Waste shells of cockle (*Clinocardium nuttalli*) as solid catalysts for transesterification of calophyllum inophyllum L. oil to biodiesel production

[1]Husni Husin, [1]Zuhra, [2]Fikri Hasfita, and [1]Wahyu Rinaldi

[1] Department of Chemical Engineering, Syiah Kuala University, Darussalam, Banda Aceh 23111, Indonesia
[2] Department of Chemical Engineering, Malikussaleh University, Aceh Utara, Lhoekseumawe 24355, Indonesia
Corresponding Author: husni_husin2002@yahoo.com

Abstract. In this work, cockle (*Clinocardium nuttalli*) shell waste is massively produced by many restorant in Banda Aceh Indonesia. The cockle (*Clinocardium nuttalli*) shell is known high calcium; therefore it is potential to be used as calcium source of catalyst for transesterification reaction. The aim of this research is to study the synthesis and characterization of *Clinocardium nuttalli* shell. *Clinocardium nuttalli* shell was prepared by calcinating the shell at 500 and 800°C. Synthesis of solid catalys was employed for transesterification reaction of calophyllum inophyllum L. oil. The reaction was carried out in batch reactor at temperature of 65°C and ratio of mrthanol:oil of 3:1 - 12:1. The synthesized samples were characterized by X-ray diffraction (XRD). Analysis data by XRD confirmed that the obtained crystal calcined at 500 °C are $CaCO_3$ calcite, $CaCO_3$ veterite, and CaO. XRD patterns of the colcined shell at 800 °C shows sharp peaks of crystalline phase of CaO. The best characteristics is obtained at calcined catalyst of 800°C with molar ratios of methanol:oil of 12:1, i.e. density 0.832 g/cm^3, viscosity 4.92 cst, and yield 84.1%.
Key words: Waste cockle shell, solid catalyst, calophyllum inophyllum L. oil, biodiesel.

Introduction

Since the potential shortages and rise of petroleum prices, and ever-increasing environmental concerns, many studies have being directed towards the exploitation of alternative renewable fuel (Alonso et al., 2009). Issues of the energy and global warming crisis, development of renewable energies, for example, solar energy (Rosseler et al., 2010), H_2 energy (Husin et al., 2011), and biodiesel (Agarwal, 2007; Gutierreze et al., 2009), have been focused worldwide.

There is an increasing worldwide concern for environmental protection and for the conservation of non-renewable natural resources (Liu et al., 2008). Biodiesel, a clean renewable fuel derived from biological sources, is a promising candidate for a diesel fuel substitute because it can be used in any diesel-engine vehicle. Biodiesel is chemically a fatty acid methyl ester (FAME) and can be produced from a direct transesterification of vegetable oils (Chen et al., 2012).

Generally transesterification is carried out in the presence of a homogeneous or heterogeneous catalyst (Noiroj et al., 2011). The homogeneous catalytic process (e.g. NaOH and KOH) however, provides some disadvantages, such as, a huge production of wastewater from washing process of catalyst residues and non reusability of the catalysts (Furuta et al., 2006). The heterogeneous catalytic process overcomes the homogeneous one since the solid catalysts can be easily recovered and potentially be reusable (Kazemian et al., 2013). Additionally, a neutralization step producing wastewater would be eliminated (Chouhan and Sarma, 2011). Because of these advantages, research on solid bases as catalysts has increased over the past decade (Liu et al., 2008). Many types of heterogeneous catalysts, such as alkaline earth metal oxides, anion exchange resins, various alkali metal compounds supported on alumina can catalyze many types of chemical reactions. Among the alkaline earth metal oxides CaO is most widely used as catalyst for transesterification and report says as high as 98% FAME yield is possible during the first cycle of reaction (Kazemian et al., 2013).

CaO is closely resembled to an environmental-friendly material. Generally, $Ca(NO_3)_2$ or $Ca(OH)_2$ is the raw material to produce CaO. Besides, there are several natural calcium sources from wastes, such as eggshell, cockle shell, and bone (Chen et al., 2012). Using wastes as raw materials for catalyst synthesis could eliminate the wastes and simultaneously produced the catalysts with high cost effectiveness.

