



BIOFUEL PRODUCTION FROM NYAMPLUNG OIL USING CATALYTIC CRACKING PROCESS WITH Zn-HZSM-5/ γ ALUMINA CATALYST

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ABSTRACT

Biofuel is one of alternative energy to solve the problem of increasing energy needs. Research on the production of biofuels from nyamplung oil is very interesting to do. This research studied the production of biofuels from nyamplung oil through catalytic cracking process. A catalyst of a Zn-HZSM-5 / γ -alumina was used in this study. The research aims were to study the composition of nyamplung oil, to get characteristic of the Zn-HZSM-5 / γ -alumina catalyst, and to study the effect of temperature and composition of the catalyst toward biogasoline, biodiesel, and bioekerosene selectivity in biofuel production. Experiments were carried out in a fixed bed reactor containing the catalyst by adjusting various temperatures and catalyst compositions. The results showed that the use of Zn-HZSM-5 / γ -alumina (1:2) catalyst produced biofuel with biodiesel selectivity of 73.86% on the reaction temperature of 450 to 550 °C. While the use of the Zn-HZSM-5 / γ -alumina (1:1) catalyst generated biofuel with a biogasoline selectivity of 54% at the reaction temperature of 500 to 550 °C.

Keywords: biofuel, fixed bed, nyamplung oil, Zn-HZSM-5, γ -alumina.

INTRODUCTION

Indonesia's National Energy Policy set out in Presidential Decree No.5/2006 suggests that the government should accelerate the implementation of the use of alternative energy to substitute fossil fuel. The use of biofuels as an energy source is driven by more than 5% in 2025 [1]. Real conditions showed that increasing environmental concerns and depletion of world oil reserves pose a great demand to find alternative sources of replacement of petroleum-based fuels, including diesel and gasoline fuels [2]. Many scientists began researching to find a new kind of energy that is cheap, easy and environmentally friendly sources of energy [3]. One of them is vegetable oil. The vegetable oil can be converted into biodiesel by esterification or transesterification process [2, 4, 5, 6, 7] produces esters of alkyl biodiesel. Completion of the combustion characteristic of alkyl ester is done by forming biodiesel ozonide [8]. Vegetable oil also can be converted into biofuel by cracking that produces a wider product of biofuels [1, 9, 10, 11, 12, 13, 14, 15].

Biofuel has many advantages compared with alkyl biodiesel ester. The advantages of this product are the biofuel is in the form of liquid fuel that is similar to the conventional diesel oil components [16] and can be produced from a variety of vegetable and animal oils. However, it is more interesting if it is derived from plants that can be cultivated well in Indonesia. Nyamplung oil is non-edible oil so that it has a potential alternative fuel to replace the use of gasoline, kerosene, and diesel fuel. The production of biofuels from plants such as palm oil had been extensively studied using zeolite as a catalyst in the

process of cracking [13, 14, 17]. HZSM-5 zeolite had a good properties and performance in the cracking process.

Another challenge of the use of zeolite catalysts in the form of solid acid in a catalytic cracking reaction is still little use for cracking various typical plant oils in Indonesia. Most reactions involving cracking of oil will reduce the ability of the catalyst active site due to the coke formation. This effect can be reduced by changing the operating parameters of the reaction process, for example by increasing pressure and decreasing temperature conversion and cracking [18]. The use of different raw materials require accurate information about the condition of cracking operations for various raw materials to produce these biofuels

Nyamplung oil is very attractive as a raw material for producing biofuels instead of fossil fuels because it has a yield of 73 wt%, environmentally friendly plant oils, the production continues to grow. Nyamplung oil has been used as a substitute for diesel fuel for fishing boat engines in Madura Indonesia. However, fishermen, who applied this oil nyamplung, complain because the engine is hot and quickly broken. Nyamplung oil is triglycerides that is very viscous and needs to convert into biodiesel or biofuel. However, the obstacle of biofuel production process requires a catalyst, especially in the catalytic cracking process. Previous research on the catalyst using a zeolite-based catalyst and HZSM-5 showed good results in the production of this biofuel, but the use of this catalyst had a drawback in the low yield of resulting liquid fraction [13]. Research to improve the selectivity of the catalyst HZSM-5 had been carried out by Roesyadi *et al.* by modifying the catalyst HZSM-5 by adding metals Ni, Cu, or Zn. The



results showed an increase in yield of gasoline but lowers kerosene and diesel. For instance, the use of the catalyst Zn/HZSM-5 provides the yield of 29.38% gasoline, 12.86% kerosene, and 4.78% diesel fuel [14]. However, these catalysts had not been tested on nyamplung oil. Research to improve product selectivity and catalyst life has also been performed by Bhatia *et al.* showed that the coating of the catalyst become a catalyst alumina composites using certain salt can protect the catalyst active site and improve the catalyst morphology [17].

