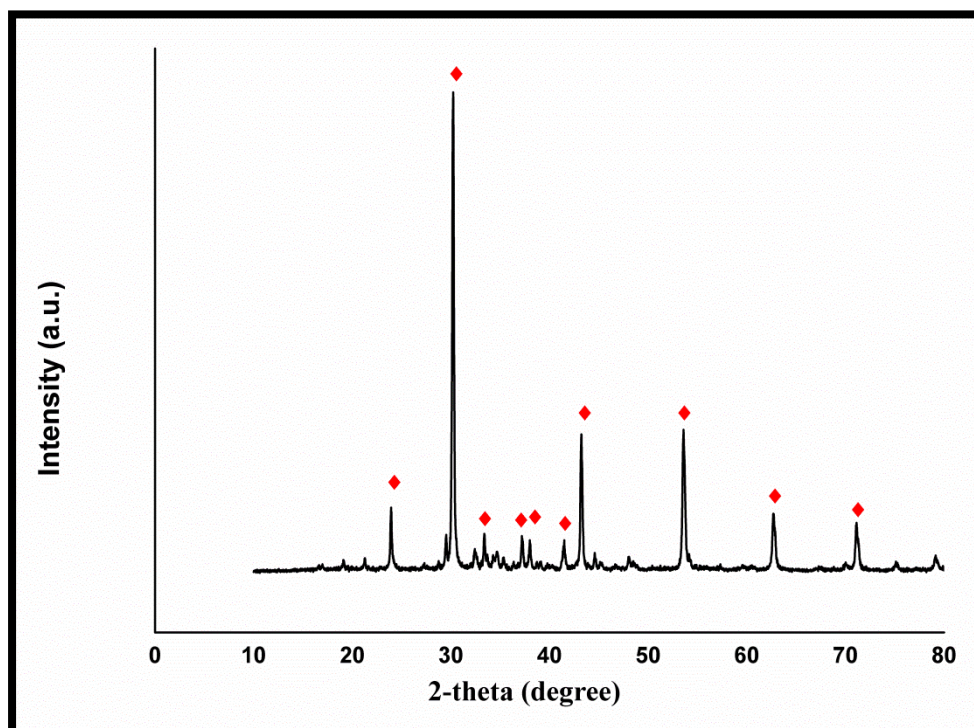


Figure 5.3 XRD pattern of the BaZrO<sub>3</sub> catalyst synthesized via co-precipitation method

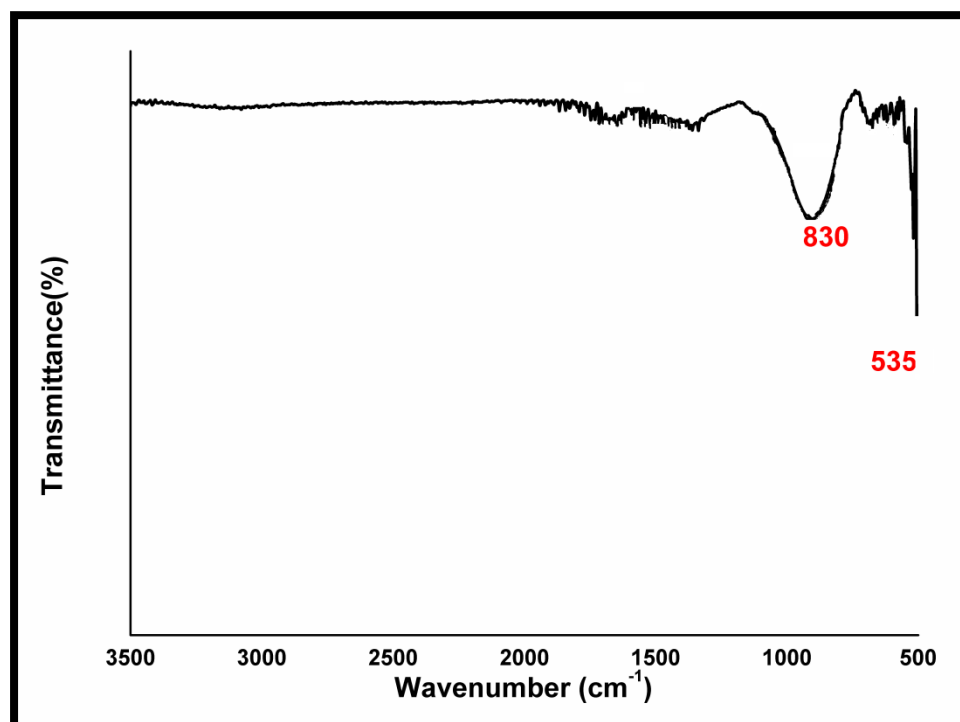


Figure 5.4 ATR-FTIR spectra of BaZrO<sub>3</sub> catalyst

### 5.3.2 X-ray diffraction (XRD)

X-ray diffraction (XRD) was used to scrutinize the crystallinity of given compound. Figure 5.3 depicts the powder X-ray diffraction (XRD) patterns for barium zirconate at 900 °C for 4 h. The prominent peaks obtained were compared with the Joint Committee on Powder Diffraction Standards (JCPDS) files. In diffractogram of barium zirconate, sharp signals of cubic phase were seen. The peaks at 23.90°, 30.15°, 33.38°, 37.33°, 41.65°, 43.20°, 53.60°, 62.71°, and 71.21° are due to barium zirconate cubical phase marked by red cubes. These peaks endorse the conversion of barium zirconate which acts as a base catalyst for transesterification of feedstock. The peaks obtained were corresponding to the standard PDF data No: 74-1299 and 06-0399 which implies the cubical barium zirconate phase. By associating the intensities of these obtained crystalline phases, it can be accomplished that the cubical phase is the major component in the catalyst.

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

Attenuated total reflectance Fourier transform infrared spectra (ATR-FTIR) of the catalyst has been taken for recognition of various phases existing on the catalyst surface. Figure 5.4 depicts the FTIR spectrum of synthesized catalyst; calcined at 900 °C for 4 h. FT-IR is more virtuous in assessing the appearance of non-crystalline phases existing in the sample. This is possible due to introduction of compound on the surface of sample which is the limitation of X-ray diffraction (XRD) technique. FTIR was used to distinguish molecular level structural transformations in barium zirconate due to calcination. As seen in Figure 5.4, the vibrations at 535 cm<sup>-1</sup> and 830 cm<sup>-1</sup> band are due to occurrence of Zr–O vibrations present in the structure [Boschini et al., 2003; Guarany et al., 2003]. These intense peaks show the transformation of barium zirconate completely

which is responsible for availability of basic sites required for transesterification reaction.

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

BET surface area of the synthesized barium zirconate ( $\text{BaZrO}_3$ ) was accompanied for surface area, pore size and pore volume determination. BET surface area and Langmuir surface area were found to be  $2.19 \text{ m}^2/\text{g}$  and  $3.14 \text{ m}^2/\text{g}$  respectively. BJH adsorption and desorption cumulative surface areas of pores were  $1.85 \text{ m}^2/\text{g}$  and  $3.76 \text{ m}^2/\text{g}$  respectively. Though, surface area was obtained to be less, catalytic activity of barium zirconate ( $\text{BaZrO}_3$ ) was higher at suitable reaction conditions. Pore volume at single point adsorption was  $0.018 \text{ cm}^3/\text{g}$  with this BJH adsorption and desorption cumulative volume were  $0.017 \text{ cm}^3/\text{g}$  and  $0.018 \text{ cm}^3/\text{g}$  respectively. BJH adsorption and desorption pore size were observed as  $376.03 \text{ \AA}$  and  $189.52 \text{ \AA}$  respectively.