In fact, many part of Aceh (Indonesia), cockle (*Clinocardium nuttalli*) has been intentionally populated as the main ingredients of food supplement or local culinary such as satays or snacks. As a result, high amount of cockle shell waste is generated and most of the wastes are abandoned. Only few farmers used it as an additional ingredient of their livestock's foods. The inorganic constituent of cockle shell is mainly calcium carbonate (ca. 95%), which two principal crystalline forms, calcite and veterite. Hence, research on the utilization of cockle shell into catalyst materials not only to treat the waste, but also more economically favorable, which may decrease the cots of biodiesel industries.

In this research, we utilize the shell of cockle (*Clinocardium nuttalli*) as the source of calcium oxide as solid catalyst for biodiesel production. The waste of cockle was calcined at temperature of 500 ^{o}C and 800 ^{o}C. The obtained catalyst were characterization by X-ray diffractometer (XRD).

Materials and Methods

Materials

Waste shells of cockle (*Clinocardium nuttalli*) were obtained from a waste of local seafood restaurant in Banda Aceh, Indonesia. Methanol with purity 99.8%, ethanol with purity 95%, potassium hydroxide with purity 99%, phenolphthalein with purity 99% were purchased from Merck Co. N_2 and O_2 supplied by Gas Company (Banda Aceh, Indonesia. Calophyllum inophyllum L. oil was got from Bogor and used with etherification.

Catalyst Preparation

The shell was washed with distilled water several times to remove any organic impurity attached to it and then allowed to drying in an oven at a temperature of 110 °C overnight. After drying, the shell was crushed using a mortar till it became powdered. It was then allowed to pass through a 0.8 mm sieve mesh. The powdered shell was then calcined in air at a temperature range of 500 and 800 °C for 4 h and then stored in a desiccators.

Catalyst characterization

X-ray diffraction (XRD) analysis was carried out using a Shimadzu XRD-7000 X-ray diffractometer, operating at 40 kV and 100 mA and using Cu Kα radiation. The diffractograms were recorded in the 2θ ranges of 15-75° with a 2θ step size of 0,02^{o}. The phases present in the samples were identified according to the Powder Diffraction (PDF) database (JCPDS-International Centre for Diffraction Data (ICDD), 2000).

Reaction study

The transesterification reaction was carried out in batch reactor with a water cooled condenser, a thermometer, and a magnetic stirrer, in a water bath. Hot plate and stirrer were used for heat generation and mixing. Appropriate amounts of methanol, calophyllum inophyllum L. oil, and catalyst were added to the reactor. The reactor was heated to 65 °C and the solid catalyst having the amounts of 3 wt.% of calcined of waste shells of cockle (*Clinocardium nuttalli*). After stirring for 3 hours, the mixture was put in a separator funnel and precipitated for 24 hours, while the catalyst was sedimented in the buttom of reactor. All experiments were performed under atmospheric pressure.

Results and Discussion

Catalyst characterization

X-ray diffraction of catalyst were performed to determine the crystal phase of the powder catalyst. Figure 1 and 2 depicts the XRD patterns of the waste cockle (*Clinocardium nuttalli*) shells samples after sintering at 500 and 800 °C, respectively. The results indicated that the cockle (*Clinocardium nuttalli*) shells calcined at 500°C exhibited peaks characteristics of $CaCO_3$ calcite (JCPDS 72-1651, 2θ diffraction peaks at 29,476°; 39,434°; 48,614°), and $CaCO_3$ veterite (JCPDS 72-1616, 2θ diffraction peaks at 17,729°; 25,454°; 30,728°.

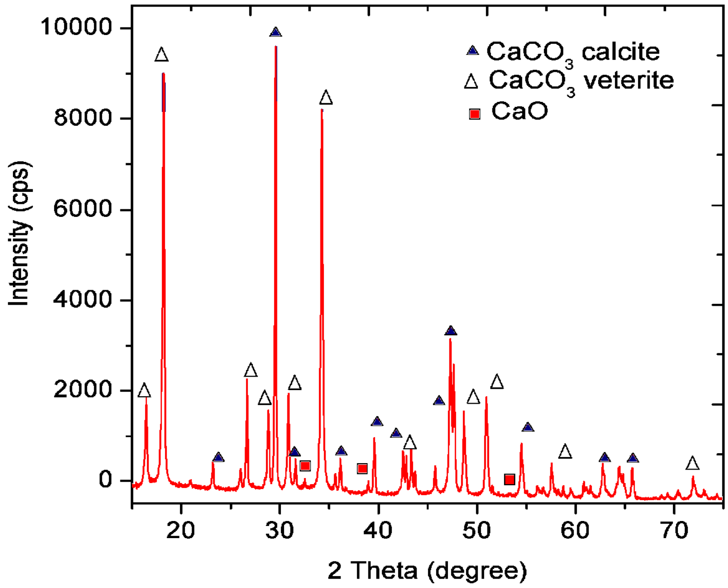

Figure 1. Powder X-ray diffraction patterns of the cockle (*Clinocardium nuttalli*) shells catalysts after calcination at temperatures 500 °C.

