***Original Research Article***

# Bi-ZnO heterogeneous catalyst for transesterification of crude jatropha oil to fatty acid methyl ester

## Abstract

The transesterification of crude jatropha oil (CJO) to biodiesel using Bi-ZnO (bi-zinc oxide) as a solid catalyst was investigated. The catalyst was prepared by co-precipitation technique, calcined and characterized with XRD, TEM and the surface area, pore volume and pore size distribution of the developed catalyst were measured using BET method to give insights into its performance. It was established that sample loading of 2.0 wt.% Bi on ZnO could exhibit the highest catalytic activity when the transesterification reaction was carried out at reflux of methanol (65 $^{o}$C), with a 12:1 molar ratio of methanol to oil and a catalyst amount of 4 wt.%, the conversion of jatropha oil was 95%during 1 h of reaction. The utilization of the catalyst for transesterification of non-edible oil will reduce dependence on food-grade oil for industrial application. The catalyst when washed using methanol and oven dried  at 80 $^{o}$C, can be reused for further tranesterification of the oil.

**Keywords**: Biodiesel; Heterogeneous catalysis; Transesterification; Bismuth loading on ZnO.

## 1. Introduction

Current concerns about the reserves shortage of fossil fuels have renewed interest in the production of renewable fuels. Fatty acid methyl esters, produced by the Transesterification of vegetable oils or animal fats with methanol and known as biodiesel, have received considerable attention due to their environmental benefits and the fact that they are derived from renewable resources [1].The advantages of biodiesel include non-toxicity, renewability, low emission profiles, excellent lubricity, biodegradability and high flashpoint. In addition, as an alternative fuel, biodiesel is virtually compatible with commercial diesel engines and no engine modifications are required [2]. Most biodiesel process currently employed the transesterification of vegetable oils with methanol using homogeneous acid or alkali catalysts [3-5].Chemically, the transesterification process is known to be a sequence of three consecutive and reversible reactions where the triglyceride is successively transformed into a diglyceride, then into a mono-glyceride and, finally into glycerol and fatty acid methyl esters. Base catalysts, such as NaOH and KOH, are usually preferred over acid catalysts due to the higher reaction rates and the lower process temperatures; hence the process is adopted for most industrial production of biodiesel. However, the homogeneous catalyst-based processes is accompanied by various disadvantages, such as separation of catalysts from the products  requires further treatment of alkaline wastewater, thus leading to multiple process steps. Therefore, the search for more environmentally friendly solid catalysts is consequent of the environmental concerns resulting from the use of homogeneous base catalysts. In the case of heterogeneous solid base catalysts, it can be easily separated from the reaction mixture and requires no additional process step which is associated with homogeneous catalysts, and have a less corrosive character. This has made biodiesel production cost cheaper and more environmentally benign [6]. Many heterogeneous base catalysts such as calcined hydrotalcites [7] and Li/CaO [8] have been developed to promote the transesterification reaction. Also, different types of heterogeneous catalysts for biodiesel synthesis have been reported ranging from strong acid catalysts to strong base catalysts[9].Zeolites, hetero-poly acids and sulphated zirconia, alkaline earth oxide based catalysts, alkali metal supported alumina are few examples [10,11]. All these materials reveal interesting results in respect with surface functions (acidic or basic) catalytic aspect. In some cases, to achieve good catalytic performance, some of the catalysts can be used only at elevated conditions, such as high temperature, high methanol content or in presence of extracting co-solvent. However, most feedstock used in transesterification such as waste cooking oil, poultry fat and other non-edible oils such as crude jatropha oil, pongamia pinnata (karanj) oil and rubber seed oil contain higher amounts of fatty acid, thus limiting the application of heterogeneous solid catalysts. Heterogeneous catalysts offer some advantages because they are environmentally friendly and present minimal disposal problems. They are also much easier to separate from liquid products and can be designed to give higher activity and longer catalyst lifetimes. In the present work, an attempt is made to prepare biodiesel from crude jatropha oil using bismuth-doped ZnO as a catalyst. The catalysts were prepared by an impregnation method followed by calcinations at higher temperatures. The catalytic activity for the transesterification reaction using high free fatty acid (FFA) jatropha oil conversion to methyl esters was investigated. In particular, much attention was paid to the influence of doped Bi amounts on the efficiency of the catalysts. Also, the dependence of the conversion to methyl esters on the reaction parameters such as the catalyst loading, the reaction time, and the molar ratio of methanol to oil was studied. Further, appropriate characterization was employed to gain insights for the catalyst performance.

