Effect of Lanthanum-Natural Zeolite, La/NZA catalyst on biodiesel production from crude palm oil

A Setianingsih, Wisrayetti, Khairat and S Bahri

Department of Chemical Engineering, University of Riau, Kampus Bina Widya Jl.HR. Soebrantas KM 12.5 Pekanbaru

E-mail: syaifulbahri@eng.unri.ac.id

Abstract. Biodiesel can be produced from vegetable oils through the trans-esterification process. In this study, potential vegetable oil of Crude Palm Oil (CPO) was used as sample. The purposes of this research were to produce biodiesel from CPO as an alternative fuel, having study the ratio of impregnation of Lanthanum on NZA, and its catalyst weight to the biodiesel yield. The La/NZA catalyst is made as followed, first the natural zeolite size was reduced using grinding, then activated using HCl 6 N and NH₄Cl 1 N, followed with the drying process. La is impregnated into NZA as solution having variations of 1 and 3% (w/w) of NZA, then it was followed with dried in an oven, calcination, oxidation and reduction. Production of biodiesel is carried out through two stages of esterification and transesterification processes. In the trans-esterification process conducted with the various variation of catalyst weight i.e. 1, 2 and 3% of La/NZA (w/w) for a total weight of 80 grams of CPO sample, having the ratio of oil : methanol 1 : 9. Reaction was lasted for 60 minutes at 60°C having 400 rpm stirring speed. From the result, the conversion of 85.37% is given by the run on using 3% La/NZA catalyst having catalyst weight 1%.

1. Introduction

Energy is decisive factor for the economic development of a country [1]. Nowadays, we know the production of the petrol oil were decreasing, and therefore increasing the energy crisis. So we need to develop production of renewable energy from vegetable oil or biomass. Biodiesel is one of the renewable alternative fuels, it has been used to combine with the petrodiesel, it called biosolar.

Biodiesel is made from vegetable oil derived from renewable natural resources. Crude palm oil is one of big source for production biodiesel because the palm oil plantation is very large. The development of biodiesel from CPO has more advantages than biodiesel from other vegetable oils, such as better physical and chemical properties.

Biodiesel, which is also known as fatty acid methyl ester (FAME), is a mixture of methyl esters resulting from the transesterification reaction of edible or non-edible vegetable oil with aliphatic alcohols with the aid of an acid or base catalyst [2]. Transesterification can be conducted homogeneously or heterogeneously. A heterogeneous catalytic process is more advantageous than a homogeneous. A heterogeneous catalyst has higher activity, easier to separate and reuse, and release less pollution to the environment than a homogeneous catalyst, therefore, the former reduces the overall production costs [3].
One of the heterogeneous catalysts is zeolite. Availability of zeolite is much enough and has not been used optimally, so zeolite has potentially to developed as a catalyst [4]. In an effort to improve the catalyst performance it is necessary to add metal to the zeolite. One of the right metals used is Lanthanum (La) which serves to increase the activity, stability and selectivity of the catalyst.

The use of La/NZA heterogeneous catalyst in the biodiesel manufacturing process is expected to increase yield and make the biodiesel production process more efficient. The aims of this research are to create and to determine the characterization of La/NZA catalyst for, producing biodiesel from CPO as an environmentally friendly for then can be used as alternative fuel.

2. Crude palm oil (CPO)
The palm oil plant (*Elaeis guineensis Jacq.*) is a plant originating from West Africa. Currently, there are 17 types of palm oil is globally traded feeding oil. The palm oil plant has the optimum growth in the area around the tropical and wet equator with temperatures ranging from 24 to 32°C in a year, abundant sunshine, high rainfall (~ 2,000 mm). Currently, Indonesia is the world's major producer of palm oil that produces more than 44% of the palm oil.

The development of CPO production in Indonesia has increased every year. This can increase the potential for producing biodiesel. Until now, palm oil is still the mostly exported in the form of CPO, while in the country about 80% of palm oil is processed into food products, especially cooking oil [5].

Palm oil produces two types of oil, namely palm kernel oil or palm kernel oil obtained from palm kernel and crude palm oil (CPO) obtained from pulp containing 50% oil [6]. CPO is the result of processed palm fruit flesh (mesocarp) through sterilization process of fresh fruit bunch, threshing, pressing and screening [7]. CPO is a bit thick yellow orange reddish.

