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Biofuel Production from Palm Olein by Catalytic Cracking Process using ZSM-5 Catalyst

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Abstract

The depletion of fossil energy reserves raises the potential in the development of renewable fuels from vegetable oils. Indonesia is the largest palm oil producer in the world, where palm oil can be converted into biofuels such as biogasoline, kerosene and biodiesel. These biofuels are environmentally friendly and free of the content of nitrogen and sulfur through catalytic cracking process. In this research, palm olein is used as feedstock using catalytic cracking process. ZSM-5 is used as a catalyst, which has a surface area of 425 m^2/g and Si/Al ratio of 50. Variables varied are the operating temperature of 375 °C - 450 °C and reaction time of 60 minutes - 150 minutes. The result shows that the highest yield of liquid product is 84.82%. This yield is obtained at a temperature of 400 °C and reaction time of 120 minutes. The yield of the liquid product in the operating conditions consisting of C_6-C_{12} amounted to 19.47 %, C_{14}-C_{16} amounted to 16.56 % and the C_{18}-C_{28} amounted to 48.80 %.

INTRODUCTION

The depletion of fossil energy sources leads to a fuel crisis as it happens today. This leads to the development of renewable fuels from plants, especially palm oil, where the fuel is environmentally friendly and free of sulfur or nitrogen This leads to the development of renewable fuels from plants, especially palm oil, where the fuel is environmentally friendly and free of sulfur or nitrogen (Chew & Bhatia, 2009; Tamunaidu & Bhatia, 2007). Palm olein is one of the alternative raw materials that can be used for renewable fuels. Palm olein is a liquid fraction of palm oil that has been fractionated (Karimah, 2014). The number of palm olein in Indonesia is so abundant that the development of palm olein utilization can be done, which is currently Indonesia is the largest palm oil producing country in the world.

Catalytic cracking is a chemical process that can be applied in the manufacture of biofuel from palm olein. Palm olein can be cracked into biofuel because it has a long carbon chain. This process can produce a number of liquid hydrocarbon fuels such as biogasoline (Rohmah et al., 2012), biodiesel (Mota et al., 2014) and kerosene (Sirajuddin et al., 2013). This process has been proven to produce biofuel from various raw materials such as palm oil, rubber seed oil, soybean oil and others. The catalytic cracking process uses heterogeneous catalysts to speed up the reaction.

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Some of the catalysts commonly used in this catalyzed cracking are Al-SBA-15 (Ooi & Bhatia, 2007), natural zeolite (Rohmah et al., 2012), silica alumina, ZSM-5 (Sirajuddin et al., 2013) and several other catalysts. Chew and Bhatia also conducted research using raw materials of crude palm oil (CPO) and cooking oil with HZSM-5 catalyst and REY catalyst. From the result of the research, it is known that HZSM-5 gives higher yield of liquid product. It also found that the use of HZSM-5 catalysts produced more gasoline components than beta zeolites which tend to produce kerosene and more biodiesel (Chew & Bhatia, 2009). Zeolite is a catalyst commonly used in catalytic cracking process. Zeolites have advantages such as thermal stability, selectivity (Taufiqurrahmi et al., 2010) and its highly ordered structure (Sprung & Bert, 2014). ZSM-5 (Zeolite Socony Mobil-5) is one of a kind zeolite that can be used as a catalyst in catalytic cracking. Zeolite ZSM-5 is aluminum-silicate with high Si content and low Al. The center on the part around Al is very acidic. Substitution of Al^{+3} by Si^{+4} requires the presence of an additional positive charge. If H^{+} exists, the acidity of the zeolite is high (Buzetzki et al., 2009).

Based on the above description, this research will examine the effect of temperature and time of operation on yield and distribution of biofuel production, and obtain the best condition for the highest biofuel yield from palm olein catalytic cracking process using ZSM-5 catalyst.

MATERIALS AND METHODS

Materials and Equipment

Palm olein used in this study are commercial oils and ZSM-5 catalysts obtained from international zeolyst with Si/Al 50 ratio. This study use a pressurized batch reactor with 4848 parr type and gas chromatography using FID (Flame Ionized Detector) to analyze raw material content and hydrocarbon content in liquid product.

Calcination of Catalyst

Catalyst NH4-ZSM-5 (CBV5524G) with Si/Al ratio of 50 is calcined at 600 °C for 6 hours to convert it into H-ZSM-5 (Chew & Bhatia, 2009).

Catalytic Cracking of Palm Olein

The reaction is carried out in a batch reactor where the operating pressure depends on reaction time and reaction temperature. Palm olein of 500 g and a catalyst of 10 g (2% of the raw material) are put into the reactor. The reaction starts when the reactor temperature has reached the reaction temperature, where in this study the reaction time is used in 60 minutes - 150 minutes and the reaction temperature of 375°C - 450°C. After the reaction is complete, the reactor is cooled to room temperature where it will form the product in three phases of liquid, solid and gas. The solid product and liquid product are separated by filtration while the amount of gas is calculated based on the mass balance by subtracting the initial amount of raw material by the amount of liquid product and the obtained solids.

