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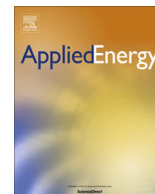
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A low cost one pot synthesis of biodiesel from waste frying oil (WFO) using a novel material, β -potassium dizirconate (β -K₂Zr₂O₅)



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HIGHLIGHTS

- A novel heterogeneous catalyst β -potassium dizirconate (β -K₂Zr₂O₅) was used for FAME production.
- 96.85% conversion of biodiesel from waste frying oil is achieved directly with the catalyst.
- The catalyst is stable up to five cycles without substantial loss in activity.

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ABSTRACT

Biodiesel was synthesized from waste frying oil (WFO) using β -potassium dizirconate (β -K₂Zr₂O₅) as a novel heterogeneous catalyst. Synthesized catalyst was characterized by X-ray diffractometry (XRD), thermogravimetric analysis (TGA), attenuated total reflectance fourier transform infrared spectroscopy (ATR-FTIR), particle size analyser, scanning electron microscopy (SEM), BET surface area and basicity. Various reaction conditions such as molar ratio of methanol: oil, catalyst amount (wt%), reaction temperature, time and reusability of catalyst were studied for transesterification reaction with the catalyst, β -K₂Zr₂O₅. High biodiesel conversion of 96.85% was observed at a 10:1 M ratio (alcohol: oil), 4 wt% catalyst at 65 °C for 2 h. WFO was characterized by GCMS and biodiesel conversion was ascertained by Fourier transform nuclear magnetic resonance (¹H and ¹³C FTNMR) spectroscopy. It was first time that β -potassium dizirconate was used as a catalyst for biodiesel synthesis. The catalyst was reused up to five times without significant loss in its activity. Physical and chemical properties of FAME such as flash point, fire point, cloud point, density, and kinematic viscosity were deliberated.

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1. Introduction

Expeditious rise in population with industrialization has resulted in energy paucity as well as global warming. According to world fact book [1], in 2014 United States, China, Japan, India and Korea are the top five countries in oil import. United States imports 9,213,000 bbl/day of crude oil whereas China, Japan, India and Korea import 5,664,000; 3,472,000; 3,272,000 and 2,590,000 bbl/day respectively. Oil consumption in these countries is 19,150,000 bbl/day for United States, China consumes 9,400,000 bbl/day, Japan, India and Korea consume 4,452,000; 3,182,000 and 2,195,000 bbl/day respectively. These countries heavily depend on the other nations for oil import, hence its obligatory to search an alternate fuel source which can reduce this oil

demand. This rapid increment in fossil fuel depletion has insisted scientists to look upon biodiesel as alternative source of energy. Biodiesel, a renewable resource of energy is eco-friendly, biodegradable, non-toxic and has potential to replace diesel fuel and fulfil the demand of world energy [2–5]. Biodiesel exhibits comparable characteristics to diesel and it also shows high cetane number, high flash point, high lubricity and low viscosity [6–9]. Biodiesel is mixture of fatty acid methyl esters (FAME) which is derived from either plant oil or animal fat [7]. Selection of feedstock plays a constitutive role in deciding the cost of biodiesel production. Recently, waste frying oil (WFO) has been reported as a potential feedstock material over the other vegetable oil sources [10–13] which improves economic viability of biodiesel. Farooq et al. reported that cost of raw material affects up to 70–95% of total production cost of biodiesel and its cost might be decreased 60–70% by utilizing waste frying oil as a feedstock which diminishes its disposal problem [14]. Currently, researchers have

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reported waste frying oil as a convenient feedstock for biodiesel production and for this biodiesel, combustion and emission characteristics were also considered [15–19]. The most frequent method used for biodiesel production is transesterification of the feedstock in presence of alcohol and catalyst (homogeneous or heterogeneous). Generally, homogeneous catalysts (acid/base) are used for biodiesel production via transesterification reaction because of their better catalytic activity [20]. However, separation of homogeneous catalysts from synthesized biodiesel needs washing with large amount of water which also results in the loss of fatty acid methyl esters (FAME), more energy accumulation and produces huge amount of waste water and this increases overall production cost of biodiesel [21,22]. Hence, heterogeneous catalysts are superior since they can be purged by filtration and can be reinvigorated and reused.

There are numerous zirconia supported catalysts that have been recognised due to their redox properties and amphoteric nature [23]. Furuta et al. [24] have reported $\text{Al}_2\text{O}_3/\text{ZrO}_2$ (2.6 wt% of Al) and $\text{TiO}_2/\text{ZrO}_2$ (11 wt% Ti) as zirconia based solid catalysts (amorphous), and obtained high conversion (>95%). This occurs because of amphoteric nature shown by zirconia. One drawback of the reaction was requirement of high temperature i.e. 448–473 K.

Santiago-Torres et al. [25] reported Na_2ZrO_3 as a basic catalyst for biodiesel production by using soybean oil feedstock and they reported a conversion efficiency of 98.3% by using 3% (by weight) catalyst at reaction time of 3 h. Intensification of basic character of zirconia has been done by applying alkali promoters like KOH [26], lanthanum oxide [27] and Mg metal [28]. Li et al. have synthesized biodiesel by using Mg–Zr as a heterogeneous catalyst [29]. Alkali zirconates have wide applications in carbon dioxide adsorption but still have very little attention for catalytic use in biodiesel production [30]. Appliance of zirconia as a support material ensued unique interface between support and active material which may yield superior activity of the synthesized catalyst [31]. Kulkarni et al. [32] have reported use of solid catalyst, tungstophosphoric acid supported hydrous zirconia for esterification and transesterification of canola oil and reported 90% of FAME yield at 200 °C. Omar and Amin [33] obtained a yield of 40% of biodiesel by using Sr/ZrO₂ catalyst for WCO. Rattanaphra et al. [34] performed transesterification of rapeseed oil by applying sulphated zirconia and attained 86% of FAME. Thus, most of the catalysts based on zirconia support necessitate high temperature for FAME production.

Gatehouse and Lloyd [35] synthesized and reported the crystal structure of Beta-potassium dizirconate ($\beta\text{-K}_2\text{Zr}_2\text{O}_5$) for the first time in 1970. They prepared single crystal of beta potassium dizirconate by thermal decomposition process and have three dimensional complex structure (orthorhombic) of distorted zirconium dioxide octahedra and potassium ions but its application in the catalytic field has not yet been explored.

The purpose of present work was to synthesize β -potassium dizirconate ($\beta\text{-K}_2\text{Zr}_2\text{O}_5$) as a heterogeneous catalyst. The synthesized catalyst was characterized by Thermo-gravimetric analysis (TGA), X-ray diffraction (XRD), Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), Particle size analyser, Scanning electron microscopy (SEM), BET surface area analyser and basicity. Then, it was applied for transesterification of waste frying oil, where the parameters such as catalyst concentration, molar ratio, temperature, time and reusability of catalyst were examined. The synthesized FAME was analysed by ¹H and ¹³C FT-NMR and the parameters such as density, cetane number, kinematic viscosity, calorific value, flash point, fire point, cloud point, pour point and ash content have been determined as per ASTM 6751 [36] standards.

2. Experimental

2.1. Materials

Waste frying oil (WFO) was obtained from hostel of the institute and zirconium dioxide (ZrO_2) from Kemphasol. The chemicals methanol and potassium carbonate (K_2CO_3) used were purchased from Merck. All the chemicals used were of analytical grade (AR).

2.2. Catalyst synthesis

Beta-potassium dizirconate ($\beta\text{-K}_2\text{Zr}_2\text{O}_5$) was synthesized via solid state reaction. In this method, zirconium dioxide (ZrO_2) and potassium carbonate (K_2CO_3) were mixed in their various Zr/K molar ratios of 0.25:1, 0.50:1, 0.75:1, 1:1 and 1.25:1. Mixing was done by ball milling for 2 h. Resultant mixture was calcined in a muffle furnace at 850 °C for 4 h. Catalyst was then ground by using pestle and mortar and then sieved to get fine powder. Finally, prepared catalyst was placed in desiccator for further application.