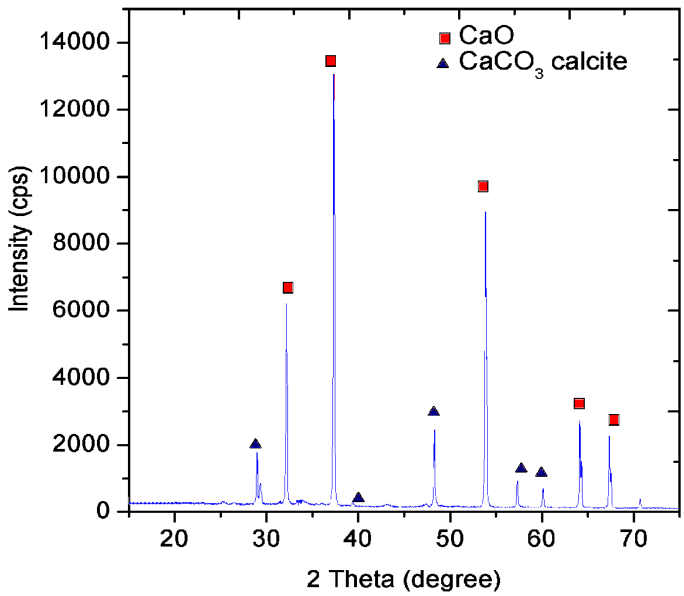

Figure 2. Powder X-ray diffraction patterns of the cockle (*Clinocardium nuttalli*) shells catalysts after calcination at temperatures 800 °C.

The cockle shell catalyst calcined at 500 °C contains calcite and veterite as the major phase and CaO as a minor phase. The highest peak of $CaCO_3$ calcite of the sample calcined at 500°C having intensity about 9700 cps, located at 2θ of 29,476°. When the calcination temperature reached 800 °C, the crystal structure of CaO (JCPDS 82-1690) was recorded.

Its diffraction peak intensity appeared at 2θ 32,29°; 37,4°; 53,87°. Only small amount of $CaCO_3$ phase appear in the diffractogram after sintering at 800 °C. This findings indicated that $CaCO_3$ was converted into crytal CaO at high temperature. The crystal phase of veterite was vanished at 800 °C. It seem that the calcite was more stabile than veterite at temperature of 800 °C.

Yield of biodiesel

To investigate the influence of preparation temperature on catalytic activity of cockle (*Clinocardium nuttalli*) shell catalyst, two samples were prepared at different calcination temperature. The effect of methanol to oil molar ratio on biodiesel yield was also investigated.

