

The Catalyst Selectivity to Cracking Product of Palm Oil

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Abstract :

It is important to develop a renewable source of energy to overcome a limited source fossil energy. Palm oil is a potential alternative and environmental friendly energy resource in Indonesia due to high production capacity of this vegetable oil. The research studied effect of catalyst to selectivity of biofuel product from cracking of palm oil. The catalyst consists of silica alumina and synthesized HZSM-5 catalyst, with or without support. The research was conducted in two steps, namely catalyst synthesized and catalytic cracking process. HZSM-5 was synthesized using Plank methods. The analysis of the synthesized catalysts use AAS (Atomis Absorption Spectroscopy), BET (Brunauer Emmet Teller). The cracking was carried out in a fixed bed microreactor with diameter of 1 cm and length of 16 cm which was filled with 0,6 gram catalyst. Composition of product if using HZSM-5 catalyst are gasoline of 28,87%; kerosene of 16,70% and diesel of 12,20%. Using silica alumina catalyst give product distribution such as diesel of 32,05% and gasoline of 2,78%.

Keywords: biofuel, catalytic cracking, HZSM-5, palm oil, silica alumina

1. Introduction

Economic growth, population, development of the area and development push will need more energy. Energy needs are met during this ingredients from renewable not namely petroleum and coal. However the energy reserves is not always able to meet the entire energy needs in the long term. In anticipation of that condition, it needs to be developed alternative energy from renewable materials. Therefore, this research to develop alternative energy from renewable materials to replace the role of fuel or coal.

Renewable energy sources derived from vegetable oils or animal fats. Some vegetable oils have been developed as alternative energy, among others, palm oil, jatropha oil, soy bean oil and so on. Indonesia's palm oil-producing countries is the second largest in the world. The production of palm oil in Indonesia is 12 million tons/year in 2010. Therefore, palm oil is one of the potential raw material for making biofuels. Palm oil has the advantage of more environmentally friendly because it is free of nitrogen and sulfur.

Various processes have been made to produce biofuels. Cracking without catalyst (thermal cracking) take place at high temperature and pressure that requires great energy. Catalytic cracking is a way to solve the long carbon chain is long enough to a simple carbon chain molecule with the aid of a catalyst. The function of catalyst is reducing the activation energy of the substance. Catalyst also control the selectivity of the product. The production of biofuels research was developed through catalytic cracking with different types of catalyst. The purpose of this research was to study the influence of catalyst to biofuel product selectivity.

Palm oil production is on the rise and the cost of production of palm oil is relatively lower than other plant oils. Indonesia as a country of tropical land that still has a quite extensive may be large to be developed both through capital investment and foreign scale plantation of the people. Palm oil contain fatty acids vary, both saturated and saturated, as in Table 1.

Schwab, et al., (1999) studied the mechanism of the thermal decomposition of triglycerides and distillation with an air sparger and nitrogen by means of distillation ASTM standard. According to Pioch, et al (1993) that the catalytic cracking of copra oil and coconut oil using a standard catalyst of petroleum ($\text{SiO}_2/\text{Al}_2\text{O}_3$) at 450°C produce gas, liquid and solid with lower molecular weights. The superheated organic column produced biogasoline and biodiesel in fractionation column. Vonghia, et al., (1995) proposed that the initial cracking occurs via two mechanisms of displacement are β -elimination dan γ -hydrogen. Leng, et al, (1999) using a fixed bed reactor to cracking palm oil by Catalyst of HZSM-5. Conversion of Palm oil is lower than canola oil, in which nearly 100% conversion [3].

Zeolite is a solid of crystal structure with microscopy shaped three dimensions, composed of aluminum, silicon and oxygen as the primary structure. Measure the diameter of the cavity between the $3-10 \text{ \AA}$. Empirical

formula of zeolite is $M_{x/n}(AlO_2)_x(SiO_2)_y \cdot mH_2O$ where M is cation of neutralising with valensi of n, where n is expressed as the number of tribes. Zeolite ZSM-5 catalyst could increase the yield of olefin and octane.

