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ORIGINAL RESEARCH PAPER

HZSM-5 CATALYST FOR CRACKING PALM OIL TO BIODIESEL: A COMPARATIVE STUDY WITH AND WITHOUT PT AND PD IMPREGNATION

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Abstract: The Needs of healthy environment and green energy poses a great demand for alternative energy. Biofuel is one of the alternative energy products that are environmentally friendly. Biofuel can be made from plant oils, especially palm oil. Cracking of palm oil into biofuel is constrained by the availability of catalysts. Moreover the available catalyst still gives a low yield. This research aims to study the effect of Pt and Pd impregnation into HZSM-5 catalyst on the catalytic properties. Another aim is to obtain the operating conditions of the catalytic cracking process of palm oil into biofuel which gives the highest yield and selectivity, especially for biodiesel and biogasoline fractions. Catalytic cracking process was carried out in a micro fixed bed reactor with diameter of 1 cm and length of 16 cm. The reactor was filled with a catalyst. The results of the study successfully prove that Pt and Pd impregnated into HZSM-5 catalyst can increase the yield and selectivity of biodiesel. Pd and Pt are highly recommended to increase the yield and selectivity of biodiesel.

Keywords: *Biofuel, biodiesel, palm oil, Pd/HZSM-5, Pt/HZSM-5*

INTRODUCTION

Alternative fuels which are environmentally friendly are needed at this time to replace petroleum-based fuels. It is triggered by the depletion of world petroleum reserves and the increase of environmental awareness [1]. Biofuel is one of very attractive alternative energies. Biofuel can be produced from plant and animal oils by a conventional method of esterification and transesterification processes. The result of this process produces biodiesel of fatty acid methyl esters (FAME). Biofuel can also be produced using cracking process to produce a product which look like a mixture of gasoline, diesel and kerosene [2]. Fuel using catalytic cracking process, especially using this catalyst is more advantageous because it does not require additional materials such as methanol and ethanol.

Biofuel is defined as liquid or gaseous fuel which can be produced from biomass utilization or bioresource substrate [3]. Biofuel is more environmentally friendly than fossil fuel. Biofuel derives from renewable raw materials, and it reduces the emission of carbon dioxide. Various studies on biofuel and the catalyst have been done by several researchers. The use of various types of catalysts to the biofuel products were carried by Farouq [4], Chew and Bhatia [5]. Study of optimization of the reactor was done by Tamunaidu and Bhatia [6]. The use of composite catalyst and deactivation study on palm oil cracking process to produce biofuel were studied by Bhatia et al [7]. Researches on the hydrocracking process of used oil to biofuel were done by Bezergianni and Kalogianni [8].

Biofuel can be produced from a variety of plant and animal oils. It would be very interesting if the oils are available in large quantities. Palm oil is one of the alternative potential oils to make substitute fuel for diesel, kerosene and gasoline. It is because palm oil production increases in Indonesia. Based on the calculation of Gapki, the realization of Indonesia's Crude Palm Oil (CPO) production in 2010 reached 21 million tons. According to data from Indonesia's agriculture ministry, CPO production in 2012 was 23.5 million tons, with a growth of 1.84 %, so that the CPO production is estimated to reach 32.9 million tons in the year 2014. These data indicate that Indonesia is the world largest palm oil producer as shown in Figure 1.

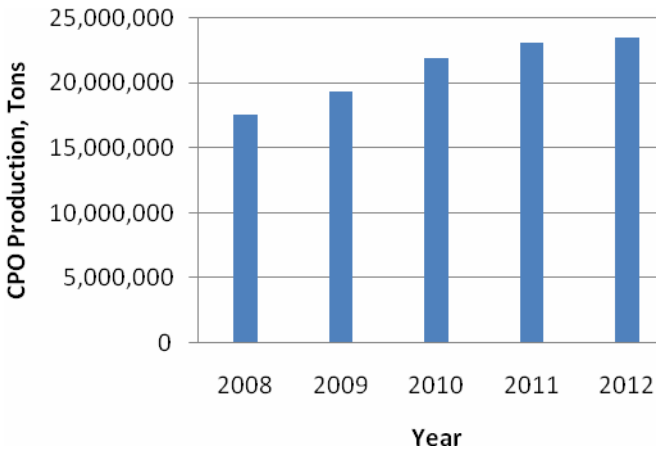

Figure 1. *Indonesia's CPO production within 5 years (2008-2012)* [9]

