



# Application of zirconia modified with KOH as heterogeneous solid base catalyst to new non-edible oil for biodiesel



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## ABSTRACT

This study seeks to investigate zirconia modified with KOH as heterogeneous solid base catalyst for transesterification of new non-edible, *Silybum marianum* (oil content 46%, FFA 0.68% and linoleic acid 65.68%) oil using methanol to biodiesel. Having screened the catalytic performance of ZrO<sub>2</sub> loaded with different K-compounds, 32% KOH loaded on ZrO<sub>2</sub> was chosen. The catalyst was prepared using incipient wetness impregnation method. Following drying (after impregnation) and calcination at 530 °C for 5 h, the catalyst was characterized by means of Hammett indicators, XRD, FTIR, SEM, TGA and N<sub>2</sub> adsorption-desorption measurements. It was found that the yield of the fatty acid methyl esters (FAME) was related to the catalyst base strength. The catalyst had granular and porous structures with high basicity and superior catalytic performance for the transesterification reaction. Maximum yield (90.8%) was obtained at 15:1 methanol to oil molar ratio, 6% catalyst amount, 60 °C reaction temperature in 2 h. The catalyst maintained sustained activity after five times of usage. The oxidative stability and iodine value were the only unsuitable properties of the biodiesel (out of range) but can easily be improved. The cetane number, flash point and the cold flow properties among others were however, comparable to international standards. The study indicated that KOH(32%)/ZrO<sub>2</sub>-5 is an economically, suitable catalyst for producing biodiesel from *S. marianum* oil which is a potential new non-edible feedstock that can contribute positively to biodiesel industry as its biodiesel can be rated as promising alternate fuel.

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## 1. Introduction

With continuous decrease in petroleum fuel coupled with the aggravation of environmental pollution caused by burning of conventional fuels, alternative fuels are gaining significant attention [1]. Biodiesel (fatty acid methyl esters, FAME), a promising alternative fuel to conventional diesel is produced by transesterification of vegetable oils, animal fats and waste cooking oils with short chain alcohols in the presence of a catalyst. It is renewable, biodegradable, has low emission profiles, high flash point, excellent lubricity and superior cetane number [2,3]. Biodiesel also reduces pollutant levels and probable carcinogens [4] and can be blended with diesel fuel or used in pure form.

Transesterification of vegetable oil to biodiesel is commonly catalyzed by bases, acids and enzymes [5–7]. On a commercial scale, NaOH or KOH (homogeneous base) are used for biodiesel

production. There are however, several setbacks including corrosion of equipment and the need to deal with waste from the neutralization of acid when using homogeneous base catalysts. For homogeneous acids, the problem has to do with the need for longer reaction time, which consequently results in much consumption of energy. Compared with homogeneous, heterogeneous catalysts can provide green and recyclable catalytic activity [8,9]. Kulkarni et al. [10] and Laosiripojana et al. [11] studied heteropolyacid impregnated on different supports (silica, zirconia, alumina, and activated carbon), SO<sub>4</sub>-ZrO<sub>2</sub> and WO<sub>3</sub>-ZrO<sub>2</sub> and indicated that the catalysts were realistic for canola oil biodiesel. Heterogeneous solid acid catalysts however, present their own setbacks, including higher reaction temperature and longer reaction time.

Studies on loading CaO, SrO, KNO<sub>3</sub> on flyash, ZnO-La<sub>2</sub>O<sub>3</sub> and zinc aluminate [12–16], with supports as solid base catalysts for biodiesel have proven promising. However, majority of the heterogeneous solid base catalysts have limited use and application. Most others are also expensive and complicated to prepare [17,18]. Currently, most of the heterogeneous base catalysts are used for transesterificating edible oils, including soybean, canola, rapeseed,

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sunflower, palm etc. [19–21]. Meanwhile, biodiesels from edible oils are presently affected by the issue of cost which emanates from the competition between edible oils for food and fuel; a major factor arousing interest for more non-edible low-cost alternative feedstocks.

In China, biodiesel is currently produced from oils including rape seed, soybean oil castor etc. Current studies indicate that there are alternative non-edible oil-yielding crops which can be used as feedstocks [22,23]. An emerging and promising of the non-edibles is *Silybum marianum* oil, which has not yet been studied for biodiesel, but gaining recognition in medicinal and pharmaceutical studies [24,25].

*S. marianum*, belonging to the compositae family is widely cultivated in China. The main provinces into its cultivation include, Guangdong, Hubei, Shanxi and Qinghai. The medicinal and pharmaceutical aspects of the plant have received attention from researchers [24,25]. For example, the extract from the seeds can be used traditionally for treatment of hepatotoxicity, acute and chronic liver diseases [24,25]. Recent studies have revealed that the seeds of the plant contain much oil [26,27]. Ghavami and Ram-in [26] reported that the content of the oil is more than 28%. Recent study by Li et al. [27] revealed that the oil content to be more than 45%. Also in silymarin industrial oil production, the oil is considered a by-product and not much used. This study was therefore undertaken to investigate biodiesel production from *S. marianum* seed oil using efficient and economical heterogeneous base solid catalyst. In our preliminary study, it was found that the heterogeneous solid base catalyst prepared from 32% KOH loaded on ZrO<sub>2</sub> under proper treatment could really render a high conversion efficiency of biodiesel from *S. marianum* oil in excess methanol.

## 2. Experimental

### 2.1. Materials

The *S. marianum* seeds were obtained from Zhongxing Pharmaceutical Co., Ltd (Zhenjiang, China). Methanol, *n*-hexane, zirconium dioxide (ZrO<sub>2</sub>), potassium hydroxide (KOH), potassium iodide (KI), potassium bromate (KBrO<sub>3</sub>), and potassium nitrate (KNO<sub>3</sub>) were obtained from Sinopharm Chemical Reagent Co. Ltd., (Shanghai, China). All solvents were AR grade and used without any purification.

### 2.2. Extraction of oil

*S. marianum* seeds were oven dried at 120 °C for 6 h for removal of excess moisture prior to its oil extraction. The dried seeds were subsequently weighed and smashed into particles of 0.5–10 mm. The extraction was done using a soxhlet extractor with *n*-hexane for 8 h. The volume of solvent per kilogram of seed was 5 L. After extraction, the oil was retrieved with rotary evaporator. The amount of oil in the seeds was then determined using Li et al. [27] method. The fatty acids composition was subsequently determined and identified using GC–MS.

### 2.3. Preparation of the catalysts

All the catalysts were prepared by incipient wetness impregnation method. Prior to the impregnation process, the catalytic carrier was calcined in a muffle at 500 °C for 4 h. The required amount of aqueous K-compound solution was slowly added to the support and kept for 24 h. After impregnation, the catalysts were dried at 115 °C for 6 h and calcined in a muffle furnace at 530 °C for 5 h. Typically, 32% KOH was impregnated with 30 ml of deionized water containing ZrO<sub>2</sub> for 24 h.