Researchers considered that the preparation of new catalyst of zeolite-based catalysts impregnated with Zn or γ -alumina can increase the selectivity and improve the catalyst morphology. It can protect the active sites of the catalyst so that it will have a longer catalyst life. This study focused on the influence of Zn and γ -alumina impregnation on the characteristics of the resulting catalyst. The resulting catalyst was also tested to produce biofuels from nyamplung oil in micro bed reactor.

Another study of HZSM-5 and MCM-41 catalysts on cracking palm oil and its performance had also been conducted. Conversion of palm oil obtained was 80 to 100 wt% where the fractional yield of gasoline 38 to 47 wt% obtained from composite catalyst. The resulting catalyst had selectivity to the formation of aromatic organic liquid product [19]. The use of zeolite-based catalysts are very effective recognized for palm oil cracking process into biofuel, however, it was deactivated by coke formation. Deactivation of ZSM-5 is due to the loss of the active sites [20]. Formation of composites catalyst can be expected to protect the active sites of catalyst. The addition of alumina in the composite catalyst increases its hydrothermal stability due to the changes on surface morphology [17].

Research on a modified zeolite catalyst preparation of natural zeolite from Blitar Indonesia had been done by Budianto *et al.* This research aims were to study the process of making the modified zeolite and examine these catalysts on converting methane and determine the best selectivity. The study was conducted with two general phases namely the process of changing the natural zeolite to be modified zeolite and testing of modified zeolites as catalysts in converting methane. The results showed that the initial characteristics of natural zeolite Blitar was a mordenite that was changed to a Cristobalit after be modified. The catalyst testing results revealed that the optimum temperature of converting methane was 300°C with a 15.78 wt% conversion but the optimum selectivity of acetylene happened at temperatures of 500°C with conversion of 1.1 wt% [21].

Study the type of reactor for catalytic cracking of oil into biodiesel had been done by Tamunaidu [22]. In this study, catalytic cracking of palm oil into biofuels had been studied using REY catalyst in fixed bed reactor at atmospheric pressure. The effects of reaction temperature (400 to 500 °C), catalyst/palm oil ratios (5 to 10) and

residence time (10 to 30 s) were studied to produce bio-premium and gas fuel. Experimental design used to study the effects of operating variables above were the result of the conversion of palm oil and hydrocarbon fuels. Response surface methodology used to determine the optimum value of operating variables in order to produce the maximum fraction of bio-gasoline in the liquid product obtained.

Beside having the advantages in the form of biofuels cracking process, the catalyst of HZSM-5 has a drawback, particularly thermal stability and its deactivation due to the formation of coke on the cracking process that closes the active sites of catalyst. Composite catalyst of HZSM-5/alumina (CZA) and Al-MCM-41/alumina (CMA) had been successfully synthesized and tested for catalytic cracking activity in the production of biofuels from palm oil characterized by structure, acidity, and surface morphology. The addition of alumina in the composite catalytic improve the hydrothermal stability due to the changes on surface morphology. Deactivation of the catalyst was studied by getting time on the data value by varying the ratio of catalyst to oil palm 8 to 16. The results showed that the presence of alumina with low concentrations may increase the hydrothermal stability and lowers the acidity of the composite. Changes in the structure of the porous composite was considered less susceptible to the formation of coke resulting in lower deactivation rate. The addition of alumina on HZSM-5 is beneficial in terms of better stability and lower shutdown without affecting the results produced gasoline fraction [17].

EXPERIMENTAL SET-UP

This research was conducted by the development of preparation methods of the catalyst Zn-HZSM-5/ γ -alumina, determining the character of catalysts, and tested for catalytic cracking reactions to produce biofuel from nyamplung oil. Nyamplung oil extracted from nyamplung seeds using compression process. Nyamplung seeds inserted into a tube equipped with a piston and pressed with a hydraulic pump. Nyamplung oil was analyzed using GC-MS to determine the composition of its compound. Materials used for this study were Zn-HZSM-5 / γ -alumina synthetically, water glass, alum / $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$, HCl 10M, NH_4Cl 2M, distilled water, hydrogen gas, zinc chloride, alumina, nitrogen gas, and nyamplung oil.

