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Characterization and Utilization of Calcium Oxide (CaO) Thermally Decomposed from Fish Bones as a Catalyst in the Production of Biodiesel from Waste Cooking Oil

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Abstract

Thermal decomposition of fish bones to obtain calcium oxide (CaO) was conducted at various temperatures of 400, 500, 800, 900, 1000, and 1100 °C. The calcium oxide was then characterized using X-ray diffractometer, FTIR spectrophotometer, and SEM analysis. The calcium oxide obtained from the decomposition at 1000 °C was then used as a catalyst in the production of biodiesel from waste cooking oil. Diffraction pattern of the calcium oxide produced from decomposition at 1000 °C showed a pattern similar to that of the calcium oxide produced by the Joint Committee on Powder Diffraction Standard (JCDPS). The diffractions of 2θ values at 1000 °C were 32.2, 37.3, 53.8, 64.1, and 67.3 deg. The FTIR spectrum of calcium oxide decomposed at 1000 °C has a specific vibration at wave-length 362 cm^{-1}, which is similar to the specific vibration of Ca-O. SEM analysis of the calcium oxide indicated that the calcium oxide's morphology shows a smaller size and a more homogeneous structure, compared to those of fish bones. The use of calcium oxide as a catalyst in the production of biodiesel from waste cooking oil resulted in iod number of 15.23 g/100 g KOH, density of 0.88 g/cm^3, viscosity of 6.00 cSt, and fatty acid value of 0.56 mg/KOH. These characteristic values meet the National Standard of Indonesia (SNI) for biodiesel.

Abstrak

Karakterisasi dan Pemanfaatan Kalsium Oksida (CaO) Hasil Dekomposisi Termal Tulang Ikan sebagai Katalis Produksi Biodiesel dari Minyak Jelantah. Telah dilakukan dekomposisi termal kalsium oksida dari tulang ikan dengan variasi temperatur 400, 500, 600, 700, 800, 900, 1000, dan 1100 °C. Kalsium oksida dikarakterisasi menggunakan difraktometer X-ray, spektrofotometer FTIR, dan analisis SEM. Kalsium oksida kemudian digunakan sebagai katalis untuk produksi biodiesel dari minyak jelantah. Pola difraksi kalsium oksida hasil dekomposisi pada temperatur dekomposisi 1000 °C menunjukkan kemiripan dengan kalsium oksida dari komite bersama standar difraksi padatan (JCPDS). Difraksi pada nilai 2θ hasil dekomposisi pada 1100 °C adalah sebesar 32,2; 37,3; 53,8; 64,1; dan 67,3. Spektra FTIR kalsium oksida hasil dekomposisi pada 1000 °C memiliki vibrasi spesifik pada bilangan gelombang 362 cm^{-1} yang mirip dengan vibrasi spesifik untuk Ca-O. Analisis SEM pada penelitian ini menunjukkan bahwa morfologi kalsium oksida itu mempunyai ukuran yang lebih kecil dan struktur yang lebih homogen daripada tulang ikan. Penggunaan kalsium oksida dalam produksi biodiesel dari minyak jelantah menghasilkan bilangan iod 15,23 g/100 g KOH, densitas 0,88 g/cm^3, viskositas 6,00 cSt, dan nilai asam lemak 0,56 mg/KOH. Nilai parameter biodiesel tersebut sesuai dengan standar nasional Indonesia (SNI) untuk biodiesel.

Keywords: biodiesel, calcium oxide, fish' bones, waste cooking oil

1. Introduction

Biodiesel is a mono-alkyl ester of fatty acid. Various renewable sources such as vegetable oil waste or cooking oil and animal fats can be converted into biodiesel [1]. The use of biodiesel for a transportation fuel has received a considerable attention in this decade because of its great potential as a substitute for fossil fuel. There are several principal reasons for selecting biodiesel as future transportation fuel: (1) it is non-toxic; (2) it contains no carbon dioxide; (3) it generates no sulfur emissions to the environment; and (4) it can be produced from a wide range of material resources available [2]. Biodiesel can be synthesized easily through the transesterification process with acid or base catalysts. Its production was mainly depending on the vegetable source [3]. Conventional acid-basecatalysts have been applied for the transesterification of vegetable oil in biodiesel production, such as hydrochloric acid, sulphuric acid, potassium hydroxide, sodium hydroxide, and calcium oxide [4]. Homogeneous conventional catalysts that are commonly used, especially the acid ones, are corrosive; therefore, the development of a heterogeneous catalyst for biodiesel production has captured a great attention. Heydarzadeh et al. (2010) mentioned γ-alumina-zirconia as an effective catalyst in the production of biodiesel from various fatty acids [5]. Macroporous-mesoporous materials can also be used for biodiesel synthesis [6]. Potassium oxide loaded with metal oxides and zeolites can also be used as a catalyst in the production of biodiesel from palm oil through the transesterification process [7]. Metal oxides such as calcium oxide, magnesium oxide, or strontium oxide are also effective as heterogeneous catalysts for biodiesel synthesis from vegetable oil [8].

