International Journal of Engineering & Technology, 7 (3.11) (2018) 228-231

International Journal of Engineering & Technology

Website: www.sciencepubco.com/index.php/IJET

Research paper

Fatty Acid Methyl Esters Production from Waste Catfish Fat (*Pangasius Hypothalamus*) Using Barnacle-Zno As A Catalyst

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Abstract

The abundance and diverse populations of Barnacle shells catching the intention as a source of calcium oxide catalyst to transesterify waste catfish fat into methyl ester. Calcium oxide supported with zinc oxide was prepared by ball milling method at 1:2 ratios, calcined for 3 h at 400 °C. The characterization of catalyst revealed both metals were well integrated into a bimetallic oxide. The optimal conditions were found to be: methanol/oil mass ratio, 10:1; catalyst amount, 11 wt% at the reaction temperature, 65 °C with 3 h of reaction time achieving 85.7% of methyl ester conversion. Both feedstock and catalyst from waste source have been successfully utilized to produce biodiesel.

Keywords: *Barnacle Shells, Fatty Acid Methyl Esters, Waste Catfish Fat.*

1. Introduction

Nowadays, the oil market is becoming more and more volatile. The world dependency on fuels is still rapidly growing by the day, but conventional fuel such as coal, natural gas, and fossil fuel is rapidly are being depleted by year. Also, previously the use of vegetable oil such as corn, rapeseed, palm oil, and soybean are often used to produce biodiesel. However, in the scale of the industry, the utilized of edible oils in the production of biodiesel may lead to a phenomenon which is food versus fuel crisis [1]. Also reported, globally almost 925 million people undernourished [2]. Therefore, the food industries will be affected due to competition with the production of biodiesel. Many researchers have been carried out the project on finding any other possible waste oils and feedstock in Malaysia. Since Malaysia is located in a geographically strategic region, of which there are plenty of natural resources that can be obtained easily. Until today, palm oil is still the main feedstock used for biodiesel production. However, palm oil is edible oil which mainly used in food industries. Hence, competition will occur between food industries and biodiesel production since both of industries used an edible material as their feedstock.

In the meantime, Malaysia is agriculture and aquaculture based country. Introduced by Thailand in the 1980's about the catfish culture and until now progressive well in this area. The retail value of catfish for 2011 in Malaysia was estimated at USD 41 million (FAO, 2015). Reported the high demand (10-15 tonnes of catfish/week) from food industries and 45 metric tonnes monthly production in Temerloh indicate a great opportunity for Malaysia to utilize non-edible oil from waste catfish fat for promising feedstock or co-source of biodiesel production. Practically, cleanup fishery processing contributes around 40 and 60 % of the total body weight as waste. Instantaneously may cut off the cost of production in the biodiesel industry [3]. [2] approved to obtain high conversion of methyl esters (96.9-97.2%) from the non-edible waste (catfish fat waste) by using calcium oxide (CaO) as a catalyst.

Other than that, transesterification process which is the process of production of biodiesel, require a demand catalyst to make sure the process is perfectly done. It requires extra cost to expense in catalyst since the cost of the catalyst is a price. Thus, this problem needs to be encounter by finding an alternative catalyst for the transesterification process of catfish oil to overcome the dependence of one type of catalyst along with reducing the cost of production of this process. Barnacle as a marine life found abundantly with various populations. It can be found at the bottom of ship, buoys, pilings, and rock on a beach. However, the abundances may move ahead of a fouling problem. Scientifically, the barnacle is a source of $CaCO_3$ compound and able of being a source of CaO which are non-toxic, high basicity and biodegradable [2]. To the best of our knowledge, no reported study uses of ball milling CaO derived from barnacle with ZnO as a catalyst to transesterify the catfish fat from waste sources for biodiesel production.