Equipment used for the preparation of the catalyst were autoclave and furnaces equipped with a thermocouple and temperature indicator, stainless steel pipe, thermometer, hotplate, stirrer, pressurized micro bed reactor, stand and clamps. While the resulting catalyst characterized by using the Brunauer Emmett Teller (BET) apparatus. The equipment series used in the cracking nyamplung oil process into biofuel was presented in Figure-1.



RESULTS AND DISCUSSIONS

Determination of nyamplung oil composition

Extraction results showed that one kg of nyamplung seeds produced 825 ml nyamplung oil. The result of nyamplung oil analysis using GC-MS was revealed at Figure-2. There were some peaks on the chromatogram of nyamplung oil at the retention time of 46.703, 50.092, 60.461, 61.846, and 66.599. It shows that

there are some compounds in nyamplung oil. The results of the analysis showed that the nyamplung oil contains palmitic acid, octadecanoid acid etc. as written at Table-1.

Characterization of catalysts

The catalyst was proved as Zn-HZSM-5 / γ -alumina (1:1) with surface area of 112.385 m²/g, pore volume of 0.019 cm³/g, pore diameter of 35.235 Å, Zn content of 4.55% of mass and Si/Al mole ratio of 24.3.

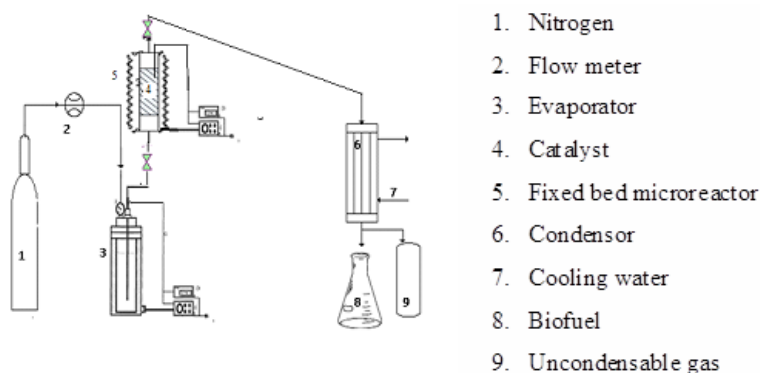


Figure-1. Equipment series of catalytic cracking.

Table-1. Composition of of Nyamplung Oil.

No.	RT/ min	Chemical name	Composition
1	46.703	Palmitic acid	12.426
2	50.092	Octadecanoid acid	54.716
3	60.461	T-butyl 2,5 dihydro 5 oxo furan 2-Y lidine) methyl-3,4 - dimethyl 1 H-pyrole carboxilate	12.953
4	61.846	4 cyclohexil-2-methyl-1(4 methylphenyl)-6-phenyl-5 (3prophynil)-1-2-dihydropyrimidin	1.793
5	65.999	1-phenyl-3methyl-5-(ethoxycarbonyl)-7-(4-methylphenyl)amino pyrazalo (3-4-D)(1,3 Diazepine)	18.112
	RT= Retention time		

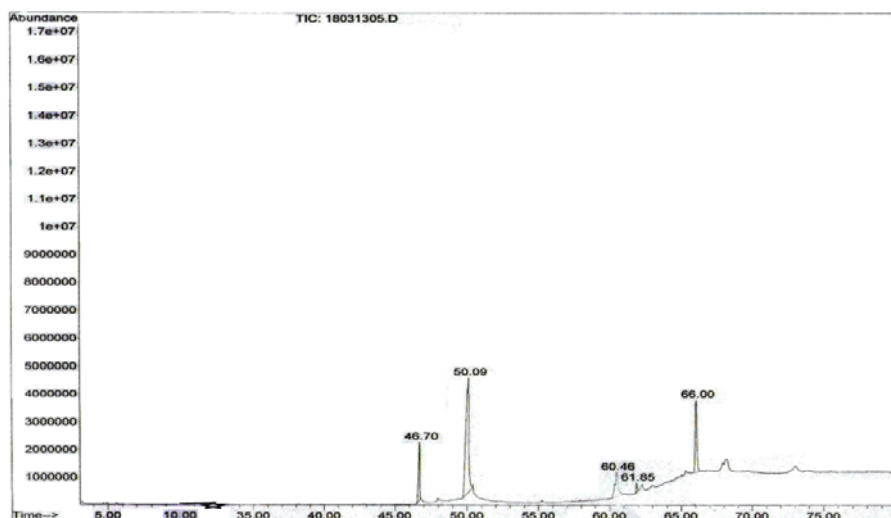


Figure-2. Chromatogram Nyamplung oil using GC-MS.