2.3. Characterization of catalyst

TGA of the catalyst was conducted with PerkinElmer Pyris 1 TGA, Thermo gravimetric Analyzer. The rate of increase of temperature was 20 °C per min. Powder X-ray diffraction (XRD) was recorded on Rigaku MiniFlex 600 at 5 deg/min scan rate over a 2 θ range of 5–80°. Diffraction pattern observed in XRD were compared with Joint Committee on Powder Diffraction Standards (JCPDS). FTIR of catalyst were recorded on ALPHA BRUKER Eco-ATR equipped with ZnSe ATR crystal in range of 500–3500 cm^{-1} . Particle size was analysed on Delsa™Nano Submicron Particle Size and Zeta Potential Particle Analyzer, Delsa™Nano UI Software Versions 2.31/2.03. Scanning electron microscopy (SEM) was performed on ZEISS EVO 18 SEM having coating of quorum model Q150R ES. Surface area was determined on Micromeritics TriStar-3000 surface area analyser by using standard Brunauer–Emmett–Teller (BET) method. Sample was degassed at 200 °C for 3 h under a nitrogen atmosphere to eradicate the physisorbed moisture of the catalyst. The catalyst basicity was measured by Hammett indicators benzene carboxylic acid titration method [37,38] by using neutral red ($H_- = 6.8$), bromothymol blue ($H_- = 7.2$), phenolphthalein ($H_- = 9.3$), Nile blue ($H_- = 10.1$), tropaeolin-O ($H_- = 11.1$) and 2, 4-dinitroaniline ($H_- = 15.0$) indicators. Physicochemical properties of prepared catalyst were observed by these characterization techniques.

GCMS of WCO were performed on Agilent 6890 GC and 5975 Mass Spectrometer at 250 °C inlet temperature, 280 °C auxiliary temperature, 50 °C for two min and at the rate of 20 °C up to 250 °C then by 50 °C to 300 °C. ¹H and ¹³C Fourier transform-nuclear magnetic resonance (FT-NMR) spectra of raw feedstock and synthesized FAME were recorded on BRUKER 500 Ascend™ 500 (advance III HD) instrument by using CDCl_3 as a solvent and TMS as internal reference.

2.4. Biodiesel production via transesterification and analysis

Waste frying oil (WFO) which is used as a feedstock was first filtered to eliminate the suspended matter present in the oil. Then it was dried in a hot air oven at 110 °C for 2 h to eliminate the moisture content. The acid value of WFO was determined as per ASTM standard and observed to be 1.76 mg KOH/g. This acid value of WFO is sufficiently low to proceed for direct transesterification. 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 1 wt% to 5 wt% of oil) has been done by dispersing it with methanol at 45 °C for 30 min with continuous stirring. After activation, oil was added to the above mixture and then refluxed for 2 h at 65 °C 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 reacting with anhydrous Na₂SO₄ [39]. Ester content present in biodiesel obtained from waste frying oil was determined by ¹H NMR using following expression [40,41]:

$$\text{ME content (\%)} = (2A_{\text{ME}}/3A_{\text{CH}_2}) * 100 \quad (1)$$

where A_{ME} represents the integration value of methyl ester proton and A_{CH_2} shows the integration value of methylene proton.

In the present study, optimization has been done by carrying out reaction with varying 'methanol: oil' molar ratio from 4:1 to 12:1 by taking 1 wt% to 5 wt% of catalyst. The reaction time varied from 30 min to 150 min and temperature from 45 °C to 75 °C.

3. Result and discussion

3.1. Characterization of catalyst

3.1.1. Thermogravimetric analysis (TGA)

Thermal characterization of the catalyst has been done by Thermogravimetry analysis (TGA) for examination of decomposition behaviour of the sample. Fig. 1 shows the thermogravimetric curve, which displays the decomposition temperature regarding weight loss of uncalcined sample. The results imply that 17.077% weight loss occurred during the heating of 20.412 mg sample from 40 °C to 900 °C at the rate of 20 °C/min when the sample was dispensed for TGA analysis. Two stages of mass loss were observed. The first weight loss is effect of water of crystallization observed at 40–200 °C, which was roughly 13.09%. Then, second weight loss of 4.12% is attributed to release of carbon dioxide up to 800 °C and after that no such weight loss was observed in the sample. TGA results show that lower temperatures are requisite hence advantageous and calcination were performed at 850 °C. This result intimates the stabilization of β -potassium dizirconate (β -K₂Zr₂O₅) phase. Experimental conditions were responsible for surface composition which leads to the composition of oxo-bond that is M–O–M. Carbonate present on the surface of oxide was responsible for catalytic poisoning in transesterification with catalyst [41].

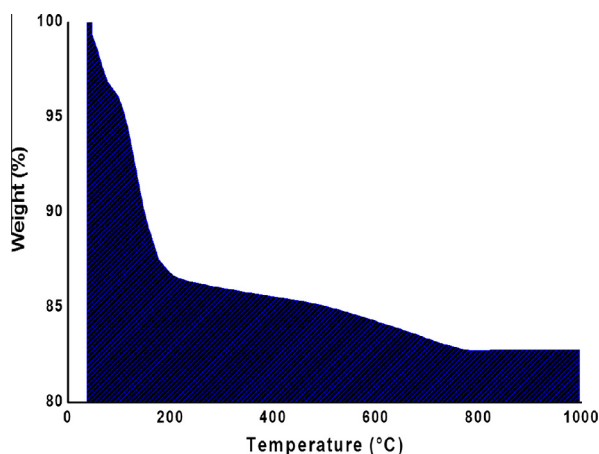


Fig. 1. TGA curve of uncalcined catalyst.

3.1.2. 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. Fig. 2 shows the X-ray diffraction (XRD) pattern of the catalyst synthesized by solid state method. From the result, it can be observed that the peaks obtained were compared with the Joint Committee on Powder Diffraction Standards (JCPDS) Diffraction Data Base. The solid state method formed β -potassium dizirconate (β -K₂Zr₂O₅) as a preeminent phase. XRD was performed in the scan range of 5–80° with 5°/min scan speed. Increment in calcination temperature is responsible for initiation of β -potassium dizirconate (β -K₂Zr₂O₅) formation due to solid state reaction between ZrO₂ and K₂CO₃. Prominent peak values are matched with mixed phase of orthorhombic β -potassium dizirconate (β -K₂Zr₂O₅), JCPDS file No. 72-1690 and monoclinic zirconia (JCPDS file No. 88-2390). The intense peaks at 13.02°, 20.01°, 30.38°, 33.19°, 35.32° and 45.95° are attributed to β -potassium dizirconate (β -K₂Zr₂O₅) phase and other phases remain inattentive, hence confirmed that catalyst has been synthesized by completion of reaction between K₂CO₃ and ZrO₂ [42] that had been used as heterogeneous catalyst for biodiesel production. The smaller peaks observed on XRD pattern were due to presence of ZrO₂. Crystallite size of potassium doped ZrO₂ 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 [43]. Our consideration was biodiesel production at amiable conditions and hence simply solid state method were chosen for catalyst synthesis.

3.1.3. Attenuated total reflectance Fourier infrared (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. Attenuated total reflectance Fourier infrared spectra (ATR-FTIR) of the catalyst were obtained for characterization. This technique is more sensitive for assimilation of phases. Fig. 3 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 [44–46]. Whereas, vibration at 630 cm⁻¹ were obtained due to presence of Zr–O–Zr stretching band [47]. 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 [44]. From Fig. 3, it has been

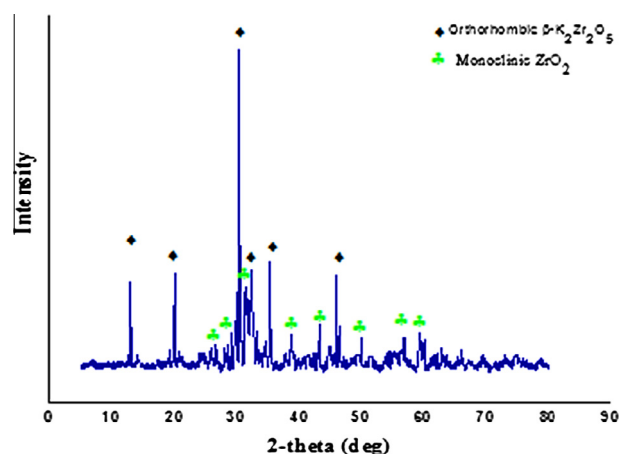


Fig. 2. XRD pattern of the β -K₂Zr₂O₅ catalyst synthesized via solid-state reaction.

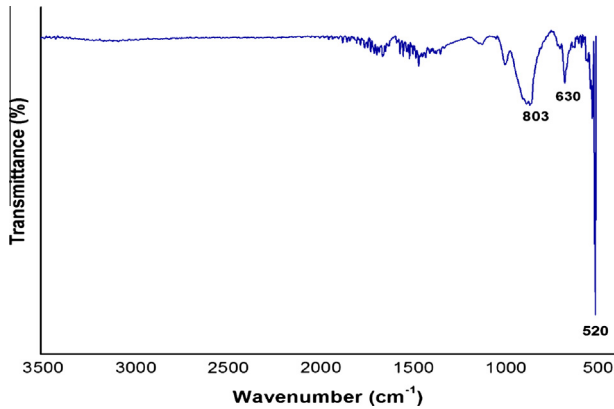


Fig. 3. FTIR spectra of β - $K_2Zr_2O_5$ catalyst.

observed that the broad peaks due to carbonate presence were observed between 1459 and 1656 cm^{-1} [48]. All the peaks present are characteristics of the material; there is no evidence for any organic content present in the synthesized sample.