## 2. Material and Methods

### 2.1. Materials

Crude Jatropha curcas oil (CJO) was purchased from Telegamadu Bdh. Sdn., Butter worths, Penang, Malaysia. The acid value was 14.47mgKOH/g, water content 3.28%, kinematic viscosity, 24.7$m^2$ $s^{-1}$ determined at 40 $^oC$, Density, 892 kg $m^{-3}$at 15 $^oC$, and refractive index was 1.467 at 30 $^oC$. Chemicals used in the catalysts synthesis such as analytical grade KOH (≥85%),$Bi(NO_3)_3.5H_2O$ (≥98%) and $Zn(NO_3)_2.6H_2O$ (≥98%) were purchased from Sigma–Aldrich Pty Ltd., Malaysia with average purity of 94 %. These reagents were used without further purification for catalyst synthesis and the Transesterification of crude jatropha oil.

## 2.2. Catalyst preparation

Bi–ZnO catalysts were prepared by co-precipitation method using bismuth and zinc nitrates with 2 M KOH. Typically, 25.2 g of both salts were dissolved in 50 mL distilled water corresponding to 0.0296 M bismuth nitrate was mixed with1.6558 M of the zinc nitrate under continuous stirring for 5 h at 33 $^{o}$C. The resulting slurry was aged in a fume hood to 70 °C until homogenized solution was obtained. Basic strength was determined by the indicator method. The solution was filtered with the filter sizes of 1.49 and 4.49 µm and oven dried at 85 °C for 12 h. The above procedure was repeated by varying ratio of Bi:Zn from 1:49 to 4:49. The synthesized catalyst was calcined at 550 $^{o}$C for 5 h before use for the reaction. The loading amounts of bismuth were calculated based on initial experimental runs.

## 2.3. Catalyst characterizations

Powder X-ray diffraction patterns were recorded on a Phillips PW 1710 diffractometer using CuKαradiationat 40 kV and 50 mA over a 2h range of 10–90. The XRD phases present in the samples were identified with the help of JCPDS (Joint Committee of the Powder Diffraction Standards) data base files. The surface area and pore size were analyzed based on the nitrogen adsorption isotherm at -196 $^{o}$C using Porosimeter Micromeritics ASAP2020, sample were degassed at 120 $^{o}$C for 3 h prior to analysis. The transmission electron microscopy was obtained to understand the structural properties of the catalyst.

## 2.4. Transesterification procedures

Crude jatropha oil is generally known to have high content of free fatty acid (FFA) greater than 1 % which must be esterifies before transesterification is carried out otherwise leads to saponification reaction lowering the yield of FAME. You did not give the percentage of FFA presence in the oil and how it was esterifies. Similarly, presence of water in the oil in excess of

1% also adversely affects transesterification reaction by hydrolysing the triglyceride. No mentioned of percentage of water in the oil was made and how it was removed.

All experiments were performed in a 250 mL round bottom flask equipped with a reflux condenser and a magnetic stirrer. The transesterification reactions were carried out with jatropha oil, at a catalyst amount of 1.0–8 wt.% and a methanol/oil molar ratio of 5:1 to 20:1. The stirrer speed was set at maximum avoid mass transfer limitations with every batch experiment conducted at reflux of methanol (65 $^{o}$C) for the required reaction time. At the end of the experiment, the heater and stirrer were switched off and the reactor was cooled to room temperature. The catalyst was separated froms the product mixture by centrifugation at 2000 rpm for 15 minute product (methyl ester) and by-product (glycerol) were further separated using a separating funnel and the denser glycerol layer was removed from the bottom after settling for 10 minute analysis of composition of methyl esters was conducted using gas chromatography GC-2010 Plus (Schimadzu, Japan) with FID detector, equipped with a fused silica capillary column. Methyl heptadecanoate (MHD) (1 g), used as an internal standard, was dissolved in 100 mL hexane. The GC analysis was carried out by preparing an accurately weighed 250 mg of sample in a 10 mL vial and was properly mixed with 5 mL of MHD to give a dilution factor of 14. The GC injection volume of prepared sample of methyl esters was 1 µL. From this, the methyl ester content of the samples was evaluated using the EN14103 application note [12].

## 3. Results and discussion

### 3.1. Characterization of the synthesized Bi-ZnO catalyst

The textural properties of the as synthesized catalyst samples were determined. According to the results shown in Table 1, the sample with the ratio 2:49 of bismuth loading on zinc has better textural properties. The properties, such as specific surface area, pore volume and average pore diameter of the samples are presented in the table. In the particular case, the BET surface area of the catalyst was found to have the highest value (30.76 $m^2/g$) amongst all other catalysts prepared.

