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By Risfidian Mohadi

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Calcium Oxide Catalyst Based on Quail Eggshell for Biodiesel Synthesis from Waste Palm Oil

Risfidian Mohadi,[1] Abi Sueb,[1] Kiki Anggraini,[1] and Aldes Lesbani,[2]*

[1] Department of Chemistry, Faculty of Mathematics and Natural Sciences, Sriwijaya University, Jl. Raya Palembang Prabumulih Km 32 Ogan Ilir 30662, South Sumatra, Indonesia
[2] Integrated Research Laboratory, Graduate School, Sriwijaya University, Jl. Padang Selasa Bukit Besar Palembang 30139, South Sumatra, Indonesia

*Corresponding email: aldeslesbani@yahoo.com

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ABSTRACT

Calcium oxide decomposed from quail eggshell was used as catalyst for biodiesel synthesis from waste palm oil. Prior to being used, the quail eggshell was decomposed at 600-1100°C to form calcium oxide and it was characterized by X-Ray measurement, FTIR, and SEM spectroscopy to analyze the functional groups and the surface morphology, followed by N_2 adsorption-desorption methods to determine the surface area. The results of X-Ray analysis powder pattern show that the decomposition of quail eggshell at 900°C gave calcium oxide that has similar characteristic to the standard CaO from Joint Committee of Powder Diffraction Standard (JCPDS). The FTIR spectrum indicated vibrations of calcium oxide from quail eggshell have a similar pattern with the calcium oxide of the standard. The SEM analysis showed that morphology of quail eggshell was changed after decomposition at 900°C and it has the mesoporous structure. The biodiesel from waste palm oil was synthesized using CaO catalyst from quail eggshell decomposed at 900°C. The biodiesel product has the density of 0.86 g/cm^3, the viscosity of 5.50 mm^2/s, the free fatty acid of 0.56 mg/KOH, and iodine number of 60.49 g I_2/100g, respectively. All those biodiesel characteristics meet the biodiesel standard by the Indonesian National Standard (SNI).

Key word: calcium oxide, waste palm oil, quail eggshell, biodiesel

INTRODUCTION

Biodiesel is an alternative renewable energy sources, known as mono-alkyl esters of long chain fatty acids, which synthesized through transesterification process from the variety of vegetable oils or animal fats using base or acid catalysts. The advantages of biodiesel as an energy source are due to its renewable, biodegradable, and low carbon dioxide or sulfur emissions to the environment. Thus, research of biodiesel has gained great attention in recent years [1]. In term of the sources, waste palm oils are non-gradable as the raw material than the fresh oils and fats due to economic reason. Currently, cooking oil from palm oils as tropical region plant is widely used in Indonesia. The production of it is not only in plant factory scale but also in home-based traditional process hence resulting in various qualities of palm oils that normally indicated by the color of the product. Fresh palm oil is a clear yellowish liquid and becomes darker after several used. Waste palm oils, which can be used as raw material for biodiesel production, are easily found as domestic and restaurant waste in Indonesia.

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The trans-esterification reaction using base catalyst has been commonly used for biodiesel production under homogeneous or heterogeneous systems [2]. Base catalyst such as potassium hydroxide, sodium hydroxide, carbonate, and correspond to sodium and potassium alkoxides have widely reported as common catalysts for trans-esterification of vegetable oils under homogeneous system [3]. Trans-esterification under homogeneous system using base catalysts provides high yield and conversion of oils to biodiesel but these catalysts have separation problems. To solve these problems, heterogeneous base catalysts have been developed due to the separation of catalyst from the reaction mixtures [4]. Heterogeneous solid base catalysts are also being considered as green catalysts due to it has less impact on the environment during the catalytic process. Among the heterogeneous catalysts, calcium oxide (CaO) has been extensively used as base catalyst for biodiesel production [5,6]. Calcium oxide is industrially produced from limestone. However some other sources are under development and exploration. Example of current calcium oxide research and development are conducted from various shells of molluscas and fowl eggshell, which are known containing calcium carbonate [7-10]. Calcium carbonate can be converted into calcium oxide at an appropriate decomposition temperature [11,12]. Fowl eggshells such as quail eggshell are often found in Indonesia since in 2015 about 20.71 thousand tons of quail egg was produced in a year[13]. These shells contain calcium carbonate that potentially used as base catalyst for biodiesel production. Chemical composition of the eggshell as well as quail eggshell are protein fibers, 96% calcium carbonate ($CaCO_3$), 1.4% magnesium carbonate ($MgCO_3$), 0.76% calcium phosphate ($Ca_3(PO_4)_2$), 4% organic matter and trace amounts of sodium, potassium, zinc, manganese, iron, copper and water [14,15].