Table 1. Composition of fatty acid in palm oil

Fatty acid (> 1%)	Composition (%)
Miristic acid	3
Palmitic acid	30
Stearic acid	3
Oleic acid	55
Linoleic acid	8
Fatty acid (< 1%)	Composition (ppm)
Carotenoid	500-700
Tokoferol / tokotrienol	600-1000
Sterol / sitosterol	218 – 370
Campesterol	90 – 151
Stigmasterol	44 – 66
colesterol	7 – 13
Other	2- 18

Literature : Hui, 1996

2. Material and Methods

2.1. Preparation of catalyst

The two tipe of catalyst were synthesized include HZSM-5 without impregnation and HZSM-5 impregnated by a solution of $CuSO_4 \cdot 5H_2O$, $NiSO_4 \cdot 7H_2O$ and $ZnSO_4 \cdot 7H_2O$. This research consisted of catalyst preparation, cracking and analysis of results. Catalysts impregnation used the Romero's procedure (1997). HZSM-5 catalyst calcinated on an oven at 110oC for 2 hours, and cooling in the desiccators. Catalytic cracking was done in a microreactor fixed bed with diameter of 1 cm, length of 16.4 cm and was filled with 0.6 g of catalyst in Figure 1. Temperature of cracking carried was 350 - 500°C and flow rate N_2 was 120-160 ml/minute. The result analyzed by gas chromatography of FID (Flame Ionization Detector).

2.2. Cracking of palm oil.

Catalytic cracking done in a microreactor coating by heater and 1 g weight of catalyst. Palm input in reactor at 350°C, then the tank are flowed by nitrogen gas with rate of 100-160 ml/min. The oil vapor and nitrogen gas flowed into the fixed bed at temperature of 350 to 500°C. Catalytic cracking was carried out during the 120 minutes. The result analyzed by gas chromatography method of FID (Flame Ionization Detector) column HP PORAPLOT QO4. The equipment of cracking can be seen in Figure 1.

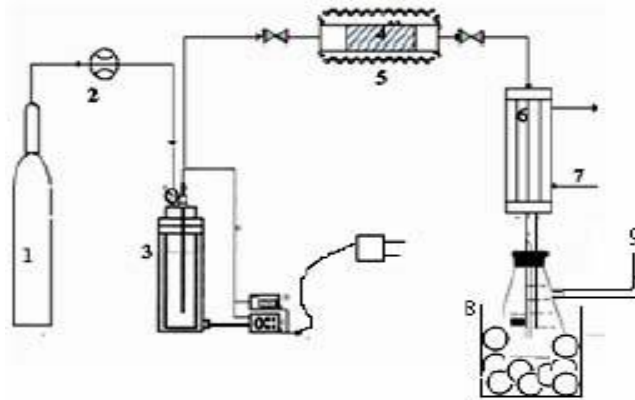
3. Result and Discussion.

3.1. Characterization of of catalyst

The synthesized catalyst were ccharacterized by mean Atomic Absorption Spectroscopy (AAS), Brunauer Emmet Teller (BET) and X-RD (X-ray Diffraction) methods. AAS to see the ratio Si/Al and the levels of catalyst of Cu, Ni and Zn. Measurement of surface area and the average pore size used the method of BET (Brunauer Emmet Teller). The type and structure of crystals catalyst analyzed using XRD. Table 2 showed results of characterization of catalyst.

Table 2. Characteristic of HZSM-5 Catalyst

The name of catalyst	Si/Al (m/m)	Ni, Cu, Zn	Pore size (Å°)	Surface area (m ² /g)
1. HZSM-5	243	0	13,255	213,3524
2. HZSM - 5 / Ni 5%		4,98	13,176	194,2372
3. HZSM - 5 / Cu 5%		5	13,249	201,1762
4. HZSM - 5/ Zn 5%		4,20	13,962	192,9966



(1) Flow rater of N_2 , (2) Flow meter, (3) heater, (4) catalyst, (5) microreactor, (6) condensor, (7) Cooling water, (8) sample of liquid, (9) sample of gas

Figure 1. Reactor for cracking palm oil

Minimum pore size length of catalyst was $8^{\circ}A$ and surface area is more than $100 \text{ m}^2/\text{g}$. [6]. Surface area increased by the addition few metal, because the surface was covered by a metal catalyst. The reducing of surface area didn't mean the reducing of the catalyst effectiveness, but adding of the active site affected the rate of the reaction [7].

