Biodiesel Production From Waste Cooking Oil Using Catalyst CaO Derived From Strombus canarium shells

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Abstract. In this article, we address the optimal biodiesel production through transesterification reaction using waste cooking oil, methanol and presence of calcium oxide (CaO) as a solid base catalyst. CaO catalyst was activated from calcined Strombus canarium shells, collected at Bangka Belitung Islands Province, Indonesia. X-Ray Diffraction and X-Ray Fluorescence (XRF) were applied to characterize the prepared catalyst. The transesterification process will produce methyl ester (biodiesel) yield of 83.5% was obtained in the optimum condition at the waste cooking oil to methanol molar ratio of 1:12, presence catalyst 3.0% wt relative to oil and temperature reaction of 65 °C for 4 h. The GC-MS analysis assured to identify the chemical composition of the synthesized biodiesel which contained methyl myristate and methyl palmitoleate as the dominant esters. As such, the uses of Strombus canarium shells as a catalyst source and waste cooking oil as a feedstock for biodiesel production.

1. Introduction
In the 19th century, the need for fossil-based fuel in the world was increasing, so the energy reserves from non-renewable resources. And the non-renewable resources lead to depletion [1]. Nowadays, the development of renewable energy or fuel is very necessary. One alternative the renewable can produced by transesterification between triglycerides with methanol and presence of suitable catalyst [2,3].

The challenge for producing biodiesel are the selection of the feedstocks and cost. One of the alternative feedstock that can be used for biodiesel production is waste cooking oil [4]. Waste cooking oil has a relatively cheap, availability, and unused. In addition, the advantage of using waste cooking oil could also help to reduce negative environmental effect from waste oil disposal [4,5].

Biodiesel is produced through transesterification reaction with catalyst should be carried out. Conventionally, to accelerate the rate of producing biodiesel using homogeneous catalysts or heterogeneous catalysts [6]. But now the use of homogeneous catalysts has begun to be reduced, because it cannot be used repeatedly and is difficult to separate with the product [7]. So the use of homogeneous catalysts is more superior because heterogeneous catalysts have several advantages such as reusability, easy separate from products, environmental compatible, high catalytic activity and low cost [1].
Calcium oxide (CaO) is a heterogeneous catalyst that is easily obtained and environmental friendly [6]. CaO was synthesized from thermal decomposition of CaCO$_3$ and Ca(OH)$_2$ [8]. CaO is the most widely used as heterogeneous base catalysts, because it has high-activated, reused, cheap, non-toxicity, and easily available [2,9]. Calcium oxide is usually found in many animal shells such as mollusks, snails and oysters. Oyster shell contains 98.5 % calcium carbonate (CaCO$_3$) [10]. Nurhayati et al (2014) [11] was reported that conversion crude palm oil to biodiesel found 87.17 % when using CaO catalyst derived from Anadara granosa.

Like other mollusks animals, the Gonggong (Strombus canarium) snails have shells that are potentially used as catalysts for biodiesel production. Strombus canarium was found in the coastal areas of Bangka Belitung island and was used as local food. This processed foods will produce unused shells. Snail shell contains calcium carbonate compounds which can be converted to CaO. CaO compounds are active catalysts in the biodiesel transesterification reaction. So in this study, we used Strombus canarium shells as catalyst in biodiesel production from waste cooking oil.

2. Materials and methods

2.1 Material
The materials used in this study was collected from the local restaurants. All the chemicals used in this study were commercially available and without further treatment.

2.2 Preparation of catalyst
The Strombus canarium shell is cleaned using water to remove sand and unwanted material that adheres to the shell. impurities that are still in the shell are removed by using distilled water. shell that has been clean and dry, calcined with the furnace at temperature 900 °C for 4 h. The calcined shells were crushed to fine powder and sieved using 200 mesh.

2.3 Transesterification process
The transesterification process was carried out in a 500 mL two-neck glass and connecting with reflux condenser and a thermometer. Waste cooking oil was placed into the reaction flask and was heated adjusting the temperature 70 °C. Methanol and CaO catalyst were added into the reaction flask. In this study, waste cooking oil to methanol molar ratio was varied from 1:8 ; 1:10; and 1:12 and a measured quantity of catalyst 3.0% relative to waste cooking oil. The reaction was carried out under constant stirring for 4 h at 65 °C. After the reaction was completed, the mixture was transferred to a separating funnel. After left overnight, this reaction will form two different layers of glycerol (lower layer) and biodiesel or methyl ester (upper layer). This layers were decanted to separating methyl ester from glycerol. To remove excess methanol and catalyst, the methyl ester was washed with a few drops of hot distilled water. Anhydrous sodium sulfate was used to remove any traces of water in methyl ester. The yield of methyl ester or biodiesel was calculated by using the equations :

\[
\text{% yield} = \frac{\text{weight of biodiesel obtained in transesterification reaction}}{\text{weight of waste cooking oil used}} \times 100\%
\]