3.1.4. Particle size analysis

The diameter of particle was measured with the particle size analyser based on the principle of dynamic light scattering

method. In this, Photon correlation spectroscopy (PCS) measures the intensity size distribution (weighted) and represented in form of histogram as shown in Fig. 4(A). Magnitude of every peak is proportional to percent of overall scattered intensity through particles. This instrument calculates intensity distributions and can convert them to volume or number distributions. A volume distribution (equivalent to weight distributions) will provide the relative volume of particles for each size present in sample. Results obtained from intensity were dependent on scattering angle, whereas in case of volume it is independent.

Volume distribution for the same sample was represented in Fig. 4(B). Number Distribution can be calculated by volume percentage result divided by cubed diameter of particles as represented in Fig. 4(C). 'ln(G1(t)) plot' displays the natural logarithmic graph in between 'G1(t) Plot and decay time' (Fig. 4(D)). This designates the presence of any noise in the signal. ACF existence can be confirmed by occurrence of smooth curve, whereas due to noise in signal, ACF touches the baseline. All analyses were repeated thrice at $25\text{ }^\circ\text{C}$ in aqueous form at $10,585\text{ cps}$ scattering intensity. Refractive index and viscosity was 1.3328 and 0.8818 cp respectively.

Overlay graph has been plotted for normalised intensity distribution as shown in Fig. 5.

From this overlay plot, it has been observed that for three nos. of repetitions, average diameter was observed to be 0.398 , 0.382 and $0.330\text{ }\mu\text{m}$ respectively as shown in Table 1.

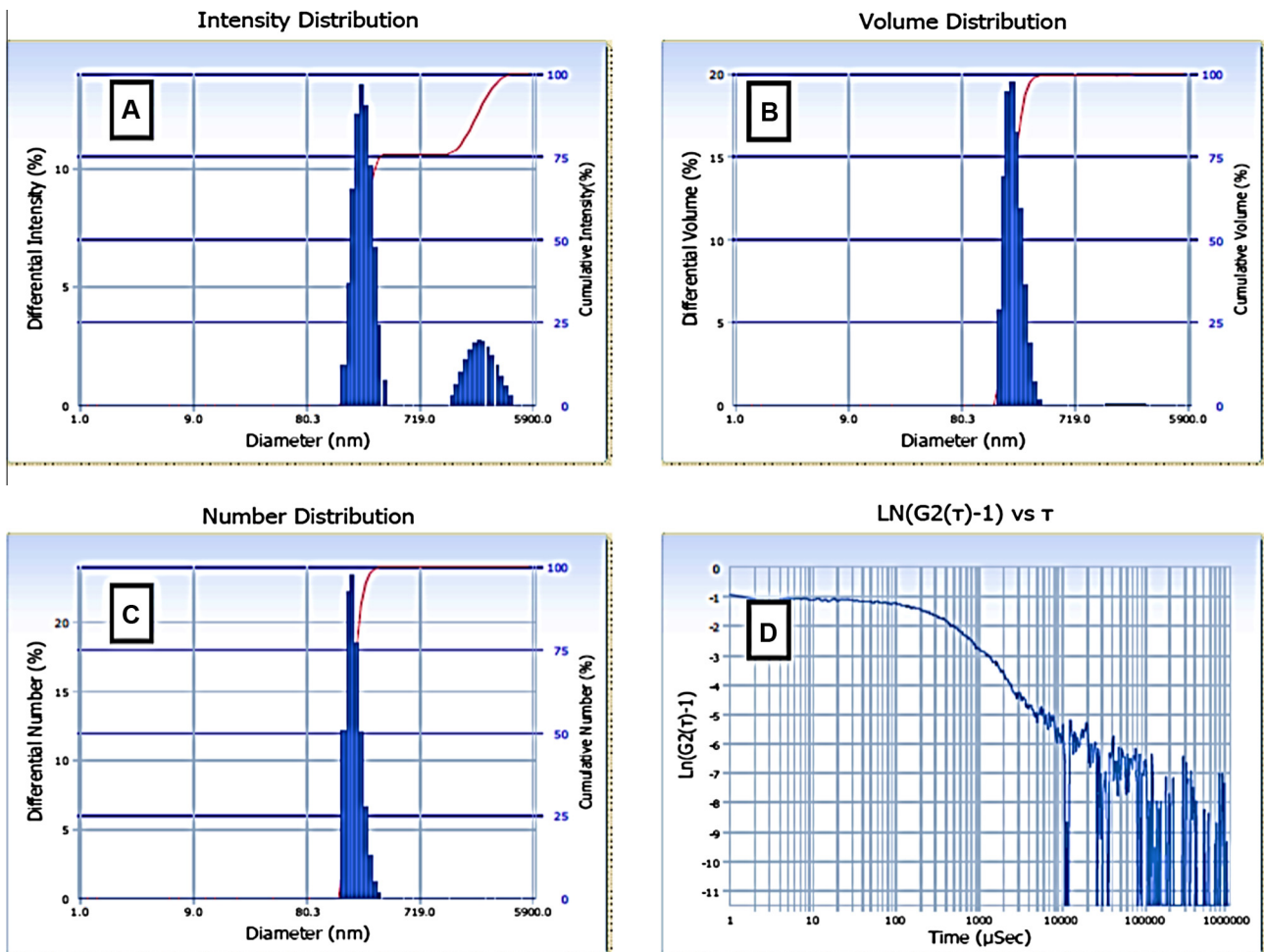


Fig. 4. Particle size distribution. (A) Diameter with respect to differential intensity. (B) Diameter with respect to differential volume. (C) Diameter with respect to differential number. (D) Natural logarithmic graph in between G1(t) plot and decay time.

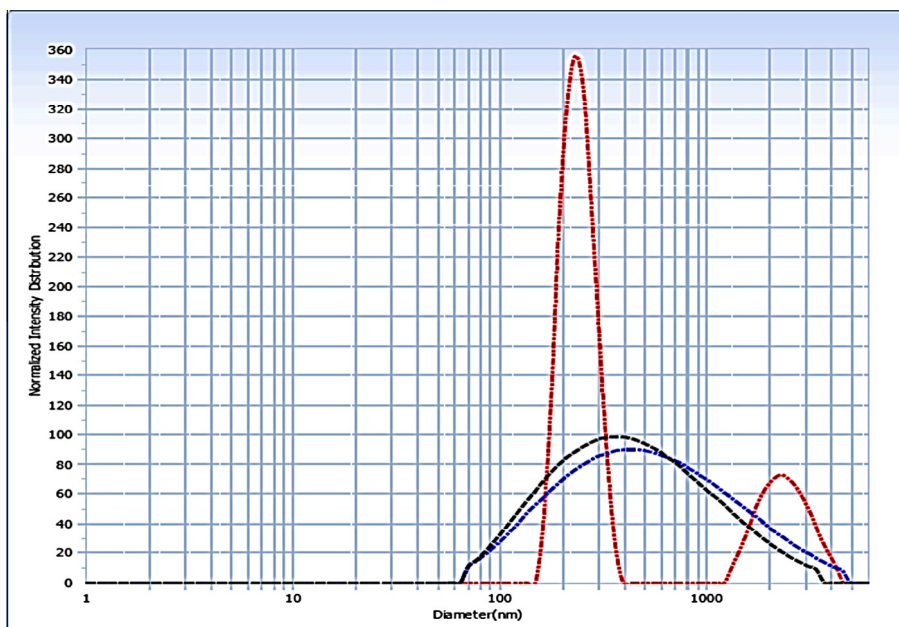


Fig. 5. Overlay plot for normalised intensity distribution.

Table 1

Normalised intensity distribution from overlay graph.

Repetition no.	Average diameter (μm)	Polydispersity index	D (10%) (μm)	D (50%) (μm)	D (90%) (μm)
1	0.398	0.414	0.133	0.388	1.30
2	0.382	0.311	0.141	0.458	1.68
3	0.330	0.239	0.182	0.243	2.36

Polydispersity index of the catalyst was 0.414, 0.311 and 0.239. A three point condition D_{10} , D_{50} , and D_{90} were considered for particulate materials. D_{10} diameter was observed to be 0.132, 0.141, 0.182 μm for three repetitions. For D_{50} and D_{90} diameter it was 0.388, 0.458, 0.243 μm and 1.30, 1.68, 2.36 μm respectively.

