



BIOFUEL PRODUCTION BY CATALYTIC CRACKING METHOD USING ZN/HZSM-5 CATALYST

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ABSTRACT

Increasing economic growth and population can improve the energy demand in all sectors, and give impact on the depletion of oil reserves. The effort to overcome this problem is increasing the production of biofuels. Biofuel is a fuel derived from vegetable oil, one of them is palm oil. Biofuel can be produced by a catalytic cracking method. In this research, we use Zn/HZSM-5 as bio-fuels catalyst. The purposes of this study are to determine the process of making Zn/HZSM-5 catalyst, determine the effect of temperature on bio-fuel producing and determine the influence of catalyst regeneration on bio- fuels yield. The method of this research was created HZSM-5 catalyst synthesis using Plank method and then impregnated with ZnSO₄·7H₂O to obtain Zn/HZSM-5 catalyst. Zn/HZSM-5 catalyst was made with various concentrations of Zn 2%, 3%, 4%, 5% and 6%. Then it was used to produce bio-fuel with a variation of Zn concentration and variation of temperature. The best result was obtained at 4% Zn concentration which has 23.97% yield of biodiesel, 2.54% yield of bio-gasoline and 1.67% yield of bio-kerosene. By increasing the operating temperature, can increase the yield of biofuels. But by regenerating the catalyst, yield of biofuel became decreased due to the active site reduction of the catalyst.

Keywords: biofuel, catalytic cracking, H-ZSM5 catalyst, catalyst regeneration.

INTRODUCTION

In 2025, Indonesia is expected to materialize in the energy mix with petroleum use less than 20% and the use of new and renewable energy to more than 5% (Widayat *et al.*, 2015; Widayat *et al.*, 2013a; Widayat *et al.*, 2012; Widayat *et al.*, 2013b). This is one of the government's efforts in addressing the depletion of petroleum reserves caused by the growing need for energy in all sectors of energy users. The largest energy used are industry and transport sector by 85% of total usage. Therefore, the development of renewable energy is more focused on biofuels.

Biofuels are non-fossil energy derived from organic materials such as vegetable oil or animal fat. One of the vegetable oil can be used to produce biofuels is palm oil. The process commonly used to produce biofuels is esterification and transesterification (Widayat *et al.*, 2015; Widayat *et al.*, 2013a; Widayat *et al.*, 2012; Widayat *et al.*, 2013b). But the weakness of this process is the separation of biofuel and glycerol and requires high temperature and high operating pressure. Another process that can be done is catalytic cracking. The catalytic cracking process can break the bond complex hydrocarbons into simpler, and this process occurred at low temperature and pressure (Widayat, 2005; Billaud *et al.*, 1995).

Catalysts are often used in the catalytic cracking process is HZSM-5 (Hydrogen Zeolite Socony Mobiles Number 5). In the production of bio-fuels can use HZSM-5 catalyst by impregnation and no impregnation. Roesyadi *et al.* (2013) conducted research into gasoline coconut oil cracking catalyst using HZSM-5 without impregnation and the impregnation of metal copper (Cu) and nickel (Ni). The catalytic cracking process takes place at temperatures of 350-500° C with N₂ purged 120-160 ml/min. On the

use of HZSM-5 catalyst obtained 17.11% gasoline, 14.89% kerosene, and 10.86% diesel. While the catalyst Ni/HZSM-5 derived 17.55% gasoline, 13.48% kerosene, 5.48% diesel and using catalyst Cu/HZSM-5 obtained 18.05% gasoline, 13.30% kerosene and 5.72% diesel (Roesyadi *et al.*, 2013). Xianhui *et al.* (2015) were cracked of camelina oil over Zn/ZSM-5. The yield of hydrocarbon biofuel obtained at Zn concentration to ZSM-5 was 20 wt%. The loading of Zn to ZSM-5 could facilitate the chemical reactions such as decarbonylation and dehydrogenation (Xianhui *et al.*, 2015a). Xianhui *et al.* (2015b) also cracked carinata oil over Zn/Na-ZSM-5 catalyst. This research yield of hydrocarbon biofuel obtained over regenerated Zn/Na-ZSM-5 increased but the coke yield and distillation residual yield decreased, compared to fresh Zn/Na-ZSM-5. Zn/Na-ZSM-5 regenerated catalyst can reduce the decarboxylation, decarbonylation, and dehydrogenation of carinata oil (Xianhui *et al.*, 2015b).

The objective of this research to production of biofuels by using Zn/ZSM-5 catalyst with palm oil as feedstock and also study of effect temperature and concentrations of Zn that loading to ZSM-5.