The uses of CaO catalysts utilization from chicken eggshell or snail shell for the synthesis of biodiesel is an interesting topic, other than using the commercially CaO because of it available at high prices. The CaO from renewable raw materials is low cost and a great number of benefits of heterogeneous catalysts compared to using base catalyst, i.e. NaOH or KOH which is likely to have a saponification reaction [16]. The utilization of CaO as heterogeneous base catalyst for biodiesel production would be a solution for most of theenvironmental problem. Eggs, snail, and crab can be produced in numerous countries in the world as an important nutrient source, represent a significant amount of waste, the utilization of eggshells, snail shells and crab shells waste to substitute the natural sources of calcium ($CaCO_3$, CaO, $Ca(OH)_2$), worthwhile to reduce the waste problem, to conserve natural resources from rock, and to develop novelty of green ceramic materials since biodiesel is considered as one of the most alternative fuel for diesel engines and it is nontoxic, renewable and biodegradable[17].

Chouhan and Sarma [18] reported that CaO derived from eggshell waste is an effective catalyst for soybean oil transesterification, resulting in 97-98% biodiesel results in 65 °C with methanol/oil molar ratio 9:1. Viriya-Empicul et al. [19] using eggshells with palm oil, biodiesel yield 95% achieved with 2 hours on the ratio of methanol to oil 12:1. Nakatani et al. [20] and Rezaei et al. [21] are used oyster/clam shells for transesterification of soybean oil and obtained biodiesel yield of 73.8% using 25% by weight of the catalyst for a reaction time 5 h. Synthesis and characterization of biodiesel using heterogeneous catalysts of clamshells and eggshells have been studied and reported by many researchers. This article explains the thermal decomposition of quail eggshell to produce calcium oxide and its used as base catalyst for biodiesel production from waste palm oil.

EXPERIMENT

Chemicals and instrumentation

Chemicals were reagent grade and used without further purification prior to being used from Merck *i.e.* ethanol, potassium hydroxide, oxalic acid, sodium sulfate, phosphoric acid, and methanol. The X-Ray powder diffraction was conducted on Shimadzu Lab X type 6000 diffractometer with Cu Kα radiation (λ = 1.54060 Å) at 40 kV and 40 mA. Sample was scanning at 1^o/min at 2θ of 0-80 deg. The Fourier Transforms Infrared (FTIR) spectrum was recorded using Shimadzu FTIR Prestige-21 using KBr disk at wavenumber 4000-250 cm^{-1}. The scanning electron microscopy (SEM) was performed using JEOL JED-2300 analysis station at an accelerated voltage of 10 kV. The nitrogen sorption-desorption analysis was performed using Quantachrome Autosorb iQ-MP instrument.

Procedure reaction

Preparation of Catalyst

Quail eggshell was obtained from the local market at 16 Ilir, Palembang, South Sumatra, Indonesia. Quail eggshell was washed and dried, then grounded by pestle and mortar until passed through 100 mm sieve. Decomposition of quail eggshell was performed in Thermoscientific Thermolyne Furnace at atmospheric condition. Quail eggshell (50 g) was placed into porcelain and sample was decomposed in a furnace at the temperature ranging from 600-1100^o C for 3 h under atmospheric condition. The decomposed quail eggshell powder was identified and characterized by X-Ray diffractometer, FTIR spectrophotometer, SEM analysis, and N_2 sorption-desorption analysis.

