

# Estimating the opportunities of ester content improvement through variation of NaOH, KI And KIO<sub>3</sub> developed impregnators on activated natural zeolite catalyst for methyl ester synthesis

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**Abstract.** The Content of esters are the number of compositions of esters formed after the esterification and / or when transesterification reaction takes place. Esters are formed by breaking up the alkyl acid carboxylic group of fatty acids or triglycerides which react with methyl groups from methanol. To increase the reaction rate, heterogeneous catalysts were synthesized using impregnators NaOH, KI and KIO<sub>3</sub>. The impregnator is carried out in the framework of natural zeolite with a concentration of 2.5% (w/ v). The zeolite framework was previously activated using 6M HCl solution for 10 hours at a temperature of 90°C. To strengthen the impregnator bond on a heterogeneous zeolite catalyst, calcination was carried out at a temperature of 600°C for 4 hours. Heterogeneous catalysts were tested on biodiesel production using a transesterification reaction. The transesterification reaction was carried out at a temperature of 65°C for 2 hours based on crude ester with 5%-10% (w/w) heterogeneous zeolite catalyst ratio shows the percentage decrease in free fatty acid content of 74.05% for zeolite/NaOH, 75.01% for zeolite/KIO<sub>3</sub> and 75.77% for zeolite/KI. Based on the results of gas chromatography analysis, it was found that zeolite/KI catalysts of 77.1591.86%.

## 1. Introduction

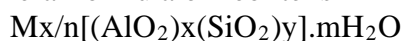
The need for reliable fuel supplies increases because of the increase in the human population and the development of developing economies in developing and developed countries (Hardy, 2015). While the availability of fuel that continues to decrease creates various innovations and technologies to overcome this. One of the innovations carried out was to shift the use of homogeneous catalysts to the methyl ester transesterification reaction into heterogeneous catalysts. This innovation can reduce the problem of separating methyl esters from soap byproducts that use water that is quite high. Heterogeneous catalysts can be synthesized from natural zeolites. According to (Weitkamp, 2000), zeolite is a material that has a wide contact surface, so it is widely used in water treatment and purification, humidity control and heterogeneous catalysts. Although zeolite has natural ability as a catalyst, treatment can increase the performance of zeolites as a catalyst. catalyst. One treatment that is carried out is activation and impregnation.

The name zeolite comes from two Greek words, zein which means boiling and lithos which means rock. It is called because this mineral has a boiling or expanding nature when heated. Where water in zeolite cavities will boil when heated at 100°C. Zeolite was first

discovered by Freiherr Axel Cronstedt, a Swedish mineralogy expert in 1756. Zeolite, according to its formation process is divided into two kinds, namely: natural zeolite (natural zeolite) and zeolite synthetic (synthetic zeolite).

While based on the size of the pores, zeolite can be classified into 3 groups, namely: zeolite with small pore (small pore zeolite), zeolite with medium pore (medium pore zeolite), and zeolite with large pore (large pore zeolite). As a catalyst, zeolite shows good performance because it has a large pore and a maximum surface. Zeolite has a hollow structure and usually this cavity is filled with water and cations that can be exchanged and have a certain pore size. The work of zeolite as a catalyst can be enlarged by activating zeolite first. Zeolite minerals are found in nature as volcanic sedimentary rocks. Zeolite's main constituents are modernit and klipnotilonit in a variety of compositions.

