Transesterification Condition of Crude Palm Oil to Biodiesel Using Solid Catalyst Zeolite/NaOH

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Abstract. The use of NaOH as a catalyst for biodiesel production has long been used and provides high conversion conversions. Homogeneous NaOH phase during the transesterification reaction causes soap to form at the end of the process. Soap is diseparasi from biodiesel by washing and decantation techniques. The presence of soap can reduce the quality of biodiesel, especially at the flash point of biodiesel. Heterogeneous catalyst zeolite / NaOH is synthesized from natural zeolite and NaOH through the impregnation method. Natural zeolite is contained in natural rock obtained from Ujong Pancu, Aceh Besar. The synthesis of natural zeolite catalyst was initiated by activating zeolite powder with 4 M HCl for 10 hours at 90oC. Activated zeolite was impregnated using 2.5% NaOH at a ratio of 1: 2 (w / v) at 90oC for 2 hours. Application of zeolite / NaOH in transesterification reaction using crude palm oil off grade. The results showed that the use of zeolite / NaOH can prevent the formation of soap with characteristics that have met SNI 04-7182-2006 standards.

1. Introduction
To deal with the fossil fuel crisis, biodiesel has been recognized as an alternative to replace the role of petroleum diesel as a fuel. Fossil fuels have caused excessive emissions resulting in global warming, severe weather changes, which can threaten the future of humanity. Compared to fossil fuels, biodiesel is superior because it can reduce environmental pollution and global warming, making it even more existent among many researchers who want to get biodiesel with high ester content and according to SNI standards.
Biodiesel can be derived from vegetable oils, animal fats, microalgae, and is biodegradable, renewable and non-toxic (Wu et al, 2016). Biodiesel is formed by binding to the alkyl group from alcohol, usually the alkyl used in the form of methyl is the first choice because of its reactive nature.
In the process of biodiesel synthesis, a catalyst is used to accelerate the reaction rate of methyl ester formation. There are 2 types of catalysts, namely homogeneous catalysts and heterogeneous catalysts. According to Pena et al (2013) base catalysts are usually preferred over acid catalysts, because of their ability to catalyze transesterification reactions at relatively low reaction temperatures and high reaction rates which are about 4000 times faster than acidic catalyst reaction rates. High biodiesel yields can also be achieved at short reaction times, and most importantly this catalyst is cheap and easy to obtain (Mansir et all, 2017). One type of homogeneous base catalyst is NaOH.
NaOH as a homogeneous base catalyst itself is widely used because of its reactive nature, but at the end of the process a product separation process is needed. In addition it requires the neutralization and separation of the final reaction mixture which leads to a series of environmental problems related to the use of large amounts of water and energy. For this reason, the role of heterogeneous catalysts as a substitute for homogeneous catalysts is needed, by using heterogeneous catalysts the product separation process is easier to do. In addition, heterogeneous catalysts have several advantages including easier
catalyst separation by physical methods, such as settling and centrifugation, and environmental pollutant reduction (Pena et al, 2013). Examples of heterogeneous catalysts that are commonly used are zeolites.

Zeolites are three-dimensional, crystalline solids, made from tetrahedral that are interrelated with alumina and silica, so they are widely used in various applications such as adsorbents, catalysts, solar energy storage, thermal adsorption storage and in the pharmaceutical industry because of their unique porous properties (Soonmin, 2017).

Zeolite as a catalyst has been recognized for its superiority, as evidenced by the large number of researchers involving zeolite as a catalyst to accelerate the reaction rate, recent studies such as those conducted by Zhang et al (2017) who analyzed the zeolite structure of fatty acid methyl esters (FAME) and Lawan et al (2019) which uses a CaO / Zeolite catalyst in biodiesel production.

Both homogeneous NaOH catalysts and zeolite heterogeneous catalysts, both have advantages as catalysts because of their nature. Therefore, in this study the biodiesel synthesis process was carried out using a zeolite / NaOH catalyst, which was a catalyst synthesized from zeolites impregnated with NaOH. Thus it is expected that the rate of formation of biodiesel can take place quickly due to the presence of zeolite / NaOH catalysts containing reactive NaOH, as well as the formation of soap and facilitate the separation of catalysts at the end of the process, to obtain biodiesel with high ester content and according to SNI 04-7182-2006 standards.

2. Method

2.1 Raw Material
The raw materials used are crude palm oil (CPO) as the triglyceride source, Methanol (p.a), zeolite/NaOH as the heterogeneous catalyst, H2SO4 98%, NaOH (p.a), hexane, ethanol. CPO as the main ingredient analyzed free fatty acid to know the initial free fatty acid content.

