CHAPTER 4

Synthesis and characterization of beta-potassium dizirconate (β-$K_2Zr_2O_5$) and its application in biodiesel production from waste vegetable oil (WVO) and *Pongamia Pinnata* (Karanja) oil

CHAPTER 4

4.1 Introduction

This chapter includes synthesis of beta-potassium dizirconate (β-$K_2Zr_2O_5$) as a heterogeneous catalyst by solid state method; characterization of catalyst by various techniques such as 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; biodiesel production via transesterification reaction of waste vegetable oil (WVO) and (*Pongamia pinnata*) Karanja oil; optimization of various reaction parameters such as catalyst concentration, molar ratio, reaction temperature, reaction time, stirring speed and catalyst reusability. Characterization of synthesized biodiesel by ^{1}H NMR; physicochemical properties of FAME derived from both feedstock as compared to petro-diesel and conclusion which are discussed in details as below have also been reported.

4.2 Synthesis of beta-potassium dizirconate (β-$K_2Zr_2O_5$)

Beta-potassium dizirconate (β-$K_2Zr_2O_5$) was synthesized via solid state reaction method and procedure was shown in Figure 4.1. In this method, zirconium dioxide (ZrO_2) and potassium carbonate (K_2CO_3) were mixed in their stoichiometric ratio of Zr/K 1:1. Mixing was done by ball milling for 2 h in presence of acetone. Resultant mixture was calcined in a muffle furnace at 850 ºC for 4h. Catalyst was ground by using pestle and mortar and then sieved to get fine powder. Finally, prepared catalysts were placed in desiccator for further application.

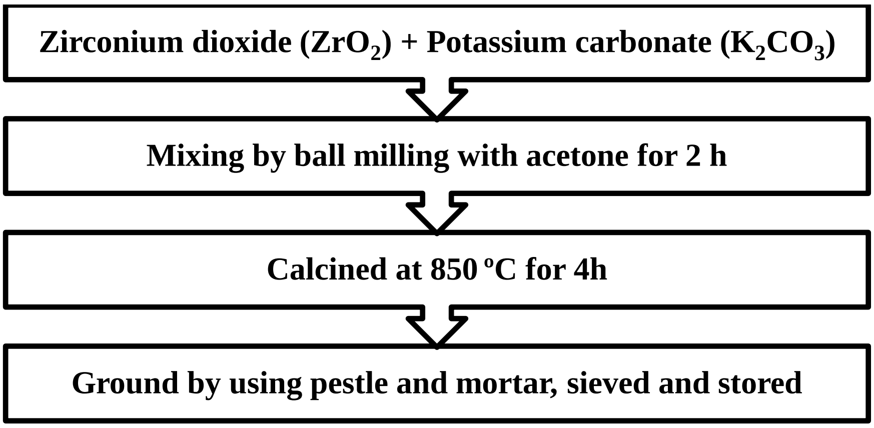

Figure 4.1 Synthesis of β-$K_2Zr_2O_5$ by solid state method

4.3 Characterization of beta-potassium dizirconate (β-$K_2Zr_2O_5$)

4.3.1 Thermogravimetric analysis (TGA)

Thermal characterization of the material has been done by thermogravimetric analysis (TGA) for examination of decomposition behaviour of the sample. Figure 4.2 shows the thermogravimetric curve, which displays the decomposition temperature regarding the weight loss of uncalcined sample. The results imply that total 17.21% weight loss occurred during the heating of 20.41 mg sample from 40 °C to 900 °C at the rate of 20 °C/min when the sample dispensed for TGA analysis. Two stages of mass loss were detected. The first weight loss was due to loss of moisture as well as crystallized water at 40-200 °C, which was approximately 13.09%. Then second weight loss of 4.12% was attributed to release of carbon dioxide up to 800 °C and after that no such weight loss was observed for sample. TGA result shows that lower temperatures are requisite hence advantageous and calcination were performed at 850 °C. This result intimates the

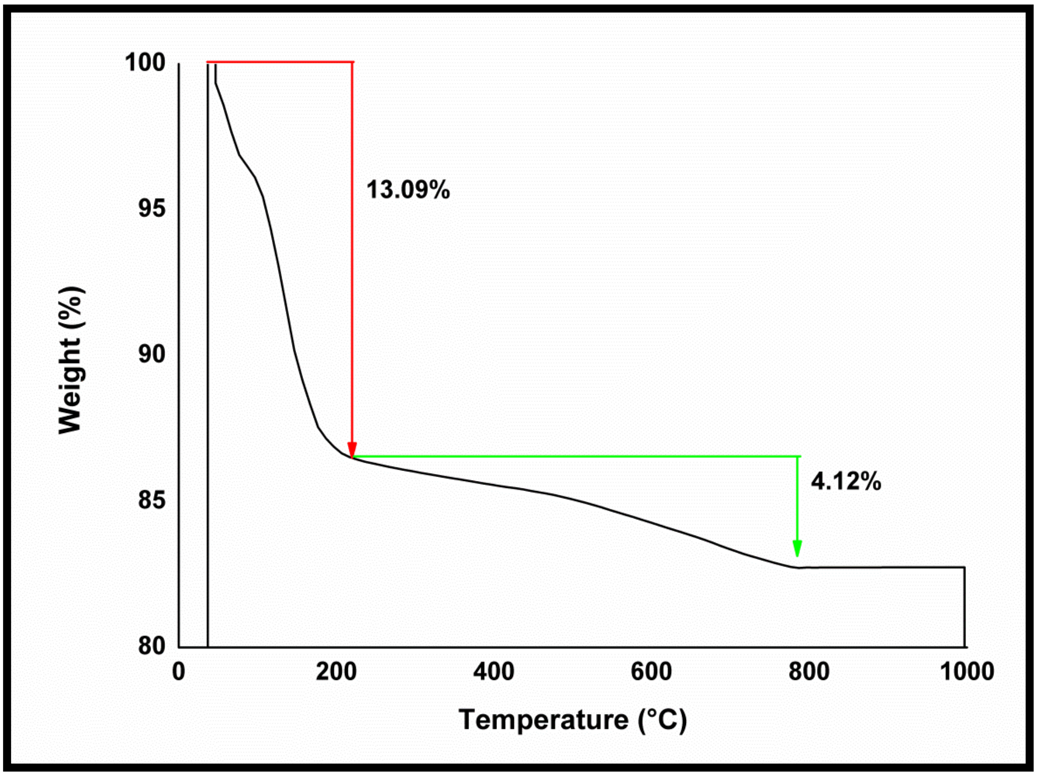

Figure 4.2 TGA curve of uncalcined β-$K_2Zr_2O_5$ catalyst

stabilization of beta-potassium dizirconate (β-$K_2Zr_2O_5$) phase. Experimental conditions were responsible for surface composition which leads to the composition of oxo-bond thatis M-O-M. Carbonate present on the surface of oxide was responsible for catalytic poisoning in transesterification with catalyst [Knothe, 2006].

4.3.2 X ray diffraction (XRD)

In order to apprehend the crystalline structure of sample during thermal decomposition, X-ray diffraction (XRD) analysis of the catalyst was performed. Figure 4.3 shows the X-ray diffraction (XRD) pattern of the catalyst synthesized by solid state method.

