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PREPARATION OF CALCIUM OXIDE FROM *Achatina fulica* AS CATALYST FOR PRODUCTION OF BIODIESEL FROM WASTE COOKING OIL

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ABSTRACT

Preparation of calcium oxide from Achatina fulica shell has been carried out systematically by decomposition for 3 h at various temperatures i.e. 600, 700, 800 and 900 °C. Formation of calcium oxide was characterized using XR diffractometer. The calcium oxide obtained with the optimum temperature decomposition was characterized using FTIR spectroscopy to indicate the functional group in the calcium oxide. The results showed that XRD pattern of materials obtained from decomposition of Achatina fulica shell at 700 °C is similar with XRD pattern of calcium oxide standard from Joint Committee on Powder Diffraction Standards (JCPDS). The IR spectra of calcium oxide appear at wavenumber 362 cm^{-1} which is characteristic of CaO vibration. Application of calcium oxide from Achatina fulica shell for synthesis of biodiesel from waste cooking oil results in biodiesel with density are in the range of ASTM standard.

Keywords: *calcium oxide; Achatina fulica shell; biodiesel; waste cooking oil*

ABSTRAK

Telah dipreparasi kalsium oksida dari Achatina fulica secara sistematis melalui dekomposisi selama 3 jam pada temperatur 600, 700, 800, dan 900 °C. Pembentukan kalsium oksida dikarakterisasi menggunakan alat XRD. Kalsium oksida yang diperoleh dari dekomposisi pada temperatur optimum dikarakterisasi lanjut menggunakan spektroskopi FTIR untuk mengidentifikasi gugus fungsional pada kalsium oksida. Hasil penelitian menunjukkan bahwa pola XRD dari cangkang Achatina fulica yang didekomposisi pada 700 °C mirip dengan pola XRD kasium oksida standar dari Joint Committee on Powder Diffraction Standards (JCPDS). Kalsium oksida yang diperoleh dari dekomposisi pada 700 °C memiliki spektra IR yang muncul pada bilangan gelombang 362 cm^{-1} yaitu vibrasi khas dari CaO. Penggunaan kalsium oksida hasil preparasi untuk sintesis biodiesel dari minyak jelantah menghasilkan biodiesel dengan densitas dan viskositas yang sesuai dengan standar ASTM.

Kata Kunci: *kalsium oksida; cangkang Achatina fulica; biodiesel; minyak jelantah*

INTRODUCTION

Biodiesel is renewable fuel, which can be synthesized from various plant oils (edible and non edible) including waste cooking oils and animal fat oils [1-2]. The advantages of biodiesel for transportation fuel due to green emissions, non-toxic, displacement of petroleum fuel, high flash point and good lubricity. Synthesis of biodiesel through transesterification of oils with alcohol using catalyst produces fatty acid alkyl esters or biodiesel with glycerol as a byproduct [3]. Fatty acid alkyl esters and glycerol are easily separated using physical or chemical process. Alcohols with low carbon chain such methanol and ethanol is commonly used for transesterification [4].

Homogeneous and heterogeneous catalysts can be used for synthesis of biodiesel from various oils [5]. Homogeneous catalysts such as NaOH and KOH are usually used for transesterification. However, heterogeneous catalysts have been explored recently because separation of product and catalyst is easy and reusability [6]. The wide ranges of heterogeneous catalysts are available such as CaO, MgO [7], macroporous-mesoporous SBA-15 [8], heteropolyacid [9-10], and KOH loaded on Al_2O_3 and NaY zeolite [11]. Among the heterogeneous catalysts that are being used in transesterification, CaO is a suitable and excellent catalyst for biodiesel production. Calcium oxide is commercially available with high price. The research to obtain CaO with low cost from renewable feedstock is intriguing topic until this time. The potential candidate for this aim is shell from several mollusk and eggshell [12]