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

Surface morphologies of the synthesized catalytic crystals were explored by using SEM-EDS. Scanning electron microscope (SEM) studies on the powder morphology of synthesized barium zirconate showed that particles are cubical in shape. Figure 5.5 shows the SEM photomicrograph of calcined catalyst at  $900 \text{ }^\circ\text{C}$  for 4 h. As shown in this (Figure 5.5), the particles got separated and appear in regular cubical shape and are uniform. The result of SEM was in conformity with the XRD as presented in Figure 5.3. The particles in separated form display larger surface area as compared to agglomerated form and hence maximum conversion of biodiesel was accomplished. The EDS is attached to scanning electron microscope (SEM) and the two techniques are commonly used together. Compositional analysis of EDS proposed that the precipitation obtained in the process consisted of barium and zirconia oxide and has been shown in Figure 5.6.



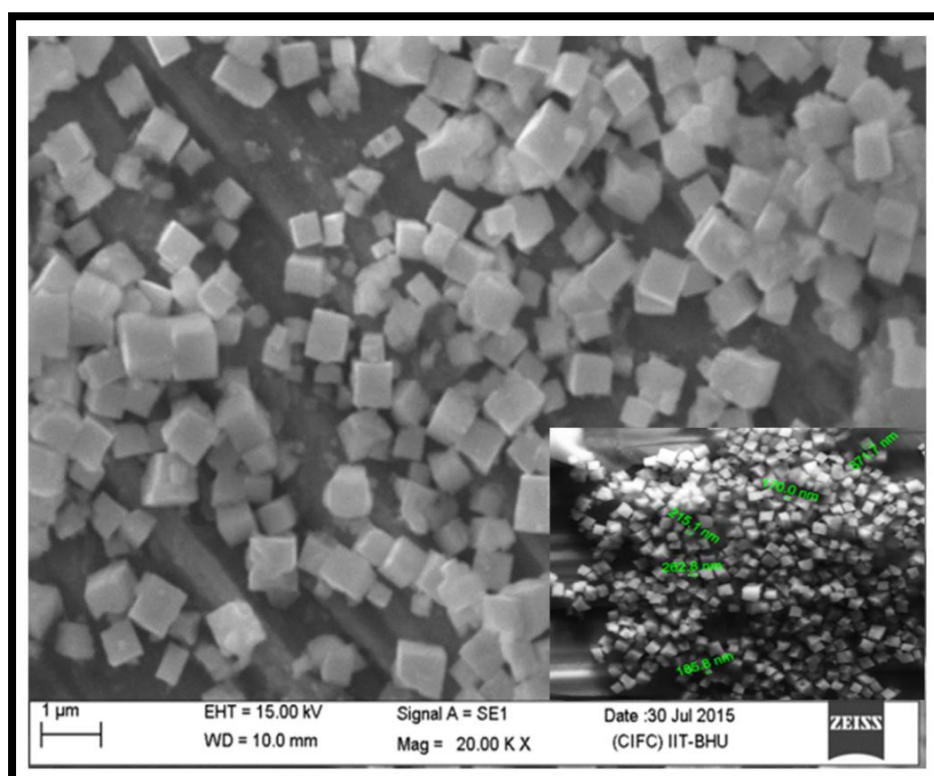


Figure 5.5 SEM image of the BaZrO<sub>3</sub> synthesized catalyst

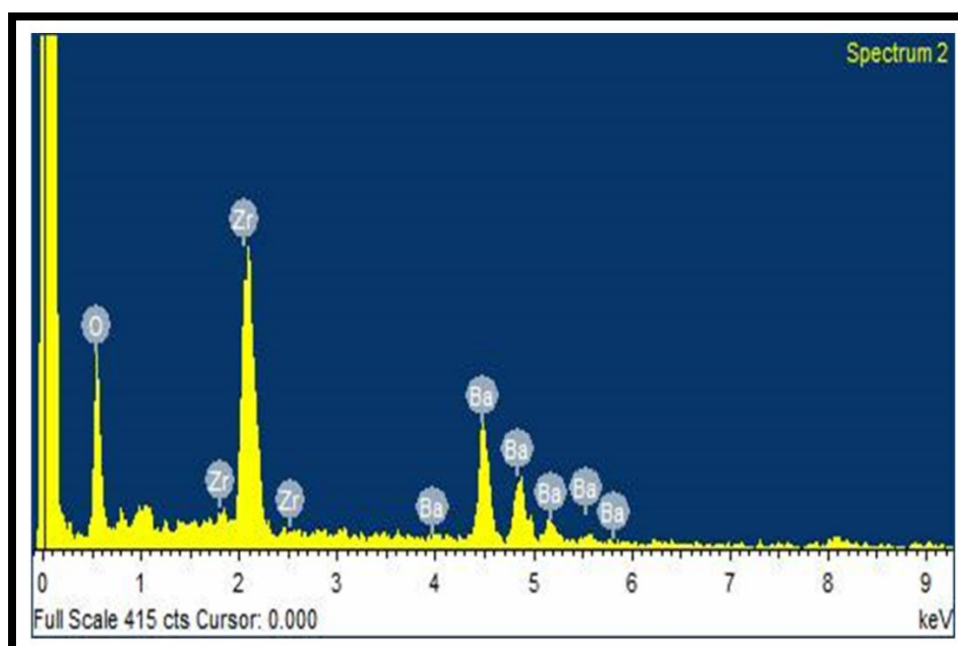


Figure 5.6 EDS image of the BaZrO<sub>3</sub> synthesized catalyst

Table 5.1 designates that calcined barium zirconate consist of 41.64 wt% Ba, 34.15 wt% Zr and 24.21 wt% O. This calcination was also effective in producing a continuous cubical structure across the joint region as shown in the Figure 5.5.