From the result, it has been observed that the peaks obtained were compared with the Joint Committee on Powder Diffraction Standards (JCPDS) data base. The solid state

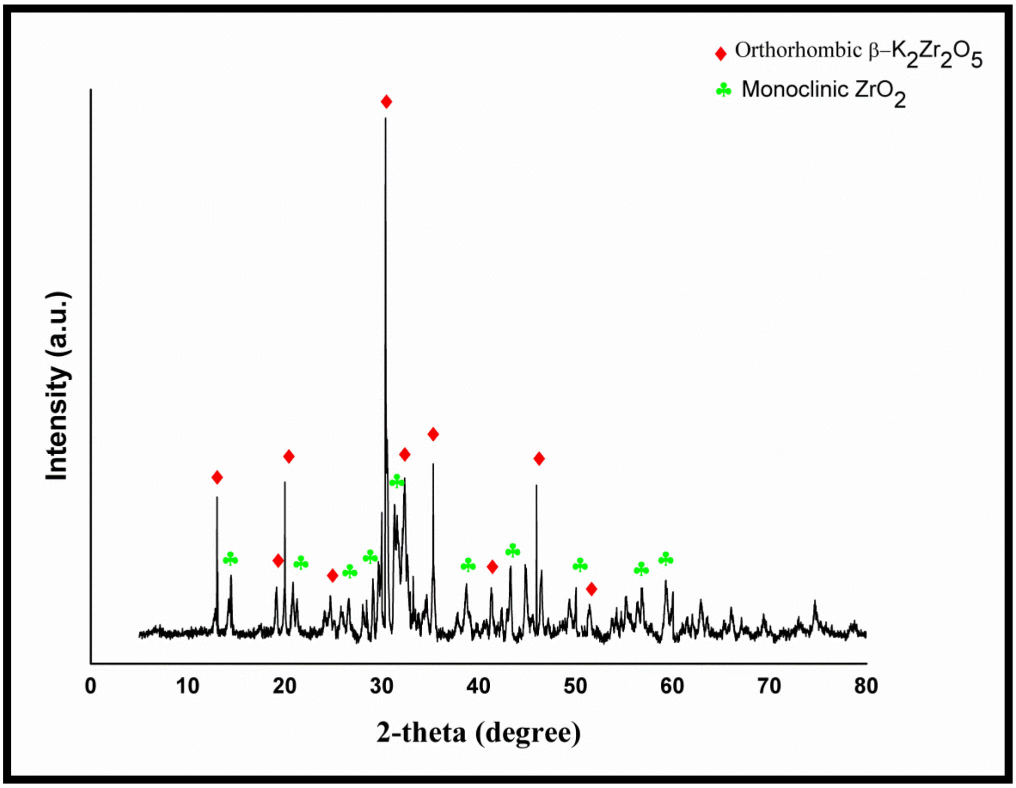

Figure 4.3 XRD pattern of the β-$K_2Zr_2O_5$ catalyst synthesized via solid-state reaction

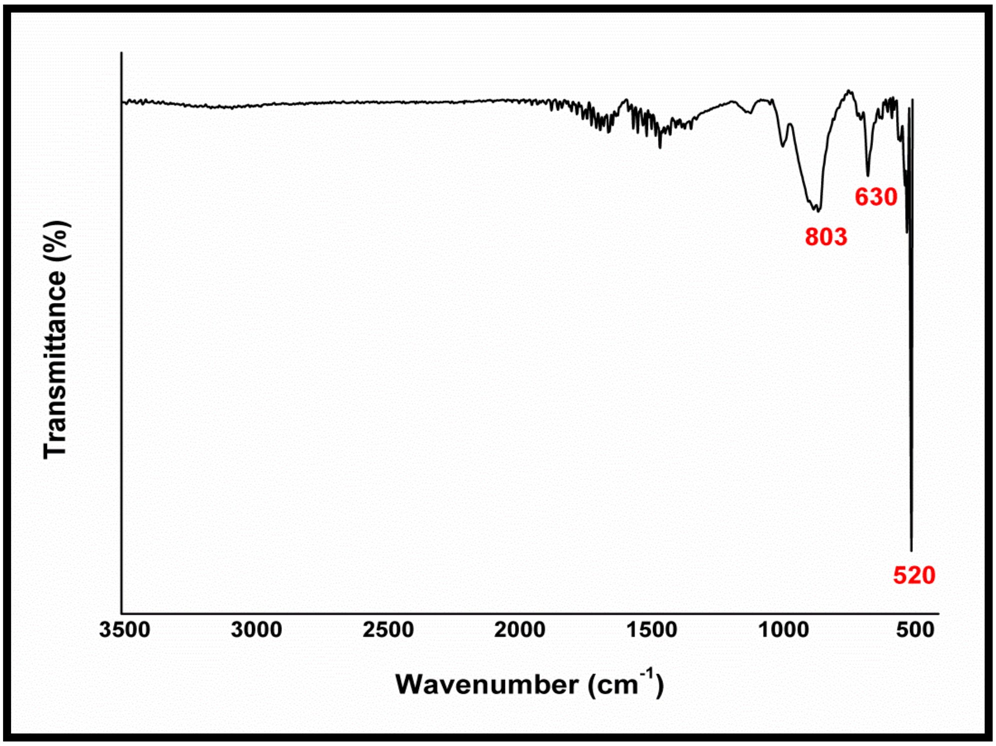

Figure 4.4 ATR-FTIR spectra of β-$K_2Zr_2O_5$ catalyst

method formed beta-potassium dizirconate (β-$K_2Zr_2O_5$) as a preeminent phase. XRD was performed in the scan range of 5º- 80º with 5º /min scan speed. Increment in calcination temperature was responsible for initiation of beta-potassium dizirconate (β-$K_2Zr_2O_5$) formation due to solid state reaction between ZrO_2 and K_2CO_3. Prominent peak values were matched with mixed phase of orthorhombic beta-potassium dizirconate (β-$K_2Zr_2O_5$) JCPDS file No. 72-1690 and monoclinic zirconia (JCPDS file no. 88-2390). The intense peaks at 13.02º, 19.15º, 20.01º, 30.38º, 33.19º, 35.32º and 45.95º attributed to beta-potassium dizirconate (β-$K_2Zr_2O_5$) phase and other phases remain inattentive, hence confirmed that catalyst has been synthesized by completion of reaction between K_2CO_3 and ZrO_2 [Xie et al., 2006] that had been used as heterogeneous catalyst for biodiesel production. The smaller peaks observed at 14.41º, 20.86º, 26.53º, 29.14º, 31.30º, 38.51º, 43.20º, 49.85º, 57.05º and 59.35º on XRD pattern were due to presence of monoclinic ZrO_2 phase. Crystallite size of potassium doped ZrO_2 increased at high calcination temperature due to sintering of particles. Zirconium oxide itself was catalytically inactive for transesterification reaction in biodiesel production. Under supercritical conditions, zirconium oxide acts as active catalyst because of acidic properties [Lima et al., 2012]. Our consideration was biodiesel production at amiable conditions and hence simply solid state method was chosen for catalyst synthesis.

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

The X-ray diffraction (XRD) technique, as mentioned previously is not more effective in estimating the appearance of non-crystalline phases present in the sample when compound acquaint on surface of the sample. Hence, attenuated total reflectance Fourier transform infrared spectra (ATR-FTIR) of the catalyst (Figure 4.4) were obtained for characterization. This technique is more sensitive for assimilation of phases. Figure 4.4 depicts the spectrum of synthesized catalyst. The intense absorption bands were observed at 803, 630 and 520 cm^{-1}. Among them, vibrations at 520 and 803 cm^{-1} occurred due to Zr-O stretching frequency [Sarkar et al., 2006; Guarany et al., 2003]. Whereas, vibration at 630 cm^{-1} were obtained due to presence of Zr-O-Zr stretching band [Borilo and Spivakova, 2012]. FT-IR results are found to be in good agreement with XRD results obtained. Bands in the range of 500 cm^{-1} and 650 cm^{-1} were supposed to appear and defined to metal-oxygen (M-O) bond which absorbed energy in that region [Sarkar et al., 2006]. From Figure, it has been observed that the broad peaks due to carbonate CO_3^{2-} were observed between 1459 to 1656 cm^{-1} [Taglieri et al., 1999]. All the peaks present are characteristics of the material; there is no evidence for any organic content presence in the synthesized sample.