Biodiesel Synthesis from Waste Palm Oil

The synthesis of biodiesel from waste palm oil was carried out in a 250 mL of Schlenk flask which was equipped with the magnetic bar. 100 mL of waste palm oil was placed into a Schlenk flask, and then 40 mL of methanol was added, followed by adding 2 g of CaO catalyst from quail eggshell. The mixtures were stirred and heated at 65^{o}C for 3 hrs. The reaction was stopped through quenching using cold water. The reaction product was left overnight followed by separation to separate the top (methyl ester) and bottom (glycerol) layers of the biodiesel samples. The top layer was mainly composed of free fatty acid methyl esters. The bottom layer was mostly made up of glycerol, salts, soap, other impurities and excess methanol. The top methyl ester layer was separated and removed from every impurity. The water washing process was used and an addition of 1 mL of H_3PO_4 for neutralization process. The resulting biodiesel was added 1 g of anhydrous Na_2SO_4 to absorb the water content and then oven to about 105°C for 30 minutes.

The result of the transesterification reaction was distilled using distillation devices. The product heating was carried out by heating-mantle at a temperature of about 200 °C to separate the biodiesel fraction by evaporating. The obtained biodiesel was characterized to determine its density (ASTM D-1298-99), viscosity (ASTM D-445), free fatty acid (ASTM D-974-08), and iodine number (AOCS Cd 1-25).

RESULT AND DISCUSSION

Preparation of CaO Catalyst from Quail Eggshell

Quail eggshell was decomposed at 600-1100^{o}C using furnace under atmospheric condition. The XRD powder patterns of decomposed quail eggshell at various temperatures and the fresh quail eggshell compared to XRD powder standard pattern of calcium oxide and calcium carbonate from JCPDS files. Quail eggshell contains calcium carbonate 63 to 69 %

[22], thus partial decomposition of quail eggshell still contains some calcium carbonate residue in the bulk material. All diffraction standard data of calcium oxide and calcium carbonate were used for determination of the optimum decomposition temperature for quail eggshell.

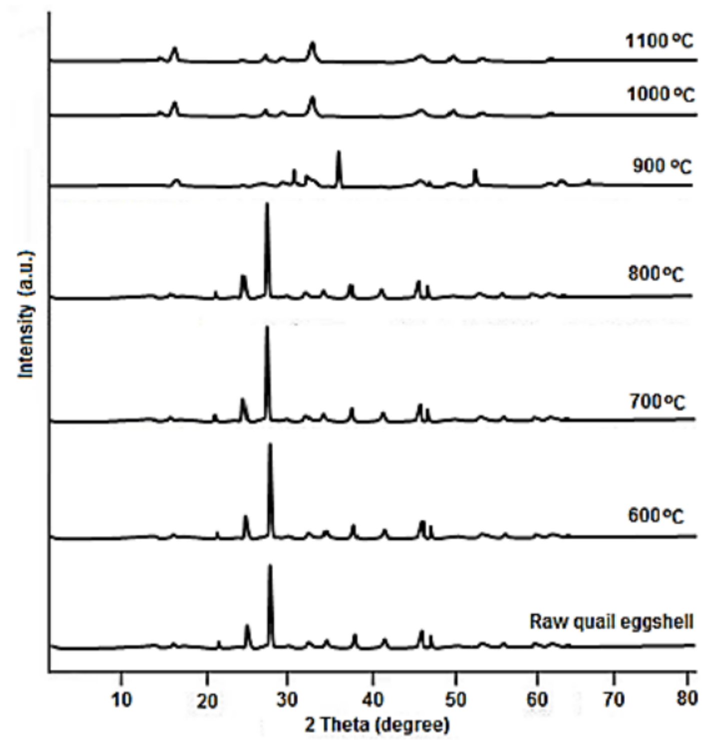

Figure 1. XRD powder patterns of decomposition of quail eggshell at various temperatures.

The XRD powder pattern of decomposition of quail eggshell at various temperatures shown in Figure 1. The XRD powder patterns of decomposition quail eggshell at lower temperatures range of 600-800°C have similar diffraction patterns with fresh quail eggshell before decomposing. Calcium carbonate is the main compound at the decomposition step. The XRD powder pattern of decomposition quail eggshell at 900°C with 2θ values of 32.2, 37.4, 53.9, 64.3, and 67.5 degrees has largely change compared to the pattern of quail eggshell decompositon at lower temperatures. The diffraction pattern of quail eggshell at 900°C is identical to the diffraction pattern of calcium oxide from JCPDS data as shown in Figure 2.