LITERATURE REVIEW

Biofuel is a fuel from organic material, named non-fossil energy. Biofuel is an alternative energy, which is can reduce gas emission and increase energy reserve (Leng Chew and Bhatia, 2008). Kinds of biodiesel are biodiesel, biokerosene, and biogasoline. Raw materials for biofuel production are from vegetable oil and animal oil. Palm oil is common use as raw materials in biofuel production. It has an oleic acid composition 38 - 52% (Widayat *et al.*, 2013). In 2012, Indonesia produces palm oil until 27 million tons.



In biofuel production, there are various processes; one of them is catalytic cracking. Cracking is a reaction of hydrocarbon breaking to simpler molecule using high temperature. In the catalytic cracking process, it uses a catalyst to increase yield product. There are three types of catalytic cracking i.e., fluid catalytic cracking, moving-bed catalytic cracking and thermo for catalytic cracking. Fluid catalytic cracking is oil breaking using catalyst by preserving fluid flow in the reactor. Moving-bed catalytic cracking is same with fluid catalytic but the catalyst was continued moving and regenerated. Thermo for catalytic cracking is done by heating oil then the oil vapors were flowing to fractionation column (Clark, 2003).

The catalyst that widely used in catalytic cracking is a zeolite. Zeolite is natural material arranged by silica and alumina. Its availability is limited, so zeolite synthetic was made to fulfill zeolite needed. Zeolite synthetic is a chemical material with the physical and chemical properties equals with natural zeolite. It makes from sodium silicate and alumina in pH base. Zeolite synthetic divided into four types i.e. zeolite low silica, zeolite medium silica, zeolite-rich silica and zeolite silica. Type of zeolite synthetic that commonly used is zeolite-rich silica. Zeolite rich silica has many types i.e. ZSM-5, ZSM-11 and ZSM-21 (Plank, 1990). In this research, ZSM-5 is used as a catalyst in biofuel production.

METHODOLOGY

Materials used in this research are palm oil (density 0.80955 g/ml, acid value 0.837, peroxide value 16.774 and FFA 0.3%). water glass from Merck Ltd and has a density (20 °C) 1296-1396 g/ml. Ethanol with industrial specification and Sodium hydroxide, Ammonium Chloride, Sulphuric Acid, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ obtained from Merck and distilled water obtained from the laboratory of Membrane Research Centre UNDIP. While the apparatus used consists of a suite of tools impregnation, calcination, and catalytic cracking. Catalyst impregnation with apparatus like presented in Figure-1. The equipment was consists of a magnetic stirrer and beaker glass. The calcination processing was used muffle furnace with Thermo Scientific mark like presented in Figure-2. The equipment for catalytic cracking showed in Figure-3. The reactor has 1/2 inch diameter and 15 cm in length.

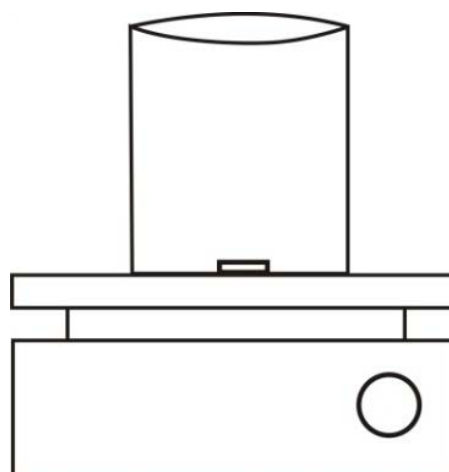


Figure-1. Catalyst impregnation instrument.

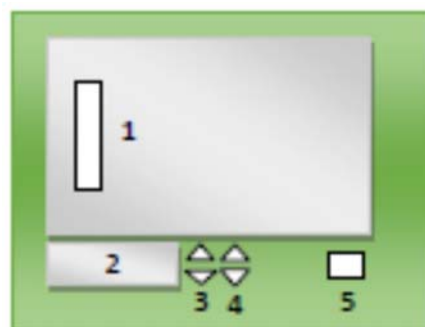


Figure 2. Catalyst calcinations instrument.

Synthesis HZSM-5 catalyst

ZSM-5 Catalyst made using Plank method [10]. The first is make a solution consisting of 360 grams of water glass (28.8% SiO_2 , 8.9% Na_2O , 62.4% H_2O) and 450 grams of H_2O and make a solution B consisting of 12.3 grams of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, 30 grams of H_2SO_4 98% and 600 grams of H_2O . Then solution B was added to the solution A while stirring with a magnetic stirrer to form a white gel. 124 grams of ethanol then added slowly and stirred for 1 hour, and pH was adjusted to 10-11. Then the gel formed inserted into an autoclave, heated to a temperature of 170 °C and stirred at 100 rpm for 48 hours, after which it was allowed to stand for 24 hours. Then filtered the crystal and washed with distilled water until the pH became 8, and then the crystals are dried in the oven at 110 °C for 14 hours.

