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Utilization of Waste Fish Bone as Catalyst in Transesterification of RBD Palm Oil

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Abstract

Biodiesel is becoming more important as it is chosen to be one of the alternative fuels to replace fossil fuel nowadays, as well as waste materials also play a significant role in cheaper and greener fuels. In this research, waste fish bones modified with potassium hydroxide (KOH) were utilized as a cost-effective catalyst in the transesterification of RBD palm oil with methanol. The waste fish bones were calcined at 900 °C for 2 h and then added with different concentration of KOH to form K⁺ impregnated calcined fish bones (K-CFB). The prepared catalysts were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy-energy dispersive X-ray (FESEM) and thermogravimetric analysis (TGA). The characterization results showed that K⁺ was successfully impregnated on calcined fish bones (CFB). Methyl ester was yielded at the highest content of 96.14 wt. % when the conditions are optimized at 5 wt. % catalyst loading, methanol to oil ratio of 12:1 and reaction time of 3 h. The CFB loaded with 10 wt. % KOH (10K-CFB) was found to be a potential heterogeneous base catalyst for transesterification due to its high catalytic activity.

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1. Introduction

Biodiesel is a renewable fuel that can be synthesized from animal fats, vegetable oils, or waste cooking oils. It consists of fatty acid methyl ester (FAME). Biodiesel does not contain petroleum, yet it can be converted into a biodiesel blend by blending with petroleum diesel. Fossil fuels are natural and non-renewable fuels created by decayed animals and plants that have been pressurized in the earth's crust under very high temperature over thousands of millions of years. Nearly 80% of the world energy demands are provided by fossil fuels such as crude oil, coal, natural gas, and heavy oils. However, the increased growth in world population and industrialization has caused the fossil fuel supplies to reduce rapidly. Moreover, the global warming due to greenhouse gasses emissions has brought about the attempts to explore new sources of energy. Biodiesel production is hence become the concern of the world because biodiesel is one of the alternative fuels [1,2]. Besides biodiesel is easy to be used, it is also biodegradable and not harmful, as well as essentially free of sulphur and aromatics. However, it has higher cetane number than conventional diesel, virtually high flash point. Nowadays, petroleum price is high, and it keeps on increasing due to increasing demands, while the price for biodiesel depends on the cost of raw material. Hence, raw materials with lower price are used to compete with petroleum diesel. Palm oil is cheap and easily available in our country as Malaysia accounts for the world's second largest palm oil production. Despite that, raw palm oil has some restrictions for the reaction of transesterification. One of the limitations that significant effect is only particular catalysts can be used due to the high content of free fatty acid (FFA) of oil [3]. In addition, crude palm oil has a few useful constituents which free fatty acids are, vitamin E, carotenoids, sterols, phospholipids, glycolipids and others [4]. Refining, bleaching and deodorization process are carried out to separate these components. The processed palm oil is found to be more suitable than the raw palm oil in biodiesel production. Therefore, refined, bleached and deodorized (RBD) palm oil was used to produce biodiesel.

In the production of biodiesel, esterification and transesterification can be used. Transesterification is normally carried out where in the process, the organic group R of an ester is exchanged with the organic group R' of an alcohol. The rate of this reaction is usually faster than others due to the usage of a catalyst [4]. With the presence of a strong acid or base catalyst, triglycerides from the plant and animal fats and oils will react with an alcohol to generate a mixture of glycerol and fatty acid methyl esters in the transesterification process [5]. The homogeneous and heterogeneous catalysts used in the transesterification reaction are usually cost intensive [6]. The waste derived green solid catalysts have gained the interest of researchers for their significance in the aspect of the present economic climates such as firm pollution regulations and increased competition. Different types of cheap and highly efficient heterogeneous catalysts synthesized from waste resources have been used to produce biodiesel successfully. Those waste resources include waste eggshell, mud crab shell, shrimp shell, oyster shell and waste mollusc shells [7]. Soon, the environmental benign heterogeneous catalysts are believed to replace the conventional homogeneous catalysts as the simplifications in the purification of product, as well as the recovery of catalyst. In

this work, transesterification is carried out to synthesis biodiesel with the use of RBD palm oil and methanol using a novel, cheap, and greatly efficient heterogeneous catalyst synthesized via the calcination of waste fish bones impregnated with K^+ ion.