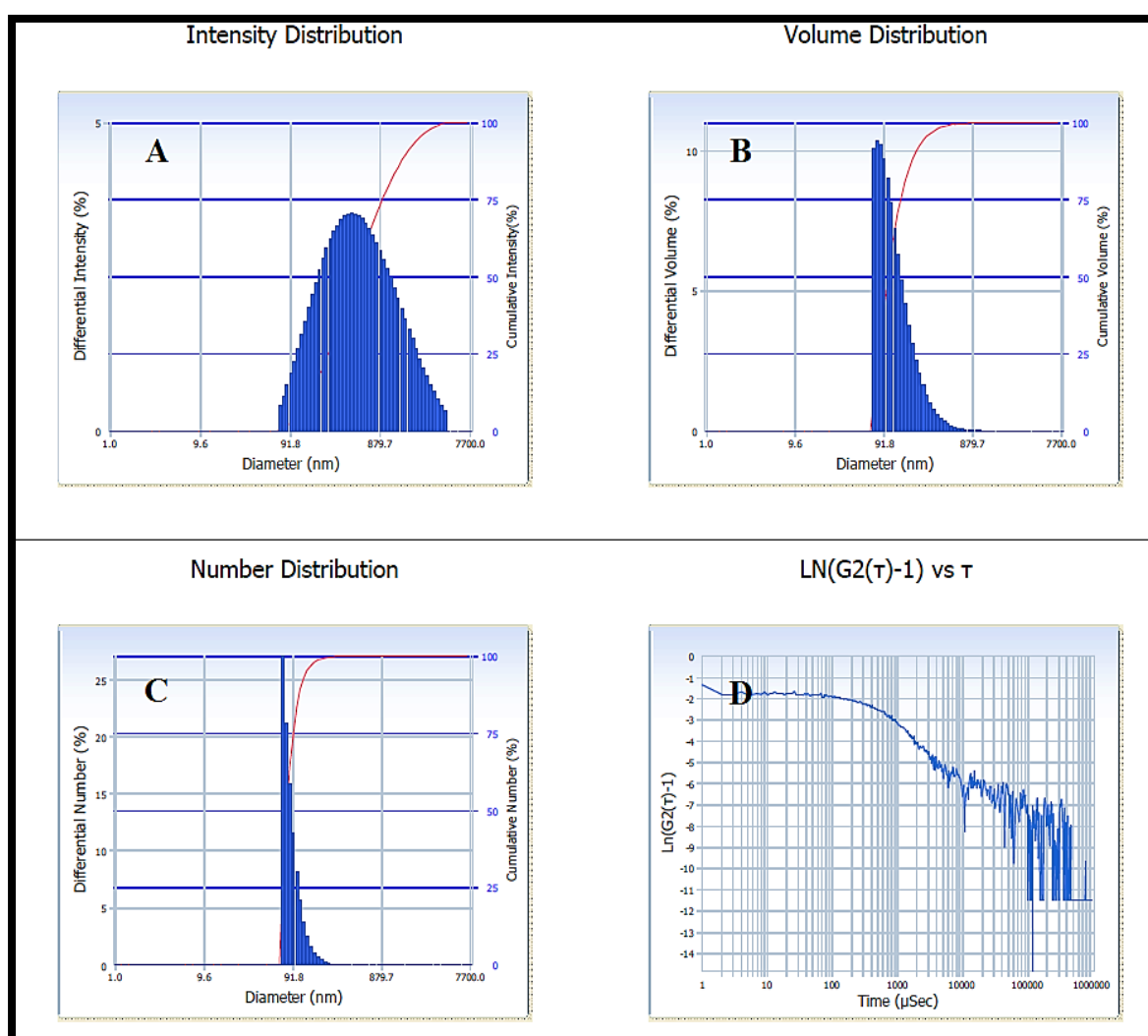
**Table 5.1** Element weight % present in BaZrO<sub>3</sub> sample

Elements	Weight (%)	Atomic (%)
O	24.21	69.08
Ba	41.64	13.83
Zr	34.15	17.09
Total	100.00	100.00

### 5.3.6 Particle size analysis

Diameter of catalyst particles was distinguished with the help of particle size analyser constructed on the dynamic light scattering principle (DLS). Intensity size distribution (weighted), volume size distribution and number size distribution were represented in the form of histogram as shown in Figure 5.7. Intensity distributions were considered (Figure 5.7(A)) and can change them to volume or number distributions by this instrument. Volume distribution was shown in Figure 5.7(B) for the same sample. Volume distribution histogram offers the relative volume of particles intended for individual size present in the sample. Number distribution histogram was achieved by volume percentage resultant divided by cubed particle diameter and represented in Figure 5.7(C).  $\ln(G2(t)-1)$  plot shows natural logarithmic graph in between  $G2(t)$  Plot and decay time (Figure 5.7(D)) which designates the presence of any noise in the signal. This analysis was performed at 25 °C temperature in aqueous form at 10585 cps scattering

intensity. Refractive index and viscosity was 1.3328 and 0.8818 cP respectively. However, polydispersity index was 0.414, diffusion constant (D) was 1.244e-008 (cm<sup>2</sup>/sec). According to intensity distribution, average diameter of particles was found to be 0.6 μm and standard deviation of 0.57 μm. Volume distribution elucidates the average diameter of particles as 0.13 μm and standard deviation of 0.07 μm, whereas number distribution graph shows average particle diameter of 0.08 μm and standard deviation of 0.02 μm.



**Figure 5.7** 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

### 5.3.7 Basicity

Lewis bases existing on mixed metal oxide were responsible for basic strength of the produced catalyst [Yan et al., 2009]. Basicity of barium zirconate was obtained by Hammett indicator benzene carboxylic acid titration method. In this titration, entire basic sites were obtained regardless of their position. Titration was performed with 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 barium zirconate was obtained as 1.21 mmol/g.

**Table 5.2** Basicity of BaZrO<sub>3</sub>

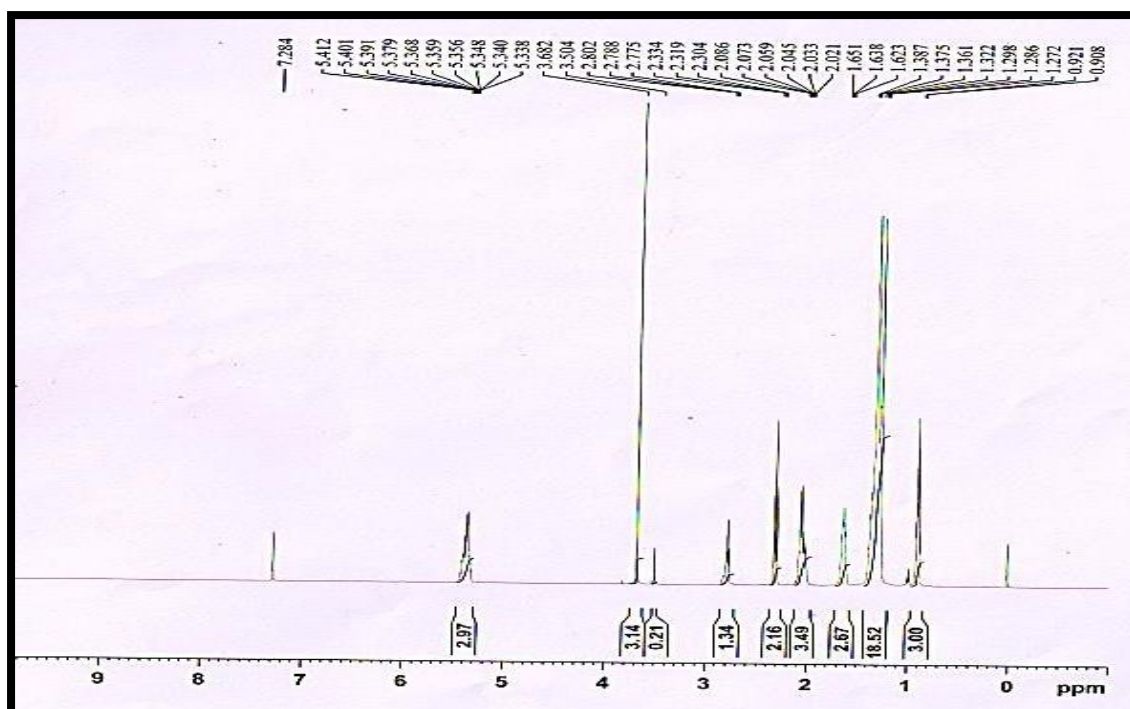
S. No.	Indicators	Basicity (mmol/g of catalyst)
1	Neutral red $pK_{BH}^+ = 6.8$	0.08
2	Bromothymol blue $pK_{BH}^+ = 7.2$	0.1
3	Phenolphthalien $pK_{BH}^+ = 9.3$	0.28
4	Nile blue $pK_{BH}^+ = 10.1$	0.42
5	Trapeolin $pK_{BH}^+ = 11.1$	0.33
6	2,4- Dinitroaniline $pK_{BH}^+ = 15.0$	-
	Total basicity	1.21