### 2.4. Characterization of the catalysts

The characterization of the basic strengths of the catalysts was performed by Hammett indicator procedure [28–30]. This method typically involves keeping 300 mg of the sample into a 1 ml solution of Hammett indicators followed by dilution with 10 ml of methanol. 2.5 h were then allowed for equilibrium to be reached, with indication from color stability. The basic strength is therefore defined as being stronger than the weakest indicator, which exhibits a color change but weaker than the strongest indicator that produces no color change. The Hammett indicators used were bromothymol blue (H<sub>7.2</sub>), phenolphthalein (H<sub>9.8</sub>), 2,4-dinitroaniline (H<sub>15</sub>) and 4-nitroaniline (H<sub>18.4</sub>). Hammett indicator benzene carboxylic acid (0.02 mol/L anhydrous ethanol solution) titration method was then used to determine the basicity of the solid catalysts.

Fourier transform infrared (FT-IR) of the catalyst samples was carried out using potassium bromide (KBr) powder method on a FTIR spectrometer (AVATAR 360, Nicolet, Madison, USA) with a resolution of 2/cm in the 500–4000/cm range. A minimum of 32 scans indicated average.

Intermediate compounds in the synthesized catalyst systems were analyzed by X-ray diffractometer using a reflection scan with nickel-filtered Cu K $\alpha$  radiation (D8, Bruker-AXS, Germany) diffractometer. The XRD measurements were performed at  $2\theta^\circ$  values between 20° and 80° [21].

The shapes and surface characteristics of the samples were examined on a field emission scanning electron microscope (S-4800, HITACHI Corp., Tokyo, Japan) at the accelerating voltage of 20-kV.

Thermogravimetric analysis (TGA) was carried out on a Netzsch instrument (STA 449C, Netzsch, Seligenstadt, Germany). The programme heating range was from room temperature to 800 °C at a heating rate of 10 °C/min under a nitrogen atmosphere. The measurement was done for 5–10 mg samples.

The nitrogen adsorption and desorption isotherms were measured at –196 °C with NDVA2000e analytical system (Quantachrome Corporation, USA). The specific surface areas were calculated using Brunauer–Emmett–Teller (BET) method. The pore size distribution and pore volumes were calculated with Barrett–Joyner–Halenda (BJH) method.

### 2.5. Transesterification of *S. marianum* biodiesel

Transesterification reaction of *S. marianum* triglycerides to fatty acid methyl esters was carried out using 30 g of oil (extracted) with varied molar ratio (9:1–17:1) of methanol to oil and catalyst in various amounts (2%, 4%, 6%, 8%, 10%); with reference to the weight of the oil. The contents were refluxed together in a 250 ml three-neck reaction flask equipped with a condenser and magnetic stirrer at different times (1–3 h) and temperatures (40, 50, 60, 65 and 70 °C). The rate of conversion was determined not to be affected by the rotational speed of the stirrer in the 400–1000 rpm range and the rotational speed was kept constant at 600 rpm during all reaction runs. After completion of the reaction, the mixture was washed with *n*-hexane to remove any absorbed fatty acid methyl esters (FAMEs) out of the solid catalyst. The mixture was subsequently, centrifuged at 5000 rpm for 10 min to ensure separation of the solid catalyst from the liquid layer containing the biodiesel and *n*-hexane. The decanted liquid phase was then transferred to a rotary vacuum evaporator to remove the *n*-hexane and any other by-products from the biodiesel. Each biodiesel sample was then kept in separatory funnel and allowed to stand for 24 h before washing with water for at least three times. Drying and analyses of the biodiesel then followed.

## 2.6. Analyses and identification of methyl esters content

The biodiesel samples were analyzed using 7890A gas chromatograph (Agilent Technology Inc. USA), equipped with a flame-ionization detector (FID) and a HP-5 capillary column (30 m × 0.32 mm × 0.25 μm). Helium was used as the carrier gas. The oven temperature ramp program was ran using Li et al. [27] method with little modification (typically the oven temperature was held at 160 °C for 1 min, then increased to 210 °C at 20 °C/min for 2 min then further increased from 210 °C to 213 °C at 0.3 °C/min for 3 min, and finally increased to 250 °C at 30 °C/min for 1 min). Hydrogen gas's flow rate was 40 mL/min and that of air was 400 mL/min. Temperature of the injector and detector were 250 °C each. The injection was done in split mode with a split ratio of 100:1. Analysis of each sample was done by dissolving 1 mL of the biodiesel with 5 mL of petroleum ether (30–60 °C) in the presence of tetradecane as the internal standard and 0.5 μL of the solution injected into GC. The yield of each biodiesel sample was determined from the content of the esters using Eq. (1) [31,32].

$$\text{Biodiesel yield(\%)} = \frac{\text{Weight of biodiesel}}{\text{Weight of oil}} \times 100 \quad (1)$$

The fatty acid methyl esters were identified using GC–MS. The brand was Agilent HP-6890 gas chromatograph (Agilent Technologies, Palo Alto, CA, USA) with a HP-5MS 5% phenylmethylsiloxane capillary column (30 m × 0.25 mm i.d., film thickness 0.25 μm; Restek, Bellefonte, PA). The carrier gas used was helium at a flow rate of 1.0 mL/min. Each biodiesel sample (1 μL) was injected into the column at a split ratio of 30:1. The oven temperature ramp program was done by applying the GC method. The fatty acids methyl esters' identification was done by comparing the obtained mass spectra with NIST05.LIB and NIST05s.LIB (National Institute of Standards and Technology) libraries data using AMDIS–Chromatogram (GC–MS system) software. All data in this study are presented as mean (values) of triplicate of experimental and GC determinations.

## 3. Results and discussion

### 3.1. Extraction of oil

The amount of oil extracted from the seeds was 46%. This value was however, comparable to Li et al. [27] study, indicating that the oil can be a promising source for biodiesel [33]. The physico-chemical properties of the oil are presented in Table 1. The free fatty acids and water content of the oil was 0.68% w/w and 0.089% w/w, respectively. The presence of a high amount of free fatty acids and water content in oils can lead to the formation of large amounts of soap that can lower the yields of esters [34]. Given the fact that the ZrO<sub>2</sub> yielded 0% from the oil with free fatty acid and water content of 0.68% w/w and 0.089% w/w, respectively (figures below 1.0%) a base catalyst (K) was chosen for the study (Table 2). The FFA and water content in the oil was closer to other oil(s) [35] (crude roselle oil, FFA 0.67% w/w, water 0.087% w/w) with high yields from base catalyst [34]. The composition of the fatty acid of an oil is also an important factor for biodiesel use in a diesel engine [36]. For example, high saturated fatty acids in oil can give higher cetane number and oxidation stability but poor cold flow properties [37]. The crude *S. marianum* oil contains high proportion of unsaturated fatty acids primarily, linoleic acid (65.68%) and a lower amount of saturated ones, typically palmitic (15.04%) and arachidic acid (5.93%) (Table 1).