Furthermore, ZSM-5 catalyst converted into HZSM-5 catalyst. ZSM-5 catalyst conversion is done by mixing the catalyst with a solution of 1M NH_4Cl . Then HZSM-5 formed is filtered, washed, and dried at 110 °C for 6 hours. The solids reduced at a temperature of 400 °C for 5 hours with hydrogen gas flow throughout the process.

Catalyst impregnation

Zn metal impregnation is done by dissolving $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ in 25 ml of distilled water with a



concentration of 2%, 3%, 4%, 5% and 6%. Then 5 grams of HZSM-5 catalyst mixed into the solution and stirred for 2 hours. The mixture obtained is filtered with suction strainer, and then dried it. The impregnated catalyst was calcined for 4 hours at 600 °C. The equipment for impregnation of the catalyst showed in Figures 1 and 2.

Catalytic cracking

The catalytic cracking process is done by inserting 2 grams of catalyst in the microreactor. Then

palm oil put into the feed tank and heated at 350 °C. Feed tank flowed by nitrogen gas with a flow rate of 130 ml/min. Then the oil vapor and nitrogen gas flowed into the packed reactor and heated at 300 °C and 400 °C subsequent catalytic cracking performed for 60 minutes. The results then analyzed using gas chromatography-mass spectrometry. The equipment used in the catalytic cracking process is showed in Figure-3.

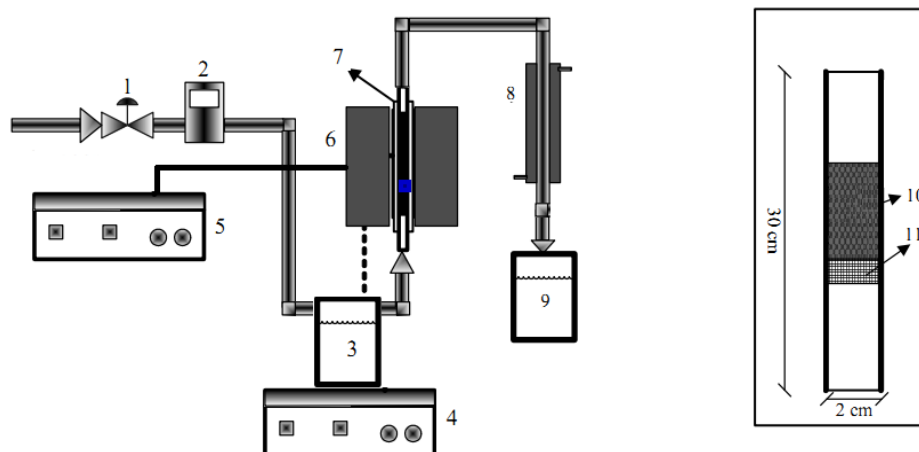


Figure-3. Catalytic cracking instrument.

RESULTS

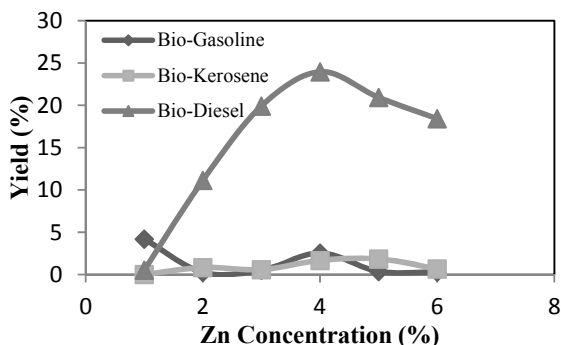


Figure-4. Effect of Zn concentration on biofuel yield.

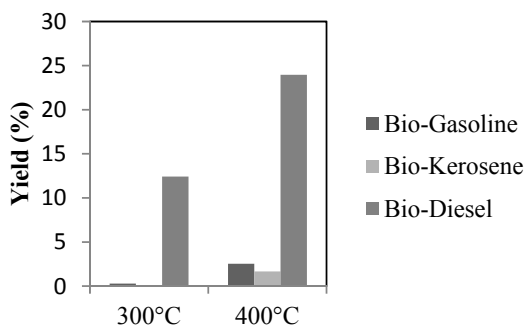


Figure-5. Effect of temperature on biofuel yield.

Table-1. Biofuel yield.