3.1.5. Scanning electron microscopy (SEM)

Surface morphology and size of particle of the synthesized catalyst have been studied by scanning electron microscope (SEM). Microstructural characteristics of synthesized sample were enhanced by using SEM (Fig. 6).

From SEM image, agglomeration of particles of irregular geometry is seen. It can be attributed to doping of potassium which forms comparatively smaller particles than ZrO_2 available commercially [49]. From Fig. 6, it is 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 [50].

3.1.6. BET surface area and basicity

BET surface area of the synthesized β -potassium dizirconate ($\beta\text{-K}_2\text{Zr}_2\text{O}_5$) was conducted to obtain surface area, pore size and pore volume. Single point surface area of the catalyst was obtained at P/P_0 0.3097 was 10.72 m^2/g . 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 β -potassium dizirconate ($\beta\text{-K}_2\text{Zr}_2\text{O}_5$) 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 \AA and 88.27 \AA . According to Horvath–Kawazoe method maximum pore volume at P/P_0 0.099 was 0.0025 cm^3/g which is very less and could be due to competent pore plugging by size of potassium ions. Strength of basic site plays substantial role in catalytic activity for transesterification reaction [49,51].

Basic strength of the synthesized catalyst was obtained because of oxide ions which are nothing but Lewis base present on mixed metal oxide apparent [37,38]. Basic site strength of β -potassium dizirconate ($\beta\text{-K}_2\text{Zr}_2\text{O}_5$) were calculated by simply Hammett indicator benzene carboxylic acid titration method. In this method total basic sites were calculated irrespective of position. This titration was held in presence of various indicators having pK_{BH^+} in between 6.8 and 15.0 (Neutral red, Bromothymol blue, Phenolphthalein, Nile blue, Trapeolin and 2,4-dinitroaniline). The total basicity of β -potassium dizirconate ($\beta\text{-K}_2\text{Zr}_2\text{O}_5$) was obtained as 1.75 mmol/g.

3.2. Characterization of feedstock (WFO) and FAME

WFO was characterized by GCMS for Fatty acid methyl esters (FAME), the biodiesel produced from WFO by transesterification were characterized by ^1H and ^{13}C NMR spectroscopy. Various reaction parameters, such as catalyst concentration wt (%), molar ratio (methanol: oil), reaction temperature, time and catalyst reusability were optimized to obtain high conversion and high yield of biodiesel.

3.2.1. Gas Chromatography Mass Spectroscopy (GCMS) of WFO

Gas Chromatography Mass Spectroscopy (GCMS) was used to demonstrate the chemical composition of WFO (Fig. 7) with the help of chromatogram.

Each peak corresponds to fatty acid present in the sample and was identified and shown in Table 2 with retention time and corresponding acid with the help of library match.

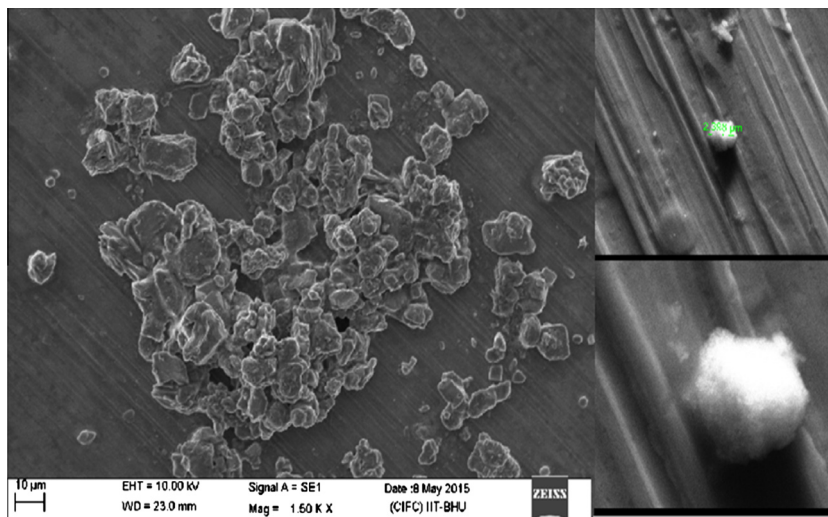


Fig. 6. SEM images of the β -K₂Zr₂O₅ synthesized catalyst.

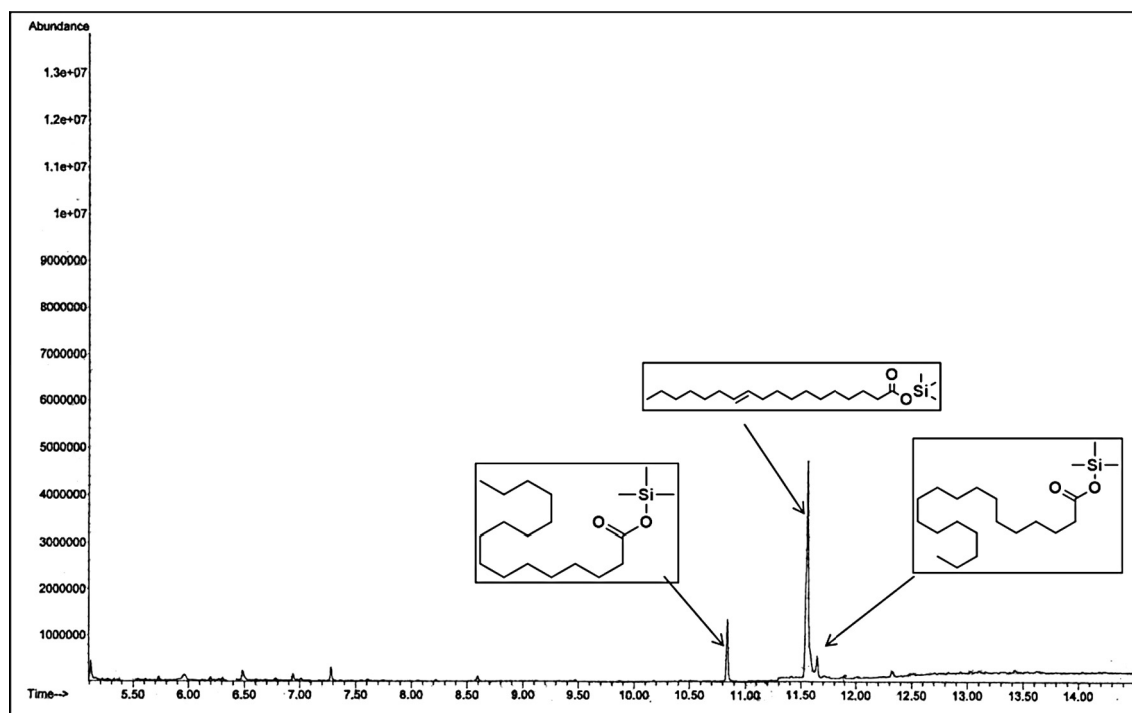


Fig. 7. GCMS Chromatogram of WFO.

Table 2
Composition of WFO from GCMS analysis.

Peak	Retention time	Structure	Library match (%)
1	10.8395	Hexadecanoic acid, trimethylsilyl ester	96
2	11.5622	11-trans-Octadecanoic acid, trimethylsilyl ester	93
3	11.6445	Octadecanoic acid, trimethylsilyl ester	96

3.2.2. ¹H and ¹³C NMR spectroscopy

¹H NMR spectrum of WFO and FAME were compared and demonstrated in Fig. 8. The conversion of FAME from WFO was calculated by taking the values of integrated signal at 3.664 ppm

(methoxy group of FAME i.e. A_{ME}) and 2.285 ppm (methylene group i.e. A_{CH₂}) Fig. 8(B).

Conversion was calculated using equation 1 and was found to be 96.85%. These two peaks were used for conformation of existence of methyl ester in FAME which were absent in WFO (Fig. 8A). Other decipherable peaks were at 0.868 ppm of terminal methyl proton; peak at 1.254 ppm was related to methylene proton on carbon chain. Signal at 1.606 ppm was due to presence of methylene proton of β -carbonyl whereas signal at 5.340 ppm was related to olefinic protons [52,53].