The production of Biofuel from palm oil using zeolite catalyst in hydrocracking process has been widely studied [10, 11]. HZSM-5 zeolite has good performance in cracking process. Zeolite catalyst has advantages in terms of providing main surface area and active site. They control the activity and selectivity of the catalyst [12]. This advantage is good enough if it is used in cracking process, but this catalyst has the disadvantage, i.e., the yield is low. This disadvantage has been improved by impregnation Cu, Ni and Zn into HZSM-5 catalyst. The results show that an increase in gasoline yield results in a decrease in kerosene and diesel yield. The use of these catalysts give the highest yield of 29.38 % gasoline, 30 % kerosene and diesel 25 % [2]. The use of Pd and Pt is assumed to give better yield and selectivity because precious metals are categorized as transitional.

Impregnation of Pd and Pt have been selected because they have a lot of electrons which are easily delocalized. It can be used to influence the reaction, especially to break covalent bonds such as cracking. This research aims to study the effect of Pt and Pd impregnation into HZSM-5 catalyst on the catalytic properties. Another aim is to obtain the operating conditions of the catalytic cracking process palm oil into biofuel which gives the highest yield and selectivity, especially for biodiesel and biogasoline fractions. Formation of Biofuel from palm oil by catalytic cracking process was carried out in a fixed bed micro-reactor. The reaction temperature was set from 350 °C to 550 °C, with the increase of 50 °C. The success of this research will give a very important contribution to the process of the production of cracking catalyst and proper operating condition in the production of biofuel, especially an increase of biodiesel and biogasoline yield.

MATERIALS AND METHOD

Materials

Raw material for the process of catalytic cracking is palm oil. Palm oil was first processed into Refined, Bleached and Deodorized (RBD) oil with refined, bleached and deodorized method. RBD oil composition used was the same as that used by Roesyadi et al, with the highest composition of oleic acid 55 % and palmitic acid 30 % [2]. The catalyst used was a synthetic zeolite. The raw material for making synthetic zeolite was aluminum sulfate $Al_2 (SO_4)_3$:18 H_2O, water glass, chloride acid, NH_4Cl, distilled water, sulfuric acid (Pro Analysis), butanol. Palladium (II) chloride anhydrous for synthesis with molar mass of 177,326 g/mol and colored dark red solid, Platinum IV chloride with a molar mass of 336.89 g/mol and brown-red colored powder. Other materials were nitrogen gas and hydrogen gas.

Method

Preparation of Catalyst

NaZSM-5 catalyst was synthesized using method of Plank et al. [13], then it was converted into HZSM-5. The catalyst was then impregnated by the solution of palladium (II) chloride and platinum (IV) chloride. Catalyst impregnation process used

procedure of Romero [14]. Pt/HZSM-5, and Pd/HZSM-5 catalysts were dried in an oven at 110 °C for 14 hours, then they were reduced at a temperature of 450 °C for 5 hours, and then they were cooled in a desiccator.

Palm Oil Catalytic Cracking Process

Catalytic cracking was done in a fixed bed microreactor with a diameter of 1 cm, 16.4 cm long and filled with 0.6 g of catalyst. Figure 2 shows the equipment used to make Biofuel from palm oil by catalytic cracking process. Palm oil was introduced into the evaporator and heated to 250 °C. Nitrogen gas was flowed into the evaporator and was distributed evenly with gas distributors submerged in the oil. Palm oil vapor formed will be carried by nitrogen gas to the reactor . The reactor temperature was maintained at 350 °C and 50 °C increased with differences of up to 550 °C. Nitrogen gas flow rate was maintained 130 $mL \cdot min^{-1}$. Biofuel products were analyzed by FID gas chromatography. The operating conditions of gas chromatography, i.e., column temperature of 50-250 °C, flow rate of nitrogen gas in the GC of 30 mL/min, temperature rise of 5 $°C \cdot min^{-1}$, initial time of 2 min, detector temperature of 250 °C, injector temperature of 250 °C. Chromatogram of biofuel was compared to the chromatogram of diesel oil, gasoline and kerosene based on rentention time similarity.

