Characteristics of Cracking Palm Oil Methyl Esters in Temperatures 280°C using Zeolite Natural Catalyst of Mamasa

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Abstract. The aim of this study is to characterize cracked products by GC-MS analysis and test the performance of natural zeolite catalysts originating from Mamasa in the catalytic crack reaction of methyl esters from palm oil for short chain hydrocarbons at 280°C. The method used for catalytic cracking of methyl ester includes 3 steps, namely the preparation of natural zeolite catalyst, catalytic cracking reaction at 280°C temperature, and analysis of cracked methyl ester. The characteristics of GC-MS cracking methyl esters indicate the addition of palmitoleic acid, and oleic acid. Cracking reaction of methyl ester at 280°C does not occur, the conversion of the reaction to form undesirable compounds namely carbon chains > C₁₅, so the natural zeolite catalyst from Mamasa is not selective for cracking reaction at 280°C.

1. Introduction

Petroleum includes an unrenewable source of energy, therefore the development of alternative fuels such as biodiesel is indispensable. The use of biodiesel as fuel, due to its chemical and physical properties are very similar to diesel fuel from petroleum [1]. The effort to improve the performance of biodiesel is through cracking reactions using catalysts or commonly called catalytic cracking. The catalytic cracking reaction is a reaction where a large hydrocarbon molecule breaks into smaller hydrocarbon molecules using a catalyst. This cracking was done at relatively lower temperatures compared to thermal cracking [2]-[3] reactions. One of the catalysts that have the potential to be used is zeolite. Zeolite as a catalyst is caused because zeolite shows considerable acid activity and is mainly due to its selexia properties. Zeolite can be grouped into two large groups namely natural zeolite and synthetic zeolite. This research uses natural zeolite as a catalyst on cracking reactions because the price is relatively inexpensive and abundant, has varied chemical and physics properties as well as not toxic so it is more environmentally friendly [4]. According to Handoko, natural zeolite generally have low catalytic activity so it needs to be activated before use. Activation is the process of increasing the capacity of adsorption so that the desired
properties are obtained according to their use. This research will test the performance of the zeolite of the Mamasa nature of a natural, for the reaction of cracking methyl esters of palm oil at a temperature of 280°C. Therefore, the characterisation of the methyl ester after cracking and determining the conversion and selectivity is expected produce methyl ester products with better characteristics.

2. Experimental

Natural Zeolite Catalyst Preparation.
Soak 100 g of natural zeolite that has been smoothed with aquades up to 500 ml at a measuring cup 1000 ml. During immersion, the mixture is stirred using an electric mixer to prevent natural zeolite from being dissolved. After immersion, the mixture is left to settle, the coarse and first deposits of zeolite are separated by pouring a subtle zeolite deposition into the other glass of the beker so that it is separated between the fine deposits and the deposits of the casters. This fine precipitate is then left for overnight to settle perfectly, then filtered using the Buchner funnel. This fine precipitate is dried in the oven for a day. After that it is soften back with mortar and weighed. Then the natural zeolite catalyst is calcined by heating in a furnace at a temperature of 500°C for 3 hours.

Palm Oil Transesterification.
Palm oil used in this study has passed the initial treatment so that the free fatty acid levels are only 0.36%. The transesterification process is carried out by heating a mixture of oil (500 grams) and methanol (113.40 grams) in a fixed bed reactor that has a cooling back. In the reactor, 5 grams of NaOH are added. The operating temperature is set to 60 °C and the reaction time is 60 minutes, calculated when the operating temperature is reached. The reaction results are transferred to a separating funnel and then allowed to stand for 12 hours. The transesterification process with homogeneous catalyst will make two layers, the bottom is glycerol and the top is biodiesel (methyl ester). The bottom layer is removed and accommodated, while the top layer is washed with warm water until the water is clear. Biodiesel is then heated in an oven at a temperature of 110 °C until the appearance is clear and there is no foam on the surface (± 2 hours). Furthermore, biodiesel was analyzed for saponification numbers.

Cracking of Methyl Esters with Natural Zeolite Catalysts
The process of cracking the methyl ester begins by flowing the N₂ gas at a rate of 0.5 mL/min. The catalytic test is done by injecting a methyl ester as much as 20 grams into a fixed bed reactor that has been heated at a temperature of 280°C. In the reactor, natural zeolite catalysts are inserted weighing 0.3 grams. Cracking reaction is held for 30 minutes. The results were analyzed saponification number and analysis figures with gas chromatography (GCMS) mass spectrometry methods.