2. Materials and methods

2.1 Materials

Black Tilapia fish are harvested in Lake Temenggor, Perak by the company Trapia Malaysia. Tilapias 6 months to 1 year old were catches for filleting process. Methyl heptadecanoate of chromatographic grade was received from Sigma-Aldrich (Switzerland). The RBD palm oil used in this study will be supplied by local store. Pure potassium hydroxide (98.9%), methanol, petroleum ether, chloroform, n-hexane, n-heptane (GC grade) and thin layer chromatography strips will be purchased from Merck.

2.2 Catalyst preparation and characterizations

Waste fish bone was cleaned using warm water to remove dirt, fibrous matters and proteins. Then the bones were dried in the oven at 105 ± 2 °C until constant weight. The bones were then roughly crushed by mortar and further crushed finely using a dry-mill grinder through 100 μ m mesh. The powder was then calcined to remove the remains of carbon and other impurities. KOH was added at 5, 10 and 15 wt. %. The catalyst active ingredients were identified by X-ray diffraction (Rigaku MiniFlex II) with $Cu K\alpha$ X-ray as a source. The catalyst was examined for thermal stability through thermogravimetric analysis (TGA) using Mettler Toledo TGA/DTA (851e instrument), from 25 to 900 °C with 10 °C/min heating rate. The size and morphology of the catalyst were identified by FE-SEM (JEOL JSM-7800 F).

2.3 Experimental setup

The transesterification reaction was carried out in a 250ml 3-neck round-bottom glass flask equipped with a condenser to reduce the losses of methanol due to the evaporation and thermo- couple thermometer. Optimization steps are important to carry out in order to figure out the best parameters achieving highest methyl ester conversion. Reaction parameters (catalyst amount, reaction period and methanol to oil molar ratio) were studied to identify the optimum reaction conditions. The experiments were carried out by using 3 – 12 wt. % catalyst, methanol to oil ratio was 8:1 – 16:1 and the reaction time was 2 – 6 hours. After the transesterification, the reaction mixture was allowed to cool. Then, to further separate the product (ME and glycerol) centrifugation at 4000 rpm for 5 min was performed. The excess methanol was evaporated before the gas chromatographic analysis. The reaction was carried out three times in order to reflect the precision and errors of the results.

2.4 Methyl ester analysis

The methyl ester content was determined using gas chromatography-flame ionization detector (GC-FID) (Agilent 7890A) using capillary DB-Wax column (length 60m x internal diameter 0.25mm x film thickness

0.25 μ m). The methyl ester content of biodiesel was calculated by following EN14103 procedure and using methyl heptadecanoate as an internal standard. The ME content was calculated using the following formula:

$$\text{Methyl ester content (\%)} = \frac{A_{\text{total}} - A_{\text{ISTD}}}{A_{\text{ISTD}}} \times \frac{C_{\text{ISTD}} \times V_{\text{ISTD}}}{W_{\text{sample}}} \times 100\%$$