RESULTS AND DISCUSSIONS

Raw Material Analysis

The fatty acid content affects the catalytic cracking process, where the content of unsaturated bonds increases the formation of aromatic hydrocarbons (Doronin et al., 2013). These aromatic hydrocarbons can polymerize which leads to the coke formation (Taufiqurrahmi & Bhatia, 2011).

Table 1 shows the results of the raw material components analysis in the palm olein using gas chromatography.

Table 1. Palm olein components.

Components	Composition % (w/w)
Lauric acid ($C_{12:0}$)	0.2208
Myristic acid ($C_{14:0}$)	1.0710
Palmitic acid ($C_{16:0}$)	38.647
Palmitoleic acid ($C_{16:1}$)	0.2048
Stearic acid ($C_{18:0}$)	3.5960
Oleic acid ($C_{18:1}$)	43.2073
Linoleic acid ($C_{18:2}$)	12.2946
Linolenic acid ($C_{18:3}$)	0.2812
Arachidic acid ($C_{20:0}$)	0.3241
Eicosenoic acid ($C_{20:1}$)	0.1526

Effect of Catalyst Calcination on Product Composition

In the catalytic cracking process of palm oil three-phase product was produced, namely in the form of solid, gas and liquid product. The effect of catalyst calcination on the composition of the product in solid phase, liquid (liquid product in the range C_6-C_{28}) and gas can be seen Figure 1, where

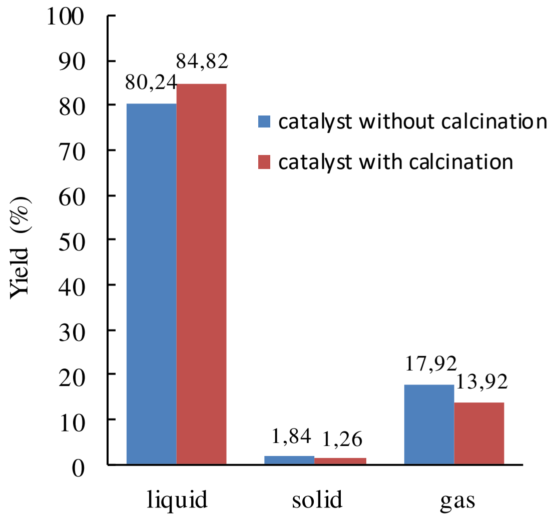

Figure 1. Effect of catalyst calcination on product composition.

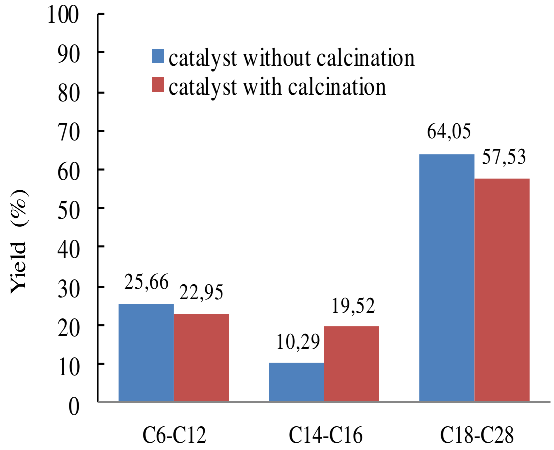

Figure 2. Effect of calcination on liquid product distribution.

the reaction is carried out under operating conditions when the temperature is 400 °C and the reaction time is 120 minutes. The results showed that the use of a catalyst by the calcination process give a higher value of the liquid product than using a catalyst without calcination, where obtained the yield of 84.82% is obtained on the use of catalyst with calcination and 80.24% on the use of catalyst without calcination. The use of catalysts with calcination also decreases gas formation by 4% and solids by 0.58% when compared with catalyst use without casination.

Figure 2 shows the effect of calcination on the liquid product yield distribution. The distribution of the liquid product formed is divided into three parts: C_6-C_{12}, C_{14}-C_{16}, and C_{18}-C_{28}. Components with carbon C_{18}-C_{28} bond on the process without using calcined catalyst is obtained value of 64.05%, and the process using calcined catalyst is obtained value of 57.53%. The C_{14}-C_{16} components have the highest value in the process by using a calcined catalyst with a value of 19.52%, and the process without using calcined catalyst is obtained value of 10.29%.