In ¹³C NMR spectrum of WFO, three peaks of carbonyl present in triglycerides (triacylglycerol backbone) were observed at 173.036, 173.457 and 173.493 ppm as shown in Fig. 9(A). Peaks at 128.094 and 130.425 were due to presence of unsaturation while other

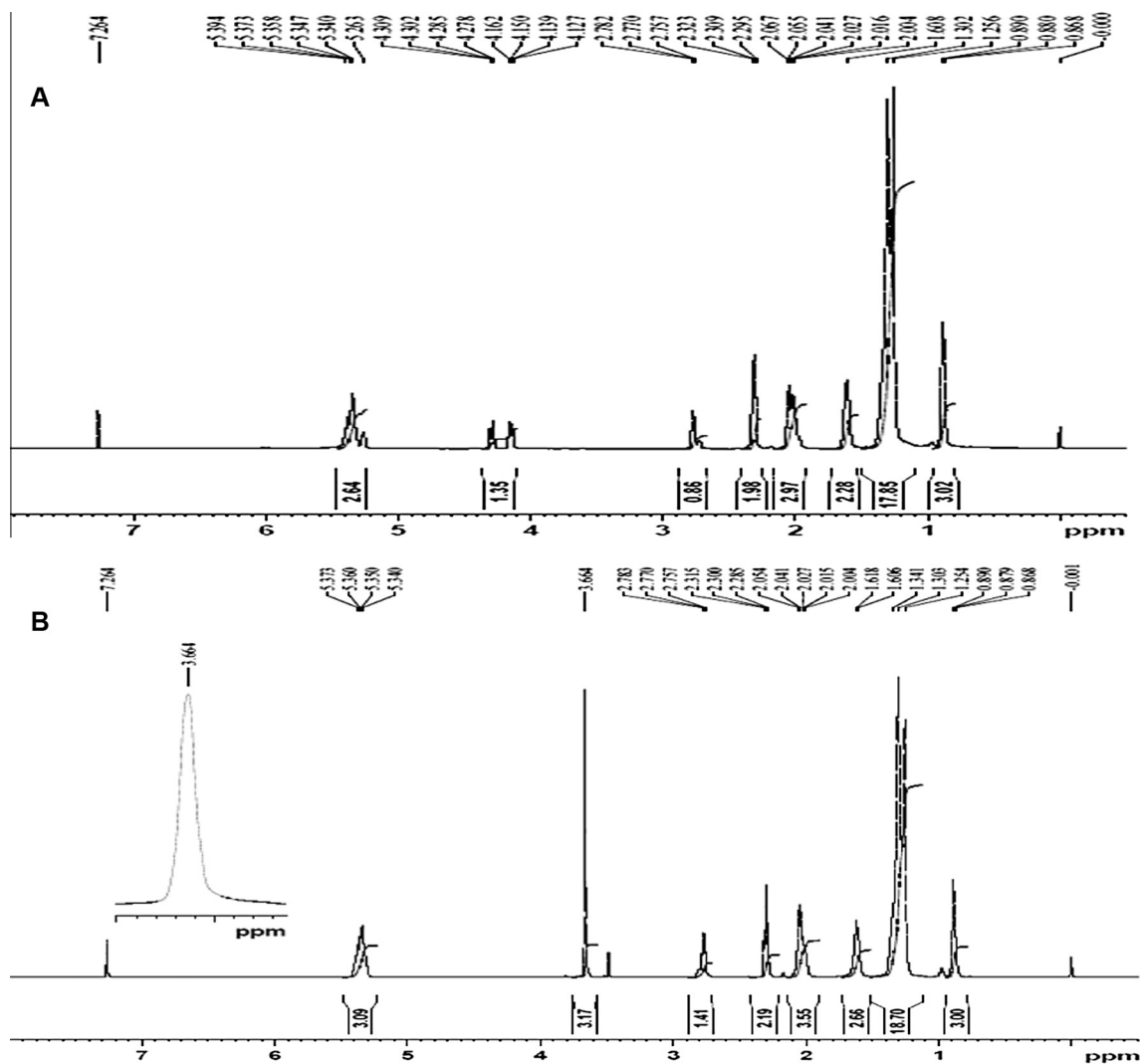


Fig. 8. (A) ^1H NMR spectrum of WFO (B) ^1H NMR spectrum of FAME obtained from $\beta\text{-K}_2\text{Zr}_2\text{O}_5$ catalyst at concentration of 4 wt%, 10:1 M ratio of methanol: oil, 2 h at 65°C .

peaks at 14.269 and 14.312 ppm were due to occurrence of terminal carbon of methyl group. Peaks obtained from 22 to 34 ppm represent the presence of methylene carbons of long chain of triglyceride. Peak at 62.304 and 69.092 ppm signifies $\alpha\text{-CH}_2\text{O}$ and $\beta\text{-CH}_2\text{O}$ of triacylglycerol.

^{13}C NMR spectrum of FAME, Fig. 9(B), exhibits the characteristic peaks of ester carbonyl ($-\text{COO}-$) and $\text{C}-\text{O}$ at 174.515 and 51.634 ppm, respectively which was absent in WFO [36]. The peaks at 130.422 and 128.119 ppm specified the unsaturation in methyl esters. Additional peaks at 14.268 and 14.313 ppm were present due to terminal carbon of methyl groups and remaining signals in between 22–34 ppm are associated to methylene carbons of long carbon chain in fatty acid methyl esters (FAME).

3.3. Effect of various reaction parameters on transesterification

The catalyst β -potassium dizirconate ($\beta\text{-K}_2\text{Zr}_2\text{O}_5$) was found to be more efficient and was used for optimization of reaction parameters for its improved catalytic activity. Sequences of transesterification process were carried out in presence of β -potassium dizirconate ($\beta\text{-K}_2\text{Zr}_2\text{O}_5$) in order to accomplish the reaction conditions for optimization and reusability of β -potassium dizirconate ($\beta\text{-K}_2\text{Zr}_2\text{O}_5$) was also assessed.

3.3.1. Effect of Zr/K ratio

Series of experiments was carried by using various Zr/K ratios for optimization purpose. Table 3 summarized the evaluation for all catalyst synthesized from various ratios. From Table 3, it has been observed that as Zr/K ratio increases from 0.25:1 to 1.25:1, FAME conversion rises. At 0.25:1, 0.50:1, 0.75:1 M ratios, % FAME conversion was found to be 60.13, 71.58, and 80.74 respectively. However, 1:1 Zr/K ratio gives conversion of 96.85 % after 2 h of reaction time at 65°C and molar ratio of 1:10 (oil:methanol) at 4.0 wt% of catalyst by transesterification reaction. Further, increment in Zr/K ratio reduces the FAME conversion and hence optimum conversion was obtained at 1.25:1 M ratio and chosen for optimization purpose.

3.3.2. Catalyst amount (wt%)

The effect of catalyst concentration on conversion of FAME was investigated from 1 wt% to 5 wt% of oil using '10:1 methanol: oil molar ratio' at 65°C for 2 h (Fig. 10(a)). The results indicated that conversion of FAME increased as catalyst concentration was raised from 1 wt% to 5 wt% where, maximum conversion (96.85%) was achieved at 4 wt% concentration. This shows that availability of active sites increased for transesterification process [54]. Further increment in catalyst concentration beyond the optimum value (4 wt%) shows reduction in FAME conversion. This reduction could