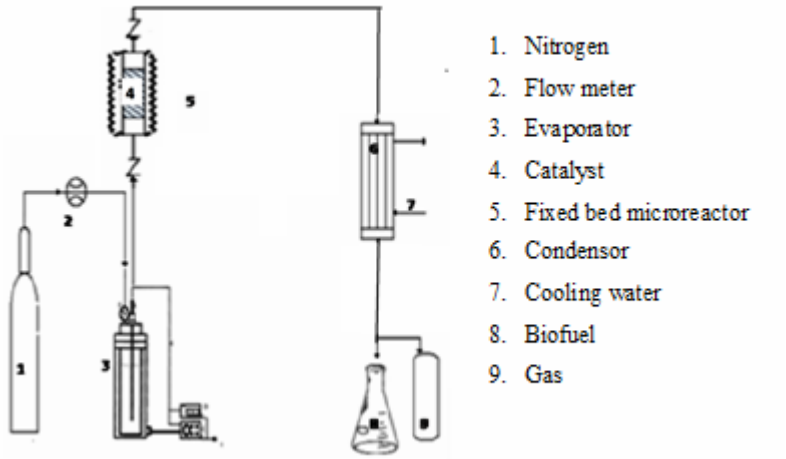

Figure 2. *The series of RBD oil cracking process equipment*

RESULTS AND DISCUSSION

RBD oil composition

Chromatogram for RBD oil is shown in Figure 3. This chromatogram is the result of the analysis of RBD oil using a gas chromatography mass spectrometry (GCMS). The figure shows that the main constituent of RBD oil is Oleic acid, palmitic acid and linoleic acid. Complete composition of RBD oil is shown in Table 2. More than 95.08% of the RBD oil is a combination of oleic acid, palmitic acid and linoleic acid.

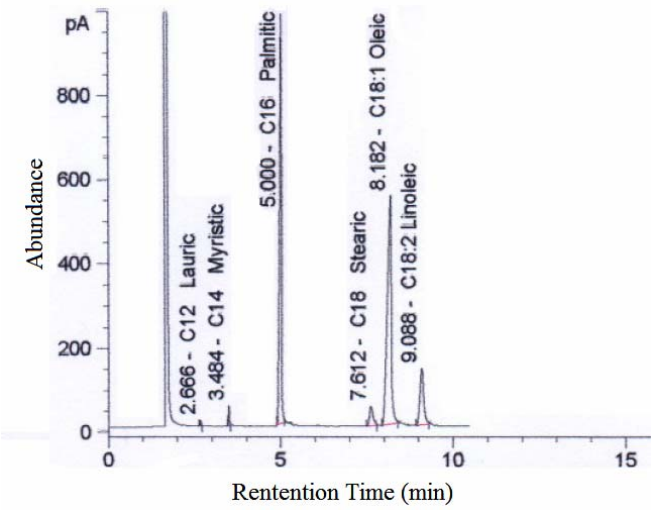

Figure 3. *Chromatogram of RBD oil produced from palm oil*

Table 1. *The composition of RBD oil*

Name of fatty acid		Fatty acid (%)
C8	Caprilic	0.000
C10	Capric	0.000
C12	Lauric	0.262
C14	Myristic	1.012
C16	Palmitic	38.201
C18	Stearic	3.637
C18:1	Oleic	45.962
C18:2	Linoleic	10.926

Characterization of catalysts

Synthetic catalysts were characterized using X-ray diffraction (XRD), Brunauer Emmett Teller (BET), and X-ray fluorescence (XRF). XRD method was used to determine the type of catalyst. BET method was used to determine the specific surface area, pore size, while the XRF method was used to determine the ratio of Si/Al and Pt and Pd content. Table 3 shows the results of the characterization of HZSM-5, Pd/HZSM-5 and Pt/HZSM5 catalysts.