The general formula of zeolite is



$M_x/n$  = charged cations

[ ] = aluminosilicate frame

X = amount of  $AlO_4$

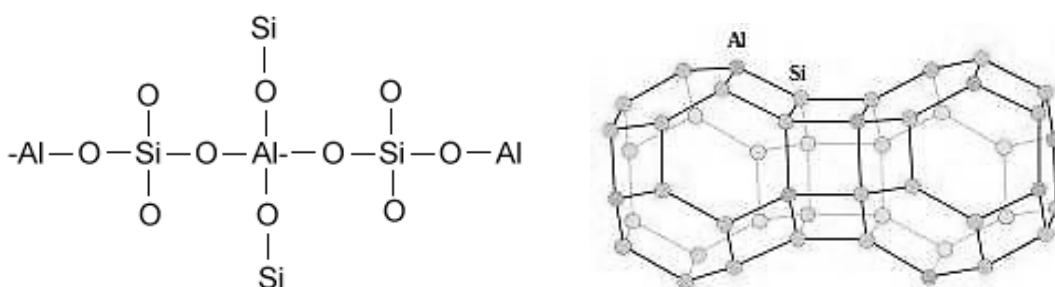
Y = amount of  $SiO_4$ , yx

Z = amount of  $H_2O$

The zeolite framework is a cavity containing cation  $M^+$  as a cation that contributes to  $AlO_4$  charge.

Zeolite characters include:

1. Physical forms can be pellets, granules, or powders. This physical form is very much required in accordance with the reaction system that will be carried out. The shape of the pellet which has a general shape of the cylinder and has a relatively large dimension will be correct for the reactor which involves the vapor phase reaction.
2. Mechanical properties are resistant to wear, hard, not easily broken, pellets can be made are important mechanical factors, especially if the reaction is carried out in a reactor involving steam or gas at high temperatures and pressures.



**Figure 1.** Zeolite Structure

The power of zeolite as a catalyst can be enlarged by activating zeolite first. Transesterification reaction is an irreversible reaction, therefore excess alcohol is used to shift the equilibrium towards the product, the oil or fat used is totally converted to form a methyl ester. The structure of zeolite (Figure 1) has been known to various kinds, but in general the structure is formed from the primary unit, in the form of tetrahedral which then becomes a secondary unit of polyhedral and forms polyhydral and finally a zeolite structure unit.

The typical structure of zeolite, which is mostly a canal and pore, causes zeolite to have a large surface area. This situation can be explained that each pore and inner canal and between crystals are considered cylindrical, then the total surface area of zeolite is the accumulation of the pore surface area (wall) and zeolite constituent canals. The more number of pores, the greater the total surface area of zeolite. zeolite's internal surface area can reach tens or even hundreds of times greater than the outer surface area. This large surface area is very beneficial in utilizing zeolite either as an adsorbent or as a heterogeneous catalyst.

Natural zeolite activation can be done both physically and chemically. Physical activation is done by reducing grain size, sieving, and heating at high temperatures, the aim is to remove organic impurities, enlarge the pore, and expand the surface. Chemical activation is done by adding acid which results in the exchange of  $H^+$  ions. (Lestari, 2010).

This series of physical and chemical activation mechanisms will eliminate impurities in the zeolite framework. The zeolite framework which has been empty of impurities can be filled by the active compound of the impregnator. This impregnator is inserted into the zeolite frame by impregnation. Impregnation is attaching the active core of the impregnator compound into the zeolite frame at a small concentration. According to (Nurhayati, 2014), impregnation is the development of a metal mixture into the support material to produce a bimetal catalyst. In this study, the impregnator variation are KI,  $KIO_3$  and NaOH to determine the most selective type of impregnator on the zeolite framework for the synthesis of methyl esters.

## **2. Method**

### **Material**

Zeolites come from Ujung Pancu, Aceh Besar in the form of bluish-green chunks of rock. HCl 6 M as an activator and impregnator of NaOH, KI and  $KIO_3$  as impregnators. The zeolite impregnation catalyst was applied to the transesterification reaction using raw ester,  $CH_3OH$  as an alkyl source

### **Apparatus**

Activation is done using erlenmeyer, spiral condenser for circulating cooling water, thermometer and heater. Transesterification reaction uses a three neck flask, condenser, agitator and stirring motor, thermometer, heater

### **Synthesis of Zeolite Catalysts**

#### **Activation of Zeolite**

The raw material for zeolite originates from the location of Ujung Pancu, Aceh Besar with the characteristics of bluish-green boulders. These zeolite rocks are destroyed and sifted to 80/100 mesh. Zeolite rock powder is then activated with 4 N HCl solution for 10 hours at  $90^\circ C$ . After that, activated zeolite was separated from HCl solution by filtration method and washed with aquadest to pH 6-7. Activated zeolite was then dried at  $105^\circ C$  Activation using HCl aims to degrade the impurities contained in zeolite rocks. The degradation of impurities is indicated by changes in the color of the mixture from green to yellow