Table 1: BET surface area, total pore volume and average pore diameter of the different ratio of as synthesized Bi-ZnO catalyst

| No. | Bi-ZnO catalyst ratio | BET surface area ($m^2/g$) | Total pore volume ($cm^3/g$) | Average pore diameter (nm) |
|---|---|---|---|---|
| 1. | 1:49 bimuth loading on zinc | 15.85 | 0.050 | 7.06 |
| 2. | 2:49 bimuth loading on zinc | 30.76 | 0.123 | 11.09 |
| 3. | 3:49 bimuth loading on zinc | 22.48 | 0.046 | 8.54 |
| 4. | 4:49 bimuth loading on zinc | 21.64 | 0.046 | 5.46 |

The mixed oxides catalyst is believed to form a synergetic network of composite heterogeneous oxides catalyst inter-locked together in one unit. The synergistic effect of this catalyst at the calcined temperature (550$^{o}$C) and time (5 h) greatly reflects on its activity. In addition to the surface area, the catalyst also possessed high total pore volumes with the value 0.123$cm^3/g$, the highest among all the formulations. The plots of relative pressure versus volume adsorbed for the catalyst is as shown in Fig.1.At low relative pressure, the isotherm exhibited a steep increase in the amount of $N_2$ adsorbed, which corresponds to the filling of micro pore with $N_2$, followed by nearly horizontal adsorption and desorption branches. At high relative pressure, hysteresis loop was observed around $P/P_o$= 0.9, indication of the inter-crystalline textural mesoporosity (mesoporous structure).All the synthesized catalyst gave pattern similar to Types IV isotherm which corresponds to mesoporous materials with characteristic feature of the hysteresis loop and is associated with capillary condensation taking place in mesopores.

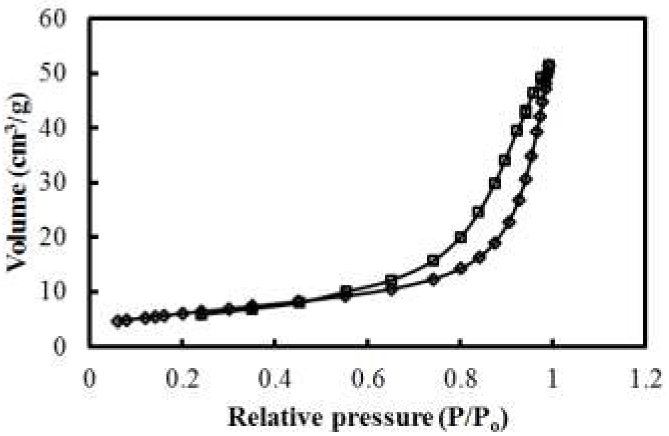

Fig.1: The Nitrogen adsorption/desorption isotherms of Bi-ZnO catalyst with ratio 2:49 calcined at temperature 550 $^{o}$C and time 5 h.

The hysteresis that appeared in the multilayer range of physisorption isotherms is associated with capillary condensation in mesopores structures and such hysteresis loop, as seen in the plot exhibited hysteresis loop of type H2. The pore structures of materials with type H2 loops are often disordered and the distribution of pore size and shape is not well defined 13]. In some cases, interpretations of the H2 loops are especially difficult but are majorly the loops identified with mesoporous materials. The surface morphology for the catalyst was done by TEM analysis as is given in Fig. 2 to further understand the structural properties of the catalyst used in this research. The figure clearly shows the typical pattern of Bi oxide surrounded by zinc ions.

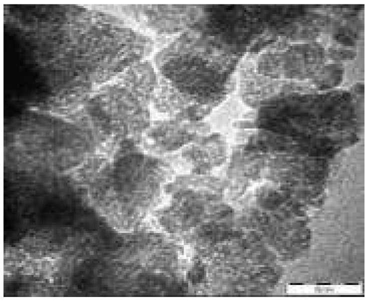

Fig.2: TEM image for the Bi-ZnO catalyst with magnification at 35KX

The cause of the blurred image of this structure could be that Zn metals are in a sub-layer covered by Bi oxide species or that the metals active sites are partially covered. The partially covered active sites are most probably responsible for the very high specific site activities observe in the performance. The observation presented here is corroborated by the reported work of Aksoylu *et al.,* (1998) [14]where nickel sites that are closely surrounded or partially covered by $MoO_x$ species are thought to be the ones that have the higher specific site activities.