Table 2. *Characterization of HZSM-5 Catalysts with Si/Al moles ratio of 24.3*

Type of catalyst	Surface area ($m^2 \cdot g^{-1}$)	Pore volume ($cm^3 \cdot g^{-1}$)	Pore diameter (Å)	Pd, Pt content (% w/w)
HZSM-5	106.508	0.002	19.302	0
Pd/HZSM-5	118.273	0.018	38.146	4.57
Pt/HZSM-5	116.234	0.016	37.235	4.78

Catalyst pore diameter was in the range of 19.302-38.146 Å. The pore volume of the catalyst was 0.002 to 0.018 $cm^3 \cdot g^{-1}$. The minimum surface area was 101.101 $m^2 \cdot g^{-1}$,

while the maximum surface area was 118.273 $m^2 \cdot g^{-1}$. The catalyst modified with impregnation of Pd and Pt showed an increase of surface area. It occurs because of the reduction process. The reduction of $PtCl_4$ and $PdCl_2$ to Pt and Pd occurs by removing the element of chlorine bonded to the metal. Space left by the element of chlorine becomes vacant and form new pores. This new pore automatically increases the surface area. The addition of surface area can improve the effectiveness of the catalyst. The addition of Pt and Pd also increases the active site; thus it affects the rate of reaction.

Effect of reaction temperature on the yield of biodiesel, biokerosene and biogasoline

In this study, it has been conducted Pt and Pd impregnation into HZSM-5 catalyst. Metal impregnation aims to add the active site on the catalyst surface, increase the surface area and increase the yield of biofuel products. So, in addition to an increase in the activity of the catalyst , there is also an increase in selectivity and yield of biodiesel . Previous researchers proved that impregnation of Ni , Cu and Zn into HZSM-5 catalyst can increase the active site and surface area of the catalyst [2]. Figure 4 to 6 show the effect of temperature on yield with HZSM-5, Pt/HZSM-5 and Pd/HZSM-5 catalysts. Experiments to study the effect of catalyst activity were done by adjusting the N_2 gas flow rate of 130 $mL \cdot min^{-1}$ and temperature variations. Figure 4 shows that HZSM-5 catalyst at 400 °C gives biodiesel yield of 25.7 %, while Pt/HZSM-5 and Pd/HZSM-5 give yield of 67.0 % and 54.3 % respectively. The highest yield of biodiesel with Pt/HZSM-5 catalyst at a temperature of 450 °C was 67,2 %. The use of Pd/HZSM-5 catalyst for the cracking process at a temperature of 500 °C give yield of 65,2 %. It proves that Pt and Pd distributed evenly give contribution to direct the product formed into biodiesel fraction. The increase of the active sites with Pt and Pd gives yield of biodiesel better than with Ni, Cu, and Zn which was only 7 % - 25 % [2].