**Table 1**  
Properties of the crude *Silybum marianum* oil.

Property	Method	Crude <i>Silybum marianum</i> oil
Density (kg/m <sup>3</sup> ) at 15 °C	ASTMD4052-96	921.4
Saponification No.		191.54
Viscosity at 40 °C, mm <sup>2</sup> /s	ASTMD 445-06	37.5
Molecular weight (g)		887.9
Water content (%) w/w	AOAC 984.20-90	0.089
FFA content (%) w/w	AOAC 940.28	0.68
Fatty acid composition <sup>a</sup> (%)	AOAC (2005), 963.22, 969.33	
(i) (Palmitic) C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>		15.04
(ii) (Stearic) C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>		2.78
(iii) (Oleic) C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>		8.79
(iv) (Arachidic) C <sub>20</sub> H <sub>40</sub> O <sub>2</sub>		5.93
(v) (Linoleic) C <sub>18</sub> H <sub>32</sub> O <sub>2</sub>		65.68

<sup>a</sup> Other fatty acids such as palmitoleic, (10-nonadecenoic, myristic, nonadecanoic, and heptadecanoic acid could be found in amounts less than 1%.

**Table 2**  
Catalytic activity and base strength of ZrO<sub>2</sub> loaded by different potassium compounds.

Catalyst	Base strength (pK <sub>BH+</sub> )	Biodiesel yield (%)
ZrO <sub>2</sub>	<7.2	0 (no reaction)
KOH	15–18.4	Heavy saponification
KI/ZrO <sub>2</sub>	<7.2	<10
K <sub>2</sub> CO <sub>3</sub> /ZrO <sub>2</sub>	<7.2	<10
KBrO <sub>3</sub> /ZrO <sub>2</sub>	<7.2	<10
C <sub>8</sub> H <sub>5</sub> O <sub>4</sub> K/ZrO <sub>2</sub>	7.2–9.8	<32.0
C <sub>4</sub> H <sub>4</sub> O <sub>6</sub> KNa·4H <sub>2</sub> O/ZrO <sub>2</sub>	9.8–15	61.2
KOH/ZrO <sub>2</sub>	9.8–15	86.4

Transesterification conditions: methanol to oil molar ratio 11:1, catalyst amount 6% w/w, reaction time 3 h, reaction temperature 60 °C, K loading amount 32%, calcination temperature 530 °C.

### 3.2. Screening of the catalyst

Screening of the catalytic activity of ZrO<sub>2</sub> loaded with different potassium compounds (KI, KBrO<sub>3</sub>, C<sub>8</sub>H<sub>5</sub>O<sub>4</sub>K, C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>KNa·4H<sub>2</sub>O and KOH) for transesterification of *S. marianum* oil was carried out. The results are presented in Table 2. In order to compare the performance of the catalysts, the same reaction conditions were used for each catalyst in all the transesterification processes. From Table 2, the pure ZrO<sub>2</sub> exhibited no catalytic activity which necessitated the loading of base (K compounds) on it.

When potassium compounds (32%) were loaded on ZrO<sub>2</sub> and activated at 530 °C for 5 h, C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>KNa·4H<sub>2</sub>O/ZrO<sub>2</sub> and KOH/ZrO<sub>2</sub> resulted in yields higher than 60% and 80%, respectively. When compared with the other catalysts, KOH/ZrO<sub>2</sub> demonstrated superior catalytic activity. The catalysts with lower yields (< 61.2%) was due to their relatively low catalytic activities. The catalytic activities were in the order: KOH/ZrO<sub>2</sub> > C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>Na·4H<sub>2</sub>O/ZrO<sub>2</sub> > C<sub>8</sub>H<sub>5</sub>O<sub>4</sub>K/ZrO<sub>2</sub> > KBrO<sub>3</sub>/ZrO<sub>2</sub> = K<sub>2</sub>CO<sub>3</sub>/ZrO<sub>2</sub> = KI/ZrO<sub>2</sub>. The loading of KI, K<sub>2</sub>CO<sub>3</sub>, KBrO<sub>3</sub> and C<sub>8</sub>H<sub>5</sub>O<sub>4</sub>K on the surface of ZrO<sub>2</sub> generated weaker base sites with base strengths ranging in between 7.2 and 9.8. Considering the base strengths and the catalytic activities, it was obvious that the activities of ZrO<sub>2</sub>-supported catalysts related with their base strengths and yields. For catalytic sites of KOH/ZrO<sub>2</sub>, K<sub>2</sub>O species were possibly formed by dehydroxylation of the OH groups which could have contributed to catalytic activity of the catalyst. From the Table 2, the results indicated that the activities of the catalysts were strongly dependent on the base strengths and the amount of base sites [38]. Reference to the yields, KOH was regarded as the best support for ZrO<sub>2</sub>. Henceforth, KOH loaded on ZrO<sub>2</sub> was selected for further investigation and its properties were studied in details.

Fixed the calcination temperature at 530 °C, KOH with varying loading amounts (20%, 25%, 30%, 32% and 35%) on ZrO<sub>2</sub> were prepared using the incipient wetness impregnation method (Table 3). The increase in the loading amount of KOH (from 20% to 32%) resulted in increase in yield from 77.7% to 86.4%. This was possibly due to the increase in the base strength of the catalyst as the loading amount of KOH increases. The catalytic activity with the active sites also increased with the loading amount. With further increase in the amount of loaded KOH to 35%, the basicity might decrease the surface basic sites after the peak was reached, resulting in the drop of the catalytic activity (82.3%). This was possibly due to the coverage of the surface basic sites by the excessive KOH. The sites might then be rendered inaccessible to incoming reactants at the 35% KOH. The optimum loading amount of 32% KOH was therefore, chosen for further investigation.

The yields of KOH(32%)/ZrO<sub>2</sub> sample calcined at different temperatures were examined (Table 3). The maximum yield of 86.4% was obtained at 530 °C. Relatively, low yields were however, obtained at temperatures below 530 °C and those above it. The slightly low yields at 630 °C might be due to the alkali metals possibly promoting vitrification of the catalyst surface upon heating at such higher temperatures. Such surface significantly becomes inert and poorly active [17]. The low yields at temperatures below 530 °C could be due to the excessive porous nature of the catalyst at that state.

