Synthesis of biodiesel using local natural zeolite as heterogeneous anion exchange catalyst

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Abstract. Production of biodiesel using homogen catalyst: alkaline catalysts, acid catalysts, biocatalysts, and supercritical methanol are very inefficient, because these catalysts have a very high cost production of biodiesel and non-ecofriendly. The heterogeneous catalyst is then used to avoid adverse reaction of biodiesel production. The heterogeneous catalysts used is ion exchanger using natural zeolit catalysts bayah banten (ZABB) and macroporous lewatit that can be used to produce biodiesel in the solid phase so that the separation is easier and can be used repeatedly. The results of biodiesel reach its optimum in engineering ion exchange catalyst natural zeolit bayah and macroporous lewatit which has been impregnated and calcinated at temperature 60°C at reaction time 2 hours, are 94.8% and 95.24%, using 100 gr.KOH/100 mL Aquadest.

1. Introduction
Fuel consumption in Indonesia is covering the fields of transport, industry and power plants. Currently the number of user equipment and diesel vehicles has been increased. In line with this increasing number, the need for fuel for diesel engines, namely diesel also increased. Another problem that arises from the use of diesel fuel is environmental pollution. Alternative energy source that produce a more environmentally friendly diesel fuel emissions and does not add to the accumulation of CO₂ in the atmosphere is required, thus reducing the effects of global warming.

Biodiesel is produced through the transesterification of vegetable oils, animal fats or waste oil with methanol using a catalyst to produce fatty acid methyl ester (FAME). Biodiesel can be used as additives in petroleum fuels, mainly for the petrodiesel (PD), known as solar, generally used by 20% biodiesel in diesel mixture known as (B20). The advantage of Biodiesel compared to petrodiesel (PD) in reducing exhaust emissions, could be described, as a high flash point, lubrication large and renewable sources. Biodiesel has a higher oxygen content than petrodiesel (PD), and when it is used in diesel engines showed a reduction in particulate emissions, carbon monoxide (CO), sulfur, polyaromatic compound, hydrocarbons (HC), smoke and noise (1).

Biodiesel in the future will be produced from raw materials that can be refurbished as oils derived from plants and animal fat so that the price of biodiesel will be competitive with petroleum.

The process of making biodiesel using homogeneous catalyst on vegetable oil have limitations and problems of both catalysts alkali, acid, lipase and supercritical including the removal of free fatty acid content, the water content in the reaction mixture, the need for downstream the processing and higher operating costs of biodiesel production.

These problems can be minimized by the use of heterogeneous catalysts in the transesterification process. The use of heterogeneous catalysts is more economical and has several advantages such as non-corrosive, environmentally friendly, easily separated from the melting product, activity and selectivity (2). Heterogeneous catalysts show high potential, strong and durable, able to free fatty acids up to 40% (3).
The use of heterogeneous catalysts is an alternative substitute of the use of homogeneous catalysts, and it is easier to separate and reuse. (4) (5) produces continuous biodiesel with ion-exchange cation acid and ion-exchange cations base by conversion is 71% with molar ratio 1:1 between jatropha oil and methanol. (6) Transesterification of biodiesel from palm oil by using KOH / zeolite as a heterogeneous catalyst at various concentrations of NaOH and reaction time to obtain maximum yield of biodiesel. The maximum yield of biodiesel produced is 95.09% at impregnation of 100 grams KOH in 100 ml of aquaest within 2 hours at 60 °C and the ratio of palm oil and methanol (1: 7), the amount of catalyst used 3% of palm oil. (7) The catalyst used was made by impregnating alumina with KI 35% for 3 hours then dried at 393 K for 16 hours. (KI / Al2O3) solids were calcined at 773 K for 3 hours, the weight of the catalyst used ranged from 1- 5% weight. Biodiesel yield at optimum is 95.2%. (3) used a heterogeneous catalyst to make biodiesel from rice bran oil with free fatty acid content (FFA) (20 - 50%). The catalyst used was Asamchlorosulfonate-Circonia (HCISO3-ZrO2). The conversion result is 92% at 120 °C, molar ratio of methanol / oil (12; 1), time 12 hours and 6% by weight of catalyst. (8) Al2O3 was modified with MgZnO as a catalyst (MgZnAlO) and activated to produce biodiesel. Effect of parameters such as molar ratio of methanol/oil, 3.32 weight catalyst, reaction time of 6 hours and operating temperature of 182 °C. Catalysts can be reused for five cycles without reactivation. The resulting biodiesel conversion is 98%. (9) Transesterification of biodiesel from palm oil by using KOH/modernit as a heterogeneous catalyst at various concentrations of NaOH and reaction time to obtain maximum yield of biodiesel. The maximum yield of biodiesel produced is 96.7%. Those researches have successfully improve the surface area of contact and the acidity increased leading to activation as a catalyst of solute is increased.

This research focused on the modification process of anion exchanger using a natural zeolit bayah banten with KOH impregnation method that can be used as a catalyst in the manufacture of biodiesel by heterogeneous catalyst transesterification using vegetable oil. As comparison, Lewatite macroporous also with the same way. Effect of base concentration (KOH) and the reaction conditions in the acquisition of biodiesel yield is observed on both heterogeneous catalysts.