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

BET surface area of the synthesized beta-potassium dizirconate (β-$K_2Zr_2O_5$) was conducted to obtain surface area, pore size and pore volume. BET surface area and Langmuir surface area was found to be 10.88 m^2/g and 16.75 m^2/g respectively. BJH adsorption and desorption cumulative surface area of pores was 13.97 m^2/g and 16.03 m^2/g respectively. Though, surface area was observed to be lesser, catalytic activity of beta-potassium dizirconate (β-$K_2Zr_2O_5$) was higher at appropriate reaction condition. Pore volume at single point adsorption was 0.036 cm^3/g with this BJH adsorption and desorption cumulative volume were 0.034 cm^3/g and 0.035 cm^3/g respectively. BJH adsorption and desorption pore size was observed as 99.78 Å and 88.27 Å.

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

Surface morphology and size of particle of the synthesized catalyst have been studied by scanning electron microscopy (SEM). Figure 4.5 represents the SEM image of the catalyst. From SEM image, agglomerations of particles of irregular geometry were observed and this was due to doping of potassium which forms comparatively smaller particles than ZrO_2 available commercially [Kaur and Ali, 2015]. From this Figure, it has been clear that size and shape of synthesized catalyst are diverse as well as non-uniform. It is observable that solid state method for guest compound and surface used for support in activation purpose is propitious for high catalytic activity of the catalyst [Xie and Li, 2006].

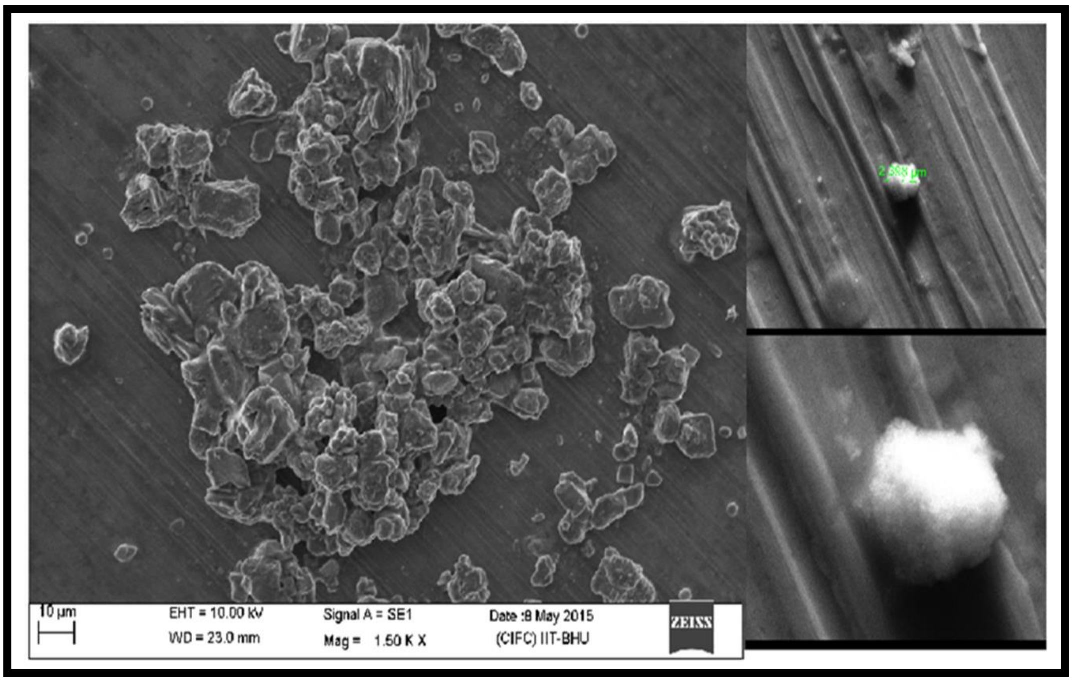

Figure 4.5 SEM image of the β-$K_2Zr_2O_5$ synthesized catalyst

Compositions present on bond interface were studied by using energy dispersive X-ray spectroscopy (EDS). The EDS is attached to the scanning electron microscope (SEM) and these two techniques were often used together. Instrument gives the signals of energy vs. signal strength in the form of histograms and associated to relative concentrations. Compositional analysis through EDS anticipated that the potassium, zirconia and oxygen are the elements exist in the sample and have been shown in Figure 4.6. While, Table 4.1 clearly described that calcined beta-potassium dizirconate (β-$K_2Zr_2O_5$) consists of 2.51 wt% K, 65.75 wt% Zr and 31.74 wt% O.

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Figure 4.6 EDS image of the β-$K_2Zr_2O_5$ synthesized catalyst

Table 4.1 Element weight % present in β-$K_2Zr_2O_5$ sample

Elements	Weight (%)	Atomic (%)
O	31.74	71.65
K	2.51	2.32
Zr	65.75	26.03
Total	100.00	100.00

4.3.6 Particle size analysis

The diameter of particle was dignified with the help of particle size analyser which is based on the dynamic light scattering (DLS) principle. Intensity size distribution (weighted) was represented in the form of histogram as shown in Figure 4.7(A). Magnitude of each peak was calculated and can convert them to volume or number distributions by this instrument related to overall scattered intensity percent throughout particles. Volume distribution for the same sample was represented in Figure 4.7(B). Volume distribution provides the relative volume of particles for each size present in sample. Number distribution was obtained by volume percentage divided by cubed diameter of particles as represented in Figure 4.7(C). ln(G2(t)-1) plot shows natural logarithmic graph in between ln(G2(t)-1) plot and decay time (Figure 4.7(D)) which indicates the presence of noise in the signal. The analyses were performed at 25 ºC temperature in aqueous form at 12527 cps scattering intensity. Refractive index and viscosity was 1.3328 and 0.8818 cP respectively. Whereas, polydispersity index was 0.239, diffusion constant (D) was 1.489e-008 (cm²/sec). According to intensity distribution average diameter of particles was 0.76 µm and standard deviation of 0.99 µm. Volume distribution shows the average diameter of particles as 0.23 µm and standard deviation of 0.15 µm, whereas, number distribution graph displays average particle diameter of 0.2 µm and standard deviation of 0.03 µm.