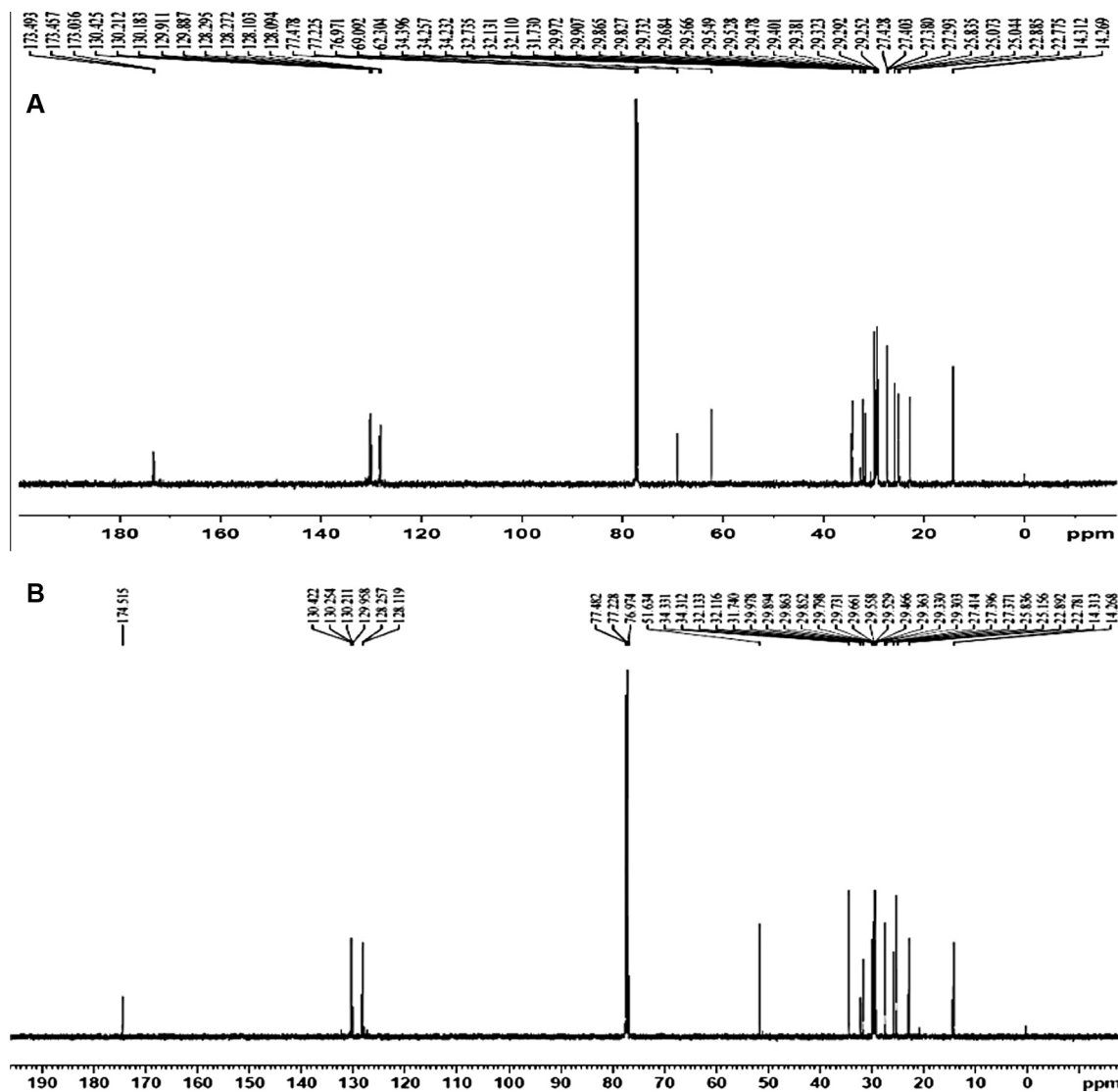


Fig. 9. (A) ^{13}C NMR spectrum of WFO (B) ^{13}C NMR spectrum of FAME obtained from $\beta\text{-K}_2\text{Zr}_2\text{O}_5$ catalyst at concentration of 4 wt%, 10:1 M ratio of methanol: oil, 2 h at 65 °C.

Table 3
Effect of various molar ratios of Zr/K on % FAME conversion.

Catalyst molar ratio (Zr/K)	% FAME Conversion
0.25:1	60.13
0.50:1	71.58
0.75:1	80.74
1:1	96.85
1.25:1	89.07

be due to soap formation which raises viscosity of reactant and ultimately inhibits the reaction [55]. As a result 4 wt% of catalyst was chosen for optimization purpose.

3.3.3. Molar ratio

Excess of methanol is essential to carry out transesterification reaction since the process is reversible as well as to enhance the reaction rate [56]. 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 [57]. The effect of methanol: oil molar ratio was studied in the range of 4:1–12:1, by keeping rest of the parameters constant, that is 4 wt% catalyst concentration at 65 °C for 2 h. The

results shows that FAME conversion significantly increases as methanol: oil molar ratios were raised from 4:1 to 12:1 (Fig. 10 (b)). Further increment in molar ratio beyond the optimum value 10:1 (where conversion obtained 96.85%) did not enhance the reaction rate. This is due to dissolution of produced glycerol into the 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 [58].

3.3.4. 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 reaction. In literature, it has been reported that catalyst based on ZrO_2 required higher reaction temperature for FAME conversion. Omar and Amin [33] synthesized 79.7% of FAME by using Zr/ZrO_2 in 2.8 h at 115.5 °C from WCO. Jitputti et al. [59] has reported transesterification of coconut oil by using $\text{KNO}_3/\text{ZrO}_2$ for 4 h at reaction temperature 200 °C and obtained 70.7% of FAME.

Effect of reaction temperature on FAME conversion was carried out in the range of 45–75 °C at 10:1 methanol:oil molar ratio, 4 wt % catalyst for 2 h as shown in Fig. 10(c). Result showed that conver-

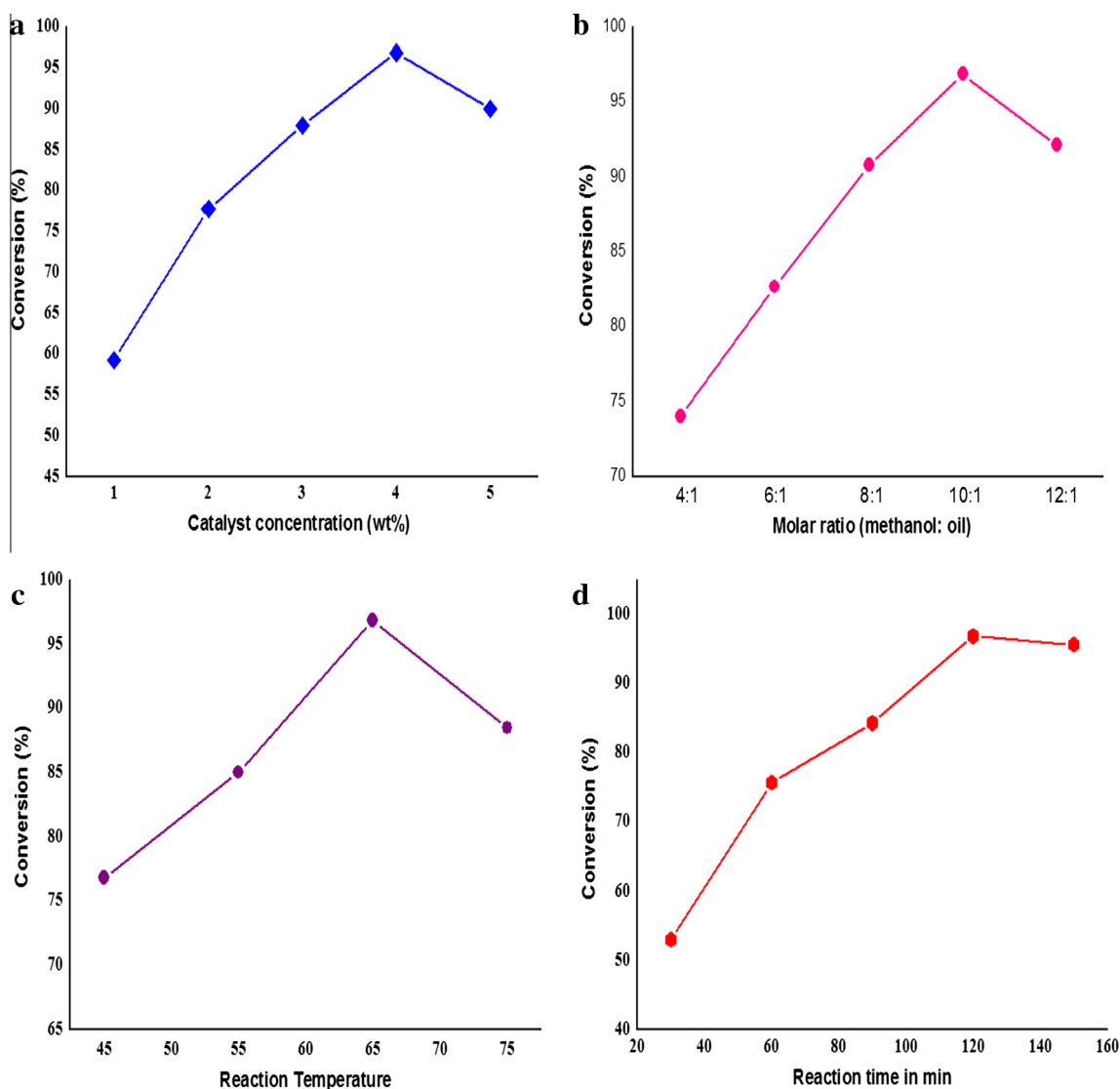


Fig. 10. (a) Effect of catalyst concentration on conversion (%) of waste cooking oil methyl esters [methanol: oil ratio, 10:1; temperature, 65 °C; time 2 h]. (b) Effect of methanol ratio to oil on conversion (%) of methyl ester [catalyst amount 4.0 wt%; reaction temperature 65 °C; reaction time 2 h]. (c) Effect of temperature on conversion (%) of methyl ester [methanol: oil ratio, 10:1; catalyst amount 4 wt%; time 2 h]. (d) Effect of reaction time on conversion (%) [catalyst amount 4.0 wt%; methanol: oil ratio, 10:1; reaction temperature 65 °C].

sion increased as the temperature was raised up to 65 °C and optimum conversion obtained was 96.85%. Further increase in temperature reduces the conversion since methanol vaporizes at high

temperature and inhibits the process [58,60]. At that temperature which surpasses the boiling temperature 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 [60].