The powder X-ray diffraction pattern of Bi-ZnO sample is depicted in Fig.3. The characteristic peaks of the parent ZnO (figure not shown)were registered in the diffraction pattern of the Bi–ZnO sample with their positions remaining essentially unaffected by the changes in Bi-loadings, which indicates that the mixture of Bi with ZnO oxides did not cause considerable distortion in the catalyst structure though the relative intensity of the ZnO peaks decreased with increase in Bi loading. The decrease in the relative intensity of the characteristic ZnO peaks observed in the sample, may be related to the effect of bismuth on the ZnO surface expressed in a stronger interaction with the ZnO, because bismuth has large cationic radius, thus may shade off the peaks characteristic of the ZnO with a decreased intensity in the samples of higher bismuth contents. The Bi oxide phase was not detected by XRD in the Bi–ZnO catalysts in the present work, as reported previously by other authors [15]. We think that the trace amounts of BiO phase may have been highly dispersed onto the surface of the ZnO as a monolayer, which does not allow its registration by XRD. The $BiZnO_x$ phase is probably formed by a solid state reaction between Bi oxide, one of the products of the loaded $Bi(NO_3)_3$ decomposition, and the ZnO, and hence could be one reason for the high activity of the calcined catalyst.

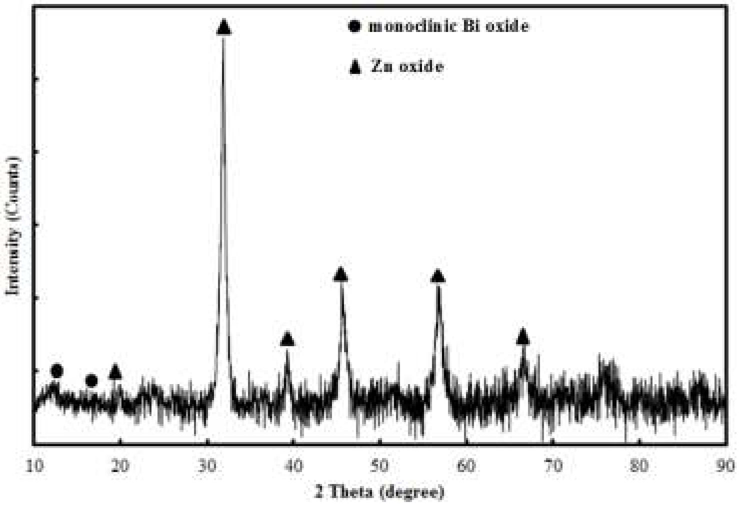

Fig. 3; XRD patterns for sample Bi-ZnO with ratio 2:49

**3.2 Transesterification of jatropha oil with methanol**

Transesterification reactions catalyzed by heterogeneous catalysts are known for their slow reaction rates. Due to the presence of heterogeneous solid catalysts, the reaction mixture initially constitutes a three-phase system, oil–methanol-catalyst, which for diffusion reasons inhibits the reaction. Stoichiometrically, 3 moles of methanol are required for each mole of triglyceride. The conversion of jatropha oil could be elevated by introducing an excess amount of methanol to shift the equilibrium to the methyl esters side, as suggested by other researchers who used heterogeneous base catalysts to study the transesterification reaction [16]. Industrially, the excess methanol can be recovered and reused after its purification. Fig. 4A, B, and C illustrates the change of the conversion under the employed reaction conditions as a function of methanol/oil molar ratio.

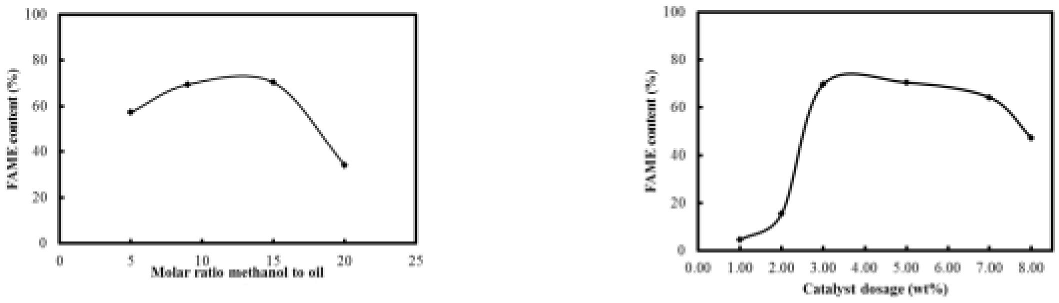

Fig.4; (A) Dependency of FAME yields on reaction time at catalyst loading of 5.0 wt %,methanol/CJO molar ratio of 12:1,temperature of 65 $^{o}$C