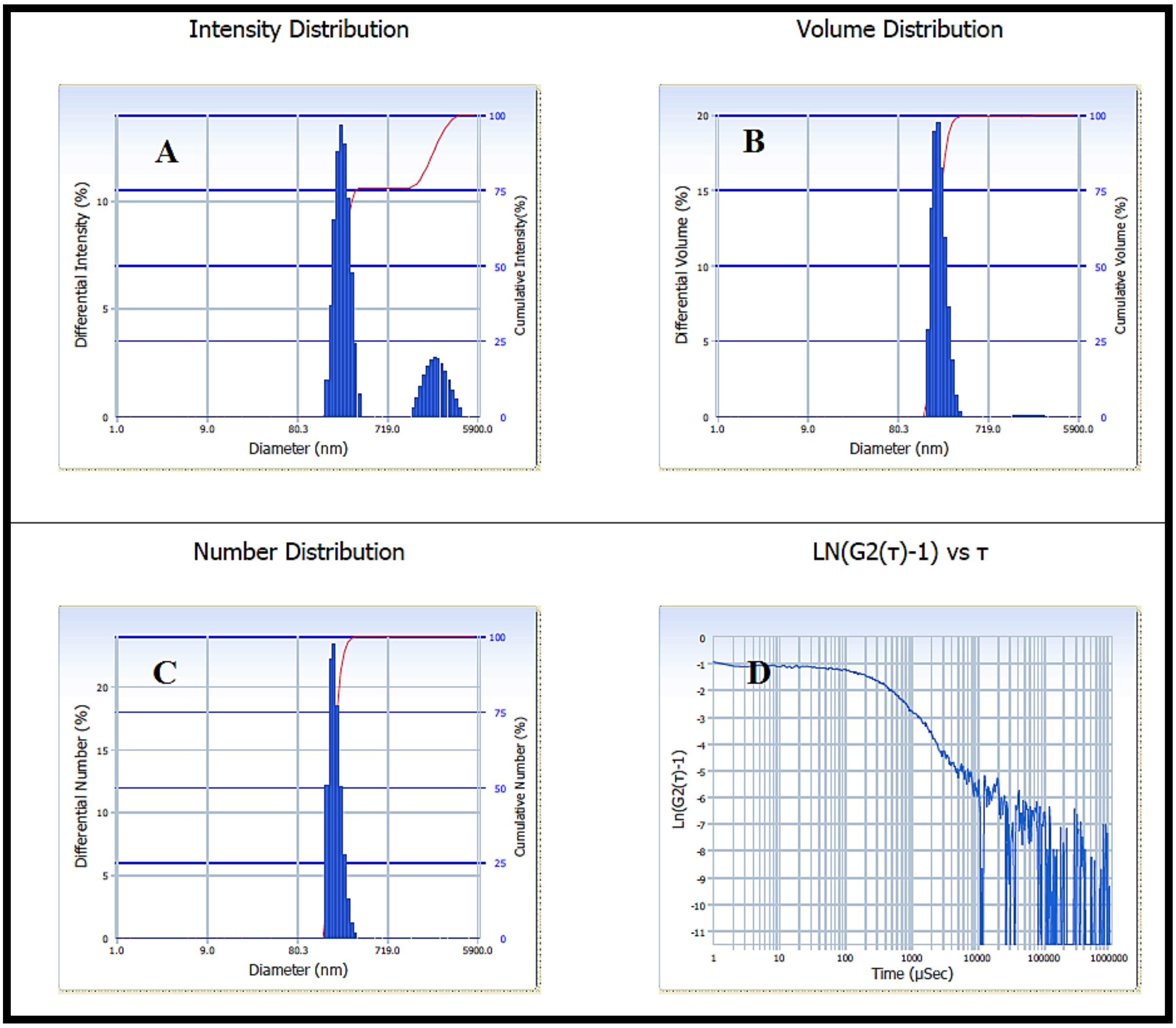

Figure 4.7 Particle size distribution (A) Diameter with respect to differential intensity (B) Diameter with respect to differential volume (C) Diameter with respect to differential number (D) Natural logarithmic graph in between ln(G2(t)-1) plot and decay time

4.3.7 Basicity

Basic strength of the synthesized catalyst was obtained because of oxide ions which are Lewis base present on mixed metal oxide apparent [Yan et al., 2009]. Basic site strength of beta-potassium dizirconate (β-$K_2Zr_2O_5$) was calculated by Hammett indicator benzene carboxylic acid titration method. In this method, total basic sites were calculated irrespective of their positions (Table 4.2). This titration was conducted in presence of

Table 4.2 Basicity of β-$K_2Zr_2O_5$

S. No.	Indicators	Basicity (mmol/g of catalyst)
1	Neutral red $pK_{BH}^{+}= 6.8$	0.05
2	Bromothymol blue $pK_{BH}^{+}=7.2$	0.09
3	Phenolphthalien $pK_{BH}^{+}= 9.3$	0.38
4	Nile blue $pK_{BH}^{+}= 10.1$	0.30
5	Trapeolin $pK_{BH}^{+}=11.1$	0.35
6	2,4- Dinitroaniline $pK_{BH}^{+}= 15.0$	0.58
	Total basicity	1.75

various indicators having pK_{BH}^{+} in between 6.8-15.0 (Neutral red, Bromothymol blue, Phenolphthalein, Nile blue, Trapeolin and 2,4-dinitroaniline) and was shown in Table 4.2. The total basicity of beta-potassium dizirconate (β-$K_2Zr_2O_5$) was obtained as 1.75 mmol/g.

4.4 Biodiesel production via transesterification and its analysis

As acid value of WVO was less (2.36 mg KOH/g) and hence direct transesterification was accomplished, however, in case of Karanja oil due to high acid value (5.60 mg/KOH) acid esterification was also performed to lower its acid value (0.52 mg KOH/g). Transesterification reaction was performed in 250 ml three neck round bottom flask equipped with mechanical stirrer, condenser and thermometer in a hot water bath. Activation of the catalyst (varied from 1.0 wt% to 5.0 wt% of oil) has been done by dispersing it with methanol at 45 ºC for 30 min with continuous stirring. After activation, oil was added to the above mixture and then refluxed for 2 h at 65 ºC under constant stirring. Reaction mixture was transferred into separating funnel overnight to separate three distinct phases of methyl ester (top), glycerol (middle) and catalyst (bottom) phases. Catalyst was collected and reused for further experiments after activation. Excessive methanol present in the methyl ester phase was evaporated by rotary evaporator and traces of water by passing through anhydrous Na_2SO_4 [Sharma and Singh, 2009]. Ester content present in biodiesel from waste vegetable oil and Karanja oil was determined by ^{1}H NMR using Equation 3.1.

In present study, optimization has been done by carrying out reaction with varying oil: methanol molar ratio from 1:4 to 1:12 by taking 1.0 wt% to 5.0 wt% of catalyst. The reaction time varied from 30 min to 150 min and temperature from 35 ºC to 75 ºC with stirring speed of 200 rpm to 700 rpm. In addition, reusability of catalyst was also performed for seven runs. The experiments were conducted thrice and uncertainties were studied. Physicochemical properties of waste cooking oil methyl ester and Karanja oil methyl ester were studied and reported. ^{1}H NMR spectrum of WVO and Karanja oil derived FAME at optimum reaction conditions was shown in Figure 4.8 and 4.9 respectively. The conversion of FAME from WVO and Karanja oil was calculated by taking the values of integrated 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:

FAME conversion of WVO(%)= (2*3.00/3*2.07)*100= 96.61% …(**Equation 4.1**)

FAME conversion Karanja oil(%)= (2*3.18/3*2.18)*100= 97.24% …(**Equation 4.2**)

and was observed to be 96.61% for WVO methyl ester and 97.24% for Karanja oil methyl ester. These two peaks were used for conformation of existence of methyl ester in FAME.

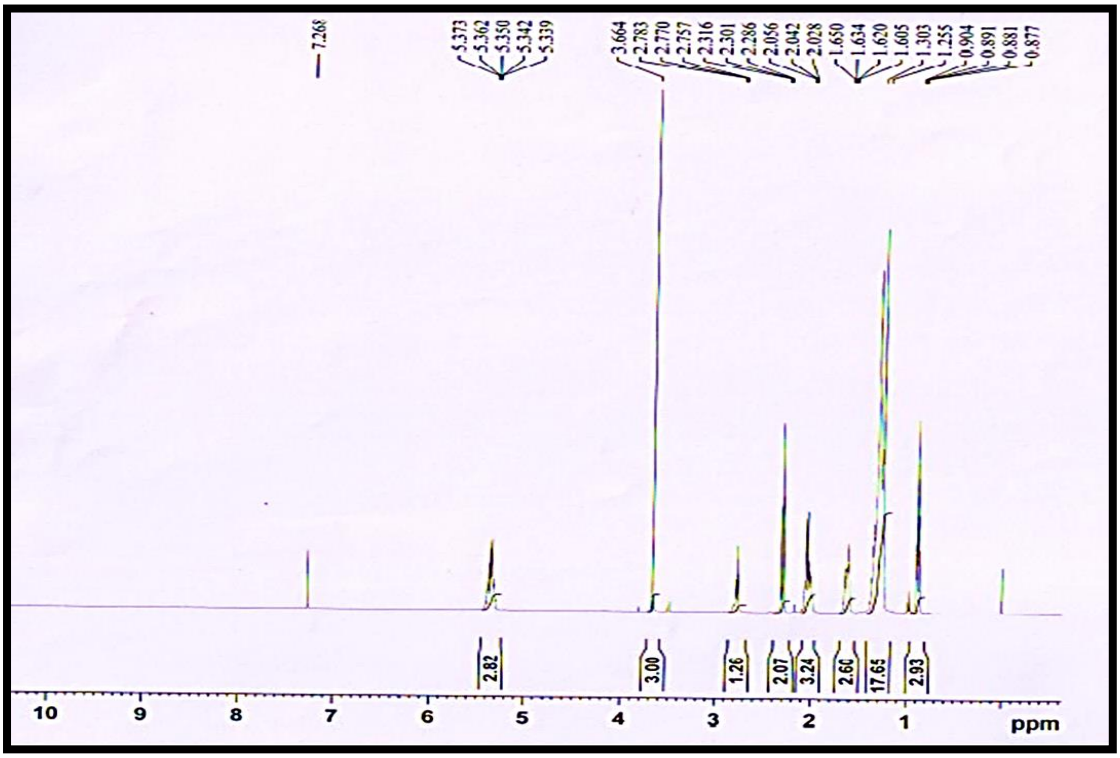

Figure 4.8 ^{1}H NMR spectrum of WVO FAME obtained at 4.0 wt% β-$K_2Zr_2O_5$, 1:10 oil: methanol, 120 min reaction time at 65 ºC temperature, 600 rpm stirring speed