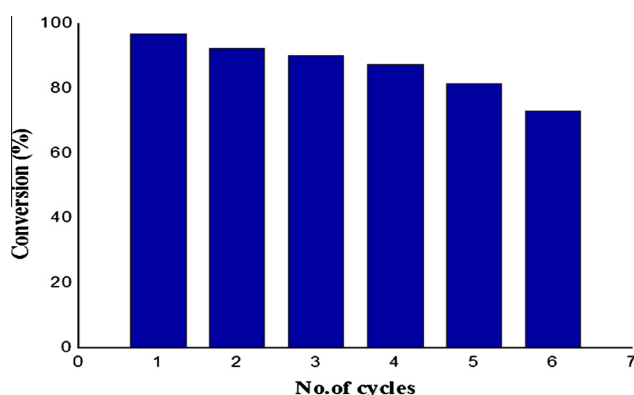


Fig. 11. β -K₂Zr₂O₅ reutilization analysis up to six transesterification reactions performed with 4 wt% of catalyst, at 65 °C for 2 h.

3.3.5. 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 as 10:1 methanol: oil molar ratio, 4 wt% catalyst at temperature 65 °C constant. Maximum conversion viz. 96.85% has been achieved at 120 min with no further increment with time and becomes constant after 120 min as shown in Fig. 10(d).

3.3.6. Catalyst reusability

Use of heterogeneous catalyst is advantageous over the homogeneous catalyst because of its reusability. This test was performed for 4 wt% catalyst only. After each run, the catalyst was washed with hot methanol to eliminate organic impurities present on the

Table 4
Characteristics of WFO methyl ester.

Parameters	ASTM test method used	ASTM-6751 biodiesel	WFO methyl ester
Acid value (mg KOH/g)	D664-07	<0.8	1.76
Density (40 °C, g cm ⁻³)	D1448-1972	0.86–0.90	0.880
Kinematic viscosity (cSt at 40 °C)	D445	1.9–6.0	4.02
Cetane number	D613	47 min	49.70
Calorific value (MJ/kg)	D6751/DIN51900	35 min	38.81
Flash point (°C)	D93	100–170	142
Fire point (°C)	D93		157
Cloud point (°C)	D2500	–3 to 12	6
Pour point (°C)	D97-05	–15 to 16	3
Ash content (%)	D482	<0.02	0.05

catalyst surface. Washed catalyst was dried in hot air oven at 110 °C for 5–6 h followed by calcination for 2 h at 600 °C. It was observed that activity of catalyst decreased continuously up to the six runs (Fig. 11).

Further, it is clear from this figure that the catalyst worked with 80% efficiency after 4 runs and also, the efficiency of catalyst decreased from ~95 to 80% in five runs. Thus, catalyst can be efficiently used for five runs without significant loss of activity. This will result in decreased cost of transesterification reaction. Catalytic activity drops since catalyst is completely covered with product which diminishes opportunity for contact of catalyst and methanol [61].

3.4. Characteristics of FAME synthesized from WFO

The synthesized FAME from WFO was characterized for its fuel and physical property 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 [36] standard as shown in Table 4. The acid value of WFO methyl ester was observed to be 1.76 mg of KOH/g and was within ASTM standard for carrying transesterification.

The density and kinematic viscosity of FAME were found to be 0.880 g cm⁻³ and 4.02 cSt at 40 °C respectively and were within ASTM limits for biodiesel. Viscosity is most essential characteristic of 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 as per ASTM standard D613. The calorific value of the fuel was observed to be 38.81 MJ/kg. The flash point as well as fire point of FAME was observed to be 142 °C and 157 °C respectively, which was within ASTM range and deliberated as safe limit for storage and transportation. Cloud point and pour point were determined as 6 °C and 3 °C respectively and were within ASTM range. Ash content obtained was found to be 0.05% and was slightly above the ASTM standard range.

4. Conclusion

β -potassium dizirconate (β -K₂Zr₂O₅), heterogeneous catalyst was synthesized, characterized by TGA, XRD, ATR-FTIR, SEM, BET and basicity. This material was successfully used for transesterification of waste frying oil for synthesis of biodiesel. Catalyst was found to be effective for transesterification of waste frying oil (WFO). The FAME produced through transesterification was characterized. At the optimized conditions of reaction that is methanol: oil molar ratio 10:1, catalyst concentration of 4 wt%, time 2 h at

65 °C reaction temperature conversion of FAME was observed to be 96.85%. Catalytic reusability has been studied and from this it was observed that catalyst has stability up to five runs. The characteristics of the FAME like acid value, density, kinematic viscosity, cetane number and calorific value, flash point, fire point, cloud point, pour point and ash content were within ASTM D6751 standard. Thus, the FAME obtained from WFO was economically feasible and retained superior quality. All of these above results intimate that β -potassium dizirconate (β -K₂Zr₂O₅) could become an alternative heterogeneous catalyst for economically viable biodiesel production.

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References

- <https://www.cia.gov/library/publications/the-world-factbook/>.
- Chattopadhyay S, Sen R. Fuel properties, engine performance and environmental benefits of biodiesel produced by a green process. *Appl Energy* 2013;105:319–26.
- Canakci M. The potential of restaurant waste lipids as biodiesel feedstocks. *Bioresour Technol* 2007;98:183–90.
- Zullaikah S, Lai CC, Vali SR, Ju YH. A two-step acid-catalyzed process for the production of biodiesel from rice bran oil. *Bioresour Technol* 2005;96:1889–96.
- Leung DYC, Wu X, Leung MKH. A review on biodiesel production using catalyzed transesterification. *Appl Energy* 2010;87:1083–95.
- Balat M, Balat H. Progress in biodiesel processing. *Appl Energy* 2010;87:1815–35.
- Lin L, Zhou C, Saritporn V, Shen X, Dong M. Opportunities and challenges for biodiesel fuel. *Appl Energy* 2011;88(4):1020–31.
- Sharma YC, Singh B. A hybrid feedstock for a very efficient preparation of biodiesel. *Fuel Process Technol* 2010;91:1267–73.
- Bari S. Performance, combustion and emission tests of a metro-bus running on biodiesel-ULSD blended (B20) fuel. *Appl Energy* 2014;124:35–43.
- Talebian-Kiakalaieh A, Amin NAS, Zarei A, Noshadi I. Transesterification of waste cooking oil by heteropoly acid (HPA) catalyst: optimization and kinetic model. *Appl Energy* 2013;102:283–92.
- Felizardo P, Neiva Correia MJ, Raposo I, Mendes JF, Berkemeier R, Bordado JM. Production of biodiesel from waste frying oils. *Waste Manage* 2006;26:487–94.
- Phan AN, Phan TM. Biodiesel production from waste frying oils. *Fuel* 2008;87:3490–6.
- Shu Q, Gao J, Nawaz Z, Liao Y, Wang D, Wang J. Synthesis of biodiesel from waste vegetable oil with large amounts of free fatty acids using a carbon-based solid acid catalyst. *Appl Energy* 2010;87:2589–96.
- Farooq M, Ramli A, Subbarao D. Biodiesel production from waste cooking oil using bifunctional heterogeneous solid catalysts. *J Clean Prod* 2013;59:131–40.
- Gupta AR, Yadav SV, Rathod VK. Enhancement in biodiesel production using waste cooking oil and calcium diglyceroxide as a heterogeneous catalyst in presence of ultrasound. *Fuel* 2015;158:800–6.
- Ferrero GO, Almeida MF, Alvin-Ferraz MCM, Dias JM. Glycerol-enriched heterogeneous catalyst for biodiesel production from soybean oil and waste frying oil. *Energy Convers Manage* 2015;89:665–71.