### 5.4 Biodiesel production via transesterification and its analysis

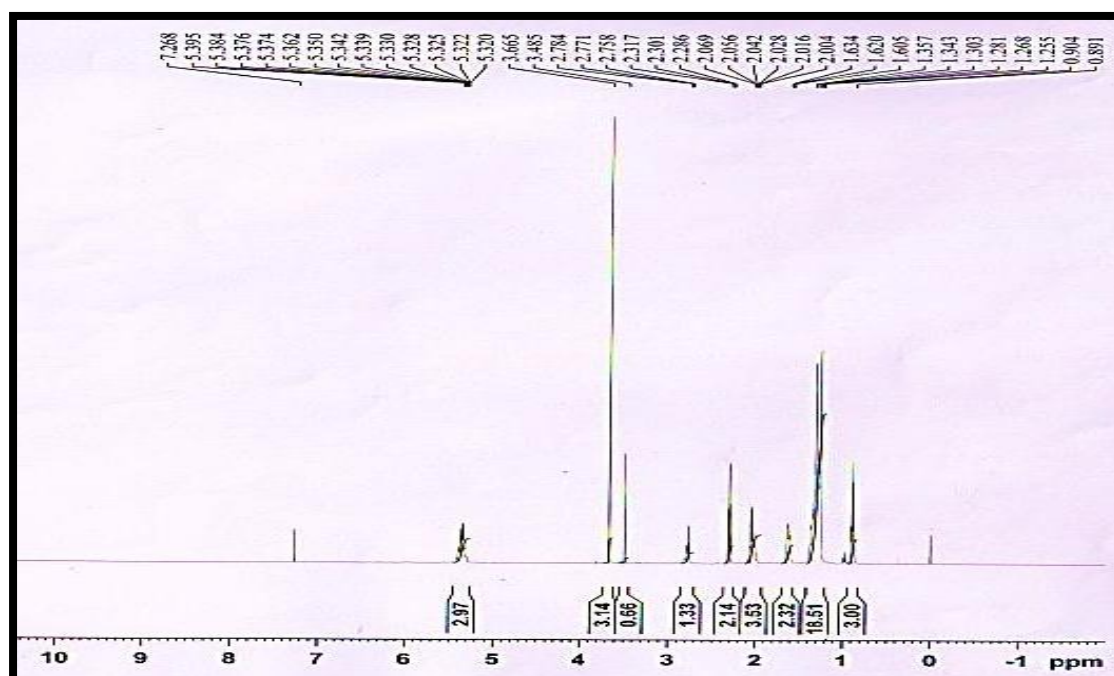
Acid value of WVO was found to be 2.36 mg KOH/g, therefore direct transesterification was performed, whereas, in case of Karanja oil, acid value (5.60 mg/KOH) was lowered by acid esterification reaction (0.52 mg KOH/g). Transesterification was carried out in 250 ml three neck round bottom flask equipped

with mechanical stirrer, condenser and thermometer in hot water bath. Activation of the catalyst (varied from 0.2 wt% to 1.4 wt% of oil) has been done through dispersing it with methanol by continuous stirring at 45 °C for 30 min. After activation, oil was added to above mixture and refluxed for 3 h at 65 °C under constant stirring. Resultant reaction mixture was transferred to separating funnel for overnight and three distinct phases of methyl ester (top), glycerol (middle) and catalyst (bottom) were observed. Catalyst was collected and recycled for further experiments after activation. Rotary evaporator was used to eliminate excess of methanol and anhydrous Na<sub>2</sub>SO<sub>4</sub> [Sharma and Singh, 2009] was used to eradicate traces of water. Formation of ester content in biodiesel obtained from waste vegetable oil and Karanja oil was confirmed by <sup>1</sup>H NMR spectra using Equation 3.1.

In present study, optimization has been performed by carrying out reaction with varying oil: methanol molar ratio from 1:6 to 1:30 by taking 0.2 wt% to 1.4 wt% of catalyst. The reaction time was varied from 30 min to 210 min and temperature from 35 °C to 75 °C with stirring speed of 200 rpm to 700 rpm. In addition to this, reusability of catalyst was also studied up to nine runs. All the experiments were conducted thrice and uncertainties were reported. Physico-chemical properties of synthesized WVO methyl ester and Karanja oil methyl ester were studied as per ASTM standards. <sup>1</sup>H NMR spectrum of WVO and Karanja oil derived FAME at optimum reaction conditions were represented in Figure 5.8 and 5.9 correspondingly. The FAME conversion of WVO and Karanja oil was calculated by considering integrated values of signal at 3.682 ppm and 3.665 ppm (methoxy group of FAME i.e. A<sub>ME</sub>) while 2.304 ppm and 2.286 ppm (methylene group i.e. A<sub>CH<sub>2</sub></sub>) respectively. Conversion was calculated as follows:



**Figure 5.8**  $^1\text{H}$  NMR spectrum of WVO FAME obtained at 1.2 wt%  $\text{BaZrO}_3$ , 1:27 oil: methanol, 180 min reaction time at 65 °C temperature, 600 rpm stirring speed



**Figure 5.9**  $^1\text{H}$  NMR spectrum of Karanja oil FAME obtained at 1.0 wt%  $\text{BaZrO}_3$ , 1:27 oil: methanol, 180 min reaction time at 65 °C temperature, 600 rpm stirring speed

FAME conversion of WVO(%)=  $(2 \times 3.14 / 3 \times 2.16) \times 100 = 96.91\%$  ...**(Equation 5.1)**

FAME conversion Karanja oil(%)=  $(2 \times 3.14 / 3 \times 2.14) \times 100 = 97.82\%$  ...**(Equation 5.2)**

and was observed to be 96.91% for WVO methyl ester and 97.82% for Karanja oil methyl ester. These two peaks were used for conformation of existence of methyl ester in FAME.

## 5.5 Effect of various reaction parameters on transesterification

The catalyst, barium zirconate ( $\text{BaZrO}_3$ ) was observed to be proficient and utilized for optimization of reaction parameters for its enhanced catalytic activity by using waste vegetable oil (WVO) and Karanja oil as feedstock. Sequence of transesterification process was performed in presence of barium zirconate ( $\text{BaZrO}_3$ ) to achieve the reaction conditions for optimization and reusability of catalyst was also evaluated.