3. Catalyst
The catalyst is a chemical that can increase the rate of reaction by lowering the activation energy and directing the reaction to achieve equilibrium without getting involved in the reaction permanently [8]. Catalysts are widely used in nature, laboratory and industry. The catalysts that are in the same phase (liquid) with the reactants are referred to as homogeneous catalysts. While the catalysts that are in different phases with the reactants (can be solids, non-mixing liquids or gases) are referred to as heterogeneous catalysts [9].

3.1 Heterogeneous catalysts
Heterogeneous catalysts consist of two types of acidic and heterogeneous catalysts. Several heterogeneous catalysts have been synthesized in both acidic and alkaline properties. The most commonly used heterogeneous base catalysts are metal oxide compounds such as alkali metals, alkaline earths as vegetable oil transesterification catalysts. The alkaline earth metal oxides (MgO, CaO, SrO, and BaO) are known as single metal oxides [10].

The use of heterogeneous solid catalysts reduces the problems posed by homogeneous catalysts. Heterogeneous catalysts can be recycled and used multiple times with better and product separation. In addition, the use of this catalyst also minimizes raw material costs and production costs. This process is environmentally friendly and can be applied to batch or continuous processes without requiring a purification stage [10]. Heterogeneous catalysts are not as homogeneous catalysts because they can reduce the cost and time of water washing and reduce the neutralization stage to separate and catalyze recovery [11].
3.2 Natural zeolite catalyst
Zeolite is a mineral, it is soft and easy to dry. The color of the zeolite is white-gray, white-greenish, or yellowish white. The size of zeolite crystals is mostly no more than 10 - 15 microns [4]. This mineral has a specificity to loses water very quickly. Zeolite consisted of a chemical compound of alumino-silicate dihydrate with sodium, potassium and barium cations.

Zeolites have a three-dimensional structure, formed from tetrahedral alumina and silica with inner cavities containing metal ions, usually alkaline freely moving water molecules. This makes the zeolite particles have a pore that can be distinguished to macropore (>50 nm), micropore (<2 nm) and between them mesopores. The basic framework of the zeolite structure consisted of tetrahedral units of AlO$_4$ and SiO$_4$ which are interconnected through the O atom.

Natural zeolites generally have low catalytic activity, low crystallinity and non-uniform pore size. Therefore, it needs to be activated before use as a catalyst. In addition to eliminating impurities found in natural zeolites, the zeolite activation process is also intended to modify the properties of zeolites, such as surface area and acidity. The increased surface area and acidity will cause the catalytic activity of the zeolite become increase. One of the advantages of zeolite is have surface area and acidity that is easily modified.

3.3 Lanthanum oxide (La$_2$O$_3$)
Lanthanum (La) is a chemical element of rare-earth metal of class III on the periodic table, which is a prototype of the lanthanide element series. Lanthanum belongs to a rare-earth group of ductile, soft, silvery white metal that is soft enough to cut with a knife. Lanthanum was discovered in 1893 by a Swedish chemist named Carl Mosander. Lanthanum is the second most reactive of rare-earth metal after europium.

Lanthanum is oxidized in air at room temperature to form La$_2$O$_3$. Lanthanum is quite electropositive, slowly lanthanum reacts with water and quickly dissolves in dilute acids, except hydrofluoric acid (HF) due to the formation of a protective fluoride layer (LaF$_3$) on the metal surface. These metals react directly with carbon, nitrogen, boron, selenium, silicon, phosphorus, sulfur and halogens.

The lanthanum metal is paramagnetic from 6 K (-267 °C, or -449 °F) to the melting point at 1,191 K (918°C, or 1,684°F) with specific gravity of 6.1545 g/cm$^3$. Lanthanum becomes superconducting at atmospheric pressure below 6.0 K (-267.2 °C, or -448.9 °F) in cubic β - f face - centered or 5.1 K (-268.1 °C, or -450.5 °F) in the close-packed hexagonal α-phase.