With the optimum calcination temperature of KOH(32%)/ZrO<sub>2</sub> at 530 °C, further investigation was carried out to determine the effect of calcination time on the catalyst performance (Table 3). The maximum yield (86.4%) was obtained at a calcination time of 5 h. Low yields were obtained at calcination times below 5 h and those above it. The yields varied with calcination time reference to the variations in the catalytic activity. 32% KOH loaded on ZrO<sub>2</sub> calcined at 530 °C for 5 h (KOH(32%)/ZrO<sub>2</sub>-5) was finally chosen for detailed investigation for transesterification of *S. marianum* oil to biodiesel.

### 3.3. Catalyst characterizations

The powdered X-ray diffraction patterns of ZrO<sub>2</sub> and KOH(32%)/ZrO<sub>2</sub>-5 samples are shown in Fig. 1. The XRD pattern of pure ZrO<sub>2</sub> exhibit typical diffraction peaks at  $2\theta^\circ = 24.2^\circ, 28.2^\circ, 31.40^\circ, 40.7^\circ,$

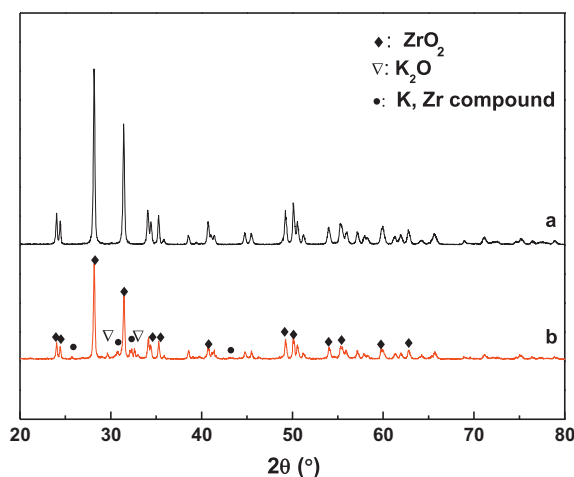


Fig. 1. XRD patterns of (a) ZrO<sub>2</sub>, (b) KOH(32%)/ZrO<sub>2</sub>-5.

50.1° and 59.9°. Upon KOH impregnation (KOH(32%)/ZrO<sub>2</sub>-5), the typical KOH peaks were observed at the Bragg angles,  $2\theta^\circ = 27^\circ, 31^\circ, 31.9^\circ$  and  $43^\circ$ . An additional K<sub>2</sub>O phase appeared clearly in the diffraction patterns of the catalyst. The peaks associated with K<sub>2</sub>O phase are observed at  $2\theta^\circ = 29.5^\circ$  and  $32.6^\circ$ . These phenomena could be as a result of the incorporation of K<sup>+</sup> ions into the vacant sites of zirconia with hydroxyl groups to form K–O–Zr on the surface during calcination [11]. The results were confirmed by FT-IR spectrum of the catalyst. The characteristic peaks of ZrO<sub>2</sub> and KOH(32%)/ZrO<sub>2</sub>-5 were similar on the XRD patterns. It was noted that the solid state reaction between KOH and ZrO<sub>2</sub> in the activation process was favorable for the catalyst to get high activity. The K<sup>+</sup> ion of KOH could have been inserted in the vacant sites of ZrO<sub>2</sub> which accelerated dissociative dispersion and decomposition of KOH to form basic sites in the activation process. The more, KOH was loaded on ZrO<sub>2</sub>, the more free vacant sites of ZrO<sub>2</sub> decreases. This results in the surface enrichment of potassium species which probably was the active sites of the catalyst [21,39]. When the amount of K<sup>+</sup> loaded on ZrO<sub>2</sub> was below the saturation uptake of K<sup>+</sup> (20–30% KOH) it could well be dispersed. But with excessive loading; thus at 35% KOH loaded on ZrO<sub>2</sub>, the KOH could not have been well dispersed and for that matter, not all but only a part of the loaded KOH might have been decomposed.

Table 3  
The effects of KOH loading amount, calcination temperature and calcination time on the yield of biodiesel.

Catalyst condition	Base strength (pK <sub>BH+</sub> )	KOH loading amount (%)	Calcination temperature (°C)	Calcination time (h)	Biodiesel yield (%)
KOH (20%)/ZrO <sub>2</sub>	9.8–15	20	530	5	77.7
KOH (25%)/ZrO <sub>2</sub>	9.8–15	25	530	5	80.5
KOH (30%)/ZrO <sub>2</sub>	9.8–15	30	530	5	84.3
KOH (32%)/ZrO <sub>2</sub>	9.8–15	32	530	5	86.4
KOH (35%)/ZrO <sub>2</sub>	9.8–15	35	530	5	82.3
250 (KOH/ZrO <sub>2</sub> )	9.8–15	32	250	5	34.2
330 (KOH/ZrO <sub>2</sub> )	9.8–15	32	330	5	68.6
450 (KOH/ZrO <sub>2</sub> )	9.8–15	32	450	5	79.8
500 (KOH/ZrO <sub>2</sub> )	9.8–15	32	500	5	84.6
530 (KOH/ZrO <sub>2</sub> )	9.8–15	32	530	5	86.4
630 (KOH/ZrO <sub>2</sub> )	9.8–15	32	630	5	83.1
3 (KOH/ZrO <sub>2</sub> )	9.8–15	32	530	3	52.3
4 (KOH/ZrO <sub>2</sub> )	9.8–15	32	530	4	79.9
5 (KOH/ZrO <sub>2</sub> )	9.8–15	32	530	5	86.4
6 (KOH/ZrO <sub>2</sub> )	9.8–15	32	530	6	84.0
7 (KOH/ZrO <sub>2</sub> )	9.8–15	32	530	7	81.5
8 (KOH/ZrO <sub>2</sub> )	9.8–15	32	530	8	78.1

Transesterification conditions: methanol to oil molar ratio 11:1, catalyst amount 6% w/w, reaction time 3 h, reaction temperature 60 °C.