where, A_{total} is the total area of ME from $C_{16:0}$ to $C_{18:2}$

A_{ISTD} is the area of methyl heptadecanoate

C_{ISTD} is the concentration of methyl heptadecanoate in mg/ml

V_{ISTD} is the volume of methyl heptadecanoate in ml

W_{sample} is the weight of sample in mg

3. Results and Discussion

In order to get information regarding the RBD palm oil used, some of the characteristics were analysed. The acid value, moisture content, iodine value, free fatty acid value, viscosity, density, saponification value and refractive index of the oil were analysed and tabulated in Table 1. TGA results (Figure 1), shows the thermogram of UCFB in the temperature range between 30 and 900 °C. This analysis exhibited an initial 5% weight loss which is from 99% to 94% corresponding to the temperature range of 40 – 200 °C. This is the first degradation stage indicating the evaporation of adsorbed water. The water adsorbed on the catalyst may due to the absorption of water molecules from the atmosphere. The second stage weight loss is from 88% to 66%, a loss of 22% resulted in the temperature range of 300 – 500 °C which can be attributed to fragmentation of macromolecules and loss of guanine and the other organic matters. There was additional 7% steady weight loss, which is from 66% to 59% at the temperature of 600 °C up to 830 °C due to decarbonation and formation of gaseous elements which eventually led to the formation of inorganic residue consisting of hydroxyapatite, as confirmed by XRD analysis. After 830 °C, there was no any further loss in weight. From this, the high thermal stability of the uncalcined fish bones is confirmed at or above 830 °C. Hence, 900 °C is the optimum temperature for calcination of UCFB because the crystallinity and optimal active sites can be increased. On the other hand, fish bones calcined beyond 1000 °C enhanced the sintering effect that ultimately reduced the surface area and resultantly the activity of the catalyst by decreasing the surface area. Figure 2 illustrated the XRD results for UCFB, CFB and K-CFB. When CFB was loaded with KOH, a new phase of KCaPO_4 at 29.141 ° was clearly showed on the diffractogram. However, there were no other peaks of KOH detected in the synthesized catalyst which might be due to the interaction of KOH with calcined fish bones and the formation of KCaPO_4 . The peaks at 26.102 °, 31.978 °, 33.112 °, 40.009 °, 46.885 ° and 49.672 ° are the characteristics of hydroxyapatite phase in the catalyst. The diffractogram of K-CFB also proposed the formation of CaO phase at 34.293 ° that is formed due to ion exchange of calcium ions of bones with potassium ions of KOH at high temperature [8]. Morphology of the UCFB, CFB and K-CFB were obtained using FESEM. FESEM micrograph (Figure 3) displays the microstructure of the UCFB, CFB and K-CFB. Figure 4a reveals the morphology of UCFB

like a mass of aggregates, while Figure 3(b) reveals the quite rough surface with a nodule like appearance where the pores are uniformly distributed throughout the irregular-shaped flat surface of the developed catalyst after calcination at 900 °C. These illustrate that UCFB has less surface area than CFB because the particle size reduction reached maximum when the bones were calcined, the carbonates were lost resulting in higher surface area. Figure 3c shows the flakes-shaped particles after impregnated K^+ on CFB which caused the particle size increases and exhibits lower surface area than CFB. The FESEM images clearly show that K^+ species were successfully impregnated into CFB.

Catalyst can speed up a reaction by lowering the activation energy of the reaction. Hence, the amount of catalyst used in the reaction plays a significant role in affecting the yield of FAME synthesized. In this research study, 10K-CFB was used as the catalyst used for carrying out the transesterification. Amount of catalyst was optimized in order to produce highest yield of methyl ester. The catalyst amount varied from 1 wt. % to 9 wt. % based on the weight of RBD palm oil. As shown in Figure 4, the conversion increased from 25.62 wt. %, 51.01 wt. % to 96.14 wt. %. As the amount of catalyst increased, ME gradually increased due to the increase of active site for reactant to undergo reaction [9]. Reaction time is one of the important parameter which can influence the yield of biodiesel. The effect of different reaction duration on the methyl ester conversion was illustrated in Figure 4. The reaction proceeds quickly as the interaction of oil and methanol is fast and the maximum yield of conversion can be reached at a short time. The yield of FAME remains constant as the equilibrium condition reached. However, unwanted reactions such as saponification may occur if the reaction time is longer than the optimum reaction time which decreases the yield of conversion. The yield of conversion decreased rapidly after the optimum reaction time because more soaps were formed. In addition, transesterification is a reversible reaction, so the reaction moves backwards when the reaction time is prolonged more than its optimum time which results in lower biodiesel yield [10]. The occurrence of glycerolysis reaction for biodiesel under this unfavourable condition which leads to lower yield of conversion [11]. It may also due to the increase in the molar ratio make the relative concentration of oil to be lowered causing the slower reaction rate and changing the reaction equilibrium [12]. From literature, the excessive amount of methanol could deactivate or dilute the catalyst affecting the interaction of catalyst in the reaction [13]. Hence, the appropriate molar ratio of methanol to oil should be 12:1 according to the experimental results.