### 5.5.1 Effect of catalyst concentration (wt%)

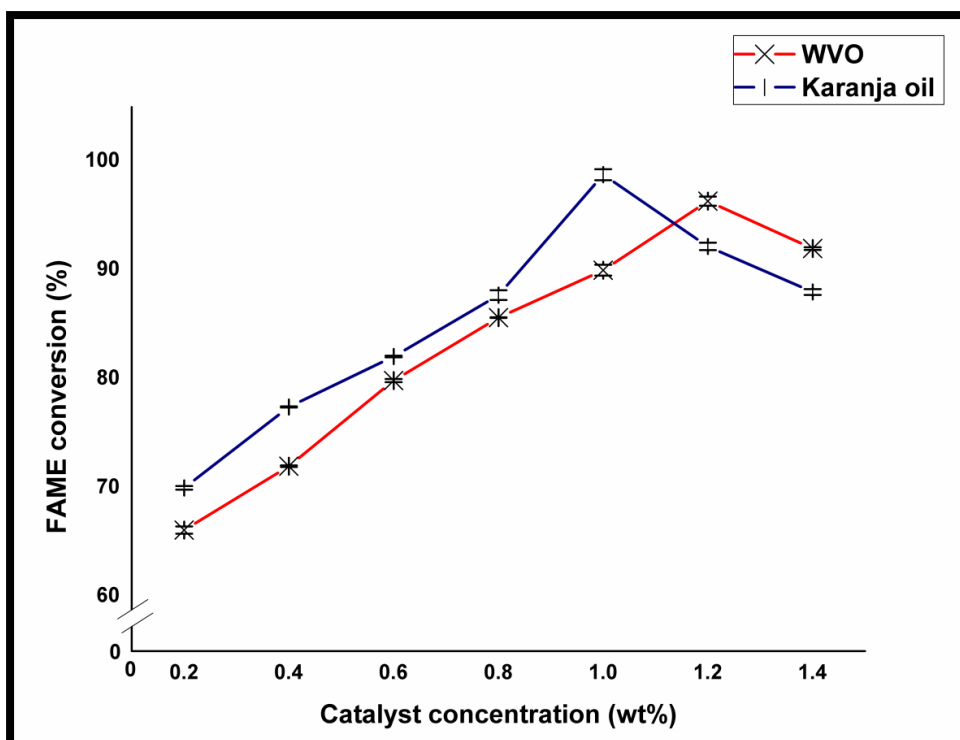
The effect of catalyst concentration on FAME conversion was elucidated from 0.2 wt% to 1.4 wt% of oil using 1:27 oil: methanol molar ratio at 65 °C for 180 min at 600 rpm stirring speed for WVO and Karanja oil (Figure 5.10). The result shows that FAME content increases as the concentration of catalyst increases from 0.2 wt% to 1.4 wt%. At 0.2, 0.4, 0.6, 0.8, 1.0, 1.2 and 1.4 wt% catalyst conversion for WVO were  $66.12 \pm 0.33\%$ ,  $72 \pm 0.07\%$ ,  $79.87 \pm 0.14\%$ ,  $85.66 \pm 0.03\%$ ,  $90.01 \pm 0.5\%$ ,  $96.91 \pm 0.42\%$ ,  $92 \pm 0.12\%$  whereas, Karanja oil shows FAME conversion of  $70 \pm 0.17\%$ ,  $77.44 \pm 0.05\%$ ,  $82.07 \pm 0.07\%$ ,  $87.71 \pm 0.45\%$ ,  $97.82 \pm 0.5\%$ ,  $92.2 \pm 0.34\%$  and  $88 \pm 0.27\%$  respectively. Hence, in case of WVO, maximum conversion ( $96.91 \pm 0.42\%$ ) was achieved at 1.2 wt% concentration and  $97.82 \pm 0.5\%$  of FAME was accomplished at 1.0 wt% catalytic concentration in Karanja oil. This is due to increment in active site of catalyst for transesterification reaction. Chemical constituent variations obtained in feedstock were responsible for this dissimilarity in optimum FAME conversion. Catalytic concentration of 1.2 wt% for WVO

and 1.0 wt% for Karanja oil were chosen for optimization purpose, since after this optimum value of catalyst, FAME conversion were decreased because of soap formation which enhances the viscosity of reactant [Xie and Zhao, 2014]. At high concentration of catalyst, viscosity of reaction mixture increases and hence some quantity of catalyst remains unused due to resistance during mass transfer, which decreases FAME conversion [Xie and Zhao, 2014]. As a result, 1.2 wt% of catalyst was chosen for optimization purpose of WVO and 1.0 wt% catalyst was used for Karanja oil.

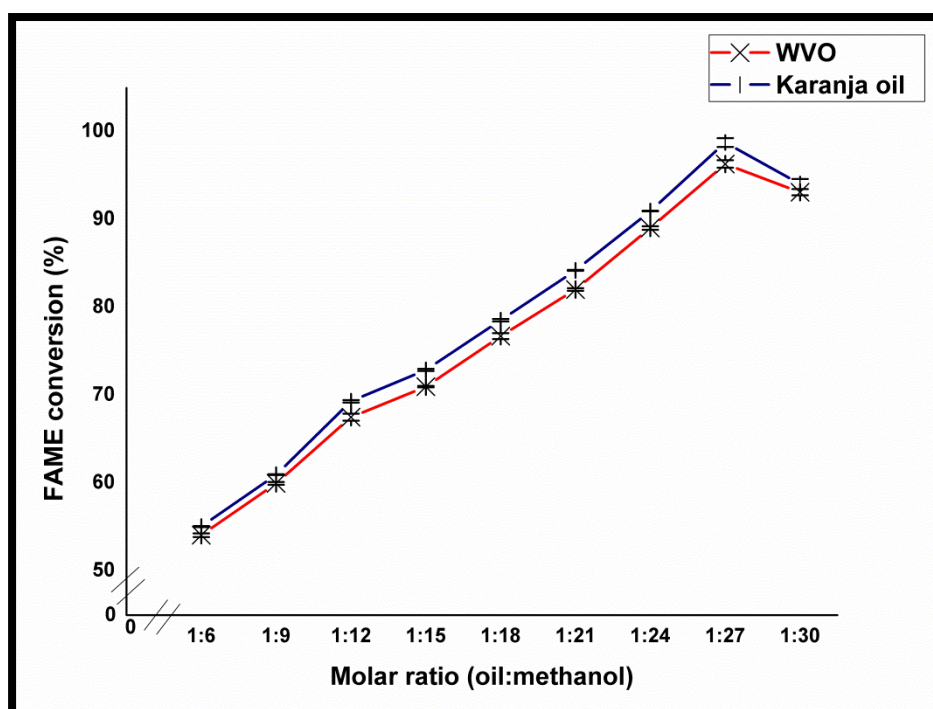
### 5.5.2 Effect of molar ratio

The molar ratio of oil: methanol significantly influences both FAME conversion and cost of final FAME production. The effect of oil: methanol molar ratio was studied from 1:6 to 1:30 by keeping other reaction variables constant as revealed in Figure 5.11. Excess of methanol is required since its effects on the rate of methanolysis. High extent of methanol promotes the formation of methoxide species which leads to shift in equilibrium in forward direction. Hence, an increase in conversion from 1:6 to 1:27 molar ratio observed as  $54.1\pm 0.21\%$ ,  $60\pm 0.15\%$ ,  $67.54\pm 0.4\%$ ,  $71\pm 0.08\%$ ,  $76.75\pm 0.33\%$ ,  $82.07\pm 0.15\%$ ,  $89.07\pm 0.2\%$ ,  $96.91\pm 0.42\%$  for WVO, however Karanja oil shows FAME conversion of  $55.08\pm 0.06\%$ ,  $61\pm 0.04\%$ ,  $69.35\pm 0.14\%$ ,  $72.91\pm 0.12\%$ ,  $78.57\pm 0.14\%$ ,  $84.24\pm 0.06\%$ ,  $90.99\pm 0.03\%$ ,  $97.82\pm 0.5\%$  for 1:6, 1:9, 1:12, 1:15, 1:18, 1:21, 1:24 and 1:27 respectively. Upon further increment in molar ratio of 1:30 FAME conversion decreases as  $93.14\pm 0.36\%$  for WVO and  $94.07\pm 0.57\%$  for Karanja oil. Glycerol formed in the final product dissolves in excessive methanol which obstructs in the transesterification reaction and with this glycerol separation becomes challenging, hence, equilibrium shift towards backward direction and ultimately FAME conversion declines [Xie and Zhao, 2014]. Hence, 1:27 molar ratio were chosen for optimization purpose.