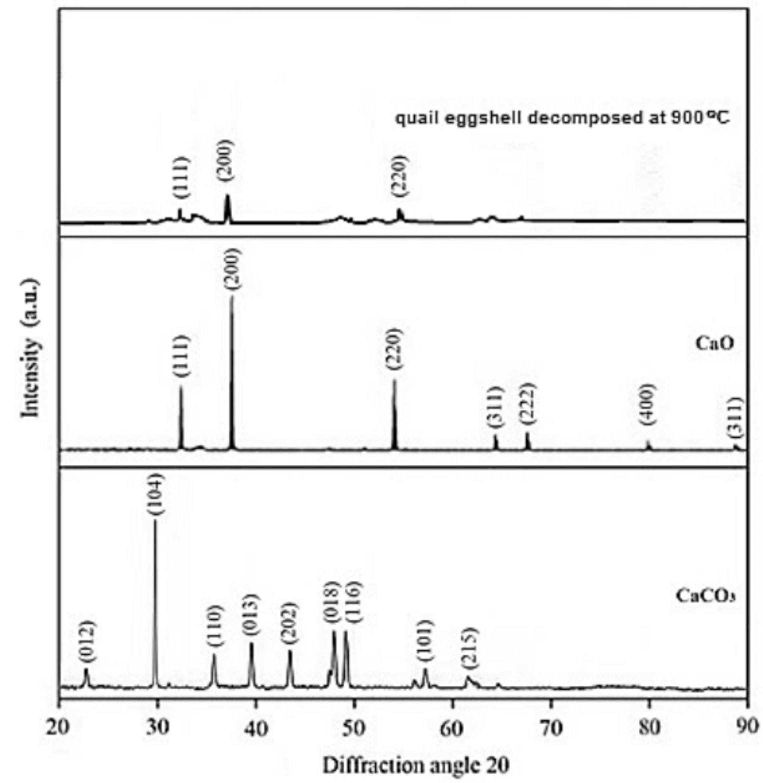

Figure 2. XRD powder patterns of calcium oxide and calcium carbonate from JCPDS and quail eggshell decomposed at 900°C.

Figure 2 shows that the XRD pattern of calcium oxide has characteristic peaks at 2θ values of 32.2, 37.3, 53.8, 64.1, and 67.3 degrees. Calcium carbonate has an XRD powder diffraction pattern at 2θ values 29.4, 39.4, 43.2, 47.4, and 48.5 degrees. By increasing the decomposition temperature to 1100°C, it was found that the diffraction pattern was significantly different from that of 600 to 800°C. It was suggested that the formation of calcium hydroxide from quail eggshell mainly occurred in this step, which was identified by 2θ peak at 28 degrees. The decomposition at 900°C was the optimum decomposition temperature for quail eggshell to form calcium oxide. This decomposition temperature was reasonably similar with decomposition of oyster, mollusca, and eggshells [19,20]. Furthermore, identification of decomposed quail eggshell using FTIR spectroscopy was also performed. The FTIR standard spectrum of calcium oxide, fresh quail eggshell and decomposed quail eggshell at 900°C are shown in Figure 3.

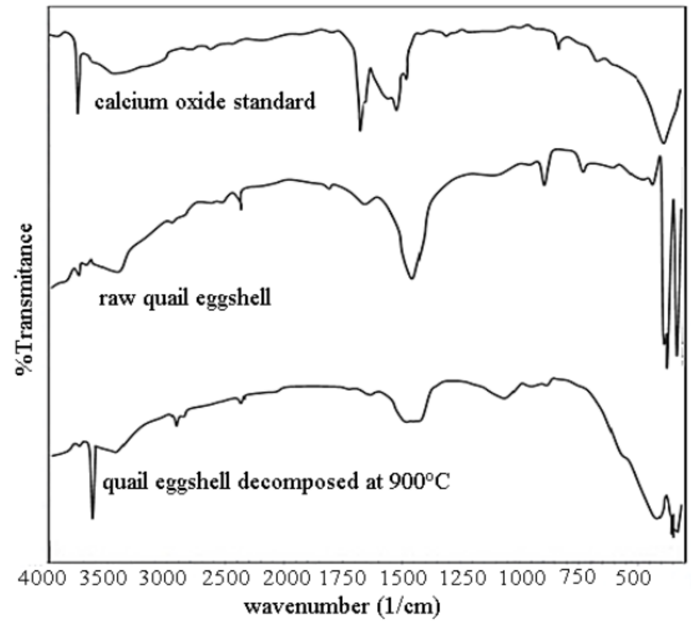

Figure 3. FTIR spectrum of calcium oxide standard, quail eggshell, and quail eggshell decomposed at 900^{o}C.