Fig. 2a and b shows the typical SEM nanographs of ZrO<sub>2</sub> and KOH(32%)/ZrO<sub>2</sub>-5 particles, respectively. The crystallites particle

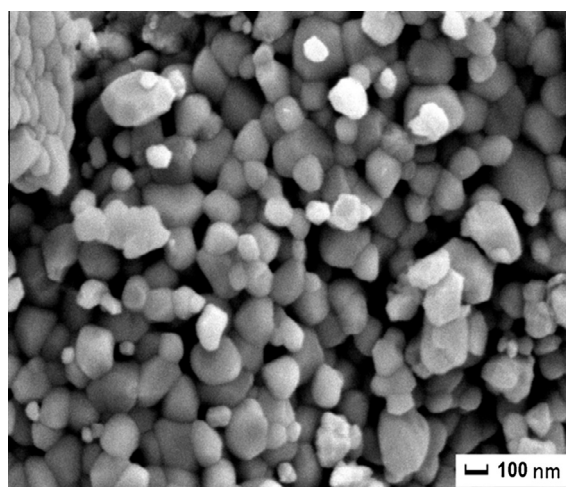


Fig. 2. (a) SEM image of ZrO<sub>2</sub>, (b) SEM image of KOH(30%)/ZrO<sub>2</sub>-5.



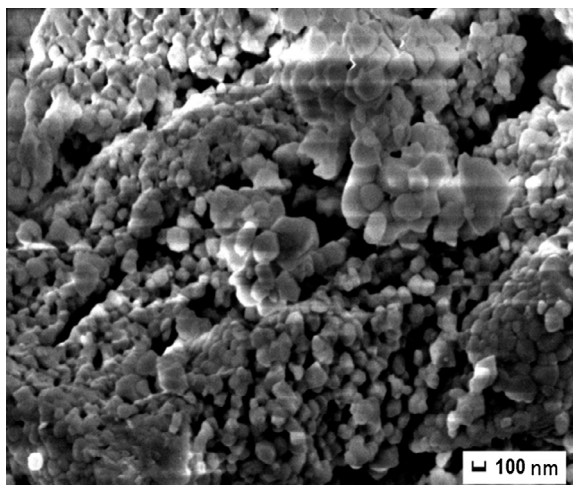
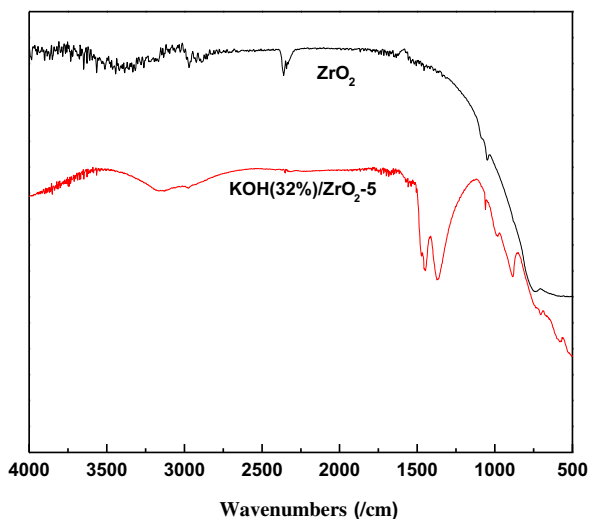


Fig. 2 (continued)

of  $ZrO_2$  and  $KOH(32\%)/ZrO_2-5$  samples were each 100 nm. Freshly crystalline morphologies were formed at the surface of the prepared catalyst. There was a reduction in the particle sizes of the catalyst as a result of loading KOH. However, no significant difference could be observed between  $ZrO_2$  and  $KOH(32\%)/ZrO_2-5$  images, indicating a good dispersion of KOH on the surface of  $ZrO_2$ . Clearly, after loading 32% KOH on  $ZrO_2$ ,  $ZrO_2$  retained its structure which was important for its catalytic activity. Potassium species could be found distributed on the surface of the support. The largest particles were  $ZrO_2$  while the smallest were  $K_2O$ . These results agree with the XRD data. It could also be seen that  $KOH(32\%)/ZrO_2-5$  had granular and porous structures. The granules made up of other smaller granules of 100 nm in diameter formed porous netlike structure which indicates that there was possible increase in contact between the catalyst and the substrates, hence improvement in the catalytic ability with increased transesterification efficiency [39].

The FTIR spectra of  $ZrO_2$  and  $KOH(32\%)/ZrO_2-5$  catalysts were also examined (Fig. 3). The spectra of  $ZrO_2$  and  $KOH(32\%)/ZrO_2-5$  indicate sharp peaks at 2450 and 750/cm, respectively. New peaks at 1550 and 1350/cm on  $KOH(32\%)/ZrO_2-5$  could be attributed to K–O and K–O–Zr bonds, respectively. The band between 3000–3300/cm regions could also be partly assigned to the stretching

Fig. 3. FTIR spectra of  $ZrO_2$  and  $KOH(32\%)/ZrO_2-5$ .

vibration of Zr–O–K groups [11] in which  $K^+$  ions could have replaced the protons of isolated hydroxyl groups to form Zr–O–K in the activation process. These results confirm the XRD data. The vibration was overlapped with the broad vibration band of OH groups which could be attributed to OH stretching vibration of the hydroxyl groups attached to the catalyst surface and the molecules of water absorbed from the atmosphere [11].

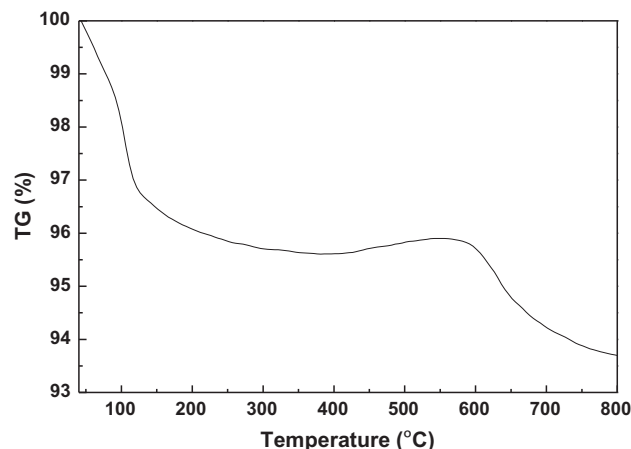
The thermal behavior of  $KOH(32\%)/ZrO_2-5$  is shown in Fig. 4. The first weight loss at lower temperature (<150 °C) corresponds to the water loss from internal and external surfaces of the catalyst. The second weight loss (200–500 °C), was due to the decomposition of KOH and  $K_2O$ . The last weight loss (above 600 °C) could be attributed to the decomposition of the residual hydroxyl groups bonded to the oxide lattice [40]. The decomposition of KOH, forming both  $K_2O$  species and K–O–Z groups in the composite was possibly the main active sites for the transesterification reaction.

