ARPN Journal of Engineering and Applied Sciences

A FACIL AND LOW COST ACTIVATED CENGAR CLAY/LA CATALYST FOR BIODIESEL PRODUCTION FROM CEIBA PENTANDRA SEED OIL

Syaiful Bahri, Panca Setia Utama and Yelmida and Khairat
Department of Chemical Engineering, Universitas Riau, Pekanbaru, Indonesia
E-Mail: syaifulbahri@eng.unri.ac.id

ABSTRACT

This paper presents the synthesis of a facil and low cost Cengar clay/La catalyst for biodiesel production from Ceiba Pentandra (CP) seedoil. The clay was activated using base (NaOH) and acid (H_2SO_4). Both activated clay were impregnated using $La_2O_3$to increase the activity of catalyst. The concentration of NaOH, H_2SO_4 and La_2O_3 loading were varied to obtain the best catalyst for biodiesel synthesis. The obtained catalyst was then calcined at 300^{o}C for 3 hours to remove the impurities and activated the catalyst. The catalysts were characterized using SEM to study the morphology of the catalyst. The performance of the catalysts was tested and compared on transesterification process of esterified CP seed oil. The result showed that Cengar clay activated using 1 N NaOH and 1% Lanthanum loading has the highest activity. The FAME yield obtained was of 86% at reaction temperature of 60^{o}C, methanol to oil molar ratio of 9:1, catalyst loading of 0.5% and transesterification reaction time of 120 min. The physicochemical properties of the produced biodiesel comply with SNI 04-1782-2006.

Keywords: cengar clay; Ceiba pentandraseedoil; biodiesel; transesterification.

1. INTRODUCTION

The conventional energy sources such as petroleum, gas, and coal are limited. Recently even though the petroleum reserve is depleted, the use of petroleum as fuel, especially for transportation, is still dominant. So it is needed an effort to provide alternative energy that can be renewed and environmentally friendly, including biodiesel. These conditions indicate the need to optimize the use of new and renewable energy for the availability of energy in the future. One alternative energy source that is renewable and environmentally friendly is biodiesel. Biodiesel is produced from a variety of oil and fat sources. Based on data from the Indonesian Energy Board, biodiesel demand increased rapidly, which is an average of 12.3% per year, in 2025 the total biodiesel demand of 16 million TOE (Tonnes Oil Equivalent) increased to 58 million TOE in 2050. So it is crucial to guarantee the availability of raw material to meet the increasing demand for biodiesel in the future

According to Koizumi (2015), only four vegetable oils that commercially used as raw material for producing biodiesel those are rapeseed oil, palm oil, soybean oil, and coconut oil. Those oils are edible, so the extensive use of this kind of oil for biodiesel production will detrimental to food security. The increasing biofuels production in a developed country will increase the world food price (Ewing and Msangi, 2009). According to the model developed by Nonhebel (2011), in the future, the need for biomass for energy is more extensive compared to biomass for food. So it is essential to search for non-edible oil that can be used to produce biodiesel. The used of non-edible oil for energy will reduce the potential of food insecurity in lower-income countries and create opportunities for these countries for producing biodiesel to increase their income.

One of the non-edible oil available in Indonesia is *Ceiba pentandra* (CP) seed oil. The productivity of 1 hectare CP tree at the age of planting 17 is 500 kg of cotton fiber and 1 ton of seeds dry cottonwood. Each cottonwood spindle contains 26% cottonwood seeds so each100 kg of logs yields 26 kg of kapok seeds. Almost all parts of the treekapok has been used for various purposes commercially, but CP seeds are still not widely used. From the CP seeds the CP oil can be extarcted and utilized as biodiesel raw material. In the process of making biodiesel, both catalysts and homogeneous or heterogeneous catalysts are needed in the form of oxides and natural minerals such as clay. In this study activated clays impregnated with Lanthanum was used. The raw material of natural clay used originates from Cengar village in Kuantan Mudik District, Kuantan Singingi Regency, Riau. Several research on this clay has been done. In addition, the potential of this natural clay reserve is quite large, about 4,313,700 m^3 spread across several locations, namely Toar Village, upstream of Batang Salo river (Cengar Village), Bukit Batabuh protected forest area, Kasang Village, Teluk Banyan Village and Air Reed Village (Bahri and Rivai, 2010).

