Low cost heterogenous catalyst from \textit{(Achatina Fulica)} snail shell and its application for biodiesel conversion via microwave irradiation

Is Fatimah, E. A. Kurniastuti, I. A. Basthiani, and A. Fakhri

Chemistry Department, Universitas Islam Indonesia, Kampus Terpadu UII, Jl. Kaliurang KM 14, Sleman, Yogyakartam Indonesia 555584.

E-mail: isfatimah@uii.ac.id

Abstract. Research on preparation of heterogenous catalyst from \textit{Achatina Fulica} snail shell and its application biodiesel conversion has been investigation. Research aimed to obtain low cost and reusable catalyst for biodiesel production. The catalyst was prepared by grinding and calcining the snail shell at 900°C for 2 hours. The obtained solid was analysed by using XRD, SEM-EDX, FTIR, and also basicity measurement. Catalyst was used in the conversion of rice bran oil transesterification at varied volume of oil methanol ratio of 20-80 under microwave and reflux methode. The transesterification result were analyzed by using GCMS.

1. Introduction

Today, more than 90% of the world's energy needs are supplied from fossil fuels. The use of fossil energy resources as human needs, especially in the fields of transport, power generation, and industrial causes of fossil energy resources dwindling, especially petroleum. The use of fossil energy sources over the years has led to increased global temperatures, also known as global warming. It is caused by high levels of carbon released as a product and waste gas. This condition lead to observe and search for alternative fuel sources that are more environmentally friendly in order to overcome the negative effects arising from petroleum-based fuels [1].

Biodiesel is the most potential alternative energy resource for developing countries. Within this scheme, Castor oil, \textit{Ricinus communis L.}, (castor bean, castor, Jatropha oil, ricin, Higuerilla, Mamona, mamoeira, palmachristi) is widely used since it is a non-food oil can easily be found and cultivated in all tropical countries in the world[2]. \textit{Ricinus communis} L grow well in tropical conditions are hot and humid and has a growing period of 4 to 5 months. Just like other vegetable oils, castor oil is a triglyceride of various fatty acids and about 10% glycerin. Fatty acids consist of about 80-90% ricinoleic acid, linoleic acid 3-6%, 2-4% and 1-5% oleic acid saturated fatty acids. The high content of ricinoleic acid is the reason castor oil is versatile in the field of technology.

Refer to the principles of green chemistry, improving effectivity and efficiency of biodiesel production can be optimized by several optimization procedures. Two of variables affecting the condition are the selection of catalysis and mechanism as well as the simpler method in synthesis. Catalysts provide active sites involved in the reaction process. Usually homogeneous catalyst of NaOH or KOH were utilized in the production but the procedure gives ineffectivity since the catalyst can not be reuse and becomes consumable chemicals. As many other organic reactions, replacement of...
homogeneous catalyst with heterogeneous form is an interesting choice. Some investigations attempted to replace homogeneous catalyst with the heterogeneous form such as CaO, CaCO$_3$, Ca(OH)$_2$ or other supported basic catalyst [3–5]. Based on some investigations, exploration on Ca-based catalyst from naturally-occurring materials were reported. For example, the conversion of ostrich egg shell, snail shell, egg shell as CaO source. In this investigation, Ca-based catalyst for biodiesel production was conducted using waste of snail (Achatina Fulica) shell. In advance, the simpler method of biodiesel production was achieved over microwave-assisted method. Research was aimed to characterize and test the catalyst for biodiesel production in the microwave-assisted method.

2. Material and Methods

2.1. Material
Castor Oil was obtained from PT. Sinar Kimia, chemicals consist of methanol, HCl, and n-hexane were purchased from Merck, Germany. Snail (Achatina Fulica) shell was obtained from Paddy field area of Sleman District, Yogyakarta.

2.2. Preparation of catalyst
Snail shell was cleaned with water to remove proteins and other substances by washing using warm water before sun-dried. The shell was crushed and followed by calcination at 900°C for 2h. The sample was characterized by x-ray diffraction (XRD), Fourier-Transform Infra Red (FTIR) and Scanning Electron Microscope-Energy dispersive x-ray (SEM-EDX). Rigaku Miniflex instrument 600 Benchtop X-Ray Diffraction (XRD) was utilized to determine crystallinity of the sample, FTIR NICOLET AVATAR to determine the functional groups contained in the sample snail calcination results and SEM JEOL microscope instrument was used for surface profile of sample.

