

SYNTHESIS OF HZSM-5 CATALYST FROM PALM OIL PLANT FLY ASH FOR CATALYTIC CRACKING PROCESS OF EMPTY FRUIT BUNCHES TO BIO-OIL

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Abstract – The need of energy increases whilst oil reserve as a primary energy resource decreases, this is the reason why seek an alternative energy source is inevitable. Biomass especially palms oil empty fruit bunches (PEFB) which are abundant in Indonesia can be processed into bio-oil by catalytic cracking process. The objective of this research is to study the effect of the concentration of NH_4NO_3 for synthesis of HZSM-5 and used it as catalyst in catalytic cracking process of PEFB. The HZSM-5 was synthesized by ion exchange of the solution of NH_4NO_3 and ZSM-5 (Si / Al = 30) at 80°C for 12 hours. The product formed is then washed, dried and calcined at 500°C for 5 hours respectively. The HZSM-5 was characterized by BET to determine surface area and then is tested its performance in the catalytic cracking process of PEFB in 1000 ml stainless steel stirred batch slurry reactor at 300 °C. Bio-oil obtained was characterized of density, viscosity and flash point respectively. The largest surface area was found of the catalyst which exchanged in 0.5 M NH_4NO_3 concentration, which having surface area 79.32 m²/g. The largest yield of bio-oil was 66.4 %. The physical characterization of bio-oil were the density = 995 g/ml, viscosity = 14.3 cp and flash point = 48 °C respectively.

Keyword: *Palm oil empty fruit bunch, catalytic cracking, HZSM-5, NH_4NO_3 .*

1. Introduction

As a tropical country Indonesia has abundance source of biomass sum around 250 billions tons per year [1]. The main sources of biomass are forest and agricultural waste such as palm oil plantation waste. In the year 2009, Indonesia has 7 million hectares palm oil and produce crude palm oil around 17.3 million tons [2]. It is mean that almost 34 millions tons of palm oil solid wastes were produced. The solid wastes were comprised of shell, fiber and empty fruit bunches respectively. The shell and fiber of palm oil are used as fuel on boiler to produce steam for palm oil plant. The empty fruit bunches just burned in incinerator and the ash produced is used as fertilizers.

Biomass can be converted into liquid fuel using selective pyrolysis process [3]. Several catalysts have been used in cracking process such as HZSM-5, Zeolite β and ultrastable Y (USY). The best catalyst which produced high conversion and high yield of conversion is HZSM-5 [4].

The HZSM-5 is made from ZSM-5 using process that has been developed in [5]. The ZSM-5 was synthesized from silica and alumina using the best condition as in [6]. For production ZSM-5, it was needed of silica and alumina sources. The sodium silicate, silicate hydrate, water glass, silica sol, silica gel, precipitated silica and calcined silica were used as the source of silica. And the sodium aluminates, aluminium sulphates and aluminium hydroxide were used as alumina sources respectively [7]. The ZSM-5 has the basic structure which has comprised of three basic functional groups of water and 76 g aluminum hydroxides were added and stirred until all the aluminum hydroxides dissolved. The sodium aluminates was settled and filtrated and dried in electric oven.

The precipitated silica and sodium aluminates were mixed having molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$ and the distilled water were added to have a suspension. And then the sodium hydroxide was added until molar ratio of $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ of 7.4 was reached. The suspension is aged into autoclave at temperature 175°C for 18 hours. The solid formed is the ZSM-5 then washed and dried respectively.

Then the ZSM-5 results was modified using ion exchange method. Ten grams of ZSM-5 was suspended into 300 ml of NH_4NO_3 solution. The concentration of NH_4NO_3 was varied from 0.5, 1.0, 1.5 and 2.0 M respectively. The suspension was heated at temperature 80°C and stirred at 100 rpm for 12 hours. The solid which is HZSM-5 was separated using filter paper and then it washed and dried, and then calcined at 500°C for 5 hours.

Na_2O , AlO_4^- tetrahedral and SiO_4 respectively that are bonds by using the same oxygen atom. The functional group AlO_4^- can be exchanged with NH_4^+ formed NH_4 -ZSM-5. And further the NH_4 -ZSM-5 will form HZSM-5 on calcination process [8].

Several catalysts have been used [9] for production of gasoline from biomass by fast pyrolysis. Using of the ZSM-5 catalyst gave better yield compared with other catalysts. But the yield was still low below 50 %. It was suggested to use combination of catalyst to have the better yield result.

In this research the ZSM-5 ($\text{Si}/\text{Al} = 30$) was synthesized from precipitated silica originated from palm oil plant fly ash and sodium aluminates [6], then the ZSM-5 was modified using NH_4NO_3 to produce HZSM-5. Then the HZSM-5 is used as a catalyst in catalytic cracking process of PEFB in stirred batch slurry reactor.