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2. Method

The crude material utilized in this work is waste catfish (Pangasius hypothalamus) fat which collected from the local market in Kuantan, Pahang, meanwhile and the barnacle shell was obtained from Tanjung Lumpur beach, Pahang, Malaysia. The chemicals purchased from Sigma–Aldrich company (Switzerland) include, phenolphthalein (H_=9.2), thin layer chromatography (TLC) plate, pH indicator strips, chloroform, and methyl heptadecanoate as an internal standard GC grades (>99.1%) were bought from Merck KGaA (Germany). 2,4-dinitroaniline (H_=15.0) and 4-nitroaniline (H_= 18.4) from Sigma-Aldrich were used as the Hammet indicator. Methanol (anhydrous, ≥99.8%) and hexane (anhydrous, ≥ 99.8%) were purchased from Hamburg (Germany).

The barnacle shells were carefully washed to remove dirt and fibrous matter several times. Dried the shell in the oven at temperature of 105 °C overnight. The dried shells were then ground to fine powder in a dry-mill blender and sieve through 75 µm mesh. The ground shell was calcined in a furnace at temperatures 900 °C for 2 h. After that, the purified shell is used as the CaO support in preparation of the catalyst. Ball milling method was used for the preparation of CaO-ZnO catalyst, CaO, and ZnO powder mixed stoichiometrically by a molar ratio of 1:2. The mixture was calcined at 400 ˚C for 3 h [4]. The basicity of the catalyst has been determined by using Hammett indicators [5]. 25 mg of catalysts were added into 1 mL of Hammett indicators solution and left to equilibrate for 2 h. The observation of the color changes of the catalyst on the Hammet indicator: phenolphthalein (H_= 9.3), 2,4-dinitroaniline (H_ = 15.0) and 4-nitroaniline (H_= 18.4) were recorded. The specific surface area of the catalyst was measured by Micromeritics (ASAP 2000) and degassed at 250 °C for 6 h using N_2 adsorption. The surface elemental composition and morphology of the catalyst was observed by Field Emission Scanning Electron Microscopy coupled with dispersive electron X-ray (FESEM-EDX) (JSM-7800F). FTIR (Perkin Elmer Spectrum 100) spectrophotometer was used to characterize the chemical structure of catalyst at 400 – 4000 cm^{-1} range.

The preparation of oil from catfish was prepared following the procedure published by [2]. The catfish was washed to uproot any contaminations in and out of the catfish body. The fat of catfish was dissolved utilized hotplate at a temperature of 100 °C to uproot the moisture content. The resultant oil (after constant weight) was then filtered through a filter paper before being stored in an amber bottle in the refrigerator. The oil content in the catfish fat was ascertained by using the equation 1 below:

$$\text{Oil content (\%)} = M_{oil} / M_{fat} \times 100 \quad (1)$$

Where, (M_{oil}) = mass of oil extracted in gram (g) and (M_{fat}) = mass of fat in gram (g). The acid value of the catfish oil was measured according to EN 14104 standards. Meanwhile, the moisture content of catfish oil was determined based on Karl Fischer titration method (784 KFT Titrino, Metrohm). The density and viscosity of oil were measured by using density meter and viscometer.

The conversion of the catfish oil into methyl ester was determined by using a 50 mL round bottom flask equipped with a reflux condenser and magnetic stirrer (Fig. 1). The transesterification reaction between oil and methanol was carried out in the liquid phase under atmospheric pressure, at 65 °C with continuous stirring. The reaction parameters (amount of catalyst, methanol to oil ratio and reaction time) were being studied to optimize the transesterification. At the end of the reaction, the denser catalysts condensed at the bottom of centrifuge tube by using a centrifuge at 4000 rpm for 4 min. Excess methanol was evaporated before the chromatographic analysis. Carefully, pour out the methyl ester on the upper layers using a dropper. The concentration of methyl ester in the sample was quantified using GC-FID (Agilent7890A) by following the European procedure EN14214 with polar capillary column (DBWax, 30m × 0.25 mm i.d × 0.25 µm) using methyl heptadecanoate as an internal standard.