Fig. 4; (B) % FAME yield at different catalyst dosage with methanol/CJO molar ratio of 12:1, reaction temperature 65°C and time 1 h

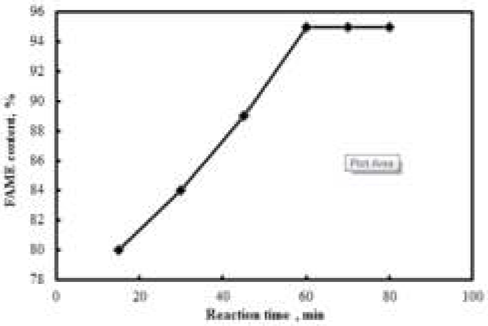

Fig.4; (C) Plot of the conversion of jatropha oil as a function of reaction time at methanol/oil ratio 12:1 at 4wt% catalyst

As shown in the graph, Fig.4 (A), the conversion to methyl esters increased from 60% to 75% when the molar ratio of methanol/oil was increased from 5:1 to 20:1. The maximum conversion was obtained at a molar ratio of about 12:1. Beyond the molar ratio of 12:1, the conversion decreased indicative of dilution effect of the reactants. Thus, a 12:1 molar ratio of methanol to oil is insufficient for the jatropha oil transesterification under the reaction conditions. The influence of the catalyst amount was examined in the present work. The catalyst amount was varied in the range between 1.0 wt.% and 8.0 wt.% referred to the starting oil weight. The obtained results, reported in Fig.4 (B), indicate that the transesterification reaction is obviously affected by the catalyst applied. By increasing the catalyst amount from 1 to 4 wt.%, the conversion to methyl esters was increased gradually and came up to its maximum of 78%. However, as the catalyst amount was raised higher than 4 wt.%, a decrease in the conversion was observed, which is possibly due to the mass transfer limitations of reactants, products and solid catalyst. Accordingly, the transesterification reaction was further studied with 4 wt.% of the catalyst for optimization of reaction time. A plot of the conversion of jatropha oil versus the reaction time is shown in Fig.4(C). As can be seen, the conversion was improved steadily in the reaction time range between 15 and 60 min, and thereafter remained almost constant of about 95% representative of near completion of the reaction. Thus, the maximum conversion is achieved after 1 h of reaction time. In order to study the stability of Bi–ZnO catalyst, it was separated by filtration, and then was initially washed with cyclohexane to remove any non-polar compounds such as methyl ester present on the surface. Further, the catalyst was washed by methanol to remove the polar compounds such as glycerol. Finally, the catalyst was heated at 80 $^oC$ overnight and further used for the next transesterification. The reaction was carried out with the same reaction conditions as before. It was shown that the reaction catalyzed by the recovered catalyst provided a 40% conversion, which was lower than the conversion over the original catalyst. The observed trend for Bi–ZnO catalysts used in jatropha oil Transesterification could be, probably, owing to the leaching of Bi species such as Bi oxide from the support catalysts. However, the Bi–ZnO catalyst was regenerated by impregnating it in fresh aqueous solution of Bi-$(NO_3)_3$ as described in the experimental section and re-calcined under the same conditions. The result shows that regeneration process could give a high conversion of 93.7%using same reaction conditions as in the case of fresh catalysts.

## 4. Conclusions

The Bi-doped ZnO prepared by an impregnation method followed by heat treatment appears to be an active catalyst in jatropha oil transesterification. The catalyst with 2.0wt% Bi on zinc oxide calcined at 550 $^oC$ for 5 h was found to give the highest catalytic activity. The Optimized reaction conditions for the transesterification were 4 wt.% Bi–ZnO catalyst, a molar ratio of methanol to oil of 12:1 and a reaction time 1 h, which resulted in a 95% conversion of oil at reflux of methanol (65 $^oC$). Furthermore, the prepared catalyst was characterized with XRD, TEM and it revealed their catalytic activity in the transesterification reaction was due to synergistic interaction of the two metals. Although, the catalyst show a good initial activity for the reaction, a decrease in catalytic activity was observed when the catalyst was reused this suggests agglomeration of oil molecules blocking the catalyst active sites.

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