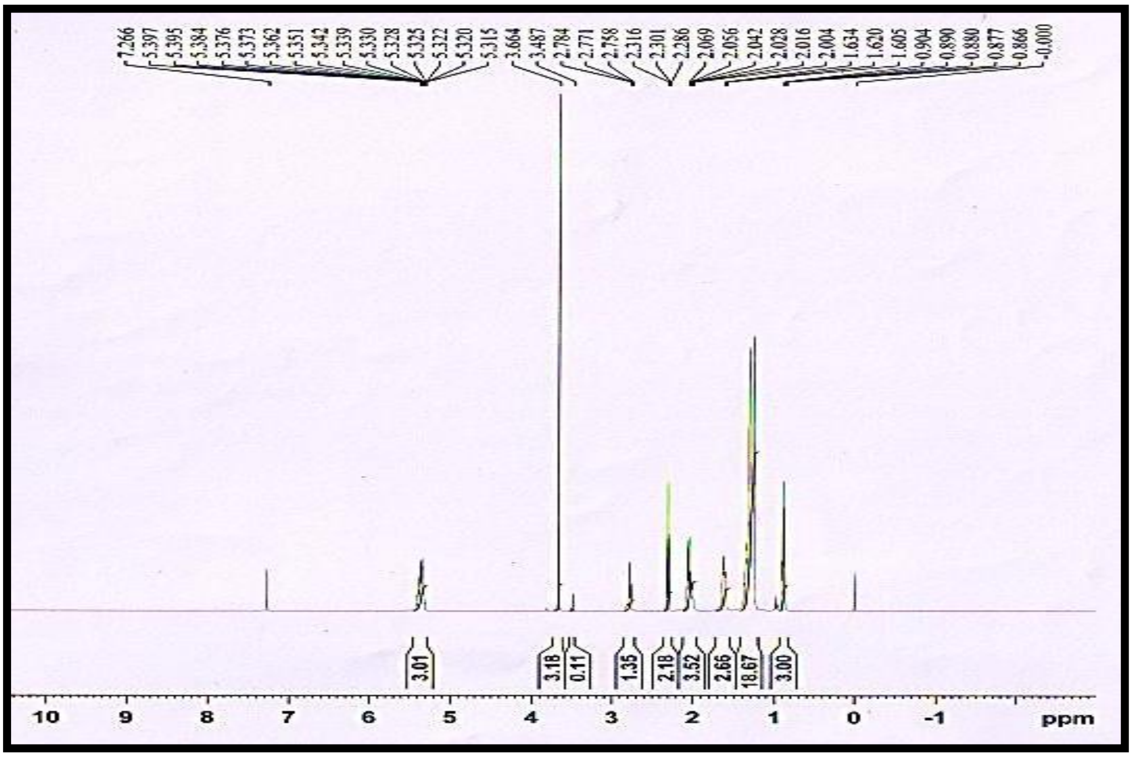

Figure 4.9 ^{1}H NMR spectrum of Karanja oil FAME obtained at 3.0 wt% β-$K_2Zr_2O_5$, 1:8 oil: methanol, 120 min reaction time at 65 ºC temperature, 600 rpm stirring speed

4.5 Effect of various reaction parameters on transesterification

The catalyst, beta-potassium dizirconate (β-$K_2Zr_2O_5$) was found to be more efficient and was used for optimization of reaction parameters for its improved catalytic activity by using waste vegetable oil (WVO) and Karanja oil as feedstock. Sequences of transesterification process were carried out in presence of beta-potassium dizirconate (β-$K_2Zr_2O_5$) in order to accomplish the reaction conditions for optimization and reusability of catalyst was also assessed.

4.5.1 Effect of catalyst concentration (wt%)

The effect of catalyst concentration on FAME conversion was investigated from 1.0 wt% to 5.0 wt% of oil using 1:10 oil: methanol molar ratio at 65 ºC for 120 min at 600 rpm stirring speed for WVO, whereas, 1:8 oil: methanol molar ratio at 65 ºC for 120 min at 600 rpm stirring speed for Karanja oil respectively (Figure 4.10). The results indicated that conversion of FAME increased as catalyst concentration was raised from 1.0 wt% to 5.0 wt%. At 1.0, 2.0, 3.0, 4.0 and 5.0 wt% catalyst concentration FAME conversion for WVO were 60.27±0.24%, 77.69±0.3%, 88±0.17%, 96.61±0.2%, 90.03±0.45%, whereas Karanja oil shows FAME conversion of 69±0.14%, 85.39±0.33%, 97.24±0.31%, 95.11±0.3% and 89.1±0.42% respectively. Where, in case of WVO maximum conversion (96.61±0.2%) was achieved at 4.0 wt% concentration while, 97.24±0.31% of FAME was accomplished at 3.0 wt% catalytic concentration in Karanja oil. This shows that availability of active sites increased for transesterification [Mutreja et al., 2014]. This difference in optimum catalytic concentration for WVO and Karanja oil was due to chemical constituents variation obtained in feedstock. Further increment in catalyst concentration beyond the optimum value shows reduction in FAME conversion. This reduction could be due to soap formation which raises viscosity of reactant and

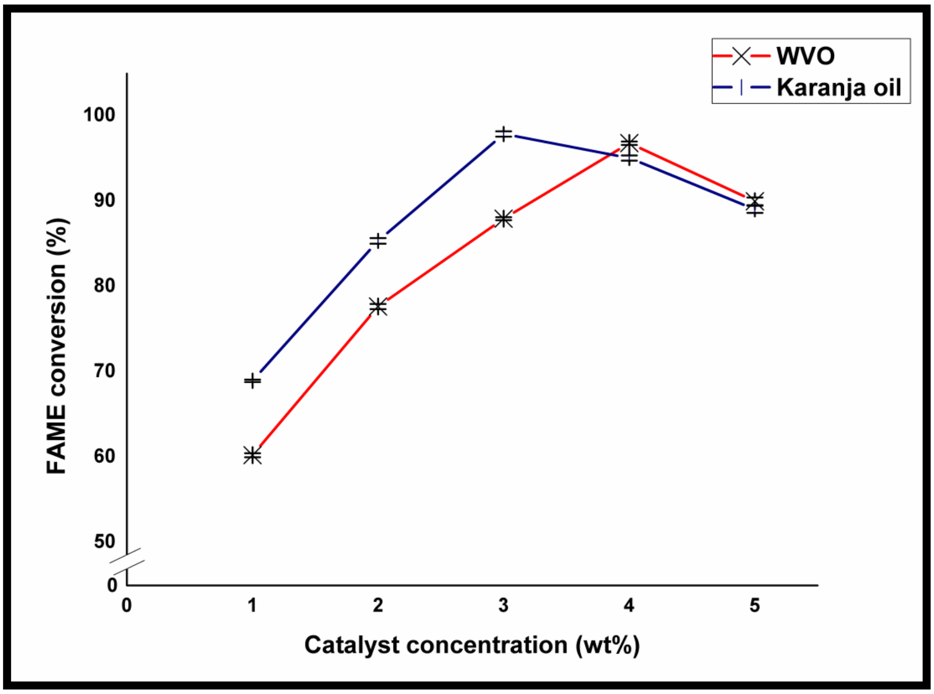

Figure 4.10 Effect of catalyst concentration on FAME conversion (%) of WVO and Karanja oil [65 ºC temperature; 120 min time; 600 rpm stirring speed; 1:10 molar ratio for WVO and 1:8 for Karanja oil]

ultimately inhibits the reaction [Sharma and Singh, 2010]. As a result, 4.0 wt% of catalyst was chosen for optimization of WVO and 3.0 wt% of catalyst was used for Karanja oil.