Clay is used as a catalyst because of its porous structure and high thermal stability, with good surface area and catalytic activity. Cengar clay catalyst has high acid stability and high temperature resistance. Meanwhile research conducted by Noda *et al* (2005), reported that one of the promising heterogeneous catalysts for biodiesel production through transesterification-esterification is metal oxide. Nasikin *et al* (2002) state that the La_2O_3 compound is a metal oxide which can act as a buffer or promoter so that it can increase the resistance of the catalyst. The development of heterogeneous catalysts is very important in the production of biodiesel production, so in this study the combination of metal La and clay is a potential catalyst for prospective biodiesel production. Clay has a good and porous structure while La is an active metal. In this research the production of biodiesel from CP seed oil with heterogeneous catalysts in the type of clay lanthanum carrier, La/Clay activated was explored. For optimizing the research data, a number of variations of La metal carrier were carried out on the clay mixture, as well as several process variables such as reaction time, temperature, stirring speed, oil: methanol ratio and catalyst: oil ratio. The results of this study are expected to be able to increase biodiesel production and quality in accordance with SNI 04-1782-2006.

2. METHODOLOGY

2.1 Material

Cengar clay was obtained from Taluk Kuantan, Riau, Indonesia. All the chemicals such as potassium hydroxide, methanol, phosporic acid and sulphuric acid used were analitycal grade (Merck). The crude CP seed oil was purchased from local market at Cilacap, Indonesia.

2.2 Pretreatment

2.2.1 Degumming

The CP seedoil was purified by degumming and neutralization to remove impurities in the oil. Gum consists of a mixture of several components, among others, phospholipids, unsubstantiated compounds, carbohydrates, proteins, water, resin acids and a small portion of free fatty acids. The process was conducted by adding 0.3% (v/v) of 85% phosphorus acid into 500 cm^3 oil in 1000 cm^3 glass reactor equipped with heater and magnetic stirrer at 80 ^oC and constant stirring speed of 400 RPM for 30 minutes (Damanik, *et al*., 2017).

2.2.2 Esterification

The Free Fatty Acids (FFA) of the crude oil used was high about23 wt%, so the esterification process to convert the FFA into methyl ester have to conduct before transesterification process. In this research 20:1 mol ratio of methanol to refined oil; 1% (v/v) sulfuric acid; temperature of 60^oC; stirring speed of 400 RPM and time 3 hours was used to convert the FFA into methyl ester in a 1000 cm^3glass reactor (Koh and Ghazi, 2011). The separating funnel was used to separate alcohol, catalyst, and impurities. The product after esterification process was analyzed for water content and FFA content.

2.3 Transesterification process

The performance of geopolymer catalysts were tested in biodiesel synthesis from CP seed oil in 250 ml round bottom flask equipped with heater, magnetic stirrer and water cooled condensor. The effect of catalyst loading, methanol to oil mol ratio, temperature and time on biodiesel yield were investigated. In this process, 100 gesterified CP seedoil was mixed with the clay catalyst and methanol then heated and stirred. Constant strirring speed of 400 RPM was used, the operating condition was time of 120 min, temperature of 60^oC, methanol to oil ratio 9:1 and catalyst loading of 0,5%. The vacuum filter was used to separate the catalyst from the product and the separating funnel was used to separate the biodiesel from glycerol, methanol, water and other impurities. The percent yield of biodiesel was calculated using the following formula (Maneerung *et al*., 2016)

$$yield\ (\%) = \left(\frac{weight\ of\ biodiesel}{weight\ of\ oil}\right) x\ 100 \qquad (1)$$

Percentage ester content was calculated by using the following equation [18,20].

$$Ester\ content\ (\%) = \left(\frac{\sum A - A_{IS}}{A_{IS}}\right)\left(\frac{C_{IS}V_{IS}}{\mathrm{m}}\right) x\ 100 \qquad (2)$$

Where $\sum A$ is a sum of the areas under all peaks from C14:0 to C24:1; A_{IS} is an area under the peak the internal standard; C_{IS} is a concentration of the solution (g/cm^3); V_{IS} is a volume of the solution (cm^3); and m is a sample weight (mg).

3. RESULT AND DISCUSSIONS

3.1 The Biodiesel Yield

The effect of Lanthanum loading on biodiesel yield using Cengar clay activated by H_2SO_4 can be seen in Figure-1.