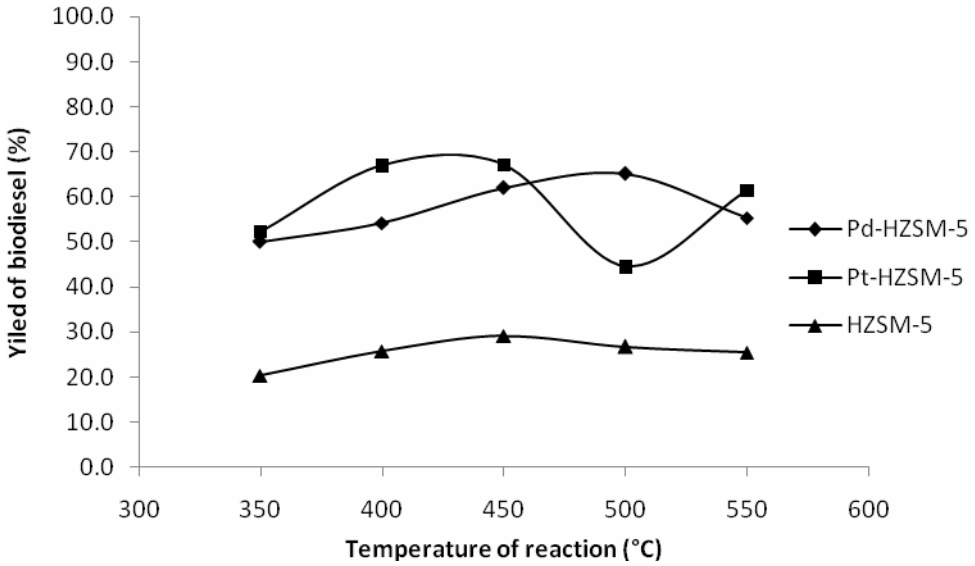

Figure 4. *Effect of reaction temperature on the yield of biodiesel for various HZSM-5 catalyst and derivatives*

Figure 5 shows the effect of reactor temperature of cracking on biokerosene yield in biofuel products with various catalysts. The use of HZSM-5 catalyst at a temperature of 350 °C gave biokerosene yield of 22.5 %. The use of Pt/HZSM-5 and Pd/HZSM-5 catalysts lowered the biokerosene yield to 10.9 % and 11.9 %. The increase of cracking process temperature with HZSM-5 and Pd/HZSM-5 catalysts decreased biokerosene yield, but the Pt/HZSM-5 catalyst gave fluctuate yield in the temperatur range of 400-550 °C. The lowest biokerosene yield was 2.9 % for Pt/HZSM-5 at 450 °C, while the highest biokeresene yield was 18,5 % with the HZSM-5 catalyst. The Pd/HZSM-5 catalyst also shows a decrease compared to HZSM-5 catalyst. The yield was only 3.4 %. It shows that Pd and Pt decrease yields of biokerosene.

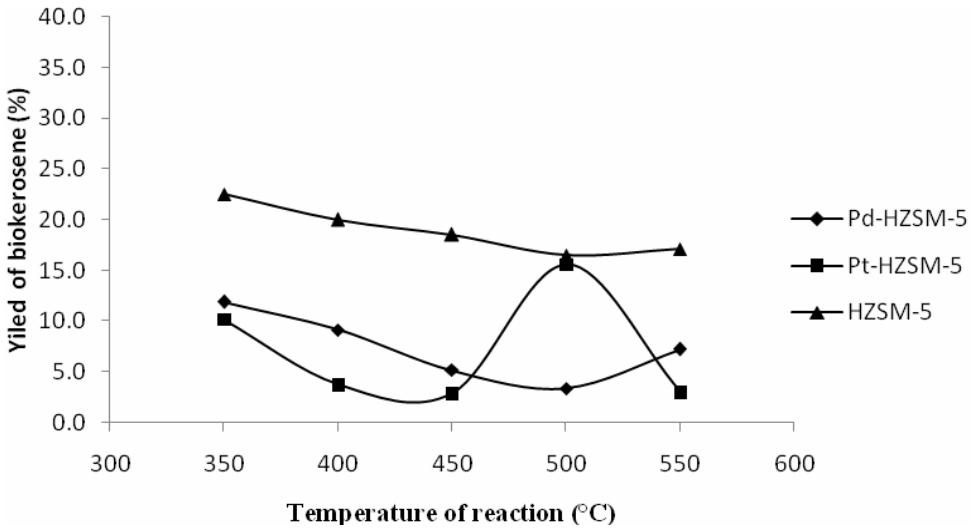

Figure 5. *Effect of reaction temperature on biokerosene yield for various catalysts*