4. Production of biodiesel

4.1. Esterification
Esterification is the reaction between a fatty acid and an alcohol using an acid catalyst. Esterification with acidic catalyst converts free fatty acid (FFA) to alkyl esters. Esterification generally uses a homogeneous acid catalyst such as sulfuric acid (H$_2$SO$_4$) and hydrochloric acid (HCl). The esterification stage is usually followed by the transesterification stage. The reaction of fatty acids to methyl ester as follows:

\[
\text{RCOOH} + \text{CH}_3\text{OH} \xrightarrow{\text{catalyst}} \text{RCOOCH}_3 + \text{H}_2\text{O}
\]

Fatty acid Methanol Methyl Ester Water
The esterification reaction is effected by several factors including free fatty acid and the amount of methanol reactant, reaction time, temperature, catalyst concentration and water content in oil. The higher amount of methanol used and the content of free fatty acids in the oil, the higher yield of methyl esters and the smaller the free fatty acid content at the end of the reaction. The longer reaction time then the yield of methyl ester obtained large. The temperature of 60 ºC already provides adequate methyl ester yield. However, the excessive amount of catalyst does not increase with the actual recovery of methyl esters [12].

4.2. Transesterification

Transesterification is the reaction between triglycerides and alcohols to form alkyl esters (biodiesel) and glycerol. The reactions that occur are as follows in Figure 1:

![Figure 1. Reaction of transesterification [12].](image)

Transesterification reactions are very sensitive to FFA levels that present in vegetable oils. The permissible FFA levels in raw materials of vegetable oil are 1 - 2.5%. High fatty acid content can lead to side reactions between the basic catalyst and fatty acid that will form the soap or known as saponification reaction. The soap in the transesterification reaction can complicate the separation process of the product (alkyl ester) with the catalyst because the soap will diffuse the mixture during leaching. Meanwhile, the formed water may react with the alkyl ester through the hydrolysis reaction to form fatty acids. This reaction actually reduces the product [12].

5. Biodiesel

Biodiesel is chemically defined as a methyl ester derived from natural oils/fats, such as vegetable oils, animal fats or used cooking oil. Biodiesel belongs to renewable fuels because its raw materials come from natural materials that can be renewed. Biodiesel is biodegradable, non-toxic and essentially sulfur-free.

Methyl ester produced as a substitute for conventional petroleum fuels, so it must fulfill biodiesel standards. The characteristics of biodiesel generally include density, kinematic viscosity, cetane number, combustion calor, pour point, incandescent point, and cloud point. Biodiesel quality standards are not based on the basic materials used in producing biodiesel but based on the performance of biodiesel [13].
6. Methods

6.1. Materials
Materials used in this research are CPO, natural zeolite, N₂ gas, O₂ gas, and H₂ gas, HCl 6 N, AgNO₃ 0,1 N, NH₄Cl 1 N, aquadest, methanol (pa), ethanol 96%, La₂O₃, H₂SO₄ 1,2 N, NaOH 0,1 N, and KOH 0,1 N.
Tools that used is mortal porcelain, sieve -100 and +200 mesh, reactor, magnetic stirrer, heating mantel, filter paper, becker glass, oven, stirrer, hot plate, furnace tube, neraca analytic, tube and regulator gases N₂, O₂, H₂, condensor, thermometer, picnometer, viscometer Oswald, flask, volatile cup, buret, erlenmeyer, pipette, gas chromatography-mass spectroscopy (GC-MS) and SEM-EDX.

6.2. Making catalyst La/NZA
The activation of natural zeolite was carried out by immersing the finely ground zeolite (-200 + 100 mesh) in 500 ml of HCl 6 N solution for 30 min at 50 °C, and refluxing while stirring with speed 200 rpm. Then it was filtered and washed repeatedly until ion Cl⁻ was not detected by AgNO₃ solution, dried at 130 °C for 3 hours in the oven. The zeolite was soaked in a 500 ml NH₄Cl 1 N solution at 90 °C for 1 week while stirring, then filtered, washed, dried.

The solid La₂O₃ dissolved in 200 ml of aquades, then the 50 gram NZA mixed into La₂O₃ solution by stirring using a magnetic stirrer while heated at 60 °C for 3 hours, then filtered and washed repeatedly, dried at 120 °C on oven for 3 hours. The amount of metal variation that is 0, 1 and 3% w/w of NZA.

The result of impregnation is La/NZA catalyst must be calcinated at 500 °C in while a 400 ml of nitrogen gas was delivered, followed by oxidation at 400 °C using 400 ml / min of oxygen gas for 2 h and reduction at 400 °C using 400 hydrogen gas ml / min for 2 hours. The catalyst was characterized using SEM-EDX.