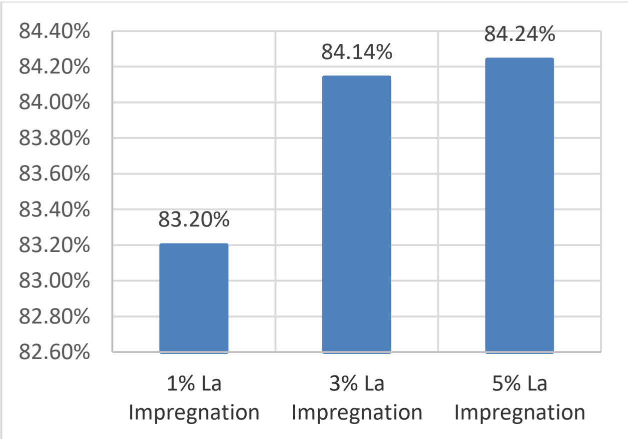

Figure-1. Effect of Lanthanum loading on biodiesel yield at clay activated by 2 N H_2SO_4.

From Figure-1, it can be seen that the biodiesel yield increase with increasing amount of Lanthanum impregnation. Even though the increasing biodiesel yield at 5% impregnation compare to 3% impregnation insignificant. According Nasikin *et al.*, the higher amount of the Lanthanum will make more active sites in the catalyst and increasing the activity of the catalyst. From this figure it can be predicted that the optimum Lanthanum impregnation is 3%.

In order to study the effect of H_2SO_4 concentration on the activity of the catalyst, H_2SO_4 concentrations for activated the Cengar clay were varied from 1N to 5N. The result can be seen in Figure-2.

ARPN Journal of Engineering and Applied Sciences

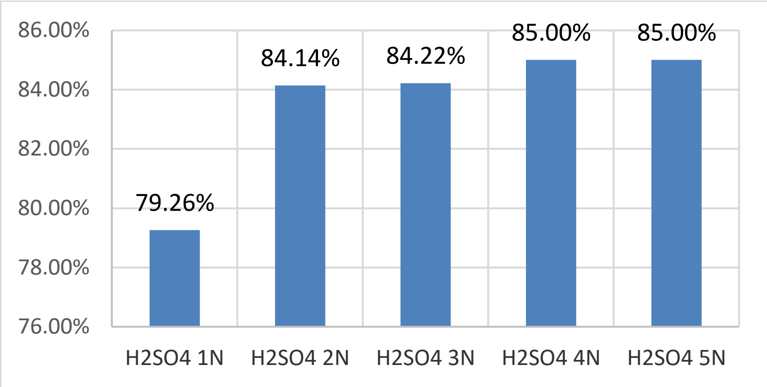

Figure-2. Effect of H_2SO_4 concentrations on biodiesel yield at 3% Lanthanum impregnation.

Figure-2 shows that the higher concentration of H_2SO_4 increase the biodiesel yield obtained. The sulfuric acid is a strong acid; it will attack the clay and dissolve part of the clay. The dissolved clay will make pore bigger, so it is easier for the oil diffuse into the catalyst and reach the active sites in the catalyst. That is why the increasing H_2SO_4 concentration in the activation process increases the activity of the catalyst and makes the biodiesel yield increases. The optimum H_2SO_4 concentration for clay activation was at 4N.

The effect of Lanthanum loading on biodiesel yield using Cengar clay activated by NaOH can be seen in Figure-3.

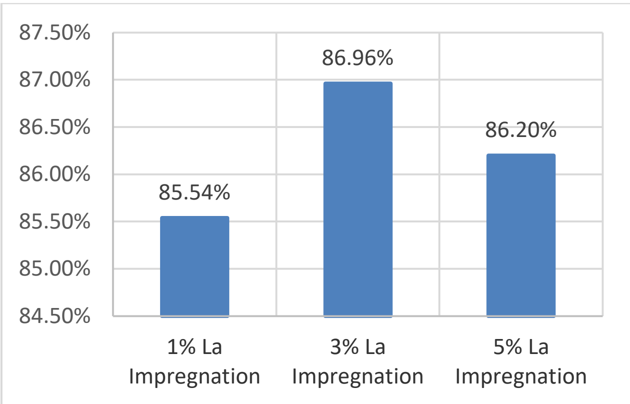

Figure-3. Effect of Lanthanum loading on biodiesel yield at clay activated by 2 N NaOH.