The BET surface area and pore volume of pure  $ZrO_2$  was  $7.02 \text{ m}^2 \text{ g}^{-1}$  and  $0.01 \text{ cm}^3 \text{ g}^{-1}$  respectively. Upon impregnation with the K compound, there was a significant reduction of the surface area and pore volume to  $3.05 \text{ m}^2 \text{ g}^{-1}$  and  $0.01 \text{ cm}^3 \text{ g}^{-1}$ , respectively; thus, the surface and pores of the catalyst support were covered upon impregnation. The pore diameters of  $ZrO_2$  and  $KOH(32\%)/ZrO_2-5$  were 17.59 and 16.91 nm, respectively. It can be seen that, the pore diameter is relatively narrow. Granados et al. [41] have reported that the dimensions of methyl oleate (oleic acid methyl ester) and glycerin are around 2.5 nm and 0.6 nm, respectively. The comparison of the mean pore size diameter of synthesized catalyst with the volume that would be occupied by triglyceride suggests that the triglyceride molecules can easily penetrate into the pores of the synthesized catalyst. Since the pores of the synthesized catalyst were 16.91 nm, most of the active sites would be utilized during the transesterification reaction.

### 3.4. Influence of transesterification reaction conditions

#### 3.4.1. Effects of methanol to oil molar ratio and reaction time

Transesterification process consists of a three consecutive reversible reactions where triglyceride is successively transformed into diglyceride, monoglyceride, and to glycerine and FAME. The molar ratio of methanol to oil and reaction time is a very important parameter that affects the conversion of triglycerides to esters [12,38,42,43]. Stoichiometrically, the molar ratio of methanol to *S. marianum* oil is 3:1. However, excess methanol (>6:1) can generally be used to increase the yield of methyl esters and also facilitate glycerine separation [42]. To investigate the effect of methanol to oil ratio using  $KOH(32\%)/ZrO_2-5$ , the transesterification experi-

Fig. 4. Thermal behavior of  $KOH(32\%)/ZrO_2-5$ .

ment was conducted by systematically changing the molar ratio of methanol to *S. marianum* oil from 9:1 to 17:1, while keeping the temperature and catalyst amount constant at 60 °C and 6% respectively and reaction time/s (1, 1.5, 2, 2.5, and 3 h (Fig. 5a)). From the Fig. 5a, it is observed that the increase in methanol to oil molar ratio (from 9:1 to 15:1) resulted in corresponding increase in yield (from 71.5% to 90.8%) at 15:1 in 2 h. Beyond molar ratio of 15:1, the excessively added methanol had no positive effect on the production yields. Obviously, altering the methanol to oil molar ratio in the range of 9:1–15:1 did affect the yield greatly. Reference to the hypothesis that methanol to oil ratio of >6:1 can increase reaction rate, in this study, the ratio of 9:1 was still low and consequently took a longer time for the reaction to relatively produce substantial yield of FAME (79.1% at 3 h); a fact that the ratio was insufficient to drive the reaction to completion [12,42]. Comparatively, methanol to oil molar ratio of 17:1 also provided high yield (90.3%) closer to the yield at 15:1 (90.8%), this ratio could be avoided for the purpose of cost minimization. The findings of this study agrees with Meher et al. [44] study. The study indicated that to increase FAME yield, an excess amount of alcohol was effective to some extent, and beyond which there could be reduction in the yield possibly due to the dilution of the oil with the excess alcohol. Methanol to oil molar ratio of 15:1 at 2 h in this case was selected as optimum.

### 3.4.2. Effects of catalyst amount and reaction time

Catalyst plays an important role in transesterification reaction [42]. Earlier studies on *Cynara cardunculus L.* indicates that the conversion of the oil to its methyl esters by transesterification without catalyst (0% NaOH) [45] was impossible. Henceforth in this study, the effects of catalyst amount on methyl ester yield was investigated at the mass ratio of KOH(32%)/ZrO<sub>2</sub>-5 to *S. marianum* oil at a varied range of 2–10% using 15:1 methanol to oil molar ratio at different reaction time/s (1, 1.5, 2, 2.5, and 3 h) (Fig. 5b). The Fig. (5b) clearly, indicates the increase in methyl ester yield (from 78.8% to 90.8%) as the catalyst amount was increased (from 2% to 6%) to a point in which the plateau value (90.8%) was reached. A further increase in the catalyst amount (beyond 6%) slightly lowered the yield. Studies by Meher et al. [44] and Encinar et al. [45] indicate that high concentrations of alkaline catalyst form soap in the presence of high free fatty acids which results from emulsion formation between the soap and water molecules that leads to low yields. Qiu et al. [21] using soybean oil also observed an increase in triglyceride conversion with increase in the amount of C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>HK loaded on ZrO<sub>2</sub> (from 2.0% and 6.0% w/w), and beyond 6.0% the

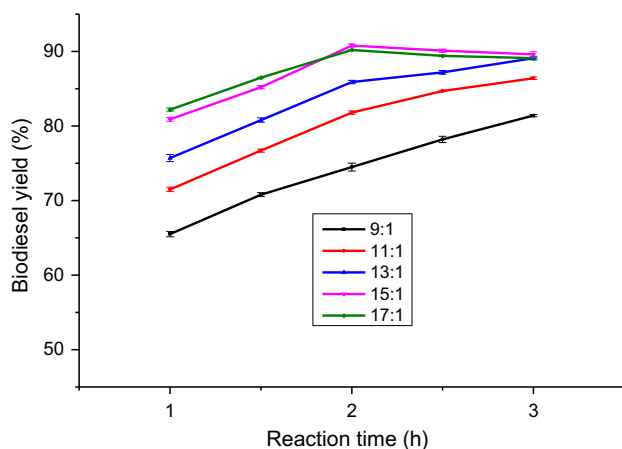


Fig. 5a. Effects of methanol to oil molar ratio and reaction time on biodiesel yield (catalyst amount of 6% w/w, reaction temperature of 60 °C).

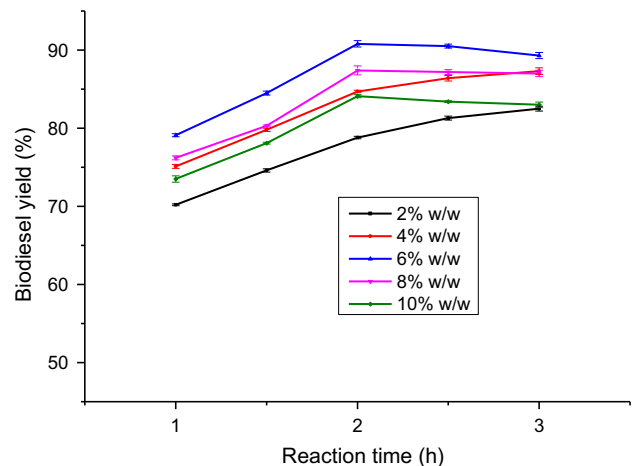
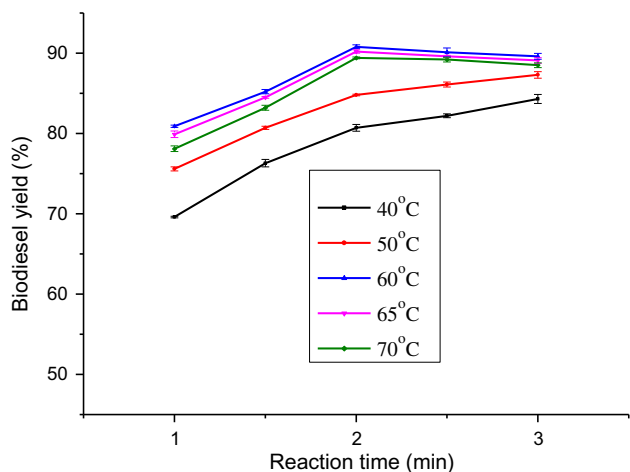