6.3. Biodiesel production
The CPO has a free fatty acid content above 2%, therefore the CPO should be esterified first using catalyst 1% H₂SO₄ 1,2 N. Transesterification process at temperature 60 °C, mole ratio oil : methanol 1 : 9, reaction time 60 minutes, with variation of catalyst weight 1, 2 and 3%. Then the product must be purified to obtain biodiesel and calculated yield.

7. Result and discussion

7.1. Characterization La/NZA catalyst
The dispersion of metals into zeolites can be determined by using SEM-EDX analysis. The result of SEM analysis can be seen in Figures 2, 3 and 4, EDX analysis can be seen in Table 1.
Figure 2. NZA catalyst surface morphology, (a) magnification 3,000 times and (b) magnification 15,000 times.

Figure 3. 1% La/NZA catalyst surface morphology, (a) magnification 3,000 times and (b) magnification 15,000 times.

Figure 4. 3% La/NZA catalyst surface morphology, (a) magnification 3,000 times and (b) magnification 15,000 times.

Figures 2, 3 and 4 shown the morphology surface of the catalyst having a characteristic crystal structure consisting of layered lamellar and there are many pores with different sizes. The crystal structure is distinctive and has many pores causing the catalyst surface area to increase. In Figures 3 and 4, there is a La metal attached to a zeolite surface with an irregular round or oval shape. This causes a morphological change in the catalyst to become more rough and there are many pores. The
porous catalyst surface structure is probably due to the calcination process at high temperatures. Calcination causes the structure on the catalyst surface to change due to the evaporation of some chemical and water compounds.

**Table 1. EDX analysis of catalysts**

| No. | Sample | NZA Composition (% weight) | 1% La/NZA Composition (% weight) | 3% La/NZA Composition (% weight) |
|-----|--------|-----------------------------|---------------------------------|---------------------------------|
| 1.  | C      | 15.94                       | 16.35                           | 13.25                           |
| 2.  | Na     | -                           | 0.83                            | -                               |
| 3.  | Al     | 8.16                        | 7.60                            | 3.60                            |
| 4.  | Si     | 74.99                       | 69.48                           | 79.33                           |
| 5.  | K      | 0.91                        | 2.13                            | 0.59                            |
| 6.  | Fe     | -                           | 0.86                            | 1.46                            |
| 7.  | Cu     | -                           | 1.02                            | -                               |
| 8.  | La     | -                           | 1.73                            | 1.77                            |
| 9.  | Si/Al Ratio | 9.19                     | 9.14                            | 22.04                           |

The results of the EDX analysis seen in Table 1 show the amount of composition of each compound or component present in the catalyst. In 1% La/NZA catalysts, impregnated La metals contained 1.73%, excess La is likely to be caused by La metal in the form of lanthanum oxide which has not been reduced by hydrogen. In the case of 3% La/NZA catalysts of impregnated La/NZA as much as 1.77%, the decrease of La content in the catalyst is probably due to the less homogeneous mixing of the impregnation process so that only a few of the La metals are impregnated into NZA and the rest soluble with aquades and when separation of the catalyst in the form of solids with liquid (aquades).

The activity and selectivity of the catalyst can be seen from the Si/Al ratio contained in the catalyst. The Si/Al ratio is very influential because if fewer Al atoms means less negative charge on the zeolite, so there are fewer balancing cations available. Zeolite with high Si compositions have high electronegativity and affinity for hydrocarbons, more stable in strong acid environments, where acidity of catalysts increases. As the Si/Al ratio increases, the cracked methyl esters become short-chain hydrocarbons into more.