- [17] Almeida VF, García-Moreno PJ, Guadix A, Guadix EM. Biodiesel production from mixtures of waste fish oil, palm oil and waste frying oil: optimization of fuel properties. *Fuel Process Technol* 2015;133:152–60.
- [18] Corro G, Sánchez N, Pal U, Bañuelos F. Biodiesel production from waste frying oil using waste animal bone and solar heat. *Waste Manage* 2015. <http://dx.doi.org/10.1016/j.wasman.2015.02.001>.
- [19] Sanli H, Canakci M, Alptekin E, Turkcan A, Ozsezen AN. Effects of waste frying oil based methyl and ethyl ester biodiesel fuels on the performance, combustion and emission characteristics of a DI diesel engine. *Fuel* 2015;159:179–87.
- [20] Sharma YC, Singh B, Upadhyay SN. Advancements in development and characterization of biodiesel: a review. *Fuel* 2008;87:2355–73.
- [21] Lam MK, Lee KT, Mohamed AR. Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste frying oil) to biodiesel: a review. *Biotechnol Adv* 2010;28:500–18.
- [22] An H, Yang WM, Maghbouli A, Li J, Chou SK, Chua KI. Performance, combustion and emission characteristics of biodiesel derived from waste cooking oils. *Appl Energy* 2013;112:493–9.
- [23] Wang Y, Huang WY, Wu Z, Chun Y, Zhu JH. Superbase derived from zirconia supported potassium nitrate. *Mater Lett* 2000;46:198–204.
- [24] Furuta S, Matsuhashi H, Arata K. Biodiesel fuel production with solid amorphous-zirconia catalysis in fixed bed reactor. *Biomass Bioenergy* 2006;30:870–3.
- [25] Santiago-Torres N, Romero-Ibarra I, Pfeiffer H. Sodium zirconate (Na_2ZrO_3) as a catalyst in a soybean oil transesterification reaction for biodiesel production. *Fuel Process Technol* 2014;120:34–9.
- [26] Agrawal S, Singh B, Sharma YC. Application of a mollusk (*Pila globosa*) as a heterogeneous catalyst for synthesis of biodiesel using used frying oil. *Ind Eng Chem Res* 2012;51:11875–80.
- [27] Sun H, Ding Y, Duan J, Zhang Q, Wang Z, Lou H, et al. Transesterification of sunflower oil to biodiesel on ZrO_2 supported La_2O_3 catalyst. *Bioresour Technol* 2010;101:953–8.
- [28] Sree R, Seshu Babu N, Sai Prasad PS, Lingaiah N. Transesterification of edible and non-edible oils over basic solid Mg/Zr catalysts. *Fuel Process Technol* 2009;90:152–7.
- [29] Li Y, Lian S, Tong D, Song R, Yang W, Fan Y, et al. One-step production of biodiesel from *Nannochloropsis* sp. on solid base Mg–Zr catalyst. *Appl Energy* 2011;88(10):3313–7.
- [30] Ding Y, Sun H, Duan J, Chen P, Lou H, Zheng X. Mesoporous Li/ZrO_2 as a solid base catalyst for biodiesel production from transesterification of soybean oil with methanol. *Catal Commun* 2011;12(7):606–10.
- [31] Mercera PDL, Ommen JG, Doesburg EBM, Burggraaf AJ, Ross JRH. Zirconia as a support for catalysts influence of additives on the thermal stability of the porous texture of monoclinic zirconia. *Appl Catal* 1991;71:363–91.
- [32] Kulkarni MG, Gopinath R, Meher LC, Dalai AK. Solid acid catalyzed biodiesel production by simultaneous esterification and transesterification. *Green Chem* 2006;8:1056–62.
- [33] Omar WNNW, Amin NAS. Biodiesel production from waste cooking oil over alkaline modified zirconia catalyst. *Fuel Process Technol* 2011;92:2397–405.
- [34] Rattanaphra D, Harvey A, Srinophakun P. Simultaneous conversion of triglyceride/free fatty acid mixtures into biodiesel using sulfated zirconia. *Top Catal* 2010;53:773–82.
- [35] Gatehouse BM, Lloyd DJ. The crystal structure of beta-potassium dizirconate: ($\beta\text{-K}_2\text{Zr}_2\text{O}_5$). *J Solid State Chem* 1970;1:478–83.
- [36] Tariq M, Ali S, Ahmad F, Ahmad M, Zafar M, Khalid N, et al. A identification, FT-IR, NMR (1H and 13C) and GC/MS studies of fatty acid methyl esters in biodiesel from rocket seed oil. *Fuel Process Technol* 2011;92:336–41.
- [37] Yan S, Kim M, Salley SO, Simon Ng KY. Oil transesterification over calcium oxides modified with lanthanum. *Appl Catal A* 2009;360:163–70.
- [38] Thitsartam W, Kawi S. An active and stable CaO-CeO_2 catalyst for transesterification of oil to biodiesel. *Green Chem* 2011;13:3423–30.
- [39] Sharma YC, Singh B. Development of biodiesel: current scenario. *Renew Sustain Energy Rev* 2009;13:1646–51.
- [40] Birla A, Singh B, Upadhyay SN, Sharma YC. Kinetics studies of synthesis of biodiesel from waste frying oil using a heterogeneous catalyst derived from snail shell. *Bioresour Technol* 2012;106:95–100.
- [41] Knothe G. Analyzing biodiesel: standards and other methods. *J Am Oil Chem Soc* 2006;83:823–33.
- [42] Xie W, Peng H, Chen L. Calcined Mg–Al hydrotalcites as solid base catalysts for methanolysis of soybean oil. *J Mol Catal A: Chem* 2006;246:24–32.
- [43] Lima J, Ghani Y, da Silva R, Batista F, Bini R, Varanda L, et al. Strontium zirconate heterogeneous catalyst for biodiesel production: synthesis, characterization and catalytic activity evaluation. *Appl Catal A* 2012;445–446:76–82.
- [44] Sarkar D, Mohapatra D, Ray S, Bhattacharyya S, Adak S, Mitra N. Synthesis and characterization of sol–gel derived ZrO_2 doped Al_2O_3 nanopowder. *Ceram Int J* 2006;33(7):1275–82.
- [45] Guarany C, Peláio L, Araújo E, Yukimitu K, Moraes J, Eiras J. Infrared studies of the monoclinic–tetragonal phase transition in $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ ceramics. *J Phys Condens Matter* 2003;15:4851–7.
- [46] Low M, McPherson R. Crystallization of gel-derived alumina and alumina–zirconia ceramics. *J Mater Sci* 1989;24:892–8.
- [47] Borilo L, Spivakova L. Synthesis and characterization of ZrO_2 thin films. *Am J Mater Sci* 2012;2(4):119–24.
- [48] Taglieri G, Tersigni M, Villa PL, Mondelli C. Synthesis by the citrate route and characterisation of BaZrO_3 , a high tech ceramic oxide: preliminary results. *Int J Inorg Mater* 1999;1:103–10.
- [49] Kaur N, Ali A. Lithium zirconate as solid catalyst for simultaneous esterification and transesterification of low quality triglycerides. *Appl Catal A* 2015;489:193–202.
- [50] Xie W, Li H. Alumina-supported potassium iodide as a heterogeneous catalyst for biodiesel production from soybean oil. *J Mol Catal A: Chem* 2006;255:1–9.
- [51] Patil PD, Deng S. Transesterification of *Camelina sativa* oil using heterogeneous metal oxide catalysts. *Energy Fuel* 2009;23:4619–24.
- [52] Monteiro MR, Ambrozini ARP, Liao LM, Ferreira AG. Determination of the content of fatty acid methyl esters (FAME) in biodiesel samples using 1H-NMR spectroscopy. *Magn Reson Chem* 2008;46:1051–4.
- [53] Samios D, Pedrotti F, Nicolau A, Martini DD, Dalcen FM. Determination of biodiesel blend levels in different diesel samples by 1H NMR. *Fuel* 2009;88:691–6.
- [54] Mutreja V, Singh S, Ali A. Potassium impregnated nanocrystalline mixed oxides of La and Mg as heterogeneous catalysts for transesterification. *Renew Energy* 2014;62:226–33.
- [55] Sharma YC, Singh B. An ideal feedstock, kusum (*Schleichera triguga*) for preparation of biodiesel: optimization of parameters. *Fuel* 2010;89:1470–4.
- [56] Wang J, Chen K, Chen C. Biodiesel production from soybean oil catalyzed by $\text{K}_2\text{SiO}_3/\text{C}$. *Chin J Catal* 2011;32:1592–6.
- [57] Obadia A, Swaroopa G, Kumar S, Jeganathan K, Ramasubbu A. Biodiesel production from palm oil using calcined waste animal bone as catalyst. *Bioresour Technol* 2012;116:512–6.
- [58] Lim B, Maniam G, Hamid S. Biodiesel from adsorbed waste oil on spent bleaching clay using CaO as a heterogeneous catalyst. *Eur J Sci Res* 2009;33:347–57.
- [59] Jitputti J, Kitiyanan B, Rangsunvigit P, Bunyakiat K, Attanatho L, Jenvanitpanjakul P. Transesterification of crude palm kernel oil and crude coconut oil by different solid catalyst. *Chem Eng J* 2006;116:61–6.
- [60] Long T, Deng Y, Gan S, Chen J. Application of choline chloride ZnCl_2 ionic liquids for preparation of biodiesel. *Chin J Chem Eng* 2010;18:322–7.
- [61] Madhuvilakku R, Mariappan R, Jeyapal S, Sundar S, Piraman S. Transesterification of palm oil catalyzed by fresh water bivalve mollusk (*Margaritifera falcata*) shell as heterogeneous catalyst. *Ind Eng Chem Res* 2013;52:17407–13.