4.5.2 Effect of molar ratio

Excess of methanol is essential to carry out the transesterification reaction since the process is reversible as well as to enhance reaction rate [Wang et al., 2011]. High amount of methoxide ion generated on the surface of catalyst due to excess of methanol addition leads to shift in equilibrium in forward direction and also increases biodiesel conversion [Obadiah et al., 2012]. The effect of oil: methanol molar ratio was studied in the range of 1:4 to 1:12, by keeping rest of the parameters constant. The results showed that FAME conversion significantly increases as oil: methanol molar ratios were raised from 1:4 to 1:12 (Figure 4.11) as 74.04±0.3%, 82.66±0.27%, 90.77±0.25%, 96.61±0.2%,

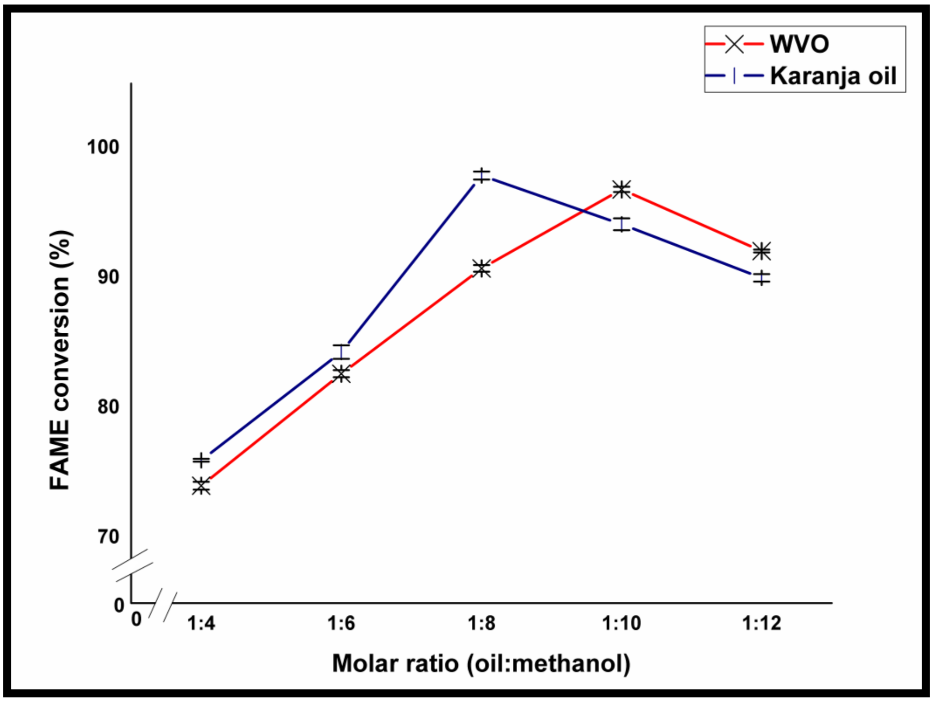

Figure 4.11 Effect of oil:methanol molar ratio on FAME conversion (%) of WVO and Karanja oil [65 ºC temperature; 120 min time; 600 rpm stirring speed; catalyst concentration of 4.0 wt% for WVO and 3.0 wt% for Karanja oil]

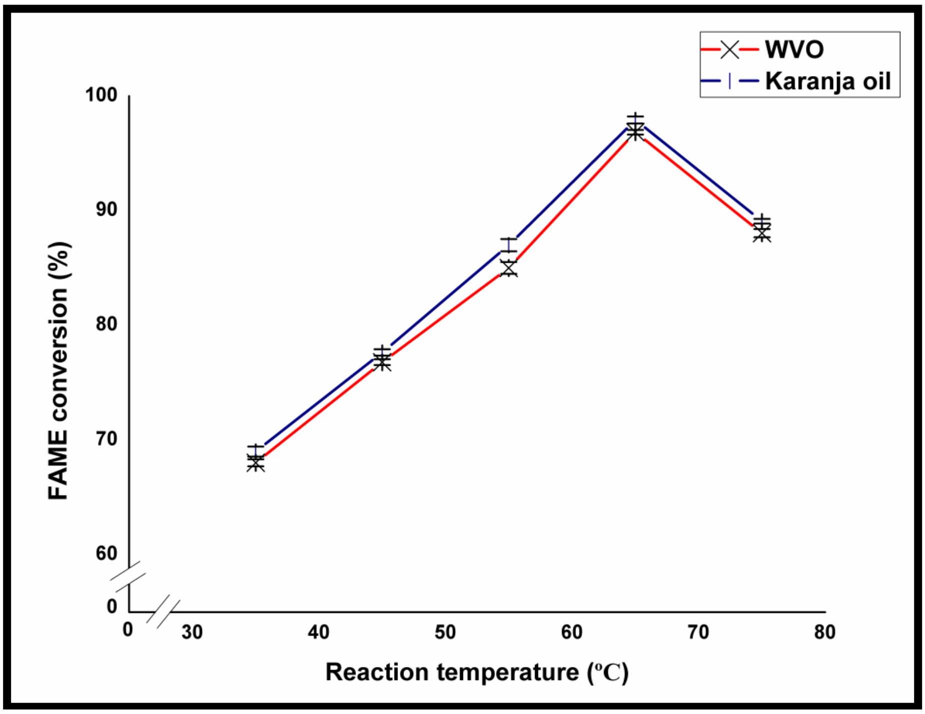

Figure 4.12 Effect of reaction temperature on FAME conversion (%) of WVO and Karanja oil [time 120 min; stirring speed 600 rpm; catalyst concentration of 4.0 wt%, 1:10 oil: methanol molar ratio for WVO and 3.0 wt% catalyst, 1:8 oil: methanol molar ratio for Karanja oil]

92.1±0.11% for WVO on the other hand Karanja oil shows FAME conversion of 76±0.11%, 84.33±0.52%, 97.24±0.31%, 94.17±0.46%, 90.05±0.29% for 1:4, 1:6, 1:8, 1:10 and 1:12 respectively. Further increment in molar ratio beyond the optimum value 1:10 for WVO and 1:8 for Karanja oil (where conversion obtained 96.61±0.2% and 97.24±0.31% respectively) did not enhance the reaction rate. This is due to dissolution of produced glycerol into excess methanol which inhibits the reaction and interrupts in glycerol separation and this resulted in reduction in FAME conversion by shifting equilibrium in opposite direction [Lim et al., 2009].

4.5.3 Effect of reaction temperature

To overcome the diffusion resistance mounted due to distinct phases of oil, methanol and heterogeneous catalyst which reduces FAME conversion, appropriate temperature is necessary for high yield of the product. In literature, it has been reported that catalyst based on ZrO_2 required higher reaction temperature for FAME conversion. Omar and Amin [2011] reported 79.7% yield of FAME by using Zr/ZrO_2 in 2.8 h at 115.5 ºC from WCO. Jitputti et al. [2006] has reported transesterification of coconut oil by using KNO_3/ZrO_2 for 4 h at reaction temperature 200 ºC and obtained 70.7% yield of FAME. Effect of reaction temperature on FAME conversion was carried out in the range of 35 ºC to 75 ºC as shown in Figure 4.12 by using other constant reaction parameters. Result showed that conversion increased as the temperature was raised up to 65 ºC as 68.02±0.3%, 76.8±0.25%, 85.01±0.51%, 96.61±0.2% for WVO while 69±0.44%, 77.65±0.28%, 87±0.54% and 97.24±0.31% for Karanja oil at 35 ºC, 45 ºC, 55 ºC and 65 ºC. Optimum conversion obtained was 96.61±0.2% for WVO and 97.24±0.31% for Karanja oil at 65 ºC. Further increase in temperature reduces the conversion, since methanol vaporizes at high temperature and inhibits the process [Long et al., 2010]. After this optimum temperature as reaction temperature increases to 75 ºC, the conversion of FAME drops to 88.05±0.36% in WVO and 89.09±0.2% in Karanja oil since it surpasses the boiling point of methanol, it starts to vaporize by forming bubbles and this inhibits the reaction and ultimately decreases the conversion of FAME obtained because of two phase interface [Long et al., 2010].