7.2. **Biodiesel characterization**

7.2.1. *The physical analysis of biodiesel*

The physical properties analysis of biodiesel can be seen in Table 2. Table 2 shown the analysis of all biodiesel products from this research and biodiesel physical properties based on SNI 04-7128-2015.
Table 2. Physical characterization of biodiesel

| Catalyst   | Weight | Density at 40ºC (kg/m³) | Viscosity at 40ºC (cSt) | Acid number (mg-KOH/g) | Flash point (ºC) | Yield (%) |
|------------|--------|--------------------------|-------------------------|------------------------|-----------------|-----------|
| NZA        | 1%     | 873                      | 5,210                   | 0,736                  | 125             | 82,87     |
|            | 2%     | 881                      | 5,121                   | 0,771                  | 127             | 83,87     |
|            | 3%     | 865                      | 4,894                   | 0,701                  | 124             | 85,25     |
| 1%La/NZA   | 1%     | 875                      | 5,413                   | 0,701                  | 124             | 84,13     |
|            | 2%     | 868                      | 5,120                   | 0,771                  | 128             | 84,25     |
|            | 3%     | 874                      | 5,082                   | 0,701                  | 125             | 84,50     |
| 3%La/NZA   | 1%     | 857                      | 5,391                   | 0,718                  | 125             | 85,37     |
|            | 2%     | 868                      | 5,049                   | 0,800                  | 128             | 84,63     |
|            | 3%     | 867                      | 4,979                   | 0,736                  | 126             | 82,00     |
| SNI 04-7128-2015 | 850 – 890 | 2,3 – 6,0 | Maks. 0,8 | Min. 100 |

Table 2. shown that the difference in yield of biodiesel is not significant, this is caused by Si/Al ratio of catalysts not much different. The biodiesel density of the research results is in the range of values based on SNI. The biodiesel density value is effected by the molecular weight of the components contained in the biodiesel. Increasing the weight of components make increasing the density. Smaller density is better to use as alternative biofuel.

The biodiesel viscosity obtained from this research is within the range of 2006 biodiesel SNI. High viscosity causes difficult biodiesel to flow, so will increasing the cost of piping installation to distribute biodiesel. The high viscosity of biodiesel is effected by the raw materials and the transesterification process temperature does not constant.

The acid number of biodiesel has a value above its maximum standard of 0.5. The acid number expresses the free fatty acid content contained in the biodiesel, the higher the acid number the more free fatty acid content. Acid numbers determine the quality of biodiesel is good or not. High acid numbers may be caused by CPO feedstock having a high FFA that is 5.472% and possibly because there is a few amount of water in biodiesel.

Flash point indicates high low volatility and the ability to burn from a fuel. The biodiesel flash point of this research has met the quality standard based on SNI that has a value above 100ºC. It states that biodiesel is at a safe limit to fire hazards during storage and during distribution. The highest flash point is 128ºC and lowest is 124ºC.

7.2.2 The chemical analysis of biodiesel

Analysis of the chemical properties of biodiesel was tested using GC - MS. Biodiesel analyzed is biodiesel with highest yield that is on the use of 3% catalyst La/NZA 1%. GC-MS analysis aims to determine the chemical compounds present in biodiesel. The result of GC-MS biodiesel analysis can be seen in Figure 5.
Figure 5. Comparison of GC-MS CPO analysis results with biodiesel.

CPO chromatogram and biodiesel on 3% La/NZA catalysts showed a significant difference. Where top five peaks in biodiesel are, first there is methyl palmitate with area of 28.57%, second methyl oleate 28.85%, 1,3-dipalmitin 6.7%, second methyl oleate 10.93% and lycopersen 9.04 %. From the chromatogram, the highest peak compounds are not all methyl esters, there are 1,3-dipalmitin glycerin and lycopersen which is a dye (carotenoid) that gives the orange to red color of the CPO. From these results it can be stated that the biodiesel obtained still needs to be purified to separate glycerin and lycopersen.

The ability of the catalyst to produce the desired product (selectivity) is affected by pressure, reaction temperature, reactant composition, pore size distribution and surface area. Glycerin and lycopersen formed may be caused by the temperature of the reaction is not constant, because when the research temperature reaction is measured only with a thermometer, sometimes up and down 1 – 3 °C. The second is probably caused by the poor pore size distribution of the catalyst, so the impregnated metals do not spread throughout the catalyst surface. Based on the discussion it can be concluded that the manufacture of biodiesel from CPO using La/NZA catalyst has produced good biodiesel.

8. Conclusions
The conclusions of this research is biodiesel from CPO can be produced using La/NZA catalyst. The best catalyst was 3% La/NZA with 1% catalyst, the highest yield 85.37%. The result is biodiesel has met the quality standard of biodiesel based on SNI 04-1782-2015.
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