Fig. 1: Transesterification set up

3. Result and Discussion

The Hammett indicator was used to test the base strength of the catalyst. The result reveals that the basic strength of 15.0 > H _> 18.0, by the color change of colorless CaO into light pinkish in phenolphthalein and yellow to light purple (2, 4-dinitroaniline) but yet cannot change color in the 4-dinitroaniline. These indicate that CaO catalyst is a strong basic catalyst with pH range falls between 15 and 18.0. However, the amphoteric characteristic property of ZnO was not able to change in phenolphthalein, 2, 4-dinitroaniline and 4-dinitroaniline. Amusingly, the CaO-ZnO catalyst presents all positive results at Hammett range 8.2 to 18.4 ($8.2 \leq H_ \leq 18.4$). Due to the supported of CaO may increase the basic strength of the catalyst and anticipated to promote the activity for transesterification [6]. Method preparation of CaO-ZnO catalysts via ball milling and calcined at 400 °C for 3 h adequate to increase the high surface basicity [7].

The determination of surface area analysis of the catalyst reveals CaO-ZnO (3.8189 m^2/g) has a lower BET surface area compare to single metals: CaO (8.250 m^2/g) and ZnO (6.9428 m^2/g). The cooperative interaction between the mixed oxides will reduce the size of the catalyst [8]. The decreasing in surface area was considering the sequence of catalyst displacement on the metal oxide. The morphology of calcined (900 °C) barnacle (CaO) shell and calcined (400 °C) CaO-ZnO catalyst were observed via FESEM (Fig. 2), showed in spherical and bulky shaped particle for CaO with range size of 2.1-7.6 µm. Meanwhile, ZnO had a spherical and rod-shaped particle with the range of size of 0.2 – 0.4 µm. When there was bind together, the small particles became inserted

into the large ones [9]. By the presence of Ca^{2+} as the major metal component in the catalysts and the previously formed Zn precipitate clusters that can be covered by Ca carbonate subsequently precipitated during aging.

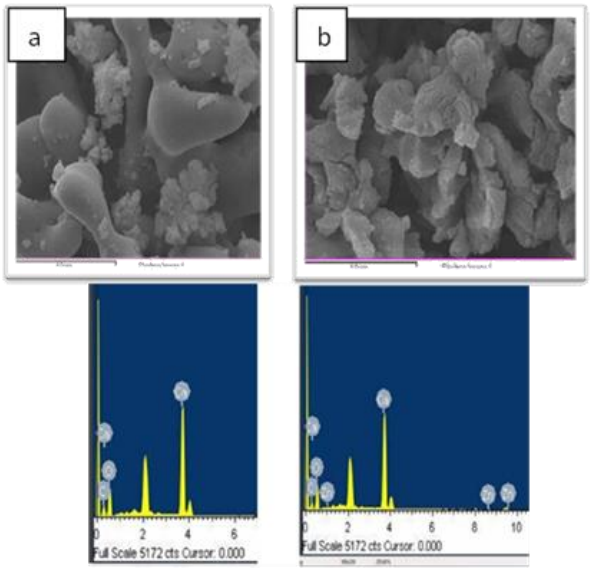


Fig. 2: FESEM-EDX micrographs of a) Barnacle (CaO), b) CaO-ZnO

According to Fig.3, the FTIR spectra of CaO-ZnO catalyst showed absorption peaks at 712 cm^{-1}, 873 cm^{-1} and had a board band at 1422 cm^{-1} which can contribute to the presence of an asymmetrical stretch, out-of-plane bend and in-plane bend vibration modes for CO_3^{-2} molecules. It is also had two sharp peaks at 3643 cm^{-1} and 3457 cm^{-1} that allocated to OH stretching vibration band which was matched with the characteristic of O-H stretching vibration of $Ca(OH)_2$ at 3643 cm^{-1} relating to OH bending mode that is observable at 873.33 cm^{-1}. Next, the H-O-H bending mode of lattice water also appears at 1635 cm^{-1}. However, the bending vibration of Zn-O-H was detected at 1137 cm^{-1} [10]. The existence of carbonates was present in all of the samples tested, which was definite by the broadband centered at 1467.2 cm^{-1}. The intense bands of $CaCO_3$ can be seen at 1467.2, 1422, 873, 712 cm^{-1} and also the band at 2511 cm^{-1} from the vibrations in the CO_2 molecule.