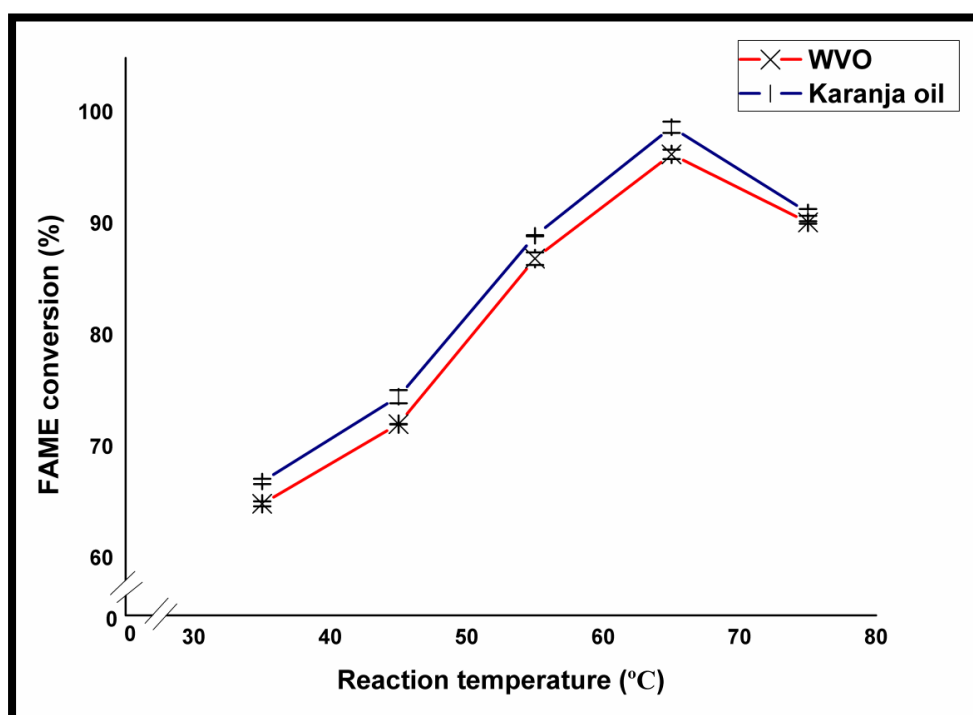
**Figure 5.10** Effect of catalyst concentration on FAME conversion (%) of WVO and Karanja oil [temperature 65 °C; time 180 min; stirring speed 600 rpm; molar ratio 1:27 oil: methanol]



**Figure 5.11** Effect of oil: methanol molar ratio on FAME conversion (%) of WVO and Karanja oil [temperature 65 °C; time 180 min; stirring speed 600 rpm; catalyst concentration of 1.2 wt% for WVO and 1.0 wt% for Karanja oil]

### 5.5.3 Effect of reaction temperature

Effect of temperature on FAME conversion is a significant parameter, since temperature influences the rate of reaction and conversion of biodiesel. Temperature effect was studied starting from 35 °C to 75 °C at other constant reaction variables condition. Substantial increment in FAME conversion observed at 35 °C, 45 °C, 55 °C and 65 °C shown in Figure 5.12 as  $65\pm 0.22\%$ ,  $72.15\pm 0.02\%$ ,  $87\pm 0.56\%$ ,  $96.91\pm 0.42\%$  for WVO, while  $67.01\pm 0.24\%$ ,  $74.62\pm 0.6\%$ ,  $89.05\pm 0.05\%$  and  $97.82\pm 0.5\%$  for Karanja oil. This effect of endorsing the transesterification reaction with the temperature can be elucidated due to endothermic reaction [Samart et al., 2009]. The maximum FAME content or conversion of  $96.91\pm 0.42\%$  and  $97.82\pm 0.5\%$  was obtained at 65 °C reaction temperature for WVO and Karanja oil respectively.

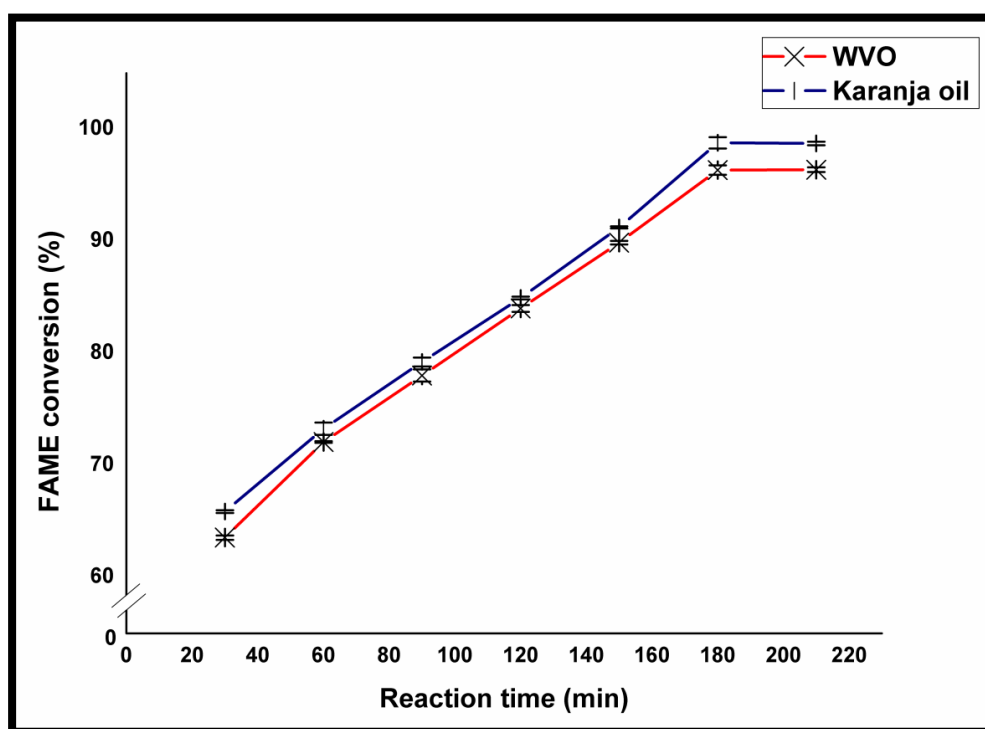


**Figure 5.12** Effect of reaction temperature on FAME conversion (%) of WVO and Karanja oil [time 180 min; stirring speed 600 rpm; 1:27 oil: methanol molar ratio; catalyst concentration of 1.2 wt% for WVO and 1.0 wt% for Karanja oil]

After this optimum temperature, when reaction temperature rises to 75 °C, the conversion of FAME declines as  $90.25\pm 0.11\%$  in WVO and  $91.15\pm 0.3\%$  in Karanja oil, this result was due to high temperature where methanol got quickly vaporized after its boiling point to form bubbles, hence impedes the reaction by forming interface of two phases [Chai et al., 2007]. Selection of low temperature is needed to save the energy requirement and therefore optimum reaction temperature obtained for FAME conversion was 65 °C.