2.3. Catalytic Activity in Biodiesel Production
Biodiesel production from castor oil was conducted over two method: reflux and microwave-assisted method. For each reaction the molar ratio of oil to methanol was 20:80. Microwave method was operated at medium power for varied time of irradiation. After each reaction, biodiesel fraction was separated using a separating funnel and the sample was analyzed using Gas Chromatography-Mass Spectra GC-MS type Shimadzu QP-2010.

3. Result and Discussion

3.1. Catalyst production from Snail Shells
Sample obtained from snail shell was characterized using XRD and the pattern is presented in Figure 1.
Figure 1. Diffractograms Catalyst Snail Shell

The pattern in Figure 1 shows that the sample contains Ca(OH)$_2$ as showed by reflections at 20 28.47, 34.014 and 50.688°.

Figure 2. IR Spectra snail shell

FTIR spectra of material (Figure 2) demonstrated the spectra of OH group at 3641.47 cm$^{-1}$. Another important spectra are at 2100-2260 cm$^{-1}$ as indication of alkyne groups, 875.4 cm$^{-1}$ as indication of (-CH). The presence of Ca-O is identified at the frequencies of 417.99 cm$^{-1}$. These results are consistent with the results of the study reported by Liu et al, (2008) that the infrared spectra of Ca(OH)$_2$ is shown from the OH groups that emerged in the area 3600-4000 cm$^{-1}$. Meanwhile, according to Alba-rubio et al, (2010), CaO group found on the tape under 600 cm$^{-1}$ is on the area around 405 cm$^{-1}$[6].

The change of surface morphology of material is illustrated in Fig 3. From EDX analysis it is found that the O content in Ca(OH)$_2$ sample was about 71.4% Wt, and Ca 27% Wt content in Ca(OH)$_2$ sample.
3.2. Catalytic activity in biodiesel production

Result of catalyst testing in biodiesel conversion at varied condition is presented in Table 1.

**Table 1.** Catalyst Activity in Biodiesel Product

| Catalyst weight (g) | Method | Reaction time | Volume | Conversion (%) |
|---------------------|--------|---------------|--------|----------------|
| 2                   | Reflux | 2 (h)         | 58 mL  | 81.5%          |
| 2                   | Reflux | 3 (h)         | 67 mL  | 86.05%         |
| 2                   | Reflux | 5 (h)         | 26 mL  | 92.49%         |
| 3                   | Reflux | 5 (h)         | 18 mL  | -              |
| 5                   | Reflux | 5 (h)         | 21 mL  | 98.96%         |

**Figure 3.** SEM profile of materials with the magnification of (a) 5000x, (b) 10000x, (c) 20000x
| Time (min) | Method | Volume (mL) | Conversion (%) |
|-----------|--------|-------------|----------------|
| 10        | Microwave | 65          | 91.65%         |
| 20        | Microwave | 56          | 95.25%         |
| 30        | Microwave | 49          | 90.13%         |

Based on data in Table 1 it can be found that both reflux and microwave produce biodiesel. On the reflux method, time of reaction as well as catalyst weight give no effect the production of biodiesel. Compared to reflux method, microwave method give higher volume and conversion with the optimum reaction time of 20 mins.

Based on the resulting data, methods reflux produce methyl ester by 98.96% at the optimum transesterification reaction for 5 hours with the use of a catalyst as 5gram, while the microwave method produced methyl ester by 95.25% at the optimum transesterification reaction for 20 minutes. Thus, it can be concluded that the differences were relatively small, the microwave method is more profitable because of the time required is much faster and simpler to use than using reflux.

4. Conclusion
Ca-based catalyst has been successfully derived from Snail shell and the material exhibits catalytic activity in biodiesel production. The material showed the dominant content of Ca(OH)$_2$ and the catalyst is active for reflux and microwave method.

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