From Figure-3, it can be seen that the biodiesel yield increase with increasing amount of Lanthanum impregnation. However using clay catalyst activated using 2N NaOH and impregnated using 5% Lanthanum will decrease the catalyst activity compared to using 3% Lanthanum impregnation. It might be if using too much Lanthanum, the Lanthanum will clog the pore in the catalyst. The pores clogged make the oil difficult to diffuse into the catalyst. From this figure it can be predicted that the optimum Lanthanum impregnation is 3%, the same with clay activated by H_2SO_4

In order to study the effect of NaOH concentration on the activity of the catalyst, NaOH concentrations for activated the Cengar clay were varied from 1N to 5N. The result can be seen in Figure-4.

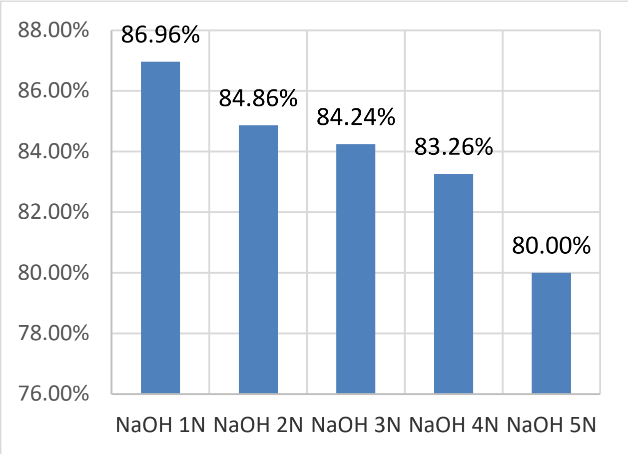

Figure-4. Effect of NaOH concentrations on biodiesel yield at 3% Lanthanum impregnation.

Figure-4 shows that the higher concentration of NaOH decrease the biodiesel yield obtained. The ultimate component of clay is silica and alumina. Both components were dissolved in high NaOH concentration. Using NaOH concentration below 1N can increase the pore size; however using concentration above 1N can destroy the clay structure and reduce the activity of the clay catalyst. That is why the increasing NaOH concentration in the activation process decrease the activity of the catalyst and makes the biodiesel yield reduced. The optimum NaOH concentration for clay activation was at 1N resulting biodiesel yield 87%. So it is can be concluded that using NaOH 1N and 3% Lanthanum impregnation is the best condition for biodiesel synthesis from CP seed oil.

3.2 Catalyst Characterization

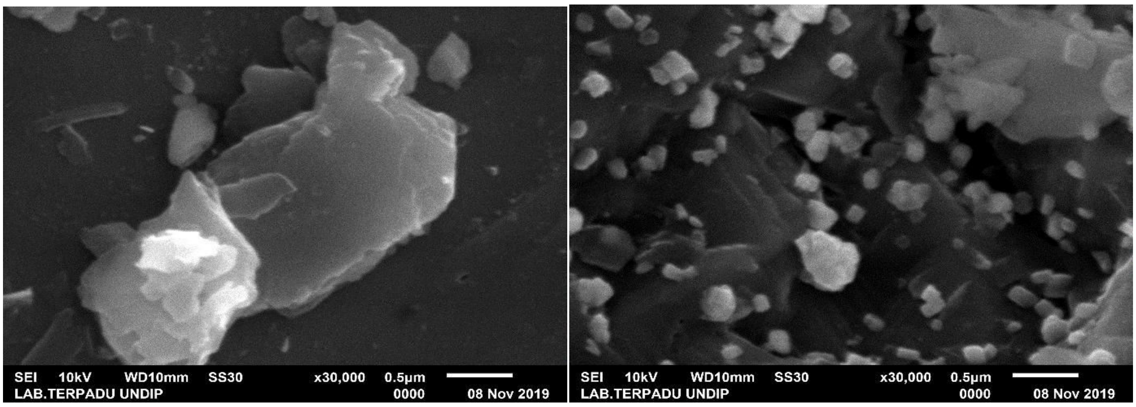

Figure-5. SEM micrograph of catalyst activated by 1N NaOH (left) impregnated 3% La(right).