3.2. Influence of temperature on yield gasoline, kerosene and diesel with HZSM-5 catalyst without impregnation and with impregnation metal of Ni, Cu and Zn

The purpose of active metal impregnation on catalyst surface added the active side on the catalyst surface, so the activity of the catalyst increased. Figure 2 to 4 showed the influence of temperature on yield of biofuels by catalyst with or without impregnation. The influence of activity catalyst was done by flow rate of N_2 gas is 130 ml/min and variations of temperature. Figure 2 shows that the highest yield of gasoline is obtained by HZSM-5 catalyst/Ni on temperature of $450^{\circ}C$ is 29,38%. This is due to Ni metal impregnation to HZSM-5 catalyst distributed evenly on the surface of the metal, so the active site catalysts having increased. Increasing of the active site followed increasing of yield of gasoline.

Figure 3 showed the highest yield of the kerosene was obtained by HZSM-5 Ni-catalyst on temperature of $500^{\circ}C$ at 14.95%. Figure 4 showed the highest yield of the diesel was obtained by HZSM-5 catalyst at 24.19%. From of the three types of impregnation catalyst, only the catalyst of HZSM-5/Ni which increased in yield with the inclusion of metal catalyst of Ni on HZSM-5.

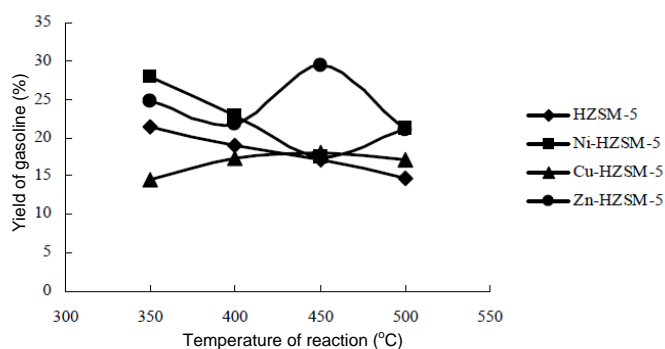


Figure 2. The influence of reaction temperature on yield of biodiesel at N_2 flow rate of 130 ml/min

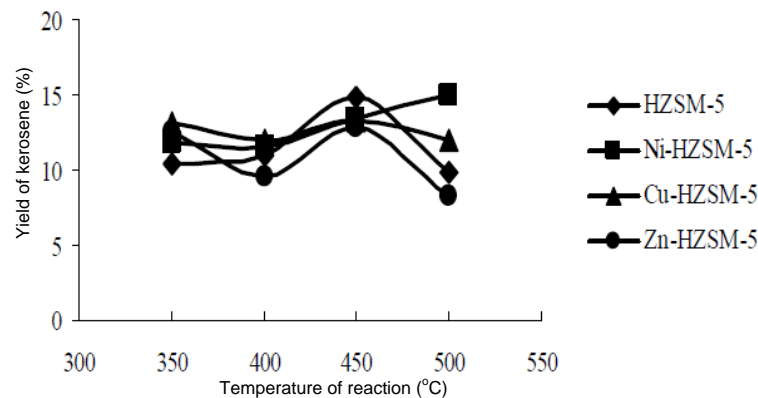


Figure 3. The influence of reaction temperature on yield of kerosene at N₂ flow rate of 130 ml/min

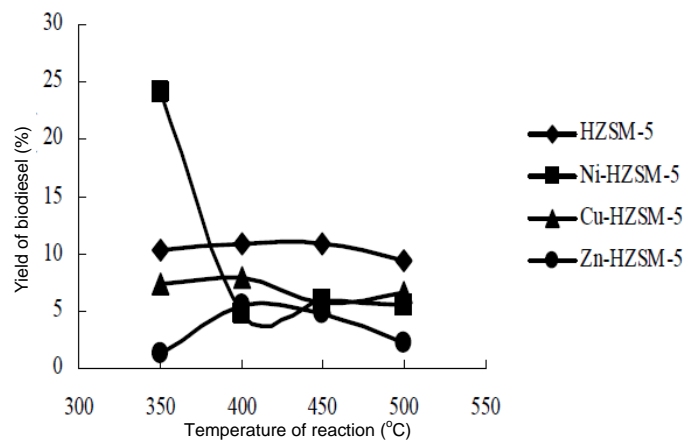


Figure 4. The influence of reaction temperature on yield of diesel for flow rate N₂ of 130 ml/min