**Figure 2.** Zeolite Color Changes During Activation

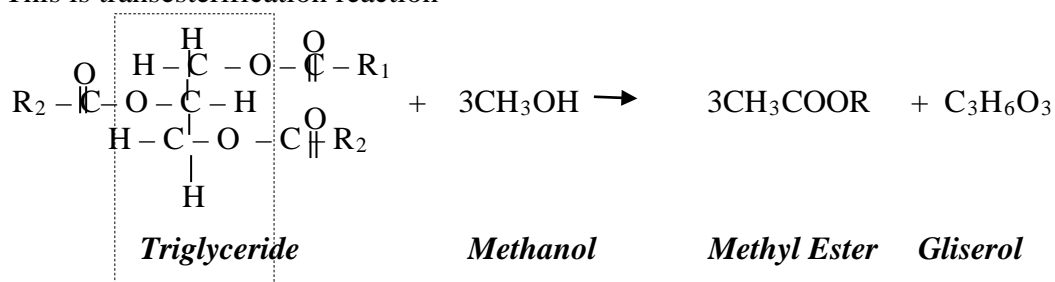
### The Development of Impregnator (Impregnation)

Activated zeolite powder mixed with impregnator solution namely NaOH, KI, KIO<sub>3</sub> on separate erlenmeyer with a concentration of 2.5%. Then the mixture was refluxed for 2 hours at a temperature of 90°C to develop the impregnator into the zeolite framework. After the reaction time is reached, the zeolite is separated from the impregnator solution and calcined at a temperature of 600°C for 4 hours to bind the active nucleus to the zeolite. Calcination aims to strengthen the pore bond between zeolite and impregnator compounds. The different types of impregnator compounds used, give different colors to the impregnated zeolite catalyst produced. The zeolite/NaOH catalyst in dark gray color is caused by the presence of Na metal impregnated in the zeolite pore. The zeolite / KIO<sub>3</sub> catalyst is yellowish white which is caused by the presence of an oxidizing agent that is trapped in the zeolite pore, while zeolite / KI is white with a powder-like texture. This is due to the fact that the compound is impregnated into the zeolite pore.

### Methyl Ester Synthesis

The embedded zeolite catalyst was applied in the synthesis of methyl esters using a transesterification reaction. The raw material is the crude ester which was obtained from the esterification stage. The content of Esters (in the form of methyl esters) only reached 50.67% with FFA content of 40.76 gr KOH/ml. When compared with the standards of SNI 01-7281-2006, esters obtained did not meet the standards when used as motor fuel. Crude ester is reacted to the next stage using a transesterification reaction using an embedded zeolite catalyst with a ratio of 10% (w/w). This aims to determine the chance of increasing the content ester in the methyl ester compound using a heterogeneous catalyst, while getting the most selective impregnator to be used in the synthesis of methyl esters. The impregnator performance was measured by the shift in free fatty acids for 2 hours of reaction and confirmed by gas chromatography to find out the ester content at the end of the reaction. Methyl esters are separated from glycerol by-products before analysis.