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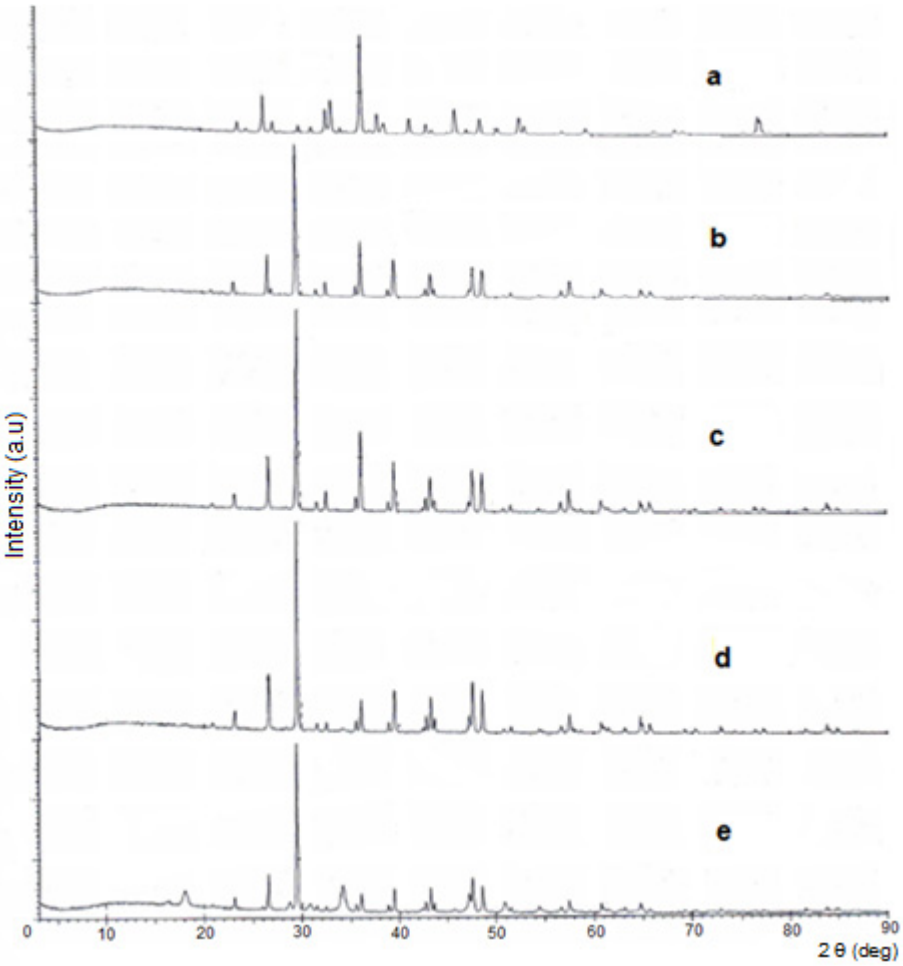

Fig 1. The XRD pattern of decomposition *Achatina fulica* at various temperatures: (a) *Achatina fulica* shell, (b) 600 °C, (c) 700 °C, (d) 800 °C, (d) 900 °C

Yang et al. [13] used shrimp shell enriched by potassium fluoride for biodiesel production with high catalytic activity. Shrimp shell was carbonized and potassium fluoride was added by impregnation method. The shrimp shell catalyst was characterized using XRD, elemental analysis, EDS and FTIR. Wei et al. [14] reported that waste eggshell could be used heterogeneously for transesterification and reused catalyst. The main chemical composition of shrimp shell and eggshell is $CaCO_3$ with base properties. By decomposition of shells in various temperatures can produce CaO, which has high catalytic activity for transesterification.

Achatina fulica (Indonesian; *bekicot)* is also containing $CaCO_3$ in the shell with high yield (88-99%) [15]. In Indonesia, the habitat of *Achatina fulica* usually is in banana tree and it is consumed with special name "crispy fried bekicot". The *Achatina fulica* shell is organic waste that can be applied as renewable CaO catalyst for biodiesel production. In the present work, the *Achatina fulica* shell has been used as raw material of heterogeneous catalyst for transesterification of waste cooking oil for biodiesel production. Waste cooking oil is used as cheaper feedstock, which can reduce the production cost for biodiesel production.

EXPERIMENTAL SECTION

Materials

All chemicals with analytical grade were purchased and used without further purification from Merck such as ethanol, potassium hydroxide, oxalic acid, sodium sulfate, phosphoric acid, and methanol. *Achatina fulica* shell was obtained from several locations in Palembang, South Sumatera. *Achatina fulica* shell was washed with water, dried in oven and grounded using a pestle and mortar to be powder whereas pass through 100 mm sieve. Meanwhile, the waste cooking oil was collected from local restaurant in Palembang, South Sumatera and used directly for biodiesel production without further special treatment.