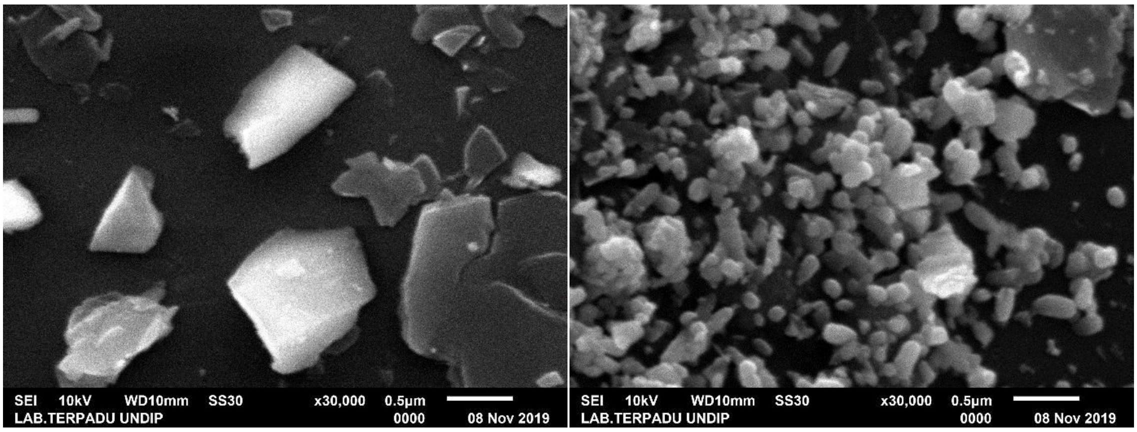

Figure-6. SEM micrograph of catalyst activated by 2N H_2SO_4 (left) impregnated 3% La(right).

Figures 5 and 6 show the micrograph of Cengar clay activated using NaOH and H_2SO_4 with and without Lanthanum impregnation. It can be seen that catalyst using Lanthanum impregnation showed many small particle compared to catalyst without Lanthanum impregnation. The small particles increase the surface area and might be increase the active sites in the catalyst. This phenomenon is in accordance with the result of biodiesel yield above.

4. CONCLUSIONS

Activated Cengar clay can be used as heterogeneous catalyst for biodiesel synthesis from CP seed oil. The best catalyst was obtained by 1N NaOH activation and 3% Lanthanum impregnation. At the operating condition of constant strirring speed of 400 RPM, time of 120 min, temperature of 60°C and catalyst loading of 0.5% the biodiesel yield obtained was of 87%.

REFERENCES

Bahri S. and Rivai R. 2010.Chemical Modification On Natural Clay And Its Application On Equilibrium Study Of The Adsorption Of Pb^{2+} In Aqueous Solution. Jurnal Sains dan Teknologi, Department of Chemical Engineering.9: 49-54.

Damanik N., Ong H. C., ChongW. T. & Silitonga A. S. 2017. Biodiesel production from Calophyllum inophyllum - palm mixed oil. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects. 39(12): 1283-1289.

Ewing M. & Msangi S. 2009. Biofuels production in developing countries: assessing tradeoffs in welfare and food security. Environmental science & policy. 12(4): 520-528.

Koh M. Y. & Ghazi T. I. M. 2011. A review of biodiesel production from Jatropha curcas L. oil. Renewable and Sustainable Energy Reviews. 15(5): 2240-2251.

Maneerung T., Kawi S., Dai Y. and Wang C. H. 2016. Sustainable biodiesel production via transesterification of waste cooking oil by using CaO catalysts prepared from chicken manure. Energy Conversion and Management.123, 487-497.

Nasikin M., Wahid A.,Supriyanto H.2002. Pengaruh promotor La_2O_3 pada ketahanan katalis Co,K/CeO2 terhadap sulfur untukCatalytic converterkendaraan diesel.(1): 37-41.

Noda L.K., Almeida R.M., Probst L.F.D., Gonçalves N.S. 2005.Characterization of sulfated TiO2 prepared by the sol-gel method and its catalytic activity in thenhexane isomerization reaction. J. Mol. Catal. A Chem. 225, 39-46.

Nonhebel S. 2012. Global food supply and the impacts of increased use of biofuels. *Energy*. 37(1): 115-121.

Siswani E. D., Kristianingrum S. & Tohari T. 2015. Synthesis of biodiesel from kapuk seed oil (Ceiba pentandra L) at variation stirring duration in transesterification process. Jurnal Sains Dasar. 4(2): 186-189.