Thus, the development of metal oxide-based catalysts for biodiesel production is an interesting topic of research. We have reported the feasibility of calcium oxide from *Achatinafulica* as a catalyst for the formation of biodiesel from waste cooking oil [9]. In this study, we aim to enlarge our study's scope by reporting the potential of using fish bones as the source of calcium oxide. Other additional benefits can be added, which include their abundance and cheap feedstock. Many studies have reported the mechanism of fish bones thermal decomposition [10-11]. The fish bones were decomposed into calcium oxide at various temperatures before being used as a catalyst in the production of biodiesel from waste cooking oil. Waste cooking oil is an attractive starting material that can increase the economical value of vegetable oil. Calcium oxide as a base catalyst can activate short chain alcohol such as methanol and ethanol to be active species. The active species can react with glycerin in vegetable or animal oils to form methylor ethyl esters (biodiesel) and glycerin as its byproduct. This reaction is well known as the transesterification reaction. Using calcium oxide as a catalyst in biodiesel synthesis is very beneficial because it is heterogeneous, non-toxic, and environmentally benign. Therefore, the objective of this study is to produce a catalyst from renewable resources such as fish bones which calcium carbonate ($CaCO_3$) rich materials that can be decomposed into calcium oxide (CaO).

2. Experiment

Chemicals such as ethanol, potassium hydroxide, oxalic acid, sodium sulfate, phosphoric acid, and methanol were purchased from Merck and used directly without any further purification. Fish bones were collected from traditional market at Plaju, Palembang, South Sumatera, Indonesia. Our fish bones were a mixture of snakehead murrel bone, climbing gouramy bone, Spanish mackerel bone, and tilapia bone. Samples were prepared by washing the bones directly with water several times, and drying them overnight in an oven at 40 °C. Dry fish bones were ground using a pestle and a mortar and the powder was sieved with a 100 mm sieve. Waste cooking oil was collected from several restaurants in Palembang, South Sumatera, Indonesia, was filtered, and was placed in plastic bottles prior to use.

Preparation of calcium oxide from fish bones. Calcium oxide from fish bones was prepared by following the procedures as reported in [12]. Dry fish bone powder (100 g) was placed into a silica cup, and then it was decomposed by using an electric furnace for 3 h at several temperatures (400, 500, 800, 900, 1000, and 1100 °C). The combusted bone was cooled at room temperature and stored in desiccators over silica gels. The combusted bone was then characterized by using XRD powder, followed by identification by using FTIR spectroscopy and SEM-EDX. The XRD powder pattern for combusted fish bones at various temperatures were compared to the XRD powder pattern of calcium oxide produced by the Joint Committee on Powder Diffraction Standards (JCPDS).

Calcium oxide characterization was carried out by using FTIR spectrophotometer Shimadzu 8201PC, X-Ray powder diffraction Shimadzu Lab X Type 6000, and SEM-EDX Jeol JED-2300. The FTIR spectrum was recorded at wave number 200-4000 cm^{-1} by using KBr disk. The XRD powder data were collected over 2θ range of 0-90 deg at a scanning speed of 1 deg. min^{-1}.

Production of biodiesel from waste cooking oil using decomposed fish bones as catalyst. Our biodiesel production protocol was adopted from Viriya-empikul et al. with a slight modification [13]. Our biodiesel production was performed in a batch reactor system (Figure 1). 100 mL waste cooking oil was poured into a1L round bottom flask; then, 40 mL methanol and 2.5 g