Table 1. XRD data of CaO, $Ca(OH)_2$ and $CaCO_3$

Sample	Decomposition temperature	Compound	2θ				
JCPDS data	-	CaO	32.2°	37.3°	58.3°	64.1°	67.3°
		$CaCO_3$	29.4°	39.4°	43.2°	47.4°	48.5°
		$Ca(OH)_2$	28.6°	34.1°	47.1°	50.8°	-
Achatina fulica shell	900 °C	CaO	-	-	-	64.7°	-
		$CaCO_3$	29.4°	39.4°	43.2°	47.5°	-
		$Ca(OH)_2$	28.6°	34.1°	47.1°	50.8°	48.5°
	800 °C	CaO	32.4°	-	-	64.7°	-
		$CaCO_3$	29.4°	39.5°	43.2°	47.5°	-
		$Ca(OH)_2$	-	-	47.2°	-	48.5°
	700 °C	CaO	32.6°	-	-	64.8°	-
		$CaCO_3$	29.6°	39.6°	43.3°	47.7°	-
		$Ca(OH)_2$	-	-	47.3°	-	48.7°
	600 °C	CaO	32.4°	-	-	64.7°	-
		$CaCO_3$	29.4°	39.4°	43.2°	47.5°	-
		$Ca(OH)_2$	-	-	47.1°	-	48.5°
	Shell before decomposition	CaO	32.6°	37.9°	-	-	-
		$CaCO_3$	29.8°	-	43.5°	-	-
		$Ca(OH)_2$	-	34.1°	47.1°	50.2°	48.8°

Instrumentation

The X-ray powder diffraction (XRD) pattern was collected from Shimadzu Lab. X type 6000. The data were collected over 2θ range of 0-90° at a scanning speed of 1° min^{-1}. The FTIR spectra were recorded using Shimadzu 8201PC.

Procedure

Decomposition of Achatina fulica shell to form calcium oxide

The decomposition procedure for *Achatina fulica* was adopted from Nakatani et al. [16] as described as follow. 100 g of dry shell was decomposed with in electric furnace in air at given temperature (600, 700, 800, and 900 °C) for 3 h and then the combusted shell was stored in desiccators over silica gel for overnight. The white solid bulk was analyzed using XRD diffractometer. The XRD pattern of combusted shell was compared with XRD pattern of calcium oxide from Joint Committee on Powder Diffraction Standards (JCPDS). The similarity XRD combusted shell with JCPDS pattern will be used as catalyst for transesterification of waste cooking oil.

Transesterification of waste cooking oil using calcium oxide as catalyst

Transesterification was carried out using 100 mL Schlenk flask, installed with thermometer, magnetic stirring, and condenser. The system was heated to 70 °C and then, 100 mL of waste cooking oil, 40 mL of methanol, and 4% (wt) catalyst were added carefully. Reaction was conducted for 3 h and stopped by quenching using 10 mL cold water. Reaction was stored overnight and 1 mL of phosphoric acid was added for neutralization. Biodiesel was obtained after separation form catalyst and glycerol. Characterization of biodiesel was performed through the determination of density (ASTM D-1298) and viscosity (ASTM D-445) after distillations of the biodiesel.

RESULT AND DISCUSSION

Decomposition and Characterization of *Achatina fulica* Shell

The decomposition products of *Achatina fulica* shell at variation temperature were identified using XRD powder as shown in Fig. 1.