Fig. 5b. Effects of catalyst amount and reaction time on biodiesel yield (methanol to oil molar ratio of 15:1, reaction temperature of 60 °C).

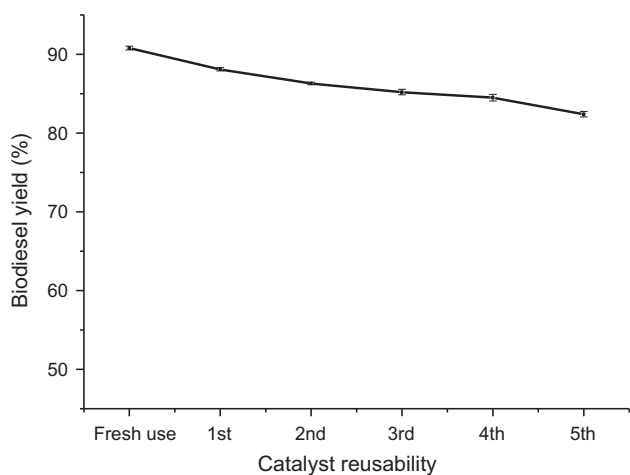
yield slight decreased. The slight drop in the yield as a result of further increase in catalyst amount (from 6% to 8%) could be due to the excessively, added catalyst, causing slight soap formation which inhibited the reaction process as a result of increase in the viscosity of the reactants [43,45]. The maximum yield in this study (i.e. 90.8%) was slightly lower than those reported by Feyzi et al. [46] for sunflower seed oil (i.e. 94.8%) after 2 h of reaction using molar ratio of 14:1 and 6% of Cs/Al/Fe<sub>3</sub>O<sub>4</sub> as catalyst but closer to yields (92.41%) of Qiu et al. [39] for soybean biodiesel after 1.5 h at 14:1 methanol to oil molar ratio with 6% of neodymium oxide loaded with potassium hydroxide, 60 °C temperature. It was observed that at low catalyst amounts (2–4%) the reaction was slow and could not reach completion even after 3 h; indicating the insufficient amount of catalyst to catalyze the process to completion. This trend however, agrees with work done by other researcher [43,45]. Catalyst amount of 6% at 2 h was considered optimum for this study.

### 3.4.3. Effects of reaction temperature and reaction time

Using heterogeneous base catalyst, the reaction mixture constitutes a three-phase system: oil–methanol–catalyst, in which the reaction can be slowed when there is diffusion resistance between these different phases. Studies indicate that reaction temperature has an important effect on base-catalyzed transesterification [43,45]. The effect of reaction temperature and time on the transesterification of crude *S. marianum* oil was investigated at different temperatures (40, 50, 60, 65 and 70 °C) and time/s (1, 1.5, 2, 2.5, and 3 h) with methanol to oil molar ratio of 15:1 and catalyst amount of 6% (Fig. 5c). As shown in Fig. 5c, the increase in temperature from 40 °C to 60 °C resulted in increased in yields of methyl esters to optimum at 60 °C (90.8%) in 2 h. It was noted that, at the starting temperature (40 °C), the reaction was slow and could not be completed even after 3 h (74.7%, 3 h). This observation agrees with those of other studies [44,45,47]. The low rate of reaction at 40–50 °C could possibly be due to the high viscosity of the oil at the lower temperatures, resulting in poor mixing between the phases of oil–methanol–catalyst [48]. The findings however, differs from that of Stavarache et al. [49] who reported that conversion of vegetable oil to methyl esters was highest (i.e. 91% at room temperature) after 10 min using mechanical stirring (1800 rpm) for 1.0% (w/w) KOH. After proceeding most efficiently at 60 °C in 2 h in which maximum yield (90.8%) was reached, the yield began to reduce upon further increase in the temperature. It is known that a more rapid reaction could be obtained at high temperatures [50]. But at higher temperature/s (beyond 60 °C), the methanol could



**Fig. 5c.** Effects of reaction temperature and reaction time on biodiesel yield (methanol to oil molar ratio of 15:1, catalyst amount of 6% w/w).



**Fig. 5d.** Catalyst reusability (methanol to oil molar ratio of 15:1, catalyst amount of 6% w/w, reaction temperature 60 °C and reaction time of 2 h).

vaporize and formed bubbles, which might inhibit the reaction on the interface. Considering the fact that maximum yield (90.8%) was obtained at 60 °C, the 60 °C in 2 h reaction temperature was chosen for the transesterification of *S. marianum* oil to biodiesel.