4.5.4 Effect of reaction time

Effect of reaction time on the FAME conversion was studied by carrying out reaction at various time ranging from 30 min to 150 min by keeping other parameters constant as shown in Figure 4.13. FAME conversion of 55.98±0.1%, 75.69±0.26%, 84.28±0.39%, 96.61±0.2%, 96.55±0.41% for WVO, whereas, 58.08±0.45%, 77±0.3%, 86.21±0.09, 97.24±0.31% and 97.20±0.27% for Karanja oil for 30,60, 90, 120 and 150 min was obtained respectively. Maximum conversion viz. 96.61±0.2% and 97.24±0.31% for WVO and Karanja oil has been achieved respectively at 120 min with no further increment with time and becomes constant after 120 min (Figure 4.13). Later rise in time longer than 120 min did not change the FAME conversion, as the transesterification is reversible and with this equilibrium was achieved at that time and no more time was obligatory in that process.

4.5.5 Effect of stirring speed

Heterogeneous catalyst, oil and alcohol are immiscible due to which exchange in catalytic active sites and other reactants were improved by stirring of reaction mixture. Mass transfer effect was removed by stirring and was liable for FAME conversion. As represented in Figure 4.14, progressive increment in FAME conversion was observed with rise in stirring speed up to 700 rpm which shows that reaction rate was controlled by

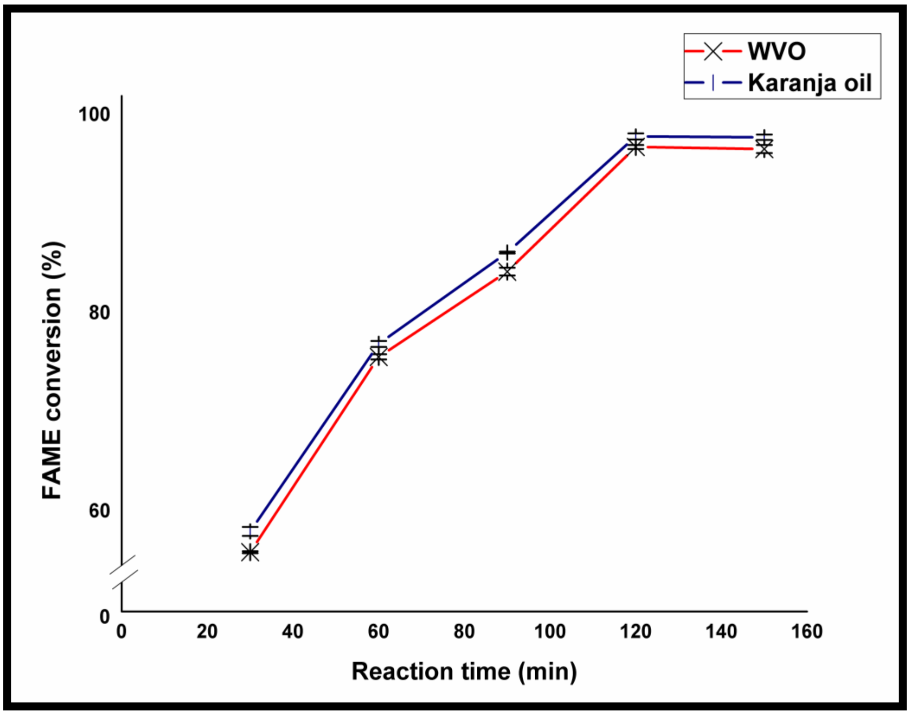

Figure 4.13 Effect of reaction time on FAME conversion (%) of WVO and Karanja oil [temperature 65 ºC; stirring speed 600 rpm; catalyst concentration of 4.0 wt%, 1:10 oil: methanol molar ratio for WVO and 3.0 wt% catalyst, 1:8 oil: methanol molar ratio for Karanja oil]

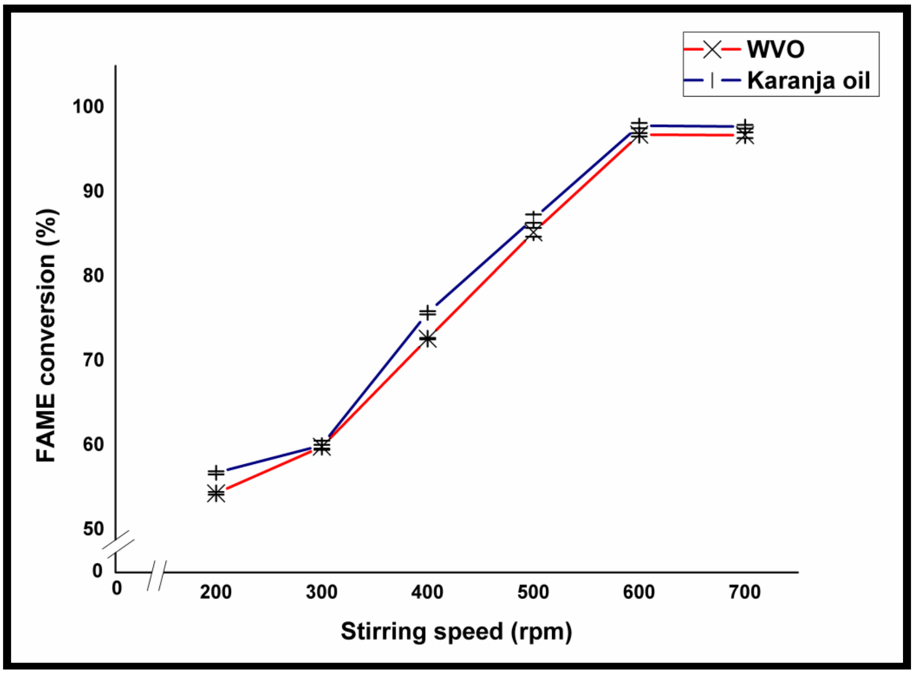

Figure 4.14 Effect of stirring speed on FAME conversion (%) of WVO and Karanja oil [time 120 min; temperature 65 ºC; catalyst concentration of 4.0 wt%, 1:10 oil: methanol molar ratio for WVO and 3.0 wt% catalyst, 1:8 oil: methanol molar ratio for Karanja oil]

external mass diffusion. At stirring speeds of 200 rpm, 300 rpm, 400 rpm, 500 rpm, 600 rpm, 700 rpm, FAME conversion was 54.38±0.16%, 59.9±0.23%, 72.69±0.08%, 85.28±0.52%, 96.61±0.2%, 96.58±0.34% for WVO, however, the conversion was 56.79±0.18%, 60.07±0.54%, 75.77±0.19%, 86.91±0.5%, 97.24±0.31% and 97.19±0.22% for Karanja oil. At 600 rpm stirring speed maximum conversion of 96.61±0.2% and 97.24±0.31% was attained for WVO and Karanja oil at other constant reaction variables. Above 600 rpm stirring speed, no significant rise in reaction rate and thus all experiments were conducted at 600 rpm to eliminate restraint existences in mass transfer

4.5.6 Effect of catalyst reusability

Use of heterogeneous catalyst is beneficial over the homogeneous catalyst because of its reusability. This test was performed (Figure 4.15) for optimized catalytic