3. Results And Discussion

Product characteristics of methyl ester
The saponification number can be used to determine the molecular weight of oil roughly. The oil composed of short C chain fatty acid esters means that it has a relatively small molecular weight that will have a large saponification number [5]. Saponification number is amount milligrams of KOH is needed to make 1 gram of oil sample, calculated until one decimal using the formula [6]:

\[
\text{Saponification number} = a \times b \times (V_0 - V_1) / c
\]

Where \(a\) is KOH molecular weight (56.1 g/mol), \(b\) is Normality of KOH solution, \(c\) is sample weight (gram), \(V_0\) is volume of HCl required in blank titration (mL), and \(V_1\) is volume of HCl needed in sample titration (mL). Analysis of the number of saponification of methyl ester before cracking i.e. 168.86 mg KOH/g and after cracking at 2800C temperature of 186.53 mg KOH/g. The number of product saponification number of cracking is greater than methyl ester before cracking.

The composition of the compounds contained in a methyl ester cracking product is analyzed using GCMS presented in the following image and table.
Each peak of the gas chromatography results, analyzed by mass spectrometry and identified as biodiesel compounds based on similarities to the standard compounds. A compound similar to a standard compound if it has the same molecular weight, similar fragment patterns, and a high price of SI (index of similarity).

Table 1. Types of compounds in methyl ester after cracking

| Peak | $T_R$ (minutes) | Compound | Amount (%) |
|------|----------------|----------|------------|
| 1    | 12.911         | Dodecanoic acid, methyl ester (asam laurat) | 0.25       |
| 2    | 15.385         | Tetradecanoic acid, methyl ester (asam miristat) | 2.14       |
| 3    | 17.667         | 9-hexadecenoic acid, methyl ester, (Z)- (asam palmitolet) | 0.24       |
| 4    | 18.109         | Hexadecanoic acid, methyl ester (asam palmiat) | 36.51      |
| 5    | 20.383         | 9,12-octadecadienoic acid (Z,E)-methyl ester (asam linoleat) | 3.42       |
| 6    | 20.670         | 9-octadecenoic acid, methyl ester (asam oleat) | 47.31      |
| 7    | 20.981         | Octadecanoic acid, methyl ester (asam 4isbani) | 8.55       |
| 8    | 21.785         | 9,11-octadecadienoic acid, methyl ester, (E,E)-(asam 9,11 octadecadienoic methyl ester) | 0.22       |
| 9    | 23.474         | 11-eicosenoic acid, methyl ester (asam gondoat methyl ester) | 0.41       |
| 10   | 23.874         | Eicosaenoic acid, methyl ester (asam arakhatat methyl ester) | 0.94       |
| **Total** |             |           | **100.00** |
Data chromatogram Figure 1. explains that in the product metilester cracking using the Mamasa natural zeolite catalyst at 280°C is composed of ten fatty acids indicated from the presence of 10 peak. Retention time indicates the time the sample constituent component is separate from other components. From data chromatogram obtained separate lauric acid first at a time of 12.911 minutes followed Miristat acid compounds at 15.385 minutes of DST. The highest fatty acids are a 47.31% oleic acid and a 36.51% palmitic acid is shown with a wider peak area than other fatty acids.

**Performance test of natural zeolite catalyst from Mamasa**

A catalyst performance test is performed by defining conversions and selectivity. The results of the performance testing of the Mamasa natural zeolite catalyst for the cracking of methyl esters at a reactor temperature of 280°C, presented in Table 2.

**Table 2.**

| No. | Compound                                 | Conversion (%) |
|-----|-----------------------------------------|----------------|
| 1   | Dodecanoic acid, methyl ester (asam laurat) | 32,38          |
| 2   | Tetradecanoic acid, methyl ester (asam miristat) | 14,39          |
| 3   | 9-hexadecenoic acid, methyl ester, (Z)-(asam palmitoleat) | 45,47          |
| 4   | Hexadecanoic acid, methyl ester(asam palmitat) | -              |
| 5   | 9,12-octadecadienoic acid (Z,Z)-, methyl ester(asam linoleat) | -              |
| 6   | 9-octadecenoic acid, methyl ester(asam oleat) | -              |

The result of the cracking reaction conversion calculation obtained from Table 2. shows only lauric acid, myristic acid and the palmitoleic acid converted, while palmitic acid, linoleic acid, and oleic acid are not converted. This fact indicates that in temperature conditions 280°C using the Mamasa natural zeolite catalyst, the reaction of cracking methyl ester does not occur. Reaction products (large hydrocarbons) are formed from cracking reactions (table 1.), so the catalyst selectivity cannot be obtained.

4. Conclusion

The characteristics of GC-MS cracking methyl esters indicate the addition of palmitoleic acid, and oleic acid. Cracking reaction of methyl ester at 280°C does not occur, the conversion of the reaction to form undesirable compounds namely carbon chains > C15, so the natural zeolite catalyst from Mamasa is not selective for cracking reaction at 280°C.

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