The data from Fig. 1 are compared to XRD pattern of shell before decomposition at XRD pattern of CaO from Joint Committee on Powder Diffraction Standards (JCPDS) file. The XRD powder pattern show that decomposition of *Achatina fulica* shell at 600-900 °C resulted the sharp spectra which the high crystallinity of the shell after decomposition at high temperature. According to Table 1, the peaks that are specific pattern of CaO were observed at 2θ 32.2°, 37.3°, 58.3°, 64.1° and 67.3°. Several peaks of $CaCO_3$ were appearing at 600 °C of temperature decomposition, which indicated that the decomposition of *Achatina fulica* shell was uncompleted and require higher temperature to convert all $CaCO_3$ in the shell sample into CaO form. However, peaks of $Ca(OH)_2$ were appeared at decomposition 900 °C due to interaction between CaO with water vapor in the air after sample decomposition. This phenomenon was also reported by Serris, et al. [17] the numerous of open pores exist inside the aggregates of CaO sample, the conversion of CaO into $Ca(OH)_2$ reaction takes place in each particle and the water vapor was easily

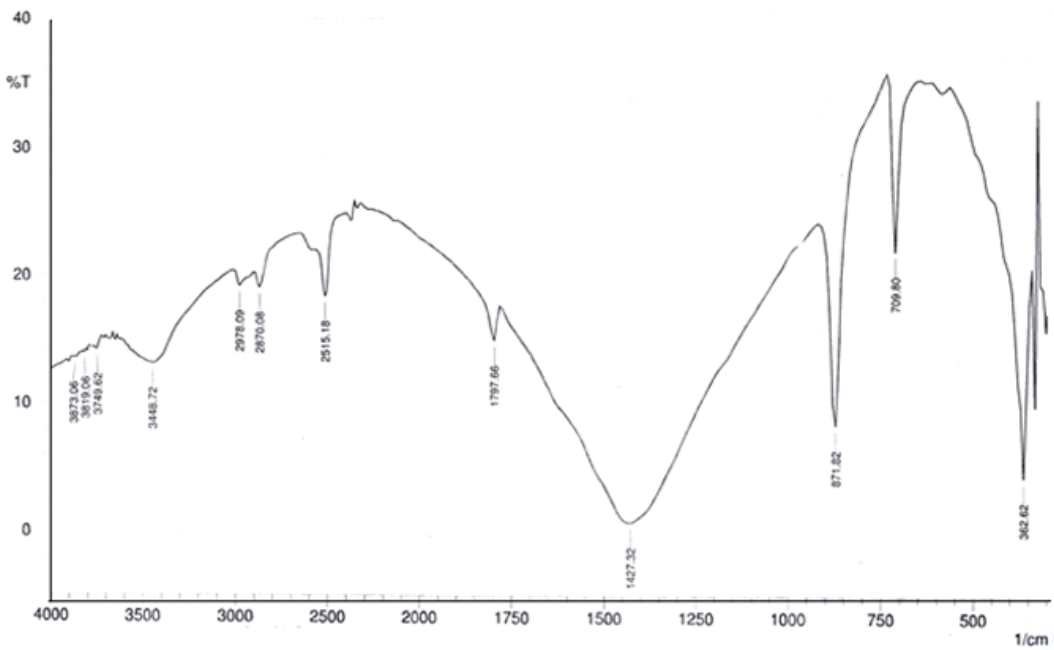

Fig 2. FTIR spectra of decomposition *Achatina fulica* at 700 °C

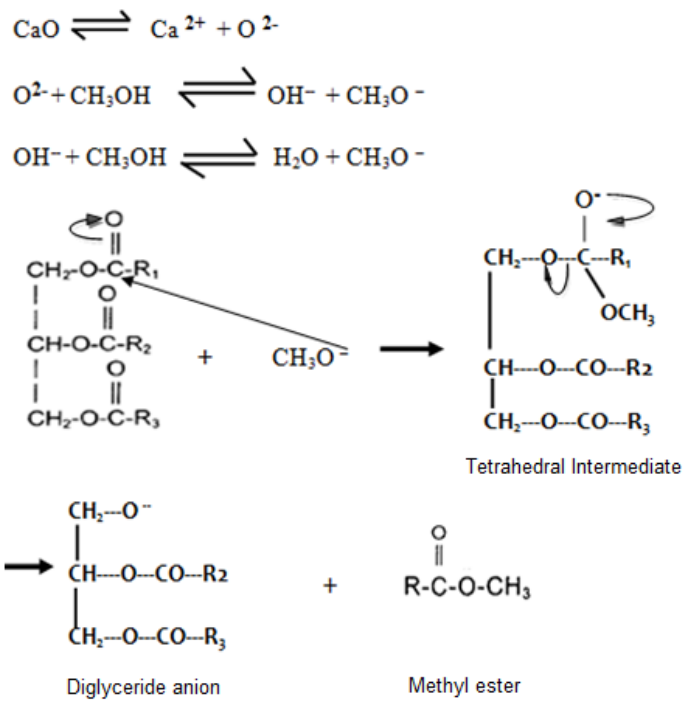

Fig 3. Reaction mechanism of catalyst to form biodiesel from waste cooking oil

circulate inside the porosity, which is in favor of a total conversion of CaO into $Ca(OH)_2$. The main peaks of CaO were observed at 700 °C and quite similar with data from JCPDS file. Although temperature decomposition at 800 °C is also similar with JCPDS but minor peaks of $Ca(OH)_2$ is appeared. The sample of *Achatina fulica* which was decomposed at 700 °C was investigated using FTIR spectroscopy. Boey et al. [18] also reported that CaO catalyst from *Scylla serrata* shell was produced by activated it at 700 °C for 2 h and applied successfully to produce biodiesel which attainment in accordance with our work.

The FTIR spectra of decomposed sample were obtained using KBr method at room temperature and the spectra were recorded at 400-4000 cm^{-1} as shown in Fig. 2. The absorption bands of decomposed sample from *Achatina fulica* shell occurred at 1427, 871, 709, and 362 cm^{-1} which can be attributed to the vibration of $CO3^{2-}$ molecules. Similar peaks also observed by Agrawal et al. [19] using *Pila globosa* as catalyst. Vibration at 1427 cm^{-1} occurred due to asymmetric stretch, while vibration at 871, 709, and 362 cm^{-1} showed out-of plane bent and in plane bent for CO_3^{2-} molecules. Furthermore, the *Achatina fulica* shell from decomposition at 700 °C is used for biodiesel production from waste cooking oil.