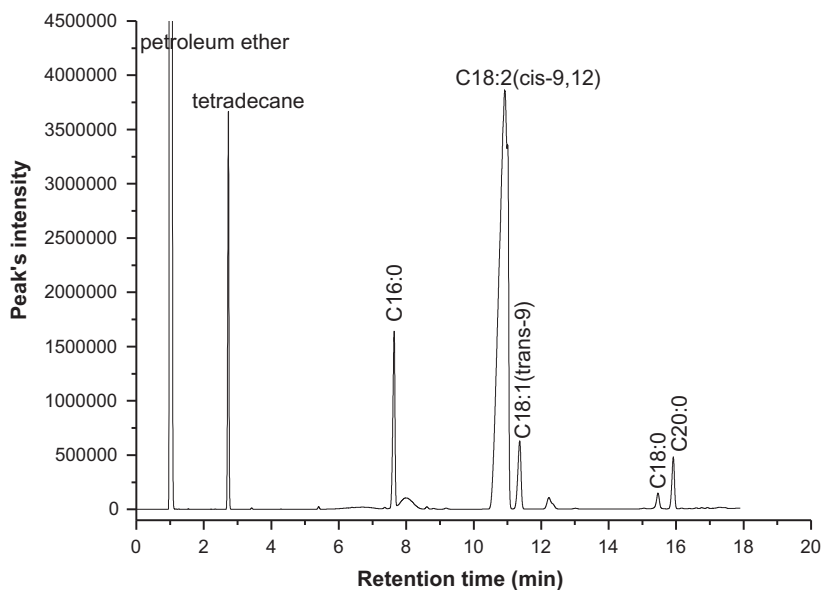
### 3.5. Catalyst regeneration

The recovery and reuse of catalyst is an important factor in shaping the economics of the use of heterogeneous catalysis for biodiesel manufacturer. Reusability of KOH(32%)/ZrO<sub>2</sub>-5 was tested by consecutively recovering and then reusing the catalyst particles up to five times in conjunction with 2 h reaction cycles in the batch reactor (Fig. 5d). For the reusability analysis, the transesterification reaction of oil with methanol was carried out repeatedly under one constant set of operating conditions (methanol to oil ratio: 15:1, catalyst amount: 6%, temperature: 60 °C, reaction time: 2 h). Upon the completion of the transesterification reaction, the catalyst particles were filtered out, recovered, washed with methanol several times, re-calcined at 530 °C for 4 h and then reused as the catalyst of the next run.

A fresh reaction mixture of methanol and *S. marianum* oil was used at each cycle of the stability tests. The typical results of methyl ester yield with reaction time as a function of the number of recycling cycles are shown in Fig. 5d. For all the five runs, the rate of reaction was very high at the end of the 2 h reaction period (with the methyl esters yield exceeding 80%). The range of reduction of the yield of methyl ester was from 90.8% (fresh use), to 82.4% (fifth reuse) (Fig. 5d). In all about 8.4% of total esters was reduced at the end of the fifth run, suggesting that the catalyst particles were stable. The reduction in the yield after each cycle of reuse was possibly due to leaching of K<sub>2</sub>O [51,52]. Sample chromatogram of the optimum reaction conditions of the maximum methyl yield is shown in Fig. 6.

### 3.6. Comparison of *S. marianum* biodiesel properties to international standards

The *S. marianum* biodiesel produced at the optimum reaction conditions were tested for their quality and the standards compared with those of PRC-GB/T 20828 (2007), European Union-EN



**Fig. 6.** Chromatogram of *Silybum marianum* methyl esters: (a) petroleum ether (solvent); (b) tetradecane (used as internal standard); (c) methyl palmitate (C16:0); (d) methyl linoleate (C18:2(cis-9,12)); (e) methyl oleate (C18:1(trans-9)); (f) methyl stearate (C18:0) and (g) methyl arachidate (C20:0).

**Table 4**  
Comparison of properties of *Silybum marianum* biodiesel to PRC, America and European Union standards.

Fuel property	Method	<i>Silybum marianum</i> biodiesel	China GB/T 20828–2007	ASTM D6751	EN 14214
Cetane number	ASTM D6890	50	≥49	≥47	≥51
Kinematic viscosity (mm <sup>2</sup> /s; 40 °C)	ASTM D445	4.3	–	1.9–6.0	3.5–5.0
Oxidative stability 110 °C (h)	EN 14112	2.3	–	≥3	≥6
Cloud point (°C)	GB/T510	0	–	Report <sup>a</sup>	Country specific <sup>a</sup>
Pour point (°C)	GB/T3535	0	–	Report <sup>a</sup>	Country specific <sup>a</sup>
Cold filter plugging point (°C)	GB/T 2540	–1	–	–	–
Flash point (°C)	ASTM D93	154	≥130	≥93	≥120
Sulfur content (% w/w)	ASTM D4294	0.002	≤0.05	≤0.05	0.020
Ash content (% w/w)	GB/T508	0.018	≤0.05	≤0.02	≤0.02
Acid value (KOH mg/kg)	ASTM D664-01	0.454	≤0.8	≤0.5	≤0.5
Water (mg/kg)	ASTM D6304	0.04	≤0.05	≤0.05	≤0.05
Density (20 °C)	SH/T0248	865	820–900	–	860–900
Iodine value g/100	EN 14111	134	–	≤120	≤120
Copper strip corrosion (50 °C; 3 h)	ASTM D 130-94	1a	–	≤No. 3a	≤No. 1a
Free glycerin (% w/w)	EN 1405	0.001	0.02	≤0.02	≤0.020
Total glycerin (% w/w)	SH/T0796	0.14	≤0.024	0.24	≤0.25

<sup>a</sup> Low temperature properties are not strictly specified, but should be agreed upon by the fuel supplier or purchaser.

14214 (2008) and American ASTM D 6751 (07b) standards (Table 4). The properties including, cetane numbers, kinematic viscosity, flash point, acid value, copper strip corrosion and water content among others, were comparable to the international standards. The alkali-catalyzed transesterification clearly reduced the viscosity of the crude *S. marianum* oil from 37.5 mm<sup>2</sup>/s to 4.3 mm<sup>2</sup>/s, and this value was closer to that of diesel (3.068 mm<sup>2</sup>/s). The pour, cloud and cold filter plugging points of biodiesel reflecting its cold weather performance [53], indicate that the methyl esters of *S. marianum* oil can be used as fuel in relatively cold-weather conditions without much problem. The flash point of the biodiesel (154 °C) was however, higher than that of diesel and when blended with diesel (67.5 °C), could be reduced [54]. The test also indicated insignificant amount of free and total glycerin in the biodiesels. The oxidative stability and iodine value of the biodiesel were however, the main problem (not within the recommended standards). But can be improved using antioxidants and other commercial additives. The remaining properties of the methyl esters were comparable to international standards.

#### 4. Conclusions

KOH(32%)/ZrO<sub>2</sub>-5 as solid base catalyst was prepared by impregnating powdered zirconia with 32% KOH followed by calcination at 530 °C for 5 h and used to transesterificate *S. marianum*; a new non-edible oil with methanol to biodiesel. The content of oil in the seeds was determined to be 46% with 0.68% FFA and 65.68% linoleic acid. The catalyst had granular and porous structures with superior catalytic activity for the transesterification reaction. The maximum yield (90.8%) was obtained at methanol to oil molar ratio of 15:1, catalyst amount of 6%, reaction temperature of 60 °C in 2 h. The catalyst maintained sustained activity after five times of use. Apart from the oxidative stability (2.3 h) and iodine value (134) of the biodiesel (properties not in the recommended range), but can easily be improved, the remaining ones including, cetane number, flash point and the cold flow properties were comparable to the Chinese, ASTM and European Union standards. The study indicates that KOH(32%)/ZrO<sub>2</sub>-5 is an economically, suitable catalyst for producing biodiesel from *S. marianum* oil which is a potential new non-edible feedstock that can contribute positively to biodiesel industry as its biodiesel can be rated as promising alternate fuel.

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