### 5.5.4 Effect of reaction time

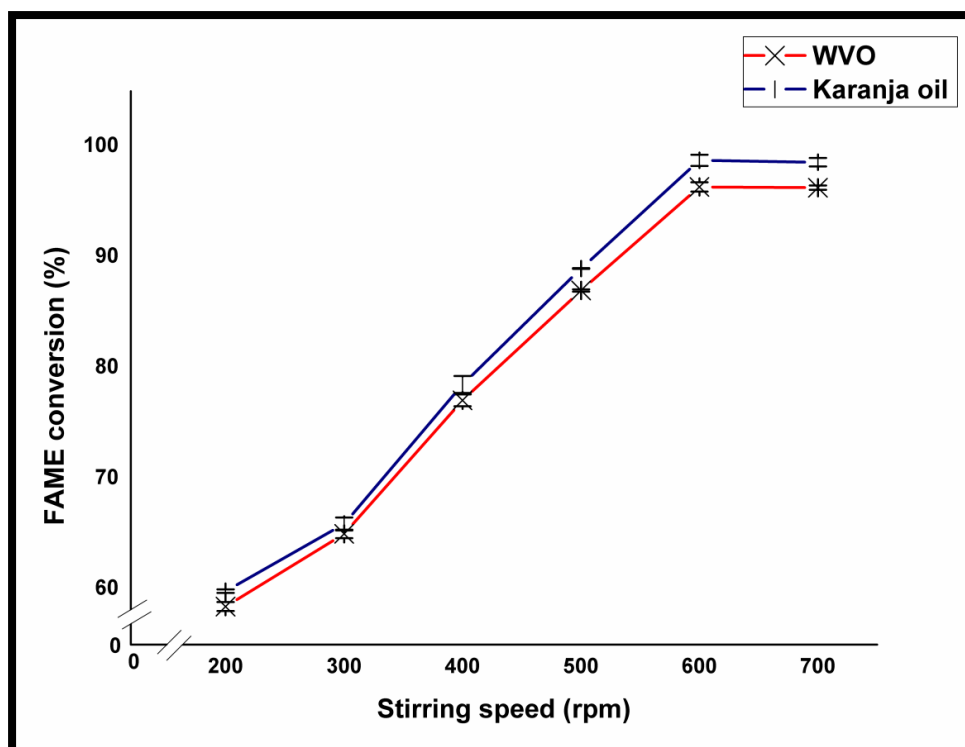
The influence of reaction time on conversion of FAME was investigated as represented in Figure 5.13. As reaction time increase from 30 min to 210 min, FAME conversion was also increased. FAME conversion of  $63.55\pm 0.2\%$ ,  $72.08\pm 0.07\%$ ,  $78.02\pm 0.54\%$ ,  $84\pm 0.3\%$ ,  $89.88\pm 0.16\%$ ,  $96.91\pm 0.42\%$  for WVO, whereas,  $65.87\pm 0.12\%$ ,  $73.28\pm 0.55\%$ ,  $79.23\pm 0.4\%$ ,  $84.94\pm 0.12$ ,  $91.25\pm 0.09\%$  and  $97.82\pm 0.5\%$  for Karanja oil for 30,60, 90, 120, 150 and 180 min respectively. Maximum conversion of FAME was obtained at optimized reaction parameters at 180 min. Further increase in reaction time from 180 min does not affects much and conversion almost remains stable i.e.  $96.39\pm 0.21\%$  and  $97.73\pm 0.15\%$  for WVO and Karanja oil respectively for 210 min of reaction time. Subsequent rise in time beyond 180 min did not alter the FAME conversion, since the transesterification is reversible reaction and equilibrium was achieved at that time and no further time was essential in that process.



**Figure 5.13** Effect of reaction time on FAME conversion (%) of WVO and Karanja oil [temperature 65 °C; stirring speed 600 rpm; 1:27 oil: methanol molar ratio; catalyst concentration of 1.2 wt% for WVO and 1.0 wt% for Karanja oil]

### 5.5.5 Effect of stirring speed

Oil, alcohol and heterogeneous catalyst are immiscible, hence to improve exchange between the active site of catalyst and reactant, stirring plays a significant role. Stirring also excludes mass transfer effect on FAME conversion. As shown in Figure 5.14, there is gradual increase in FAME conversion with increment in stirring speed starting from 200 rpm to 600 rpm at the interval of 100 rpm as  $58.44 \pm 0.4\%$ ,  $65 \pm 0.39\%$ ,  $77.07 \pm 0.54\%$ ,  $87 \pm 0.1\%$ ,  $96.91 \pm 0.42\%$  for WVO, however,  $59.83 \pm 0.16\%$ ,  $65.9 \pm 0.59\%$ ,  $78.51 \pm 0.77\%$ ,  $88.98 \pm 0.04\%$  and  $97.82 \pm 0.5\%$  for Karanja oil and this assumes that rate of reaction was restricted by exterior mass diffusion. Above 600 rpm, i.e. at 700 rpm no noteworthy rise in FAME conversion seen as it was  $96.29 \pm 0.2\%$  and  $97.59 \pm 0.38\%$  for



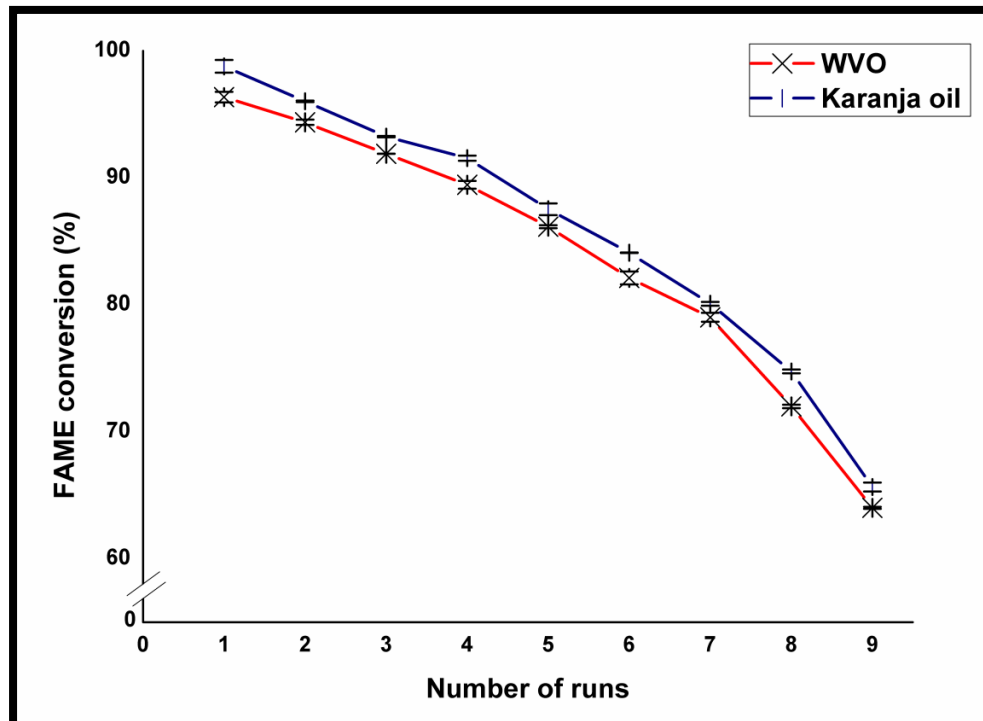
**Figure 5.14** Effect of stirring speed on FAME conversion (%) of WVO and Karanja oil [time 180 min; temperature 65 °C; 1:27 oil: methanol molar ratio; catalyst concentration of 1.2 wt% for WVO and 1.0 wt% for Karanja oil]

WVO and Karanja oil respectively, thus all experiments were conducted at 600 rpm to remove mass transfer limitations.