Table 1. Oil characterizations

Parameters	Present	[14]	[15]
Acid value, mg KOH/g	4.69	-	0.6 – 4.65
Moisture content, %	0.11	0.1	-
Iodine value, mg I ₂ /g	50.2	47 – 55.83	46.0 – 56.0
FFA value, %	3.5	-	3.17 – 5.0
Viscosity, cP	72.1	-	45.0 – 49.0
Density, g/cm ³	0.9087	0.89 – 0.92	0.892 – 0.889
Saponification value, mg KOH/g	207.57	196 – 208.2	190.0 – 209.0
Refractive index	1.4661	1.46	-

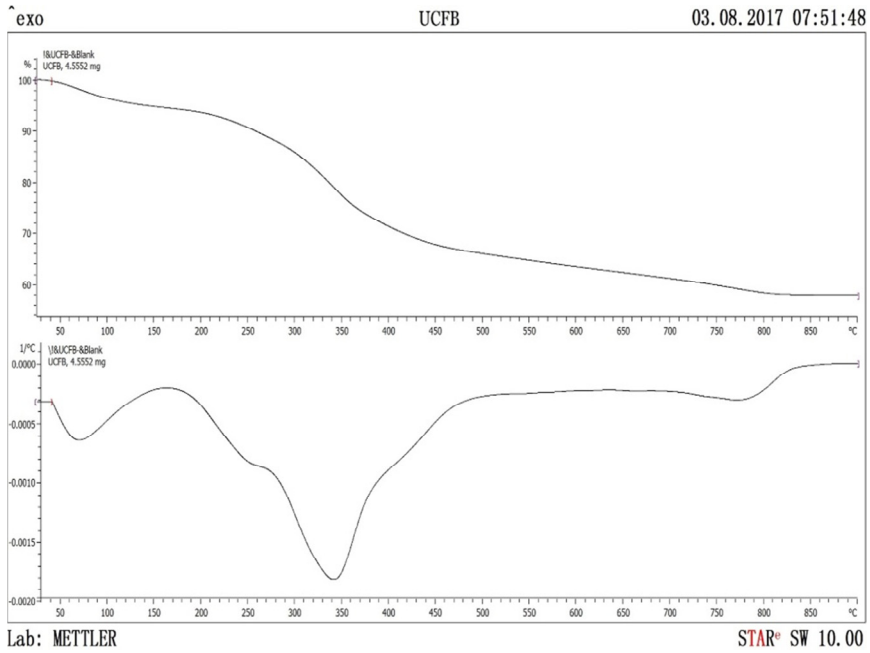


Figure 1. TGA thermogram of UCB

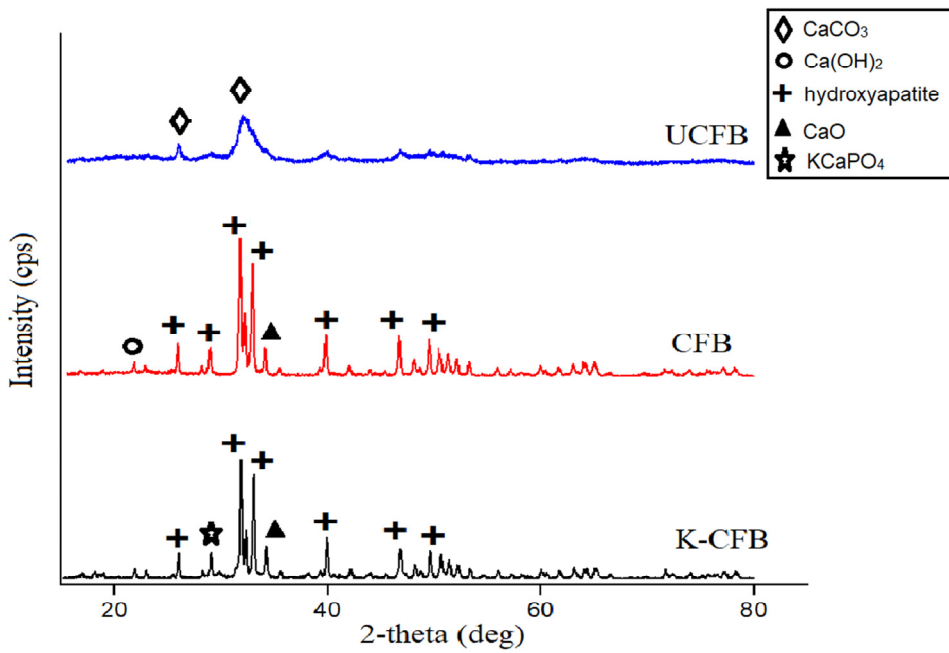


Figure 2. XRD result of UCFB, CFB and K-CFB.

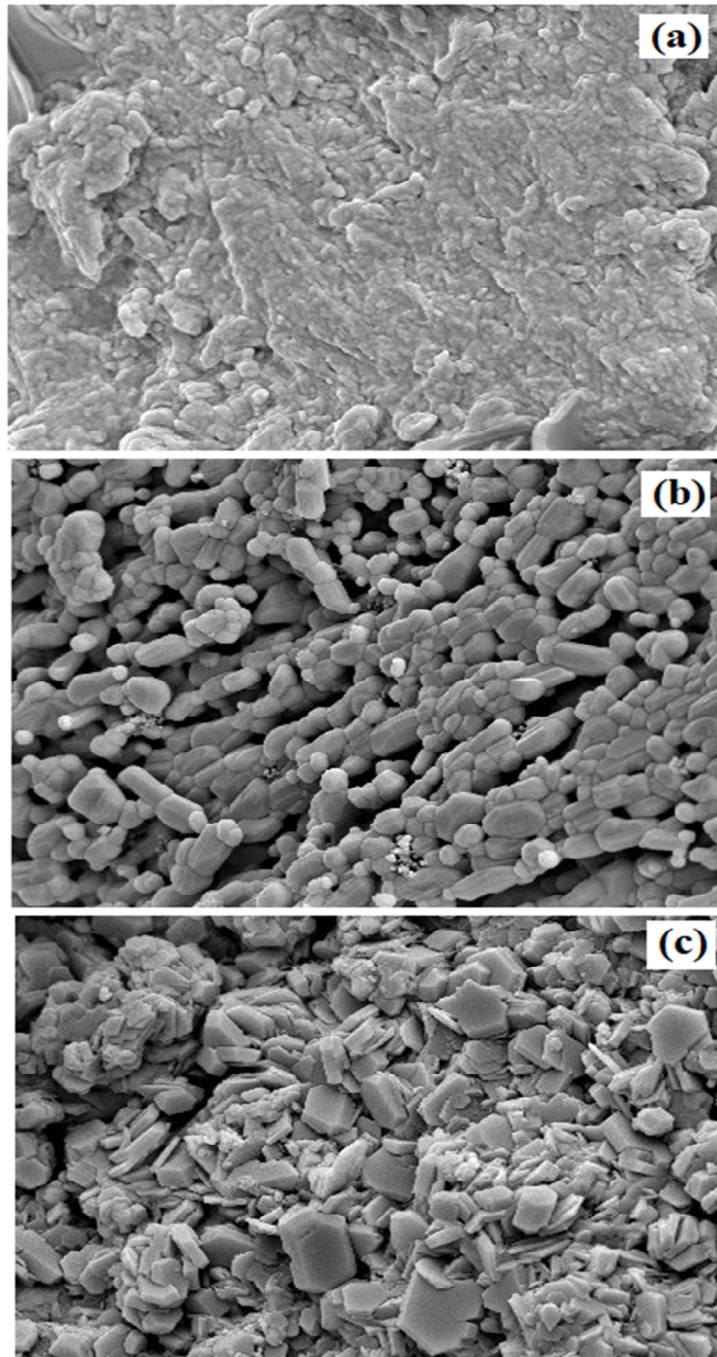


Figure 3. FESEM images of (a) UCFB, (b) CFB and (c) K-CFB under 10,000 magnification.