2. Research Methodology

The silica in palm oil plant fly ash was extracted using 2.0 N of NaOH for 4 hours in stirred batch extractor at 105°C having the volume of liquid and mass of solid ratio is 600 ml : 100 g ash respectively. The extracted silica was precipitated using HCl at pH 8.5, and further the precipitated silica then washed and dried. The precipitated silica was used as silica source of the synthesis of ZSM-5. And the alumina source was sodium aluminates made from $\text{Al}(\text{OH})_3$ and NaOH. The sodium aluminates was made of 109.5 g sodium hydroxide which was dissolved in 1000 ml distilled

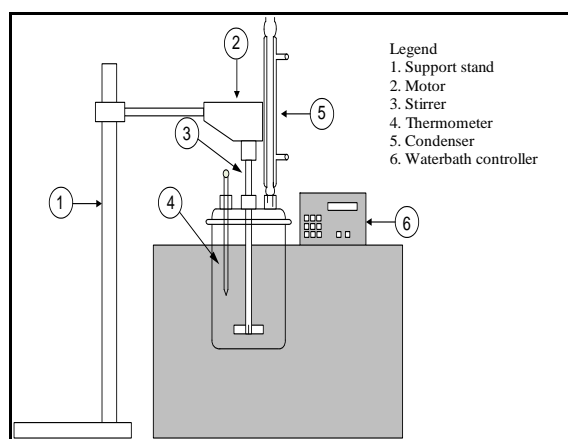


Figure 1. Equipment for producing ZSM-5

The product HZSM-5 was characterized using BET for its specific surface area and then is tested its performance in catalytic cracking of PEFB to bio-oil. The catalytic cracking of PEFB was done in 1000 ml stainless steel stirred batch slurry reactor. The 50 grams of PEFB which have cut in to small pieces of 0.5 cm, 500 ml of thermo oil of Silinap 280 M and 0.5 grams HZSM-5 were put altogether into the reactor. The cracking process was done at temperature 300°C and

400 rpm stirring speed and flowed by the N_2 gas with volumetric rate of 1.3 mls^{-1} to ensure there was no oxygen in the reactor and as well as a carrier gas. The bio-oil vapor produced was condensed in water cooled condenser and collected in Erlenmeyer. After there was no bio oil produced, the bio oil was weighed to know the bio oil yield. The density of bio-oil was measured using picnometer and weighing with digital analytical balance. The viscosity of bio-oil was measured using Ostwald viscometer. The flash point was measured using Cleveland open cup apparatus.

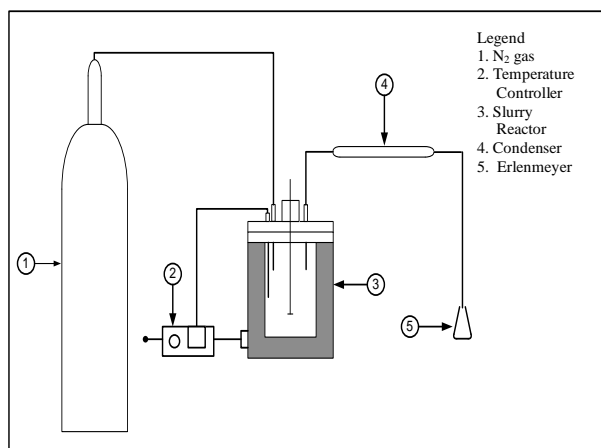


Figure 2. Equipment for PEFB Cracking

3. Results and Discussions

3.1. Effect of NH_4NO_3 Concentration.

The ratio of functional group especially Si/Al is the important indicator of characteristic of zeolite. The acidity and thermal stability will increase with increasing of molar ratio of Si/Al [10]. The AlO_4^- in the ZSM-5 can be exchanged with proton, metal cations. And in this study was used of ion NH_4^+ to increase its acidity, thermal stability and specific surface area of ZSM-5 [8].

In this research HZSM-5 was synthesized using ion exchange process using NH_4NO_3 solution. The concentration of NH_4NO_3 solution was varied of 0.5, 1.0, 1.5 and 2.0 M respectively. According to [11] the objective of the ion exchange process is to increase catalyst acidity and to increase catalyst surface area.

Table 1. Specific Surface Area (SSA) of HZSM-5

No	Catalyst	SSA (m^2g^{-1})
1	Prepared with NH_4NO_3 0.5 M	79.32
2	Prepared with NH_4NO_3 1.0 M	44.14
3	Prepared with NH_4NO_3 1.5 M	71.22
4	Prepared with NH_4NO_3 2.0 M	27.41

In table 1, it was seen that variation of concentration of NH_4NO_3 influenced the SSA of the catalyst. The largest SSA of the product HZSM-5 was the HSM-5 which was treated with 0.5 M NH_4NO_3 solution. The way the ions NH_4^+ bond to HZSM-5 influenced the SSA of the catalyst. If the ions flock into the pore of the catalyst it will reduce the SSA but if the ions NH_4^+ spreaded evenly in the surface of catalyst will increase the SSA [12]. That is the possibilities why the increasing of concentration of NH_4NO_3 solution not always increase the SSA of the catalyst HZSM-5.

3.2. The Performance of HZSM-5 Catalyst

The performance of catalyst to convert PEFB into bio-oil can be seen in Figure 3.