This is transesterification reaction

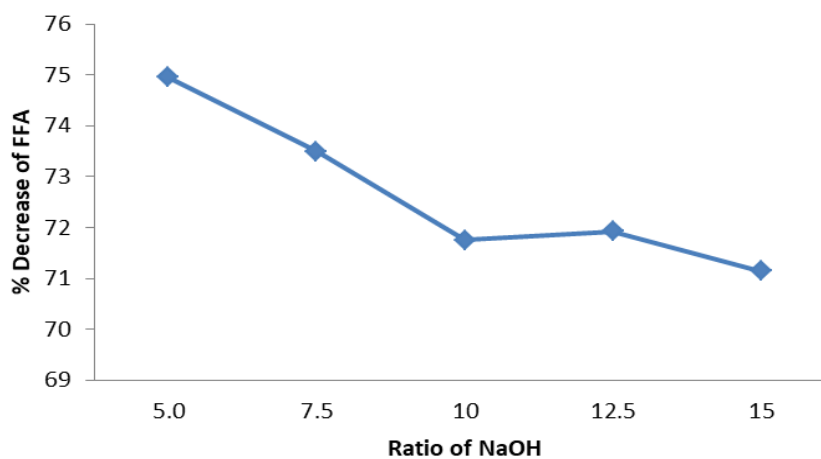


### 3. Results and Discussion

#### The Effect of NaOH Performance on Activated Zeolite Catalysts to Decreased FFA

The performance of NaOH in activated natural zeolite Ujung Pancu is based on the fact that NaOH compounds are the most reactive metal hydroxides compared to other base compounds. In addition, NaOH has been tested as a homogeneous catalyst in the synthesis of methyl esters and provides the acquisition of content esters that match SNI 01-7182-2006 standards. (Kurniasih, 2012). But the use of alkaline metal has a disadvantage, because along the transesterification reaction takes place, the saponification reaction between free fatty acids from triglycerides reacts with NaOH. This condition is overcome by carrying out NaOH active nucleid in the zeolite framework so as to prevent the occurrence of free fatty acid saponification reactions. NaOH metal is applied to the zeolite framework by impregnation method with a concentration of 2.5% NaOH solution. Impregnation was carried out by refluxing zeolite and NaOH solution at a temperature of 90°C for 2 hours. The advantage of the impregnation method is that it can use an impregnator compound in a low concentration. The embedded zeolite/NaOH catalyst is calcined at a temperature of 600°C for 4 hours. From the research results obtained, zeolite/NaOH catalysts have a harder texture than activated zeolite and the colour are dark gray.

Zeolite/NaOH catalyst was applied to the synthesis of methyl esters with a ratio of 5%-10% (w/w) from the raw material, with reaction conditions of 65°C and 65 ml of methanol as a methyl source. The opportunity to increase the content of esters is measured by decreasing free fatty acid (FFA) from the beginning of the reaction to the end of the reaction. The decrease in free fatty acids indicates that the fatty acids from the raw material have bind to the methyl group of methanol so that there is no free fatty acid. The reasearch show that zeolite/NaOH can decreased the FFA to 74.05%.

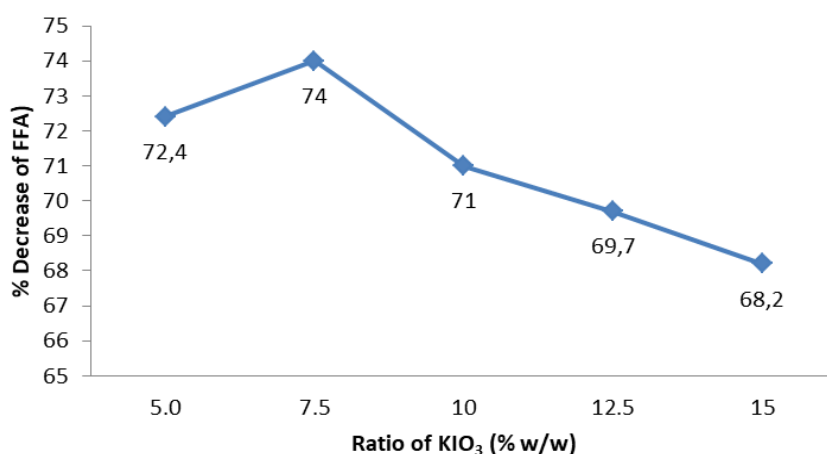


**Figure 3.** Effect of Zeolite/ NaOH against Decreasing FFA

#### The Effect of KIO<sub>3</sub> Performance on Activated Zeolite Catalysts to Decreased FFA

The second impregnator is KIO<sub>3</sub> which has radioactive properties. KIO<sub>3</sub> is applied to the zeolite framework at the same concentration of 2.5%. From the results of the study it was revealed that the zeolite / KIO<sub>3</sub> catalyst produced had a very fragile structure (scattered), and the colour is brownish yellow. When applied to the synthesis of methyl esters, zeolite/KIO<sub>3</sub> was able to increase the FFA to 75.01%. But when compared with the previous impregnator, the increase in content esters was higher using embedded zeolite/NaOH.