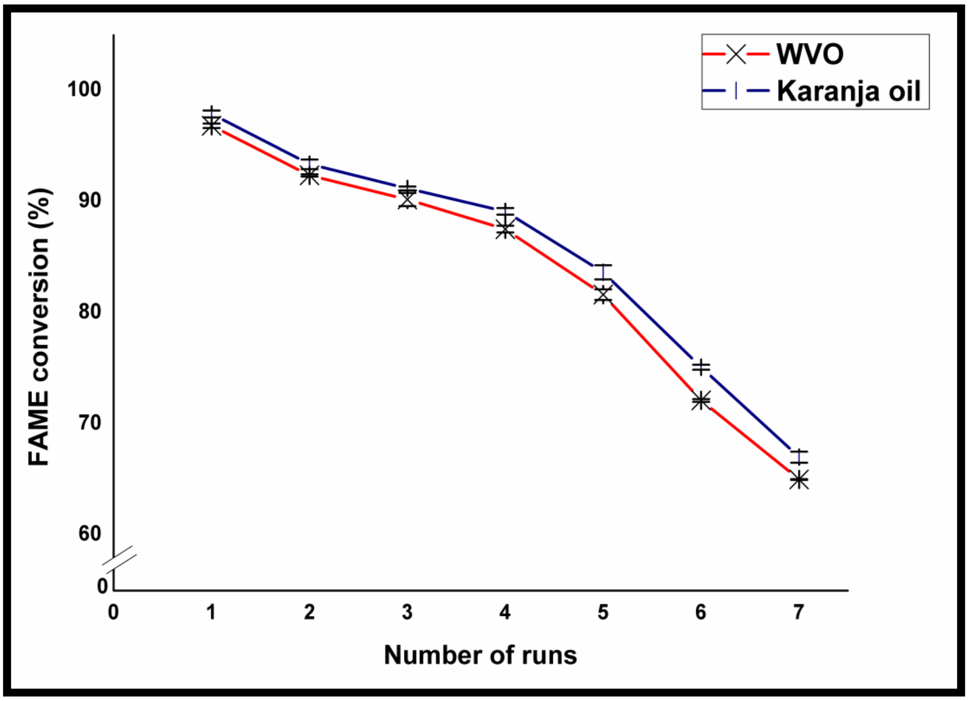

Figure 4.15 Beta-potassium dizirconate (β-$K_2Zr_2O_5$) reusability analysis up to seven runs [1:10 M ratio of oil: methanol, 4.0 wt% of catalyst at 65 ºC for 120 min and 600 rpm stirring speed for WVO and 1:8 M ratio of oil: methanol, 3.0 wt% of catalyst at 65 ºC for 120 min and 600 rpm stirring speed for Karanja oil]

concentration i.e. 3.0 wt% for Karanja oil whereas 4.0 wt% for WVO. After each run, the catalyst was washed with hot methanol to eliminate organic impurities present on the catalyst surface. Washed catalyst was dried in hot air oven at 120 ºC for 3-4 h followed by calcination for 2 h at 600 ºC. It was observed that activity of catalyst decreased continuously up to seven runs. Further, it has been observed from this figure that the catalyst worked with >65% efficiency after 7 runs and also, the efficiency of catalyst decreased from 96.61±0.2% to 92.38±0.1%, 90.21±0.6%, 87.54±0.31%, 81.65±0.47%, 72.12±0.12% and 65±0.04% for WVO and 97.24±0.31% to 93.38±0.43%, 91.21±0.18%, 89.14±0.3%, 83.91±0.02%, 75.12±0.22% and 67.02±0.5% for Karanja oil in seven runs. Thus, catalyst can be efficiently used for seven runs with >65% of FAME conversion. This will result in decrement in cost of biodiesel production. Catalytic activity drops since catalyst is covered with reactant as well as product in contact which diminishes opportunity for contact of catalyst and methanol [Madhuvilakku et al., 2013].

4.6 Characteristics of FAME synthesized from WVO and Karanja oil

The synthesized FAME from WVO and Karanja oil was characterized for its fuel and physical properties retaining methods of American Society for Testing and Materials (ASTM). Fuel characteristics as well as various parameters of FAME were accomplished as per ASTM D6751 [Tariq et al., 2011] standards as shown in Table 4.3.

The acid value of WVO methyl ester and Karanja oil methyl ester was observed to be 0.83 mg of KOH/g and 0.51 mg of KOH/g respectively that was within ASTM standard. The density and kinematic viscosity of WVO FAME were found to be 0.880 g cm^{-3} and 4.02 cSt at 40 ºC, respectively, whereas density and kinematic viscosity of Karanja oil FAME were observed to be 0.851 g cm^{-3} and 3.93 cSt at 40 ºC respectively and also within ASTM range of biodiesel. Viscosity is most essential characteristic of

Table 4.3 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	0.83	0.51
Density (40 ºC, g cm^{-3})	D1448-1972	0.880	0.851
Kinematic viscosity (cSt at 40 ºC)	D445	4.02	3.93
Cetane number	D613	49.70	47
Calorific value (MJ/Kg)	D6751/ DIN51900	38.81	39.12
Flash point (ºC)	D93	142	140
Fire point (ºC)	D93	157	151
Cloud point (ºC)	D2500	6	5
Pour point (ºC)	D97-05	3	3
Ash content (%)	D482	0.05	0.02

biodiesel, since it disturbs fuel injection equipment's operation. Viscosity is directly commensurable to density and by performing simply transesterification reaction viscosity can be decreased. Cetane number of the biodiesel plays an important role for fuel quality and correlates it with combustion quality and ignition delay time; hence a competent cetane number is obligatory for good engine performance. Cetane number of FAME was observed to be 49.70 and 47 for WVO and Karanja oil as per ASTM standard D613.The calorific values of the fuels were observed to be 38.81 MJ/kg and 39.12 MJ/kg respectively. The flash points as well as fire points were observed to be 142 ºC; 157 ºC for WVO methyl ester and 140 ºC; 151 ºC for Karanja oil methyl ester, respectively, which was within ASTM range and were deliberated as safe for their storage and transportation. Cloud points and pour points were found to be 6 ºC; 3 ºC and 5 ºC; 3 ºC respectively and were within ASTM limits. Ash content obtained for WVO methyl ester was found to be 0.05% and was slightly above the ASTM standard range while, Karanja oil methyl ester shows ash content of 0.02% which was within ASTM limits.

From these results, it has been cleared that beta-potassium dizirconate used as a catalyst for biodiesel production has significant potential to produce FAME from oil on large scale as well as has capability to replace petro-diesel.

4.7 Conclusion

Beta-potassium dizirconate (β-$K_2Zr_2O_5$), heterogeneous catalyst was synthesized and was characterized by TGA, XRD, ATR-FTIR, SEM, EDS, BET, BJH, particle size and basicity. This material was successfully used for transesterification of waste vegetable oil and Karanja oil for synthesis of biodiesel. The FAME produced through transesterification was also characterized. The optimized conditions of reaction for WVO were oil: methanol molar ratio 1:10, catalyst concentration of 4.0 wt%, time 120 min at 65 ºC reaction temperature and 600 rpm stirring speed, conversion of FAME was observed to be 96.61±0.2%. While, optimized condition for Karanja oil was oil: methanol molar ratio 1:8, catalyst concentration of 3.0 wt%, time 120 min at 65 ºC reaction temperature and 600 rpm stirring speed conversion of FAME was observed to be 97.24±0.31%. Catalytic reusability has been studied and it was observed that catalyst has stability up to seven runs (FAME conversion>65%). The characteristics of the FAME like acid value, density, kinematic viscosity, cetane number, calorific value, flash point, fire point, cloud point, pour point and ash content were within ASTM D6751 standards.

Thus, the FAME obtained from WVO and Karanja oil was economically feasible and retained a superior quality. The above results intimate that beta-potassium dizirconate (β-$K_2Zr_2O_5$) could become an alternative heterogeneous catalyst for economically viable biodiesel production at large scale.