Biodiesel Production Using Decomposed *Achatina fulica* Shell and Waste Cooking Oil

In this work, waste cooking oil was mixed with methanol and catalyzed by decomposed *Achatina fulica* shell at 700 °C. After complete the reaction, the mixture was separated into 3 parts in the separation funnel. Catalyst with heterogeneous system was appeared in the bottom of funnel while biodiesel in the top of funnel. Thus glycerol as by product formed in the middle of the funnel. The ability of decomposed

catalyst for biodiesel production is great factor to obtain biodiesel with properties in the range of ASTM, thus the effect of waste cooking oil/methanol, temperature reaction, catalyst weight, reaction time and reusability catalyst did not studied in this research. Mechanism reaction of catalyst in the reaction to form biodiesel is shown in Fig. 3. Catalyst formed Ca^{2+} and O^{2-} in the reaction mixture before react with methanol. This process is called disassociation of CaO. After reaction with methanol, the species that called "methoxide anion" react with oil to form tetrahedral intermediate. The rearrangement of tetrahedral intermediate was formed diglyceride anion and methyl ester (biodiesel) [18]. The characterization of biodiesel in this research was carried out systematically i.e. density and viscosity after distillation of product due to quality of biodiesel, which indicated from purity of compound.

Density and viscosity of biodiesel was performed based on ASTM D-1298 and ASTM D-445, respectively. The data was carried out three times with high reproducibility data. Density is one of vital parameter in the characterization of biodiesel. According to ASTM D-1298 and ASTM D-1298, biodiesel standard has density in the range of 0.82-0.90 g/cm^3 and viscosity in the range of 2.0-5.0 cst. The results of characterization of biodiesel from waste cooking oil catalyzed by decomposed *Achatina fulica* shell gave density 0.90 g/cm^3 and viscosity 4.52 cst. These values are appropriate with the biodiesel standard from ASTM, thus it can be a potential candidate for renewable energy in the future.

CONCLUSION

The decomposition of *Achatina fulica* shell to form calcium oxide was successful carried out at 700 °C. Analysis using XRD diffractometer and FT-IR spectroscopy were indicated the existence of calcium oxide after decomposition of *Achatina fulica* shell. The Application of calcium oxide for synthesis biodiesel from waste cooking oil produces biodiesel which viscosity 4.52 cst and density 0.997 g/cm^3 that are in the range of ASTM standard.

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