The acid value, moisture content, viscosity, density, and saponification value of catfish oil were 3.70 mg KOH/g, 0.62% using Karl Fischer method, 65.5 mm2/s, 913 kg/m3 and 217.56 mg KOH/g, respectively. The low moisture content of oil may inhibit the conversion of methyl ester because the possibility of moisture to react with the basic catalyst is low, thus resulting less formation of soap occur during transesterification process [11]. It was found the fatty acid profile that catfish oil consisted of 45.96% palmitic acid and 54.04% oleic acid. Palmitic acid is saturated fatty acids, whereas oleic acid is unsaturated fatty acids. Thus, it can conclude that unsaturated fatty acids were predominantly in the catfish oil. However, reported by [12] the lauric acid for Pangasius Pangasius is 13.36%, and P. sutchi is 4.26%. Dissimilarity can be attributed to the fact that different intake of the food chain and their environment habitation [2].

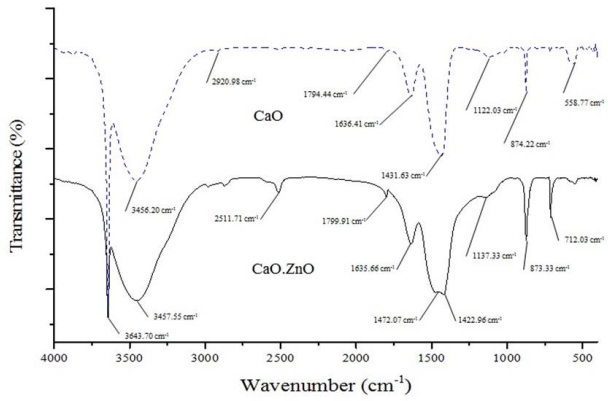


Fig. 3: FTIR spectra of CaO-ZnO catalyst

In this study, the solid basic catalyst, CaO-ZnO was capable of catalyzing transesterification of catfish oil consecutively. Catalyst amount has a substantial effect on the methyl ester conversion of the reaction. Therefore it is significant to optimize the catalyst loading to optimize the methyl ester yield. The catalyst amount was varied from 4 wt. % to 16 wt. % (based on Catfish oil weight). As shown in Fig. 4(a), the conversion of methyl ester increased from 43.94 to 85.7 % with increasing catalyst amount from 4 to 11 wt. %. However, further increase of catalyst amount decreased the methyl ester yield. Hence, the optimum catalyst loading to achieve highest methyl ester yield is at 11 wt. %.

The methanol to catfish oil molar ratio is another important parameter that affects the yield of methyl ester conversion. The methanol to catfish oil ratio was varied from 4:1 to 16:1. Supposedly, an excess of methanol is required to shift the equilibrium of the transesterification reactions towards the direction of methyl ester production. Transesterification of catfish oil was carried out by 11 wt.% of CaO-ZnO catalyst at 65 °C constant temperatures for 3 h reaction time. It was observed that the methyl ester yield was frequently raised from 11.58 % (MeOH/ oil) ratio to 85.7 % at 10:1 methanol to catfish oil ratio. However, at 12:1 MeOH/oil ratio the percentage of methyl ester yield was started to decrease and slightly dropping from 14:1 to 16:1 MeOH/oil ratio. Observably, the highest methyl ester content of 11 wt. % of methanol: oil ratio of 10:1. Conversely, further increasing of methanol/oil ratio brought negative effects on methyl ester conversion. Excess of methanol used will make the reaction became slow in rate [13]. The excess amount of methanol will increase the tendency to dilute the oil during transesterification reaction. On the other hand, at 12:1 MeOH/oil ratio was observed to be a drop in methyl ester yield due to emulsification of catfish oil that would cause by an excess of OH groups in methanol to restrict the yield of methyl ester production in the reaction. [14] found that the emulsification of catfish oil will make a methyl ester hard to separate from the glycerol. As a result, the yield of methyl ester started to decrease. Therefore, the optimum parameter of methanol to oil ratio of 10:1 was preferred as the methyl ester conversion was the highest (85.7%) percentage obtain by using 11 wt.% of CaO-ZnO catalyst at 65 °C for 3 h reaction time.