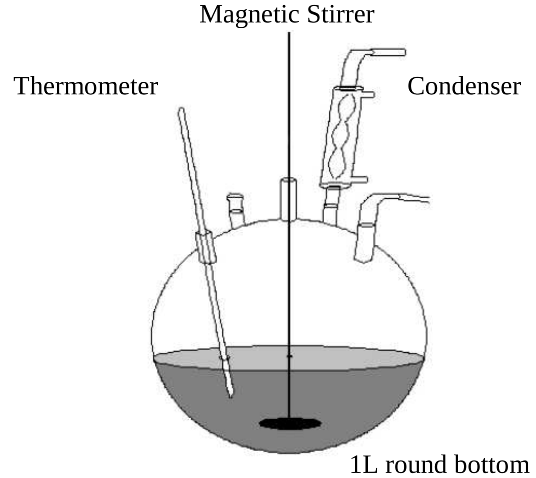


Figure 1. Batch Reactor Equipment for Biodiesel Production

of combusted fish bones were added, mixed, and heated at 70 °C for 3 h. Reaction was stopped by quenching the mixture with 10 mL cold water. 1 mL phosphoric acid was added into the prepared mixture for neutralization. The mixture was then stored overnight. This crude product of biodiesel was then collected after being separated from the catalyst and glycerol. Pure biodiesel was obtained after the distillation of the crude biodiesel. The resulting biodiesel was characterized by determining its viscosity (ASTM D-445), density (ASTM D-1298), fatty acid value (ASTM D-974), and iod number (AOCS Cd 1-25).

3. Results and Discussion

The XRD patterns of thermally decomposed of fish bones are shown in Figure 2. XRD patterns in Figure 2 are compared to the calcium oxide produced by the JCPDS. Diffraction 2θ from JCPDS for calcium oxide being used is at 32.2, 37.3, 53.8, 64.1, and 67.3 deg. Therefore, we emphasized the patterns in Figure 2 with these values. The XRD pattern of the fish bones shows a wide peak at 30-35 deg. This pattern indicates the presence of calcium in the fish bones. Decomposition of fish bones was conducted at various temperatures ranging from 400 to 500 and from 800 to 1100 °C. The XRD pattern of those fish bones decomposed at temperatures 400 and 500 °C is similar to that of our original fish bones, so we started the decomposition from 800 °C. The decomposition at 800 °C shows a XRD pattern with a high peak, which indicates a high degree of crystallinity, and there is a similarity between the XRD pattern found in the fish bones decomposed at 800 °C and those at 900-1100 °C. Thus, we focused on selecting the same calcium oxides pattern with JCPDS data at temperature 900-1100 °C [14].

The characteristic pattern of decomposition at 900 °C shows the presence of calcium oxide at 32.3 and 64.1 deg, while the same process at 1000 °C results in 32.3, 53.8, and 64.1 deg. A more detailed study shows decomposition evidence at 1100 °C, and this result has a pattern similar to that produced by decomposition at 900 °C. Thus, it can be concluded that the decomposition at 1000 °C shows the nearest pattern to that shown by JCPDS's calcium oxide. Temperatures chosen for decomposing fish bones in our research are quite similar to those used in several other experiments by other researchers who decomposed a variety of shells, as shown in Table 1.

Table 1 shows various renewable sources for the preparation of a catalyst in biodiesel synthesis from vegetable and animal oils. The temperature selected for the decomposition to obtain calcium oxide is above 700 °C. This can be prepared by burning those shells in a furnace at 2-4 h.

These results can be used as basic references for the preparation of calcium oxide from various animal shells, which include the fish bones we use in this research. We found that the appropriate temperature for the decomposition of our fish bones is 1000 °C, and this result is comparable to those obtained from the decomposition of other animal shells, as shown in our comparison data (Table 1).

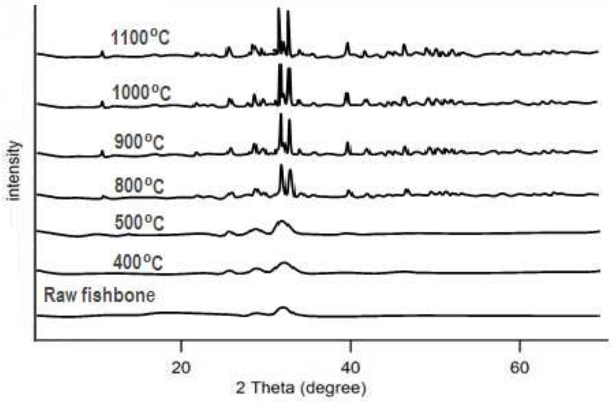


Figure 2. XRD Pattern of Fish' Bones with various Decomposition Temperatures

Table 1. Decomposition of Several Shells to Obtain Calcium Oxide as a Catalyst in Biodiesel Production

Sample	Decomposition temperature (^{o}C)	Time of decomposition (h)
Mollusk (*Pilaglobosa*)	900	2.5
Freshwater mussel shell	900	4
Waste fish (*Labeorohita*)	900	2
Various shells: egg shell, golden apple snail, meretrix venus	800	2-4
Oyster shell	1000	3
Crab shell (*Scylla serrata*)	above 700	2
Waste egg shell	1000	2
Snail shell (*Achatina fulica*)	700	3
Fish bone	1000	3

Further characterization of our results was carried out through FTIR spectrophotometer and SEM analysis. The FTIR spectra of calcium oxide and our fish bones are presented in Figure 3, while the SEM photo analysis is shown in Figure 4.