2. Materials and method

2.1 Materials
Zeolite obtained from natural Bayah Banten that has been crushed by using crusher with a particle size <50 mesh is prior to use. Lewatit was purchased from Sigma-Aldrich Chemical Co., Lewatit MR64 Form Chloride Anion Exchange resin cross linked, Polystyrene matrix, free base, medium base macroporous. Vegetable oil obtained from restaurants at Cilegon after three-time usage. KOH Made in Germany with index-No.019-002-00-8, Brand KGA, 6427 / Darmstadt Germany, Tel +49 (6) 615172-2440 Millipore EMD Corporation. Methanol for analysis made in German.

2.2. Method
The research methodology focused on ion exchange on as heterogeneous catalysts for biodiesel synthesis to obtain optimal results with variation of time, the catalyst and temperature by first activating anion exchange, the Natural zeolit bayah Banten (ZABBrht) and Lewatit mesoporous. The research is conducted at the Laboratory of Bioprocess Engineering Department of Chemical Engineering, Faculty of Engineering, University of Indonesia, Campus UI Depok 16424.

3. Catalyst preparation anion exchanger (zeolite and mesoporous Lewatit)
3.1. Zeolit
Preparation of Zeolit is done to make the zeolite has the ability as a base catalyst, while the steps are as follows, taken from the zeolite used natural zeolite bayah banten (ZABBbrht) offerings through the stages of destruction, then screening to obtain a desired zeolite size in accordance with the size of its diameter. Activation of natural zeolite bayah banten (ZABBbrht) is done to modify the structure of the
framework or the non-zeolite framework with the aim to enhance its power. Zeolite activation is done by physically and chemically. Physically aim is to evaporate the water caught in the pores of the Zeolite’s structure, and the process is conducted at a temperature 110 °C so that the surface area of the pores of the crystals increases for approximately 24 hours. Chemical activation is done by using an alkaline solution KOH aims to clean the surface of the pores, removing impurities compounds and rearrange the location of atoms exchange. The impregnation process is carried out by using a solution of KOH / 100mL of distilled water to the zeolite at a temperature of 60 °C, for 2 hours and then the mixture is placed in a preheated oven at 60 °C for 24 hours and separated by a vacuum pump filter with filter paper, dry it in an oven temperature of 110 °C for 24 hours and Zeolite calcination to keep the catalyst obtained to be relatively stable at high temperatures. This process is done by heated the zeolite at a temperature of 450°C. Calcination time is calculated starting from temperature 450 °C for 4 hours. The catalyst is then cooled and ready to use.

3.2. Lewatit Mesoporous
Preparation Lewatit is made to make Lewatit have the ability as a basic catalyst. The steps are as follows, the catalyst is kept at a temperature of 110 °C for approximately 24 hours. Then, the process of impregnation is carried out by using a solution of KOH / 100mL of distilled water to Lewatit at a temperature of 60 °C, for 2 hours and then the mixture is placed in a preheated oven at 60 °C for 24 hours and separated by a vacuum pump filter with filter paper, dry it in an oven temperature of 110 °C for 24 hours for 24 hours. The catalyst is then cooled and ready to use.

4. Results and discussion

4.1. The effect of various grams of KOH / 100mL towards percent yield of biodiesel

![Figure 1](image.png)

**Figure 1.** The Effect of various grams of KOH / 100 mL towards percent yield of biodiesel.

Experiments were performed to determine the effect of various gram KOH / 100ml zeolite to the acquisition percent yield biodiesel using used cooking oil. The optimum conditions of biodiesel is reached when using the ratio of reactants to methanol (1: 7) (Kusuma at al, 2013) to move to the right reaction and collide wider.

Zeolite Optimum condition was achieved in 75 grams of KOH / 100 mL with a percent yield 92.28%, is caused by many methoxide trapped in zeolites. Lewatit optimum condition was achieved in
50 grams of KOH / 100 ml of distilled water with 98.88% percent biodiesel yield caused by the amount of metal oxides that react.

4.2. The effect of various Gram KOH / 100mL towards the product density

![Graph of density vs. KOH concentration](image)

**Figure 2.** The effect of various Gram KOH / 100 mL towards the product density.

Figure 2 in zeolite chart showed that the higher use of gram KOH / 100mL resulted the lower the density produced. The density will affect the quality of biodiesel produced, the smaller the value the greater density caloric value.

On the use of catalysts Lewatit optimum conditions achieved with the use of a solution of 100 g KOH / 100mL distilled water. All the conditions included in the density of standard biodiesel.

4.3. The effect of various Gram KOH / 100mL towards biodiesel viscosity

![Graph of viscosity vs. KOH concentration](image)

**Figure 3.** The effect of various gram KOH / 100mL towards biodiesel viscosity.
The more catalysts used the lower the viscosity of the resulting, it indicates that the more sodium methoxide is reacting with cooking oil so that the process of cracking the larger chains of fat is successful and results to the lower viscosity grades. Low viscosity grades of biodiesel will be more easily flow in order to improve the performance of the engine combustion system.

5. Conclusions
Based on the research that has been done, it can be concluded that biodiesel production using natural zeolite bayah banten (ZABBrht) as heterogeneous catalysts can be carried out with specific preparation and treatment and the biodiesel produced meets the Indonesia National Standard (SNI).

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