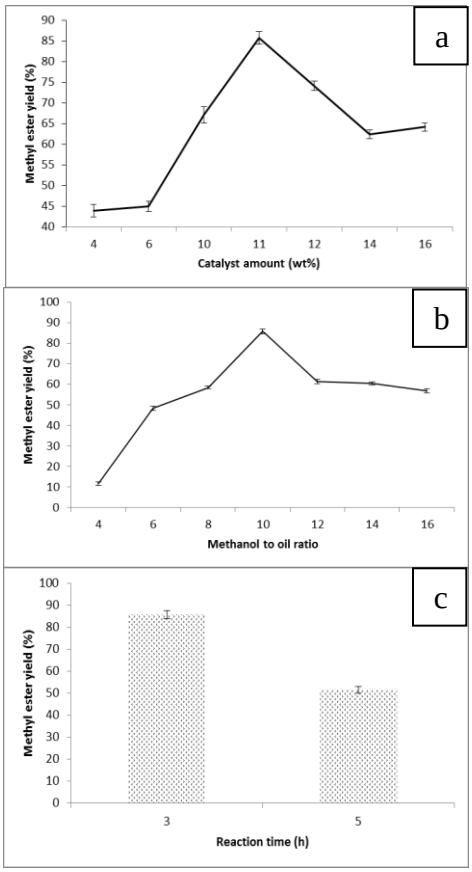


Fig. 4: Effect of (a) catalyst amount; (b) methanol/oil molar ratio and (c) reaction duration on the methyl ester content.

Fig. 4(c) presents the average yield of methyl ester for 3 h, and 5 h were 85.7% and 51.6% respectively. However, theoretically, transesterification need a certain period to reaching a complete mixing and diffusion of methanol, oil, and catalyst to make sure that the reaction will take place effectively. In conclusion, a longer time is better to overcome the mass transfer limitations and reduce the poor mixing of the mixture. Notwithstanding, [14] and [2] had stated that the methyl ester conversion was capable of reaching a certain high yield but later will decline gradually in a longer reaction time. Reverse reaction of transesterification will happen when they are in a longer reaction time because the methyl ester could shift back to more free fatty acids that can cause the formation of soap. Therefore, it is vital to find the optimize reaction interval to obtain a high yield of methyl ester conversion. Hence, 3 h reaction time was selected for the transesterification of catfish oil since the methyl ester yield was higher (85.7%) than that of 5 h (51.6%) by using 11 wt. % of CaO-ZnO catalyst at 65 °C and 10:1 methanol to oil ratio.

4. Conclusion

As a summary, CaO-ZnO catalyst was capable of enhancing the catalytic performances of both single metal oxides (Barnacle-CaO and ZnO). The combination of both single metal oxides able to enhanced the synergic consequence between the metallic ions of CaO and ZnO. This synergic effect was verified in the catalytic performance in the transesterification of catfish oil in this study. Thus, it was proven that a CaO-ZnO catalyst capable of yielding 85.7% of methyl ester in 3 h of reaction time at 65 °C with MeOH/oil mass ratio, 10:1; catalyst amount, 11 wt%. The use of this type of oil as a low-cost feedstock offers a cost-efficient and eco-friendly alternative to the existing feedstock for biodiesel production.

Acknowledgement

The authors would like to thank Ministry of Higher Education, Malaysia, Universiti Malaysia Pahang and Universiti Teknologi MARA Pahang for funding the research project under FRGS Grant (RDU 150110), UMP PGRS (170311) and the scholarship (Khazaai, S.N.M).

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