Transesterification for the synthesis of methyl ester was carried out at 65°C temperature and constant stirring of 400 rpm (1.000 rpm scale) for 2 hours. When zeolite /  $\text{KIO}_3$  is applied as a catalyst, the mixed system forms a kind of sludge. This is due to the fragile texture of zeolite/ $\text{KIO}_3$  and changes to very smooth after the impregnation process. The sludge that is formed affects the homogeneity of the mixture so that it is difficult to reduce equilibrium towards the product. The impregnator selectivity was measured based on the decrease in FFA during transesterification. Zeolite/ $\text{KIO}_3$  showed low selectivity, compared to zeolite/ $\text{NaOH}$ . Whereas zeolite/ $\text{NaOH}$  has given a decrease FFA in the 30 minutes. This may be due to higher reactivity and alkalinity of  $\text{NaOH}$  than  $\text{KIO}_3$



**Figure 4.** Effect of Zeolite/ $\text{KIO}_3$  against Decrease in FFA

### **The Effect of KI Performance on Activated Zeolite Catalysts to Decreased FFA**

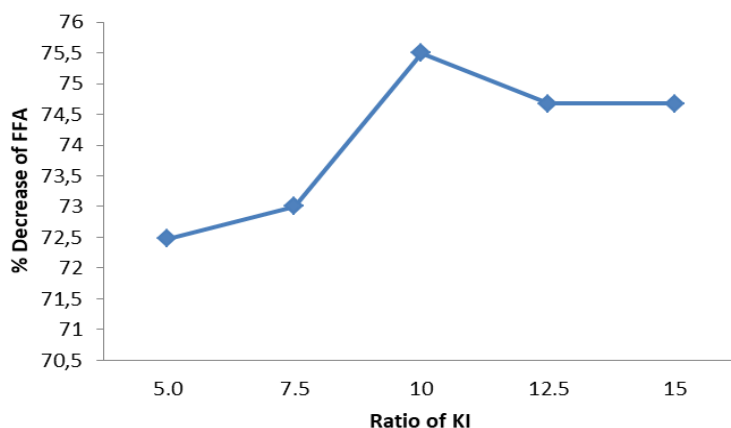
KI is non ionic and is not easy to absorb water (non hygroscopic). This trait is one of the hallmarks of KI so that it is used as an impregnator. In the synthesis of these embodied zeolite catalysts, the effect of water is very high on the bound water content which can reduce the performance of the catalyst while causing a hydrolysis reaction. Hydrolysis will cause a breakdown of the triglyceride chain and increase free fatty acids.

The concentration of KI which is applied to the zeolite framework is 2.5%. From the results of the study it was obtained that the texture of zeolite/KI catalysts were dense, slightly brittle and white. Unlike zeolite/ $\text{NaOH}$  which has a dark color, this is caused by the reactivity of Na metal which is higher than KI. This zeolite/KI catalyst was applied to the synthesis of methyl esters. Based on the FFA analysis it is known that zeolite/KI provides the lowest FFA reduction compared to the other 2 impregnators. The zeolite/KI catalyst can reduced FFA to 75.77%

Activated zeolites carried by different impregnators caused differences in texture. Previously the color of zeolite was bluish green, then changed to pure white. Development with  $\text{NaOH}$  causes the zeolite texture to become harder and tighter. While the zeolite that  $\text{KIO}_3$  carries has a very fine texture, brittle and scattered compared to zeolite/  $\text{NaOH}$  and zeolite/KI.