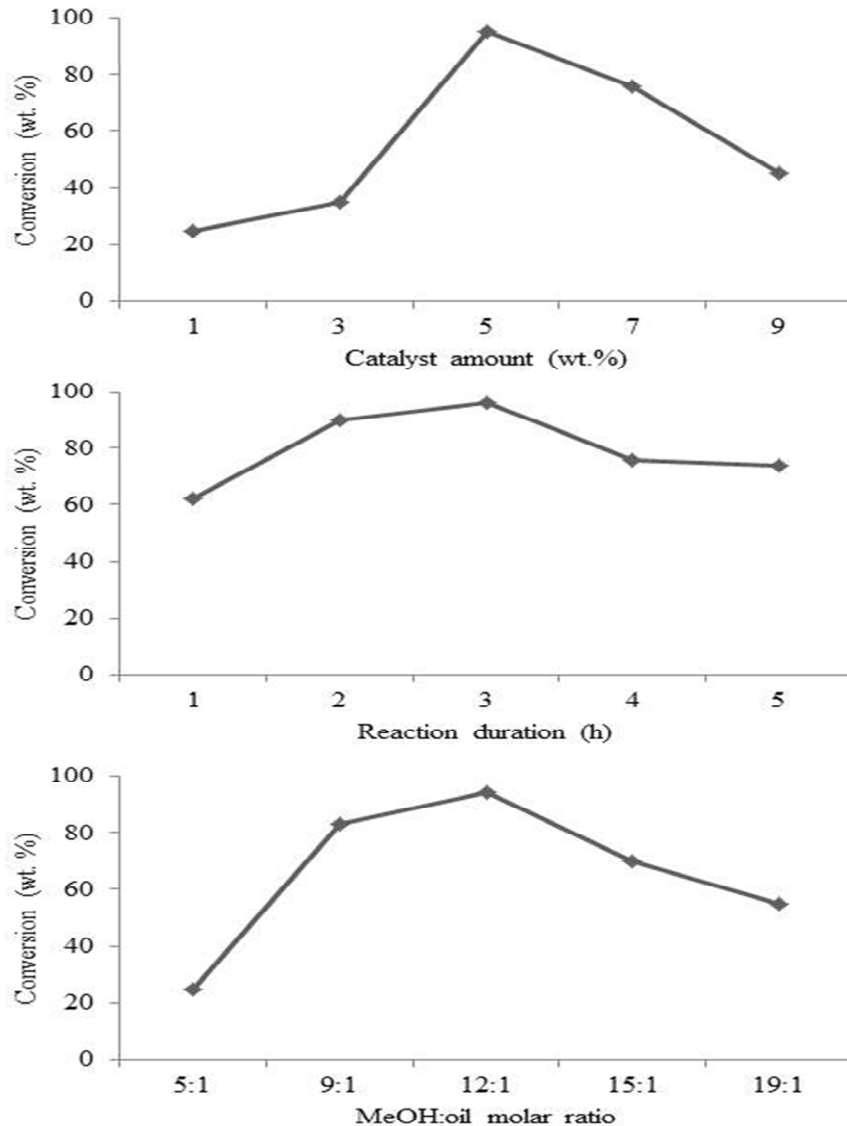


Figure 4. Effect of catalyst amount, reaction duration and MeOH to oil molar ratio on ME conversion for 10K-CFB

4. Conclusions

In this research study, a novel heterogeneous catalyst was successfully synthesized from waste calcined fish bone loaded with KOH. The catalyst was calcined at 900 °C which is known as the optimum calcination temperature for waste animal bones to form hydroxyapatite. The KOH was added to the CFB by using wet impregnation method. The results revealed that K-CFB has high specific surface area and higher biodiesel yield that could be obtained at moderate methanol to oil molar ratio and lower catalyst amount. Highest conversion of ME in this study was found to be 96.14 wt. %. The optimum conditions were determined which were catalyst amount of 5

wt. %, methanol to oil ratio of 12:1 and reaction time of 3 h. The 10K-CFB catalyst seems to be a promising solid base catalyst for the production of biodiesel or other fuels and chemicals.

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