Characteristics of biofuels

Effect of reaction temperature on biogasoline production by cracking process of nyamplung oil was presented at Figure-3. It can be seen that the composition ratio Zn-HZSM-5/ γ -alumina (1:1) provides a stable yield of 49.19 to 54.30 wt% in the temperature range of 350 to 550 °C. It might occur because the active site of the catalyst Zn-HZSM-5 was protected by γ -alumina. The yield of biogasoline in this study was higher than that of

cracking hazelnut oil using catalyst Zn-HZSM-5 [1]. It was also higher than the yield of cracking using catalyst CoMo/ γ -Al₂O₃ when used the same sample that reached 31wt% [15]. Figure-3 also shows that the use of the catalyst Zn-HZSM-5/ γ -alumina (1:2) affects the yield of the biofuel. It tends to fall at the temperature rise. This occurred because the high concentration of γ -alumina cause cracking product tend to form biodiesel fractions.

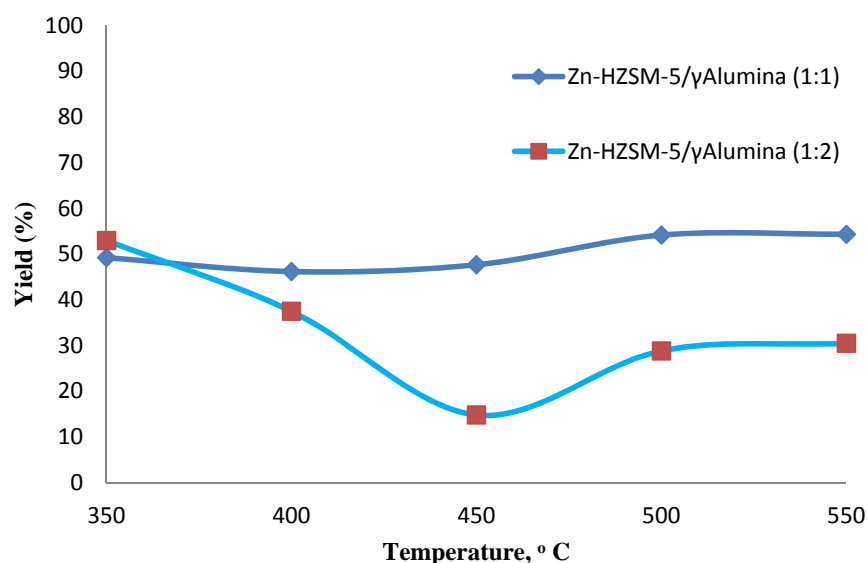


Figure-3. Effect of reaction temperature on selectivity of biogasoline on cracking process of nyamplung oil using catalyst Zn-HZSM-5/ γ Alumina (1:1).

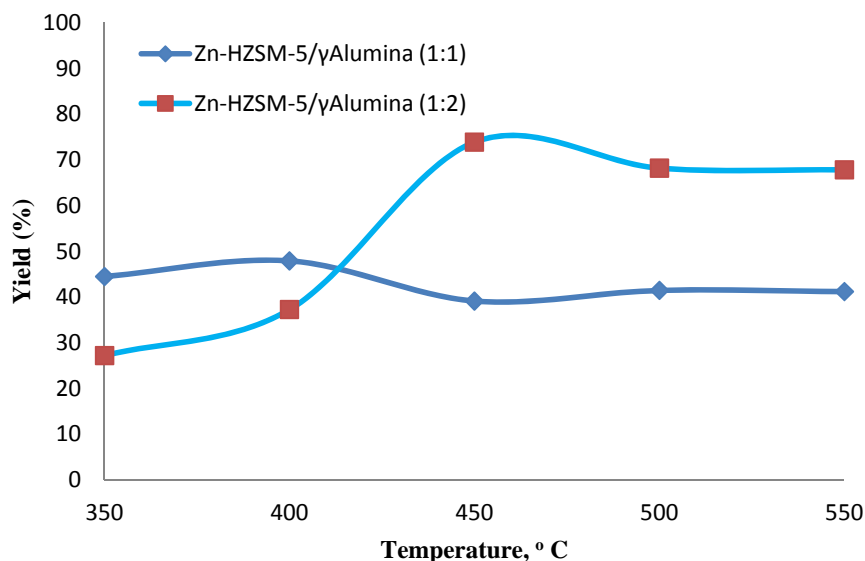


Figure-4. Effect of reaction temperature on selectivity of biodiesel on cracking process of nyamplung oil using catalyst Zn-HZSM-5/γ Alumina (1:2).