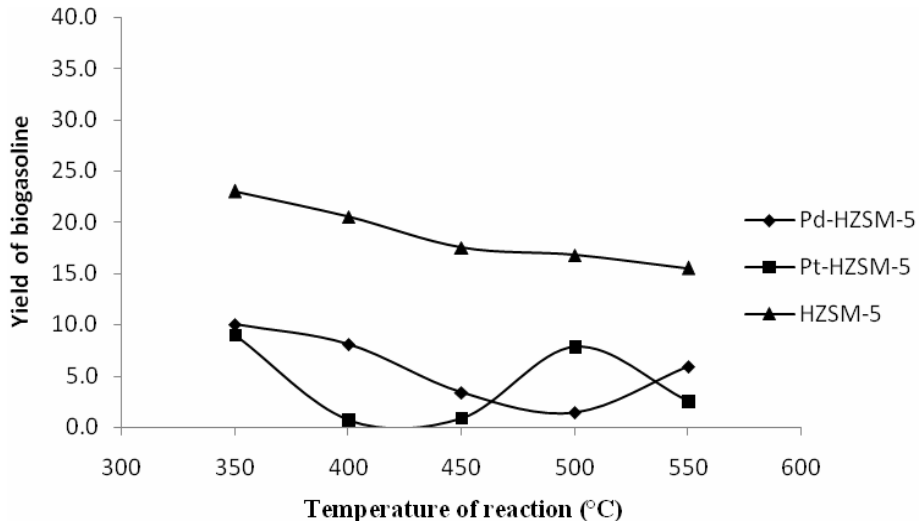

Figure 6. *Effect of reaction temperature on biogasoline yield for various catalysts*

Figure 6 shows the effect of cracking reaction temperature on biogasoline yield with various catalysts. The highest biogasoline yield was 23.0 % at a temperature of 350 °C, while the lowest yield was 0.7 % at a temperature of 400 °C. HZSM-5 catalyst at temperature range of 350-550 °C decreases the yield by increasing temperature, while Pd/HZSM-5 and Pt/HZSM-5 catalysts decrease and fluctuate the yield due to temperature rise. Figure 4-6 show that the Pd/HZSM-5 and Pt/HZSM-5 direct the formation of biodiesel fraction and an increase in product yield.

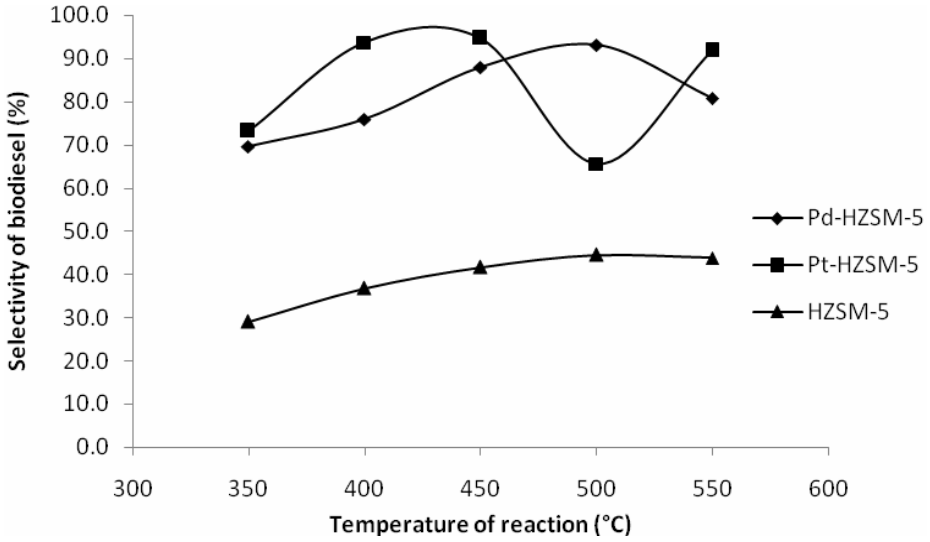

Figure 7. *Effect of reaction temperature on the selectivity of biodiesel for various catalysts*

Figure 7-9 show the effect of reaction temperature on the selectivity of biodiesel, biokerosene and biogasoline. Figure 7 shows that the highest selectivity of biodiesel with HZSM-5, Pt/ HZSM-5 and Pd/HZSM-5 catalysts were 44,5 %, 94.6 % and 93.2 % respectively. The increase of selectivity of biodiesel proves that the presence of Pt and Pd direct the product of biodiesel to form biofuel factions. However, the best temperature of the selectivity with Pt/HZSM-5 and Pd/HZSM-5 were different, i.e., a temperature of 450 °C and 500 °C respectively. This difference could be occured due to the differences in the activation energy for each of catalysts and for the moment the data to calculate the activation energy is not sufficient, so it needs to be proven in the future.