Figure 3 show the vibration of decomposed quail eggshell at 900^o C was a resemblance to the vibration of commercial calcium oxide standard. Vibration of calcium oxide should be appeared in wavenumber at 250 - 400 cm^{-1}[23,24]. The FTIR spectrum of calcium oxide decomposed from quail eggshell showed three specific vibrations of calcium oxide were detected in wavenumber at 316.3 cm^{-1}, 941.3 cm^{-1}, and 1442.8 cm^{-1}. These vibrations are unique for calcium oxide for Ca-O, O-C-O and C-O assigned as stretching vibrations. These wavenumbers were found in both calcium oxide standard and decomposed quail eggshell at 900^{o}C. Data of XRD powder pattern and FTIR spectrum of decomposed quail eggshell at 900^{o}C are appropriate with calcium oxide standard. Thus, the surface morphology of calcium oxide was identified using SEM as shown in Figure 4.

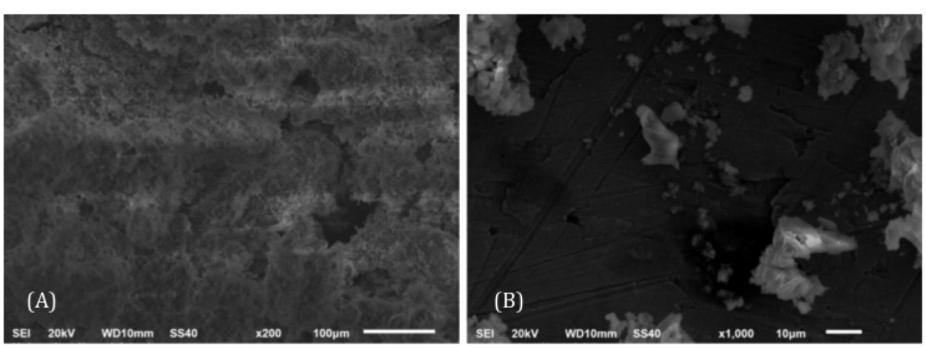

Figure 4. SEM images of (A) quail eggshell and (B) decomposed quail eggshell at 900^{o}C.

The quail eggshell is shown in tube particles with regular size. Decomposition of quail eggshell at 900°C gives block shapes with irregular size. This morphology is identical to shapes of several types of mollusc shells [25,26]. The surface area of calcium oxide after decomposition at 900°C was measured using nitrogen adsorption-desorption, as shown in Figure 5.

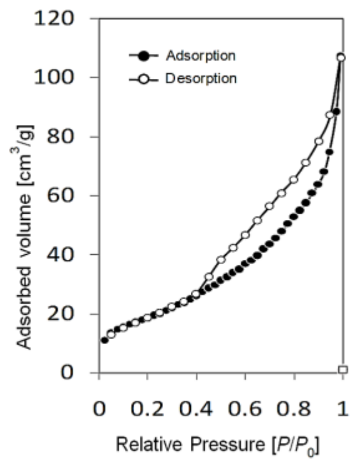

Figure 5. N_2 Sorption desorption of CaO from quail eggshell decomposed at 900°C.

Table 1. Textural properties of CaO from quail eggshell decomposed at 900°C.

CaO	Surface area (S_{BET}, m^2/g)	Pore volume (V_{BJH}, cm^3/g)	Pore diameter ($\varnothing_{BJH}$, nm)
Value	68	1.65	6.6

The data was calculated using BET equation and give a surface area of decomposed quail eggshell at 900°C of 68 m^2/g (Table 1), classifies as mesoporous materials. Mesoporous material that derived from mollusc and waste shells was also found after decomposition of waste fish (*Labeo rohita*) at 900°C [27]. These results are largely different to surface area of decomposed eggshell at 800°C due to preparation step of calcium oxide [28].