The FTIR spectrum of ground fish bones shows a broad peak at wave number 1041 cm^{-1}. This peak is related to calcium carbonate. The decomposition of fish bones at 1000 °C resulted in two sharp peaks at wave numbers 1620 cm^{-1} and 1420 cm^{-1}. The peak intensity of ground fish bones at wave number 570 cm^{-1} decreases and eventually shows only a single peak at 871 cm^{-1}. A peak at wave number 871 cm^{-1} is a unique vibration for calcium oxide, which was assigned as a vibration of Ca-O [20]. The calcium oxide obtained from the decomposition of fish bones at 1000 °C was also characterized by using SEM to identify the morphology of the resulting bulky powder, as shown in Figure 4.

The morphologies of fish bones and fish bones decomposed at 1000 °C showed differences in size and structure. The structure of fish bones showed a granular solid with unsymmetrical form. Decomposition at 1000 °C changed the fish bones' structure, making it smaller in size and more uniform in shape. Therefore, fish bones decomposed at 1000 °C could be used in the production of biodiesel from waste cooking oil.

Biodiesel was characterized by determining its density, viscosity, iod number, and fatty acid value by using a standard method. The results of the analysis of our biodiesel are shown in Table 2. We have chosen four parameters for our biodiesel analysis from the original eighteen SNI parameters because of their simplicity, but without minimizing their confidence for testing biodiesel products to meet the SNI standard. Moreover, all of the other fourteen parameters are more suited to industrial scale productions and must be performed in a different scale of laboratory setting.

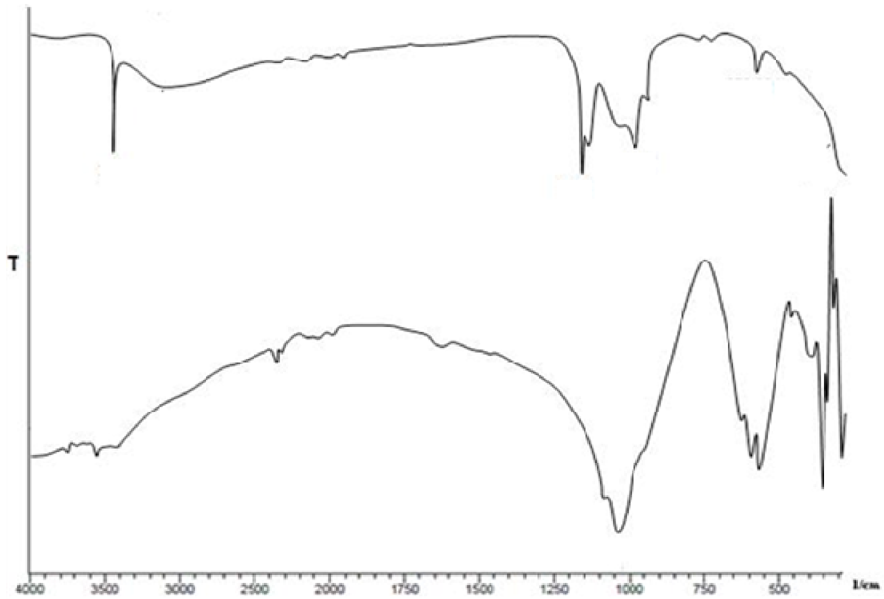
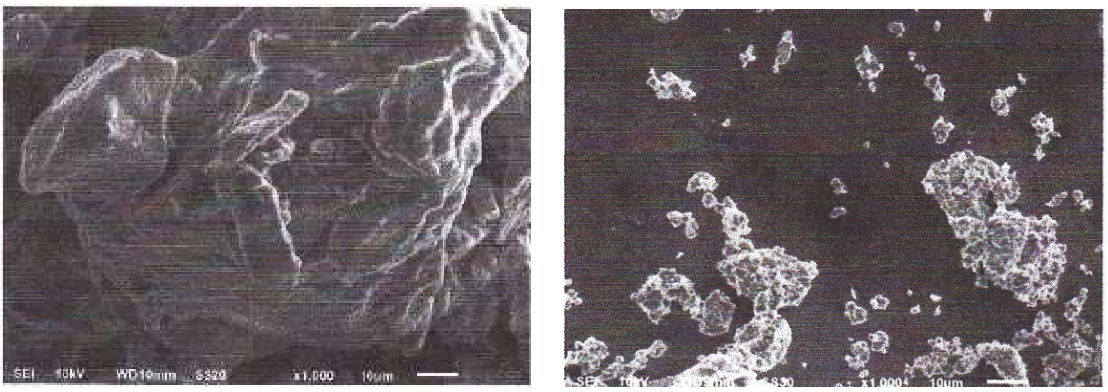