2.2 Esterification
At first, crude palm oil (CPO) was performed free fatty acid (FFA) analysis to determine the free fatty acid content before esterification reaction was performed. CPO is reacted with methanol and an H2SO4 as the acid catalyst. It is added with a ratio of 15% (w/v). The esterification reaction is pre-treatment process for CPO to reduce free fatty acid (FFA). The reaction lasts for 120 minutes, at temperature 65°C and 400 rpm on stirring speed (scale of 1000 rpm). If CPO as triglyceride source contains many FFA, it will interfere the formation of ester bonds with methanol.

2.3 Transesterification
The transesterification reaction is also called alcoholization, is the conversion stage of triglyceride (vegetable oil) to alkyl ester, reacted with the alcohol to produce a by-product of glycerol. The CPO from esterification reaction is referred to crude ester. It is used as a feedstock in the transesterification reaction. crude ester is reacted with methanol with the addition of zeolite/NaOH heterogeneous catalyst, temperature, mole ratio and reaction time according to the Taguchi design Reactan are stirring at speed of 400 rpm (scale 1000 rpm).

The reaction temperature is adjusted to the boiling point of methanol. After the reaction time is reached, the transesterification reaction is stopped. Crude products are separated by separating funnels using the decantation method. Biodiesel is in the upper layer, and glycerol is in the lower layer.

Biodiesel which has been separated from glycerol is purified using aquadest to remove the formed side products. Crude biodiesel is then distilled to take up excess methanol. Distillation is carried out at a temperature of 68°C. Pure biodiesel is then carried out a final ALB analysis to determine the decrease in ALB content.
3. Characteristic analysis

Biodiesel products with the highest ester content, characteristics were analyzed in the form of density, viscosity, acid number, flash point. The results of product analysis are adjusted to SNI 04-7182-2006 standards.

4. Result and Discussion

Biodiesel production uses a heterogeneous zeolite/NaOH catalyst with a catalyst ratio of 0.5% -2.5% (w/w). The use of zeolite / NaOH allows the recycle of the catalyst because the catalyst is not homogeneous in the mixture so that it is easily separated at the time of purification. From the results of the study (Figure 1 and 2), obtained the highest ester content at a catalyst ratio of 2.5% (w/w) of 63.51%.

The use of zeolite/NaOH catalyst also does not result in the formation of byproducts in the form of soap in large quantities, because the core of NaOH has been trapped in the zeolite framework so that it does not form a saponification reaction with free fatty acids in triglycerides (CPO).

![Figure 1. Correlation of Zeolite / NaOH Catalyst Ratio to Ester Content](image1)

| Retention Time | Komponen   | %     |
|---------------|------------|-------|
| 19,2          | Trigliserida | 9.89  |
| 11,06         | Monogliserida | 15.2  |
| 15,4          | Digliserida  | 11.2  |
| 5,14          | Ester       | 63.51 |

![Figure 2. Gas Chromatography Zeolite / NaOH Catalyst Biodiesel Product 2.5% (w/w)](image2)
5. Product Characterization

Product characterization aims to determine the extent to which biodiesel products exhibit properties as alternative fuels. Products containing large quantities of esters have properties close to or in accordance with biodiesel standards. The characteristics tested include acid number, density, kinematic viscosity, no flame, water content, total glycerol which is considered to have a major influence to determine the quality of a body cell product. In this research, the product with the highest ester content to be determined for the analysis of the characteristics includes:

| Parameter | Biodiesel Zeolite/NaOH | Standard SNI 04-7182-2006 |
|-----------|------------------------|--------------------------|
| Acid Value | 0.4                    | Maks 0.8 mg KOH/gL       |
| Density   | 0.860                  | 0.850-0.890 kg/liter     |
| Kinematic Viscosity | 3.7               | 2.3-6.0 mm²/s           |
| Flash Point | 110                 | Min 100°C               |
| Water Content | 0.01               | Maks 0.02%              |
| Glycerol Total | 0.24              | Maks 0.24%              |

The Table 1 shows that the characteristics of zeolite / NaOH biodiesel meet SNI 04-7182-2006 standards.

6. Conclusion and Suggestions

Based on the results of gas chromatography analysis of biodiesel products with zeolite/NaOH catalysts, it is recommended to increase the zeolite/NaOH catalyst ratio above 2.5% (w/w) to improve the alkaline atmosphere in the reaction mixture system.

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