In addition to affecting the reaction system, the catalyst texture which is too fragile greatly affects the time of separation. Methyl esters synthesized with zeolite/ $\text{KIO}_3$  catalysts are harder to repair because the catalyst is in the form of sludge. Based on gas chromatography analysis, content esters were obtained at 79.1937% by zeolite/ $\text{NaOH}$  while zeolite/ $\text{KIO}_3$  at 75.889% and zeolite/KI at 75.77%. higher content esters than zeolite/KI. The

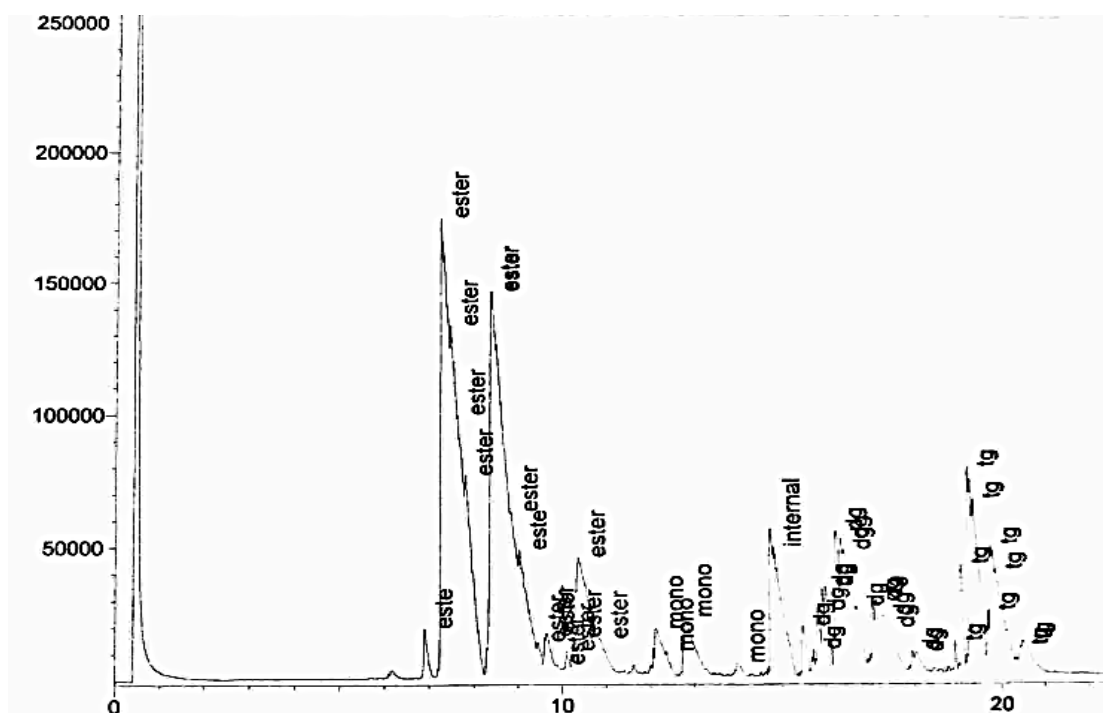
results obtained are 40.56%. This may be based on differences in the structure of zeolites as a framework because they come from different natural sources. The use of zeolites in catalytic process for biodiesel production provides a number of advantages including the ease of separation from the liquid products, regenerability, and no toxicity, corrosion for environmental pollution.[17].



**Figure 5.** Effect of Zeolite/KI against Decrease in FFA

### Product characteristics

Biodiesel products produced using zeolite/KI catalysts are confirmed using gas chromatography to determine product composition. From the results of the analysis it was found that the methyl ester formed was 79.1937%, diglyceride at 12.1171%, monoglyceride at 7.0219% and triglycerides unreacted at 1.6673%.



**Figure 5.** Chromatogram of Biodiesel with zeolite/KI

#### **4. Conclusion**

Based on the results of the study it was found that zeolite/KI catalysts performed better than zeolite which was impregnated with NaOH and KIO<sub>3</sub> compounds. Zeolite/KI can reduce FFA by 75.77% after it was applied in synthesis biodiesel at a temperature of 65°C for 2 hours. Based on gas chromatography analysis, content esters were zeolite/KI at 75.77%. Higher content esters than zeolite/KI.

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