3.3. Influence of temperature on the selectivity of gasoline, kerosene and diesel for Ni/Cu/Zn-HZSM-5 catalyst

Figure 5 to 7 showed the influence of temperature on biofuel selectivity at catalytic cracking with or without impregnation of catalyst. Figure 5 showed selectivity of gasoline by HZSM-5 catalyst on 400°C at 0,43, by Ni/HZSM-5 catalyst on 350°C at 0,85, by Zn/HZSM-5 catalyst on 450°C at 0,40 and by Cu/HZSM-5 catalyst on 500°C at 0,45. Figure 6 showed selectivity of kerosene by HZSM-5 catalyst on 450°C at 0,26, by Ni/HZSM-5 catalyst on 350°C at 0,34, by Zn/HZSM-5 catalyst on 350°C at 0,19 and by Cu/HZSM-5 catalyst on 400°C at 0,22. Figure 7 showed selectivity of diesel by HZSM-5 catalyst on 400°C at 0,24, by Ni/HZSM-5 catalyst on 350°C at 0,7, by Zn/HZSM-5 catalyst on 350°C at 0,10 and by Cu/HZSM-5 catalyst on 400°C at 0,13. Ni-HZSM-5 catalyst was selectivity of gasoline, kerosene, diesel at temperature of 350°C because adding of Ni metal followed increasing acid side of HZSM-5.

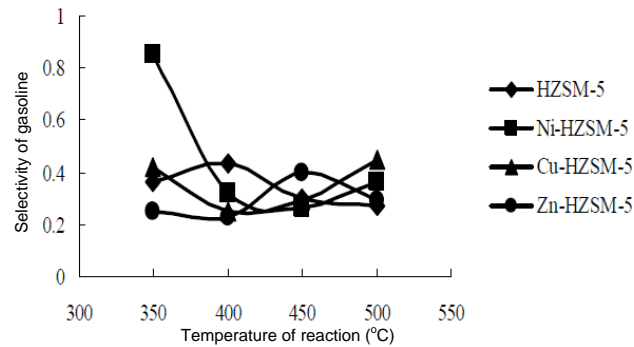


Figure 5. The influence of reaction temperature on selectivity of gasoline for flow rate N_2 of 130 ml/min

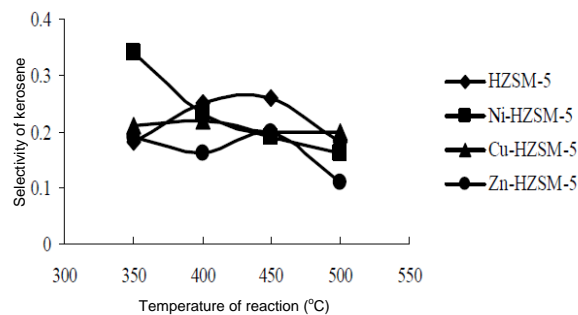


Figure 6. The influence of reaction temperature on selectivity of kerosene for flow rate N_2 of 130 ml/min

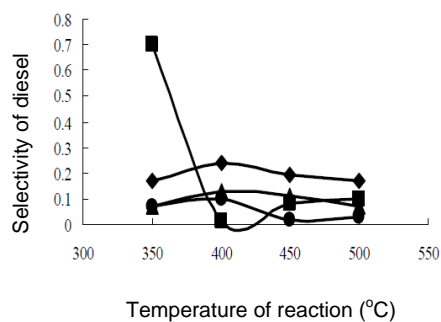


Figure 7. The influence of reaction temperature to selectivity of diesel for flow rate N_2 of 130 ml/min

4. Conclusion

Cracking product of vegetable oil was more friendly than cracking product of crude oil. Using of HZSM-5 catalyst with or without impregnation decrease activation energy of cracking reaction. The result of characteristic catalyst that the surface area and pore size suitable with the criteria of a standard catalyst. The product distribution at reactor temperature of 450°C and rate of N_2 gas of 130 ml/min by catalyst HZSM-5 were 17,11% of gasoline, 14,89% of kerosene and 10,86% of diesel. For the same condition by catalyst Ni/HZSM-5 were 17,55% of gasoline, 13,48% of kerosene and 5,84% of diesel. And then by catalyst Cu/HZSM-5 were 18,05% of gasoline, 13,30% of kerosene and 5,72% of diesel. All of the catalyst selected to formation of gasoline and kerosene.

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