Component	Yield (%)	
	New catalyst	Regeneration catalyst
Bio-Gasoline	2.54	0.23
Bio-Kerosene	1.67	0.27
Bio-Diesel	23.97	16.17

DISCUSSIONS

Effect of Zn concentration on biofuel yield

The use of HZSM-5 catalyst produced the highest yield of bio-gasoline, but the uses of zeolite synthesis the yield generated mostly leads to bio-diesel product as showed in Figure-4. This is caused HZSM-5 catalyst has a high acidity because it has a core of Bronsted acid very high and the core of Lewis bit. In addition, this catalyst also has a very high selectivity and small pore size so that molecules such as cyclohexane and aromatic compounds can diffuse easily into the pore HZSM-5. The catalytic cracking reaction occurs in the gas phase for the formation of gasoline, solar oil (Roesyadi *et al.*, 2013) and also hydrocarbon fuels (Xianhui *et al.*, 2015a; Xianhui *et al.*, 2015b). In this research, catalytic cracking with Zn/ZSM-5 catalyst can increase of bio-diesel yield to 23.97%. This is due to the function of specific catalyst to form a reaction directs certain products. So the use of zeolite catalysts in the synthesis of the use of HZSM-5 will produce different



products although using the same raw materials (Wilczura-Wachnik, 2013). The yield of biodiesel was obtained highest on catalytic cracking of palm oil with Zn concentration 4% loading to ZSM-5.

The use of synthetic zeolite catalyst by impregnation of 4% Zn produced bio-diesel, bio-kerosene, and bio-diesel in a maximum yield 2.54%, 1.67% and 23.97%. The function of loading Zn to HZSM-5 is to increase the active side of catalyst (Xianhui *et al.*, 2015a; Xianhui *et al.*, 2015b). So by impregnated catalyst with %Zn will affect the cracking process. In this experiment showed that the more %Zn were added to the impregnation process, increase the number of cracked compounds and also shown in the increase in the yield of biodiesel, bio-kerosene, and biodiesel. However, by the addition of Zn exceeds 4% decrease the number of cracked compounds? It caused by the addition of Zn is more than 4% will make the active site of the catalyst more widely so the reaction rate becomes faster cracking causes the formation of coke which is faster anyway. The coke formation will cause the pores of the catalyst covered (Roesyadi *et al.*, 2013). So the surface area of the catalyst is reduced and the formation of the products will decline. The concentration of Zn loading was less if compared with Xianhui *et al.* (2015a). Xianhui *et al.* were used Zn loading until 30% (Xianhui *et al.*, 2015a; Xianhui *et al.*, 2015b). So, this experiment was advantages in the use of Zn.

Effect of temperature on biofuel yield

In Figure-5 showed the higher temperature of the cracking process will produce a greater yield. The increase in yield can be interpreted as increasing the cracking reactions occur. A cracking reaction is an endothermic reaction where the reaction involves carbon chain termination process, to crack a carbon chain required large heat energy (Wilczura-Wachnik, 2013). At a temperature of 300 °C showed a formation of biodiesel, bio-kerosene, and bio-diesel as a result of palm oil cracking. In these conditions, bio-diesel formed larger than bio-diesel and bio-kerosene. This is due to the hydrocarbon chains on bio-diesel are longer than the chain of bio-diesel and bio-kerosene. So in the cracking process will form a long chain hydrocarbon product first? However, at a temperature of 400 °C can increase the yield of biodiesel and biokerosene became 2.54% and 1.67%, and the yield of biodiesel became 23.97%.

Effect of catalyst regeneration on biofuel yield

In Table-1 listed the difference in yield generated by a new catalyst (fresh) and the regenerated catalyst. By using the new catalyst produces a bio-gasoline yield of 2.54%, 1.67% bio-kerosene and bio-diesel 23.97%. While used the regenerated catalyst, it produces a bio-gasoline yield of 0.23%, 0.27% bio-kerosene and bio-diesel 16.17%. Use of the catalyst within the specified time will lead to changes the character of the catalyst which in turn will result in a decrease in catalyst activity. This was due to undergo reduction catalyst active sites. Reduced active site of the catalyst is due to the species or compounds are adsorbed firmly on the catalyst surface so that the active

catalyst sites covered by the species or the compound (Xianhui *et al.*, 2015b). On regenerated catalyst decreased catalytically active sites are indicated by a decrease in the formation of bio-gasoline yield, the yield drop caused by the coke that remains on the surface of the catalyst so it covers the sides of the active catalyst (Trisunaryati and Emmanuel, 2009).

CONCLUSIONS

The best result was obtained at 4% Zn concentration which has 23.97% yield of biodiesel, 2.54% yield of bio-gasoline and 1.67% yield of bio-kerosene. By increasing the operating temperature, can increase the yield of biofuels. But by regenerating the catalyst, yield of biofuel became decreased due to the active site reduction of the catalyst.

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