Calcination of the ZSM-5 catalyst has changed the zeolite cation from NH_4^+ to H^+ (Chew and Bhatia, 2009) and can also change the acidity of the catalyst (Lu et al., 2005). From the research conducted at temperature of 400 °C and at the time of reaction of 120 minutes, the liquid product formed has a shorter chain carbon content (<C_{16}) larger on the catalyst with calcination than the catalyst without calcination, but the long chain hydrocarbon content (>C_{18}) is greater in the catalytic cracking process using a catalyst without calcination.

Effect of Temperature and Reaction Time on Liquid Product Yield

The effect of reaction time and reaction temperature at 375°C - 450°C on the yield of liquid product can be seen in Figure 3. In the figure can be seen that the highest yield of liquid product is obtained at a temperature of 400°C and at reaction time of 120 minutes with a value of 84.82% and decreased at a later time. At the reaction temperature of 425°C and 450°C, the yield of liquid product showed a downward trend with increasing reaction time, with maximum liquid product yield value at minute 60 with value of 81.94% and 74.06% respectively. At 375°C, the yield of liquid product is still increased until the reaction time of 150 minutes, where the lowest yield of liquid product is obtained at 375°C at reaction time of 60 minutes with the value of 54.44%, and the highest yield is obtained at reaction time of 150 minutes with the value of 83.04 %.

The results of this study are in accordance with the predictions of Li, et al (2014) which states that the yield of liquid product increases with increasing reaction temperature, but will decrease after obtaining maximum yield value by increasing the reaction temperature. This is because some liquid product will be cracked into gas product and will decrease yield on liquid product. This makes the product liquid yield of catalytic cracking

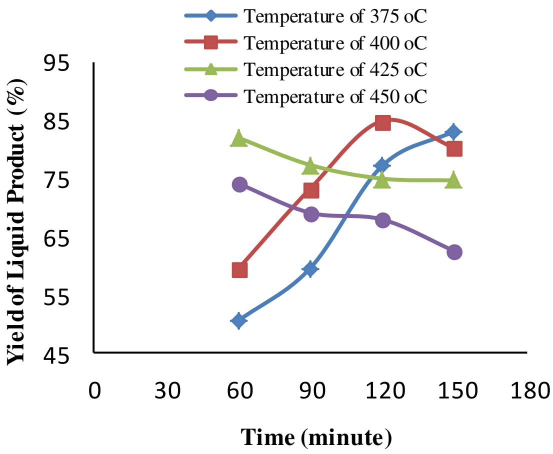

Figure 3. Effect of reaction time on yield of liquid product at temperature of 375 °C - 450 °C.

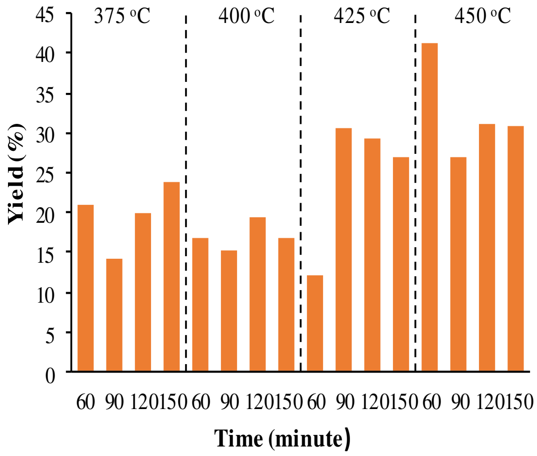

Figure 4. Influence of reaction time and temperature reaction to liquid product distribution of C_6-C_{12}.

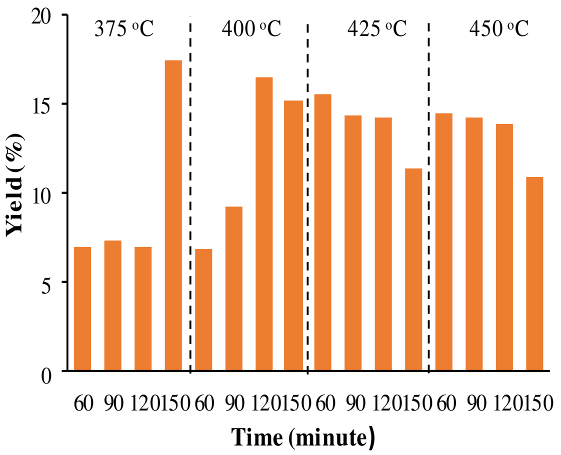

Figure 4. Influence of reaction time and temperature reaction to liquid product distribution of C_{14}-C_{16}.