Biodiesel Synthesis from Waste Palm Oil

CaO from decomposed quail eggshell at 900°C was applied as a base catalyst in biodiesel production via transesterification reaction of waste palm oil with methanol [29]. The physiochemical properties of waste palm oil are shown in Table 2.

Table 2. Physiochemical properties of waste palm oil

Properties	Value	Unit
Density	0.90	(g/cm^3)
Viscosity	56.68	(mm^2/s)
Free fatty acid	2.80	(mg/KOH)
Iodine number	124.36	(g I_2/100 g)

Methanol is commonly used for biodiesel synthesis in addition to the other types of alcohol such as ethanol or propanol [30]. Biodiesel properties were identified after purification process using ASTM methods. The yield of biodiesel after purification was 98% based waste palm oil. The biodiesel properties *e.g.* density, viscosity, free fatty acid, and iodine number were analysed and assigned based on Indonesian National Standard (SNI 7182:2015) parameters as presented in Table 3.

Table 3. Properties of biodiesel from waste frying palm oil.

Properties	Biodiesel	Biodiesel standard (SNI 7182:2015)	Unit
Density	0.86	0.85-0.89	(g/cm^3)
Viscosity	5.50	2.30-6.00	(mm^2/s)
Free fatty acid	0.56	Max 0.80	(mg/KOH)
Iodine number	60.49	Max 115	(g I_2/100 g)

Table 3 shows the properties of the biodiesel product were meet the parameters standard in SNI 7182:2015. Calcium oxide based quail eggshell as catalyst for biodiesel production was a heterogeneous system. The transesterification reaction mechanism of biodiesel production using waste palm oil containing triglyceride and methanol is illustrated in Figure 6. The formation of biodiesel from glyceride involved three steps reaction mechanisms *i.e.* methoxide ion reacts with the catalyst (step 1), reaction of carbonyl carbon of triglyceride with step 1 to form a tetrahedral intermediate (step 2), and the intermediate forms a mole of methyl ester and diglyceride anion (step 3). The reaction was repeated to form three moles of methyl ester (biodiesel) [31,32].

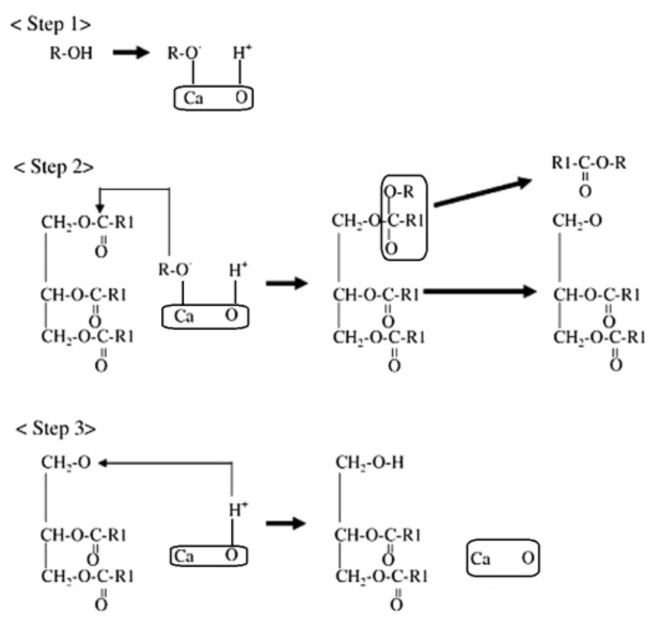

Figure 6. Calcium oxide catalysed transesterification of triglyceride with methanol in heterogeneous system purposed by Jerry et al. [33].

Moreover, this study showed the use of decomposed quail eggshell as catalyst for biodiesel production is beneficial as a renewable source, inexpensive material, and involved simple process to obtain calcium oxide and biodiesel.

CONCLUSION

Decomposition of quail eggshell at 900°C produced calcium oxide similar with calcium oxide standard. Application of the calcium oxide as catalyst for biodiesel synthesis from waste palm oil resulted biodiesel with density, viscosity, free fatty acid, and iodine number in the range of biodiesel standard from Indonesian National Standard (SNI).

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