Figure 8 shows that the reaction temperature affects the biokerosene selectivity. At a temperature of 350 °C, the different types of catalysts had an effect on the selectivity of biokerosene. Temperature rise decreases the selectivity of biokerosene, but Pd/HZSM-5 catalyst fluctuated the selectivity of biokerosene. The Pt/HZSM-5 and Pd/HZSM-5 catalysts reduce the formation of biokerosene more than that of HZSM-5 at temperature range of 350-550 °C.

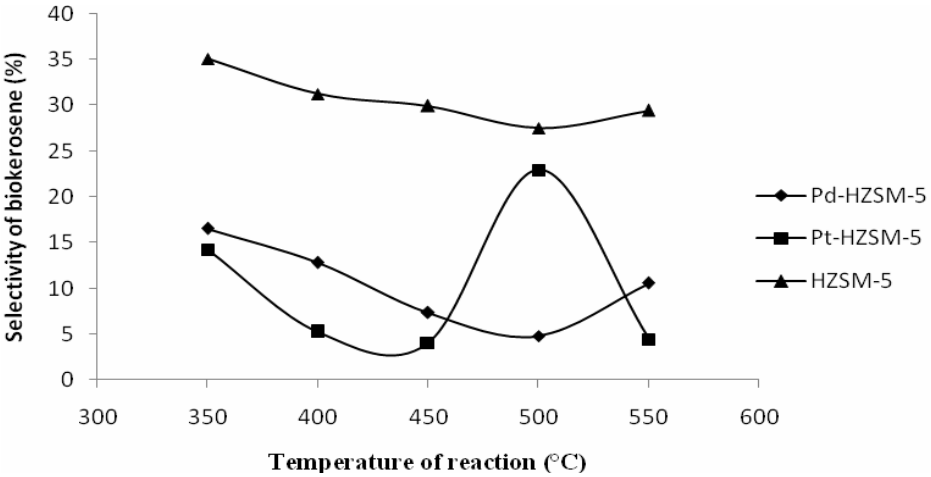

Figure 8. *Effect of reaction temperature on the selectivity of biokerosen, for various catalysts*

Figure 9 shows the effect of reaction temperature on the selectivity of biogasoline. At a temperature of 350 °C, the biogasoline selectivity for these three types of catalysts was different, i.e. for HZSM-5, Pt/HZSM-5 and Pd/HZSM-5 catalyst was 35.9 %, 12.6 % and 13.9 % respectively. It indicates that the impregnation of Pt and Pd can decrease the yield of biogasoline. Increasing the temperature decreased the biogasoline selectivity, although fluctuation also occurred. The lowest biogasoline selectivity was 1 % for Pd/HZSM-5 catalyst at a temperature of 400 °C.

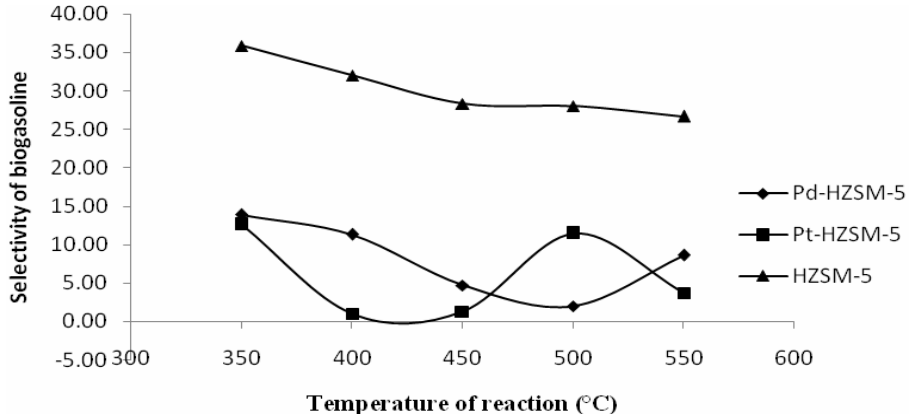

Figure 9*. Effect of reaction temperatur on the selectivity of biogasoline, for various catalysts*