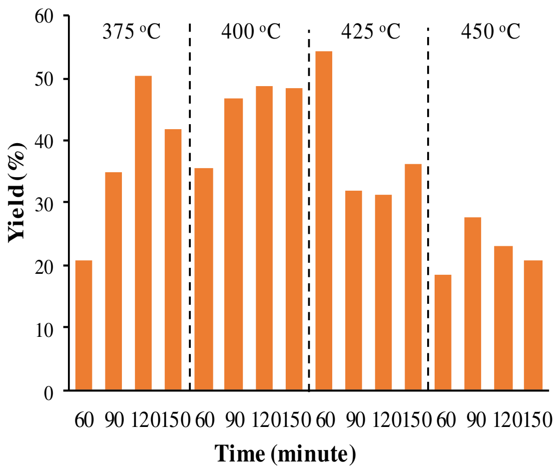

Figure 4. Influence of reaction time and temperature reaction to liquid product distribution of C_{18}-C_{28}.

decrease with increasing time and reaction temperature after reaching the maximum value.

Compared to the similar studies with this study performed by Li, et al. (2014) and Sirajuddin, et al. (2013), the results obtained in this study are quite good. In a study conducted by Li, et al (2014), they performed catalytic cracking process using rubber seed oil as raw material and USY as catalyst. They could achieve the highest liquid product yield about 75.6% at temperature of 420°C in 90 minutes. While in research conducted by Sirajuddin, et al. (2013), they did a catalytic cracking process by using a fix bed micro reactor using palm oil as a raw material and HZSM-5 as catalyst, with variation of temperature and N_2 flow rate. They achieved the highest yield consists of gasoline of 28.87%, kerosene of 16.70% and diesel of 1.2%. This yield is obtained at a temperature of 450°C and N_2 flow rate of 100 ml/min.

Liquid Product Distribution at Various Temperature and Reaction Time

Liquid product of the catalytic cracking process of palm olein contains hydrocarbons with varying amounts of C chains, where the product distributions are grouped by carbon bonds, carbon bonds of C_5-C_{12} are identified as gasoline, carbon bonds of C_{13}-C_{14} are identified as jet, carbon bonds of C_{15}-C_{17} are identified as kerosene fuels and carbon bonds of C_{18}-C_{28} are identified as gas oil/diesel (Ortega et al., 2006). The effect of reaction time and reaction temperature on the distribution of liquid product of C_6-C_{12}, C_{14}-C_{16} and C_{18}-C_{28} in the temperature range of 375ºC - 450ºC can be seen in Figures 4, 5 and 6, where these distributions are obtained from liquid product analysis by using gas chromatography.

Figure 4 shows that the highest yield of liquid product of C_6-C_{12} chain is obtained at temperature of 450°C and reaction time of 60 minutes with value of 41.21%. In Figure 5 can be seen that the highest yield of liquid product of C_{14}-C_{16} chain is obtained at 375ºC and reaction time 150 minutes with value 17.42%, and figure 6 shows the liquid product with the highest of C_{18}-C_{28} chain is obtained at temperature of 425ºC and reaction time of 60 minutes with a value of 54.17%.

From the results of this study also obtained that the longer reaction time and higher reaction temperature gives different values to the value of the liquid product distribution,where the complexity of the reaction of palm olein catalytic cracking process can provide many possible reactions or products formed. In this catalytic cracking process, there are several processes occurring such as cracking, deoxygenation, oligomerization, aromatization, alkylation, isomerization and polymerization (Doronin et al., 2013).

Thermal decomposition of triglycerides and heavy oxygenated hydrocarbon groups always start at a temperature of 240 ºC - 300 ºC and this catalytic cracking temperature is in the range of 300 ºC - 500 ºC (Luque et al., 2011). From the results of this study also are found the patterns of product distribution, where the liquid product of C6-C12 at a temperature of 450 °C in all the reaction time and temperature of 425 ° C in reaction time 90 minutes - 150 minutes have higher yield than other operating conditions. Liquid product of C_{14}-C_{16} at temperature of 375 °C and reaction time of 150 minutes, at temperature of 400 °C and reaction time of 120 minutes - 150 minutes, and at temperature of 425 °C and 450 °C in a reaction time of 60 °C - 120 °C have a higher yield than other operating conditions. Liquid product between C_{18}-C_{28} at temperature of 375 °C and reaction time of 120 minutes - 150 minutes, at 400 °C of temperature and reaction time of 90 minutes - 120 minutes, and 425 °C of temperature at reaction time of 60 minutes has a higher yield value than other operating conditions. From the results obtained above, it is found that the highest liquid product for C_6-C_{12}, C_{14}-C_{16} and C_{18}-C_{28} is not obtained under one operating condition, but each product has the best temperature and time conditions to obtain the highest yield value, so it can be stated that the liquid product composition produced will fluctuate when the temperature and reaction time are changed.

CONCLUSIONS

The use of ZSM-5 catalysts with calcination produces more products with short carbon chains than by using a catalyst without calcination. The variation of reaction temperature and reaction time in the catalytic cracking process of palm olein provide a fluctuating dispersion pattern for catalytic cracking products. In this research, the highest liquid product yield is 84.82% at reaction temperature of 400 ºC and reaction time of 120 minutes.

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