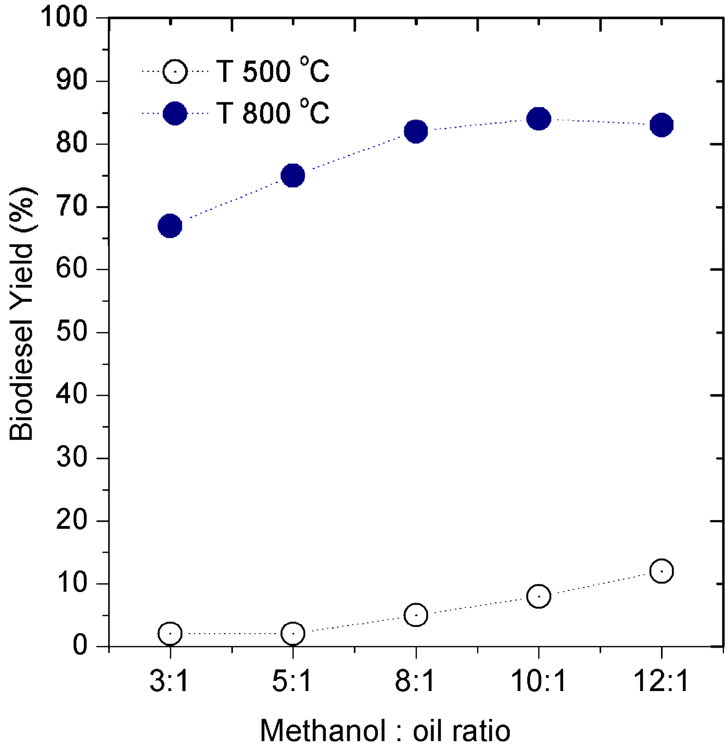

Figure 3. Yield of biodiesel at different of molar ratio metnaol: oil

Figure 3 depicts the FAME yield % with respect to the different methanol to oil molar ratio employed for transesterification. Transesterification was carried out with 3:1, 5:1, 8:1, 10:1 and 12:1 methanol to oil molar ratio. As can be seen, the yield of biodiesel increased with increasing methanol to oil ratio. This is due to the formation of methoxy species on the cockle shell catalyst surface which helps in shifting the reaction towards forward direction. The optimum molar ratio is found to be 10:1 over the catalyst calcined at 800 °C. The best characteristics is obtained at calcined catalyst of 800°C with amount of catalyst 3%, i.e. density 0.832 g/cm^3, viscosity 4.92 cst, and FAME 84.1%.

Conclusions

The waste cockle (*Clinocardium nuttalli*) shell catalyst was successfully synthesis and employed for biodiesel production via transesterification. After calcination at 800 °C, almost all *Clinocardium nuttalli* shell catalysts mainly consisted of CaO phase with high crystallinity as confirmed by XRD. The best characteristics is depicted at calcined catalyst of 800°C with molar ratio methanol oil of 10:1, i.e. density 0.832 g/cm^3, viscosity 4.92 cst, and biodiesel 84.1%. The study can be further extended to investigate more operating condition, making both the oil and catalyst from reusable materials.

Acknowledgements

We would like to thank the Ministry of Education of Repulbik Indonesia for financial support through competitive research grants (Hibah Bersaing) 2013.

References

Agarwal AK. 2007. Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines. Progress in Energy and Combustion Science 33:233-271.

Alonso DM, Granados ML, Mariscal R, Douhal A. 2009. Surface chemical promotion of Ca oxide catalysts in biodiesel production reaction by the addition of monoglycerides, diglycerides and glycerol. J Catal 276:229-236.

Chen C-L, Huang C-C, Tran D-T, Chang J-S. 2012. Biodiesel synthesis via heterogeneous catalysis using modified strontium oxides as the catalysts. Bioresource Technology 113:8-13.

Chouhan APS, Sarma AK. 2011. Modern heterogeneous catalysts for biodiesel production: A comprehensive review. Renewable and Sustainable Energy Reviews 15:4378 -4399.

Furuta S, Matsuhashi H, Arata K. 2006. Biodiesel Fuel Production with solid amorphous-zirconia catalysis in fixed bed reactor. Biomass and Bioenergy 30:870-873.

Gutierreze LF, Sanchez OJ, Cardona CA. 2009. Process integration possibilities for biodiesel production from palm oil using ethanol obtained from lignocellulosic residues of oil palm industry. Bioresour Technol 100:1227-1237.

Husin H, Chen HM, Su WN, Pan CJ, Chuang WT, Sheu HS, Hwang BJ. 2011. Green fabrication of La-doped $NaTaO_3$ via H_2O_2 assisted sol-gel route for photocatalytic hydrogen production. Appl. Catal., B 102:343-351.

Kazemian H, Turowec B, M.N.Siddiquee, Rohani S. 2013. Biodiesel production using cesium modified mesoporous ordered silica as heterogeneous base catalyst. Fuel 103:719-724.

Liu X, Piao X, Wang Y, Zhu S, He H. 2008. Calcium methoxide as a solid base catalyst for the transesterification of soybean oil to biodiesel with methanol. Fuel 87:1076-1082.

Noiroj K, Intarapong P, Luengnaruemitchai A, Jai-In S. 2011. A comparative study of KOH/Al_2O_3 catalysts for biodiesel production via transesterification from palm oil. Renewable Energy 34:1145-1150.

Rosseler O, Muthukonda V, Shankar, Du MK-L, Schmidlin L, Keller N, Keller V. 2010. Solar light photocatalytic hydrogen production from water over Pt and Au/TiO_2(anatase/rutile) photocatalysts: Influence of noble metal and porogen promotion. Journal of Catalysis 269:179-190.