CONCLUSIONS

The production of biofuel from palm oil can reduce the consumption of fossil energy. Besides, biofuel is environmentally friendly. HZSM-5 catalyst impregnated by Pd and

Pt increased the yield of biofuel. The addition of Pd and Pt into HZSM-5 catalyst also increased the selectivity of biodiesel. The Pt/HZSM-5 catalyst gave the highest selectivity and yield of biodiesel high of 94.6 % and 67.2 % respectively at a temperature of 450 °C. The Pd/HZSM-5 catalyst gave the highest selectivity and yield of biodiesel that is 93.2 % and 65.2 % respectively at a temperature of 500°C. Pt and Pd impregnation increased biodiesel yield and selectivity higher than that of HZSM-5 catalyst. The Pt/HZSM-5 and Pd/HZSM-5 catalyst are recommended for palm oil cracking process into biofuel, especially that is rich of biodiesel.

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REFERENCES

1. Leung, D.Y.C., Wu, X., Leung, M.K.H.: A review on biodiesel production using catalyzed transesterification, *Applied Energy*, **2010**, **87**, 1083–1095.
2. Roesyadi, A., Prajitno, D.H., Nurjannah, N., Savitri, S.D.: HZSM-5 Catalyst for Cracking Palm Oil to Gasoline: A Comparative Study with and without Impregnation, *Bulletin of Chemical Reaction Engineering & Catalysis*, **2013, 7** (3), 185 – 190.
3. Stocker, M.: Biofuel and Biomass-to-Liquid Fuels In The Biorefinery: Catalytic Conversion of Lignocellulosic Biomass Using Porous Materials. *Angew. Chem. Int*, **2008, 47**, 9200–9211.
4. Farouq, A., Twaiq, A., Mohamad, R., Bhatia, S.: Performance of Composite In Palm Oil for the Production of Liquid Fuels and Chemicals, *Fuel Processing Technology*, **2004, 85**, 1283-1300.
5. Chew, T.L., Bhatia, S.: Catalytic Processes Towards the Production of Biofuel in a Palm Oil and Oil Palm Biomass-Based Biorefinery, *Bioresource Technology*, **2008, 99**, 7911–7922
6. Tamunaidu, P., Bhatia, S.: Catalytic Cracking Of Palm Oil For The Production Of Biofuel: Optimization Studies, *Bioresource Technology*, **2007, 98**, 3593–3601.
7. Bhatia, S, Mohamed, A.R., Noor, A.A.S.: Composites as cracking catalysts in the production of biofuel from palm oil: Deactivation studies, *Chemical Engineering Journal*, **2009, 155**, 347–354.
8. Bezergianni, S., Kalogianni: Hydrocracking of used cooking oil for Biofuel Production, *Bioresource Technology*, **2009, 100**, 3927–3932.
9. http://deptan.go.id/infoeksekutif/bun/bun-asem2012/**produksi**-kelapasawit.pdf, **Produksi** Kelapa Sawit Menurut Provinsi di Indonesia, 2008 – 2012, Aceessed Januari 27, 2012.
10. Ooi, Y.-S., Zakaria, R., Mohamed, A.R., Bhatia, S.: Catalytic Conversion Of Palm Oi Based Fatty *Acid* Mixture To Liquid Fuel, *Biomass and Bioenergy*, **2004**, **27**, 477-484.
11. Ooi, Y.-S., Zakaria, R., Mohamed, A.R., Bhatia, S.: "Hydrothermal Stability And Catalytic Activity Of Mesoporous Aluminum-Containing SBA-15", *Catal. Commun.*, **2004**, **5**, hal. 441–445.
12. Gosselink, J.W., van Veen, J.A.R.: Coping with catalyst deactivation in hydrocarbon processing, *Studies in Surface Science and Catalysis*, **1999**, **126**, 3–16.
13. Plank, C.J., Rosiski, E.J., Rubin, M.K.: Method for producing zeolites, United states patent, **1979**, **4175144,** 1-8.
14. Romero, M.D.: Influence of the preparation methode and metal precussor compound on the bifunctional Ni/HZSM-5 catalysts, *Industrial Engineering Chemistry Research*, **1997**, **36** (9), 3533-3540.