Figure-4 shows the relationship between temperature of cracking nyamplung oil to the yield of biodiesel using catalyst Zn-HZSM-5/γ-Alumina (1:1) and Zn-HZSM-5/γ-Alumina (1: 2). Based on the diagram, it shows that the optimum temperature for producing biodiesel achieved at 450°C. At the temperatures of 350 °C biodiesel yield was 27.20 wt% then increased to 73.86 wt% at a temperature of 450°C, but afterward it slowly decreases until reaches 67.82 wt% at a temperature of 550 °C. The phenomenon might occur due to the rising temperature could increase the active site of catalyst, but

at the temperatures higher than 450 °C the active sites of catalyst was decrease. This occurrence showed similarity with the type of HZSM-5 and Cu-HZSM-5 catalyst were used for palm oil cracking in producing biodiesel [14] and the use of Zn-HZSM-5 catalyst for palm oil cracking to produce biofuel [13]. The catalyst of Zn-HZSM-5/γ-Alumina (1:1) tend to be stable against temperature. The stability might happened because of a balanced composition of active sites of Zn-HZSM-5 and γ-Alumina that more resistant to temperature rise.

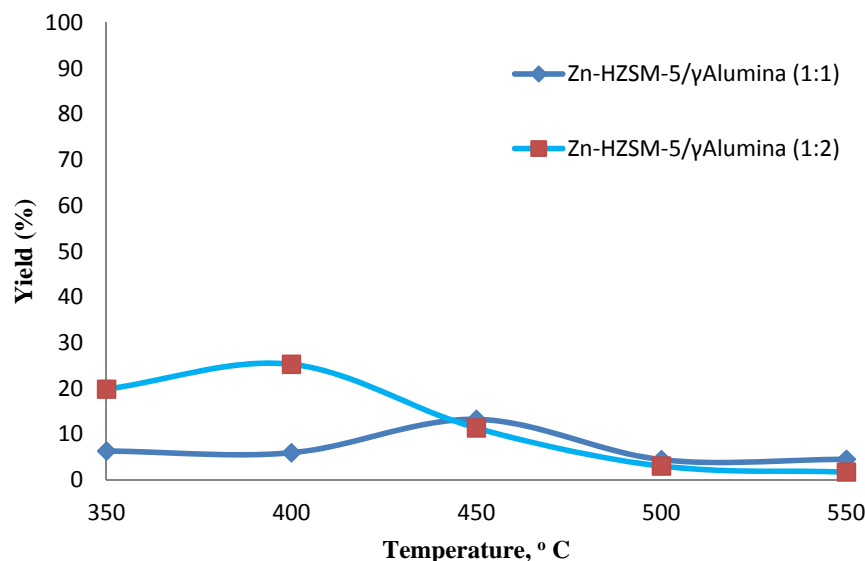


Figure-5. Effect of reaction temperature on the yield of biokerosene at various catalyst composition.

Actually biokerosene fraction was undesirable in the biofuel preparation. Its use has been replaced by liquefied petroleum gas (LPG) in Indonesian market. Figure-5 shows the relationship between temperature processes to biokerosene yield. The catalyst of Zn-HZSM-5/γ-Alumina gave biokerosene yield in the range of 20 to 3 wt%. This study showed conformity with the use of CoMo / γ-Al₂O₃ catalysts in producing biofuel from oil nyamplung where biokerosene yield reached 17.3 wt% [15].

CONCLUSIONS

The catalyst Zn-HZSM5/γ-Alumina can be used for cracking nyamplung oil into biofuel. The catalyst composition Zn-HZSM5/γ-Alumina affect selectivity of biogasoline and biodiesel production. The use of Zn-HZSM-5/γ-Alumina catalyst (1:1) to produce biofuels had high selectivity to biogasoline and biodiesel of 54% and 41% respectively, while Zn-HZSM-5/γ-Alumina (1:2) to produce biodiesel had high selectivity of 73.86%. Temperature also affects the biofuels obtained. At high temperature the selectivity product of biodiesel and biogasoline higher than that of at low temperature. The best selectivity of biodiesel production when it used catalyst composition of Zn-HZSM5/γ-Alumina (1:2) performed at temperatures of 450-550°C was 73.86%. While biogasoline selectivity of 54% was obtained on the composition of the catalyst Zn-HZSM-5/γ-Alumina of 1:1 which is operated at the temperature of 500-550°C.

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