Figure 3. FTIR Spectra of Fish Bones decomposed at 1000 °C (above) and of Ground Fish Bones (below)



(A) **(B)**

Figure 4. SEM Analysis for Fish Bones (A) and Calcium Oxide (B)

Table 2. Analysis of Biodiesel

Parameter	Result	Method	SNI standard [21]
Iod Number	15.23 g/100 g KOH	AOCS Cd 1-25	Max. 115 g/100 g KOH
Density	0.88 g/cm^3	ASTM D-1298	0.85-0.89 g/cm^3
Viscosity	6.00 cSt	ASTM D-445	2.3-6.0 mm^2/s (cSt)
Fatty acid value	0.56 mg/KOH	ASTM D-974	Max. 0.8 mg/KOH

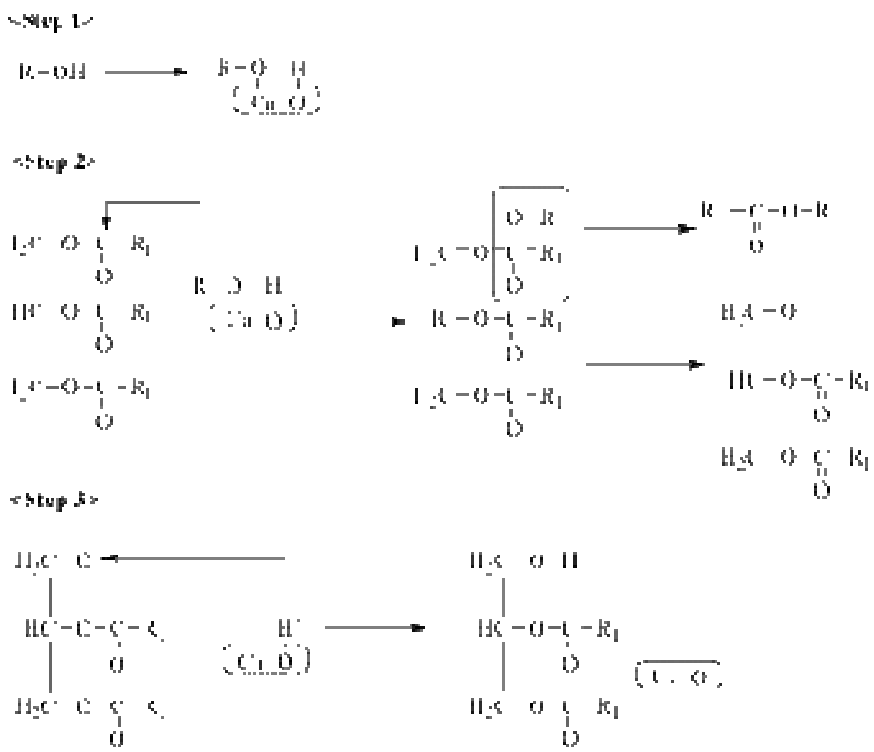


Figure 5. Plausible Biodiesel Synthesis using Calcium Oxide in a Heterogeneous System

Based on the analysis results in Table 2, all biodiesel parameters in this study fulfill the SNI standard. Therefore, it can be concluded that the calcium oxide obtained from the decomposition of our fish bone mixture at 1000 °C can be used as a potential and more economical catalyst in biodiesel production (SNI 04-7182-2006). A plausible mechanism for biodiesel synthesis using calcium oxide extracted from fish bones is presented in more detail in Figure 5.

4. Conclusion

The XRD pattern of fish bones decomposed at 1000 °C is similar to that of the calcium oxide produced by the JCPDS. In addition to that, the characterization of fish bones decomposed at 1000 °C as a catalyst in the production of biodiesel from waste cooking oil shows viscosity of 6.00 cSt, density of 0.88 g/cm^3, acid value of 0.56 mg/KOH, and iod number of 15.23 g/cm^3. All of these characterization data meet the Indonesia National Standard (SNI) for biodiesel.

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