3. Result and Discussion

3.1 The catalyst characterization
XRD and XRF analyzes were carried out to determine the chemical composition of the catalyst derived from the Strombus canarium shell. XRF analyses revealed that the Strombus canarium shells contain 97.8% of pure CaO. Birla et al (2012) [12] also have been reported that CaO in snail shells achieved 98.35%. There is a high CaO content in this Strombus canarium shell, so this snail shell can be used as a base-catalyst in biodiesel production.
The X-ray diffraction (XRD) patterns characterizing the structural properties catalyst from calcined *Strombus canarium* shells are presented in Figure 1. This pattern was accordance with the standard XRD pattern of CaO from the International Centre for Diffraction Data (ICDD). The main peaks for CaO after calcination were observed at 2θ = 32.16°; 37.31°; 53.82°; 64.11°, and the 2θ value in ICDD are 32.19°; 37.35°; 53.85°; 64.14°. The major peaks were indicating of calcium oxide (CaO). the other peaks obtained at 2θ = 3.1; 29.4; 36.05; 39.4; 43.2; 48.6; 57.5, and 60.8 were for CaCO3 and the peaks appeared at 2θ = 47.1 was in Ca(OH)2. The results of XRF and XRD analyses confirmed that the experimental conditions used in the calcinations are suitable to form calcium oxide (CaO).

### 3.2 GC/MS analysis

![GC-MS chromatogram of biodiesel production](image)

GC-MS analysis was used to determine the chemical composition of the synthesized biodiesel. Figure 2 presents a typical chromatogram for the synthesized biodiesel and the results are reported in table 1. Eight major peaks were observed in chromatogram. The methyl ester as the dominant
esters that was found in the synthesized biodiesel and it was formed methyl oleate (39.76%), methyl palmitate (32.04%), methyl linoleate (10.89%), methyl isostearate (8.02%), and methyl octadecenoate (3.16%). Methyl ester compounds was obtained according to the content of fatty acids contained in palm oil that used in this biodiesel synthesis. Mahesh et al (2015) [13] also found that biodiesel produced from waste cooking oil using KBr impregnated CaO as catalyst contained methyl oleate, methyl palmitate, methyl linoleate, and methyl isostearate.

| No. | Retention Time (minutes) | Peak area % | Molecular weight | Molecular formula | Name of compound                                      |
|-----|--------------------------|-------------|------------------|-------------------|-------------------------------------------------------|
| 1   | 8.651                    | 0.97        | 242              | C₁₅H₃₀O₂          | Tetradecanoic acid, methyl ester (Methyl myristate)   |
| 2   | 12.398                   | 0.52        | 268              | C₁₇H₃₂O₂          | 9-Hexadecenoic acid, methyl ester, (Z)- (Methyl palmitoleate) |
| 3   | 12.983                   | 32.04       | 270              | C₁₇H₃₄O₂          | Hexadecanoic acid, methyl ester (Methyl palmitate)    |
| 4   | 16.562                   | 10.89       | 294              | C₁₉H₃₄O₂          | 9,12-Octadecadienoic acid (Z,Z)-, methyl ester (Methyl linoleate) |
| 5   | 16.798                   | 39.76       | 296              | C₁₉H₃₆O₂          | 9-Octadecenoic acid (Z)-, methyl ester (Methyl oleate) |
| 6   | 16.836                   | 3.16        | 296              | C₁₉H₃₆O₂          | 9-Octadecenoic acid, methyl ester (methyl octadec-9-enoate) |
| 7   | 17.226                   | 8.02        | 298              | C₁₀H₃₈O₂          | Heptadecanoic acid, 16-methyl-, methyl ester (Methyl isostearate) |
| 8   | 21.365                   | 0.66        | 326              | C₂₁H₄₂O₂          | Eicosanoic acid, methyl ester (Arachidic acid methyl ester) |

3.3 Effect of waste cooking oil to methanol molar ratio
The most important factor in producing biodiesel is methanol to oil molar ratio [12]. Transesterification reactions are reversible reactions. If the amount of methanol is excessive, the equilibrium of the reaction will shift to the right so that the resulting biodiesel will be more. But if the amount of methanol added exceeds the optimum condition, the glycerol formed will dissolve in methanol so that the amount of biodiesel produced will be small. The yield of biodiesel 83.5% was obtained at waste cooking oil to methanol molar ratio 1:12. Sirisomboonchai et al (2017) [14] was reported that conversion waste cooking oil to biodiesel found 86% when using CaO catalyst derived from waste scallop shell.

4. Conclusion
The highly activated CaO catalyst from calcined Strombus canarium shells, collected at Bangka Belitung Islands Province, Indonesia. The transesterification process will produce methyl ester (biodiesel) yield of 83.5% was obtained at the waste cooking oil to methanol molar ratio of 1:12, presence catalyst 3.0% wt relative to oil and temperature reaction of 65 °C for 4 h. This methyl ester was confirmed to find out its functional groups. Moreover, the GC-MS analysis assured to identify the composition of compound. The results of this study indicated that the use of Strombus canarium shells as a catalyst in the synthesis of biodiesel from waste cooking oil is effective and efficient.
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