### 5.5.6 Effect of catalyst reusability

Homogeneous catalyst cannot be reused since limitation in separation after its usage. However, heterogeneous catalysts can be recycled and reused several times. Activity of catalyst falls only when surface of catalyst is entirely surrounded with the product which lessens occurrence for methanol and catalytic surface contact [Sun et al., 2010]. Catalytic activity was performed by using 1.2 wt% catalyst for WVO and 1.0 wt% catalyst for Karanja oil at each step. After every successful run, the catalyst was washed with hot methanol to remove organic impurities exist on the surface of catalyst.

The washed catalyst was dried in oven for 3-4 h at 120 °C and for activation calcination has been performed at 600 °C for 2 h. From Figure 5.15, it has been observed that catalytic activity continuously diminished from first cycle to ninth cycles as we got FAME conversion of  $96.91\pm 0.42\%$ ,  $94.38\pm 0.2\%$ ,  $91.9\pm 0.01\%$ ,  $89.45\pm 0.3\%$ ,  $86.15\pm 0.12\%$ ,  $82.12\pm 0.51\%$ ,  $79.02\pm 0.35\%$ ,  $72\pm 0.14\%$ ,  $64.01\pm 0.08\%$  for WVO, while  $97.82\pm 0.5\%$ ,  $96.03\pm 0.06\%$ ,  $93.25\pm 0.05\%$ ,  $91.55\pm 0.2\%$ ,  $87.53\pm 0.46\%$ ,  $84.1\pm 0.02\%$ ,  $80.08\pm 0.15\%$ ,  $74.75\pm 0.15\%$ ,  $65.65\pm 0.35\%$ , in Karanja oil. Hence, barium zirconate can be reused up to consecutive nine runs for transesterification reaction with admirable activity. The reason behind this loss in activity may be due to deposition of organic species on the surface of catalyst responsible for deactivation of catalyst through blockage of catalytic active sites.



**Figure 5.15** Barium zirconate ( $\text{BaZrO}_3$ ) reusability analysis up to nine runs [1:27 M ratio of oil: methanol at 65 °C for 180 min and 600 rpm stirring speed; 1.2 wt% of catalyst for WVO and 1.0 wt% for Karanja oil]

Barium zirconate, the catalyst used for nine runs, can be reused in other fields such as thermal barrier coating material for aerospace industry, for high temperature superconductor manufacturing due to its less reactivity towards corrosive compound, thermal stability, weak thermal conductivity and good mechanical property [Viviani et al., 2001; Erb et al., 1995; Vassen et al., 2000].

### 5.6 Characteristics of FAME synthesized from WVO and Karanja oil

Physicochemical properties of FAME produced were investigated as well as compared with the reported properties as per ASTM standards. As shown in the Table 5.3 properties of WVO methyl ester and Karanja oil methyl ester were characterized and accomplished as per ASTM D6751 [Tariq et al., 2011] standards.

**Table 5.3** 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	0.79	0.52
Density (40 °C, g cm <sup>-3</sup> )	D1448-1972	0.863	0.795
Kinematic viscosity (cSt at 40 °C)	D445	4.79	5.3
Cetane number	D613	46.05	44
Calorific value (MJ/Kg)	D6751/ DIN51900	38	37.13
Flash point (°C)	D93	123	98.3
Fire point (°C)	D93	137	114
Cloud point (°C)	D2500	6	7
Pour point (°C)	D97-05	4	5
Ash content (%)	D482	0.04	0.03

The acid value of WVO methyl ester and Karanja oil methyl ester were found to be 0.79 mg of KOH/g and 0.52 mg of KOH/g respectively and were within ASTM standard. The density and kinematic viscosity of WVO FAME were observed as  $0.863 \text{ g cm}^{-3}$  and 4.79 cSt at 40 °C respectively and were within ASTM range for biodiesel. Density and kinematic viscosity of Karanja oil FAME were observed to be  $0.795 \text{ g cm}^{-3}$  and 5.3 cSt at 40 °C and also within ASTM limit of biodiesel. Viscosity is directly related to density and by executing simply transesterification reaction viscosity can be lessened which affects on fuel injection property. Cetane number of FAME was observed to be 46.05 and 44 for WVO and Karanja oil as per ASTM standards D613. Cetane number of the biodiesel plays a significant role for quality of fuel and relates with combustion quality as well as ignition delay time; therefore, cetane number in good agreement is necessary for better engine performance. The calorific value of the FAME was observed to be 38 MJ/kg and 37.13 MJ/kg. The flash point as well as fire point was observed to be 123 °C; 137 °C and 98.3 °C; 114 °C respectively for WVO methyl ester and Karanja oil methyl ester, which was considered as safe limit for transportation and storage. Cloud point and pour point was found to be 6 °C; 4 °C and 7 °C; 5 °C respectively. Ash content obtained for WVO methyl ester was found to be 0.04% whereas, Karanja oil methyl ester shows ash content of 0.03%.

From the study, it has been perceived that barium zirconate used as a catalyst in the experiments has good potential to produce FAME from oil on large scale and has ability to replace petro-diesel.



**5.7 Conclusion**

Barium zirconate ( $\text{BaZrO}_3$ ) heterogeneous catalyst has been synthesized by co-precipitation method and characterized by TGA, XRD, ATR-FTIR, SEM, EDS, BET, particle size, BJH analysis and basicity techniques. Barium zirconate was proved to be a virtuous catalyst for transesterification of waste vegetable oil and Karanja oil as feedstocks. FAME obtained was characterized at different reaction parameters. Under optimized condition of transesterification reaction for WVO at molar ratio of 1:27 oil: methanol, 1.2 wt% catalytic concentration, 65 °C reaction temperature, 180 min time of reaction and 600 rpm of stirring speed FAME conversion was  $96.91 \pm 0.42\%$ , whereas Karanja oil showed FAME conversion of  $97.82 \pm 0.5\%$  at 1:27 oil: methanol molar ratio, 1.0 wt% catalyst, 65 °C reaction temperature, 180 min time of reaction and 600 rpm of stirring speed. The catalyst has been recovered, recycled and was stable up to nine runs (FAME conversion > 64%). The physicochemical properties of WVO methyl ester and Karanja oil methyl ester have been studied and were found within ASTM standards. Thus, barium zirconate ( $\text{BaZrO}_3$ ) could become an attractive alternative catalyst for large scale production of economically feasible biodiesel.