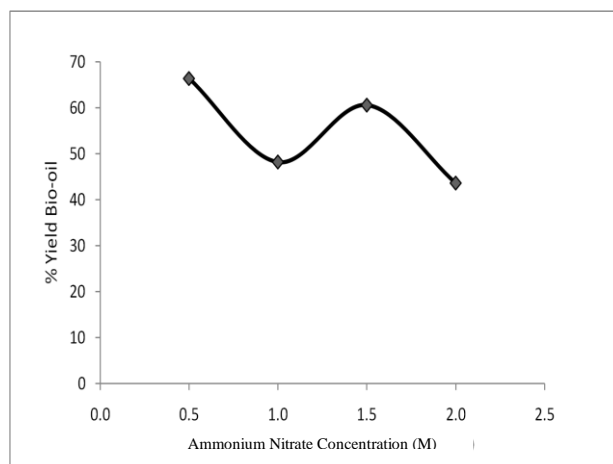


Figure 3. The influence of NH_4NO_3 concentration on preparation of HZSM-5 catalyst on yield of bio oil

The performance of the catalyst on conversion of PEFB to bio-oil was given in Figure 3. The performance of the catalyst HZSM-5 was influenced by the concentration NH_4NO_3 solution used in ion exchange process on the synthesis of the HZSM-5. From table 1 and figure 3, the performance of HZSM-5 catalysts to produced bio-oil is related to their SSA values. The larger the SSA of catalyst showed the larger yield of bio-oil. The best result of 66.4 % was approximately twice than result given by run without catalyst process. The best result was given by the HZSM-5 which was treated with 0.5 M NH_4NO_3 which is as well having the highest SSA.

The physical characterization of the bio-oil produced is given table 2.

Table 2. Physical Characteristic of Bio-oil Product.

No.	Parameter	Standar Bio-oil [13]	Bio-oil	
			Without Catalyst	HZSM-5

1	Density (grml ⁻¹)	0.94-1.2	1.021	0.995
2	Viscosity (cp)	10-150	17.45	14.3
3	Flash point (°C)	48-55	53	48

It was seen that bio-oil produce from run without catalyst has lower density, viscosity and flash point compared to bio-oil produce using the catalyst HZSM-5.

3.3. Comparison with other research results.

The comparison of bio-oil produced of this research with other research results showed in table 3.

Table 3, Comparison with other research results.

No	Researcher	Research method	Bio-oil Yield
1	Abdullah and Gerhauser (2008)	Palm oil empty fruit bunch , fluidized bed reactor, without catalyst, temperature 500°C	61,3%
2.	Carlson, et.al. (2008)	Saw dust, fast pyrolysis , fluidized bed reactor, catalyst : ZSM-5, temperature 600°C	31%
3	Sunarno, et.al (2011)	Palm oil empty fruit bunch , slurry reactor, catalyst : HZSM-5, temperature 500°C	66,4%

4. Conclusions

The Concentration of NH₄NO₃ in the preparation of HZSM-5 proved in influenced the SSA of the HZSM-5. The concentration of NH₄NO₃ of 0.5 M gave the largest SSA of 79.32 m²g⁻¹ and then gave the largest yield of bio-oil produced of 66.4 %. Physical characteristic of bio-oil produced using HZSM-5 catalyst has given lower density, viscosity and flash point compared with the bio-oil produced of the run without catalyst eventhought this results is still in range of the standard of bio-oil.

5. References

[1] Suwono, A. *Indonesia's Potential Contribution of Biomass in Sustainable Energy Develompment*. Thermodynamics Laboratory. IURC for Engineering Sciences. Bandung Institute of Technology. Bandung. Indonesia. 2004

[2] Direktorat Jendral Perkebunan. *Statistik Kelapa Sawit*. Departemen Kehutanan dan Perkebunan. Jakarta. 2009

[3] Hyun, P.J., Hyeon, H.S., Ji, Y.H. and Jong, J.K. Catalytic Pyrolysis of Japanese Larch Using Spent HZSM-5. *Korean J Chem* 27 (2010) : 73-75.

[4] Twaiq., Farouq, A., Noor, Z., Asmawati, Mohamed, A. R., Bhatia, S. Catalytic Conversion of Palm Oil over Mesoporous Aluminosilicate MCM-41 for the Production of Liquid Hydrocarbon Fuels. *Fuel Processing Technology* 84 (2003): 105-120.

[5] Lacheen, Howard., Iglesia, Enrique. Stability, Structure, and Oxidation State of Mo/H-ZSM-5 Catalyst During Reaction of CH₄-CO₂ Mixtures. *Journal of Catalysis* 230 (2005) : 173-185.

[6] Misidian, D. Pembuatan CoMo/ZSM-5 dari Abu Sawit Sebagai Katalis pada Pengolahan Biomassa Menjadi Bahan Bakar Cair. *Laporan Penelitian*. Pekanbaru : Universitas Riau. 2009.

[7] Zahrina, I., Saputra, E., Evelyn, Santoso, I. A., Ramelo, R. Sintesis ZSM-5 Tanpa Templat Menggunakan Silika Terpresipitasi Asal Abu Sawit Sebagai Sumber Silika. *Jurnal Natur Indonesia* 9 (2006) : 45-50.

[8] Zheng, S., Surface Modification of HZSM-5 Zeolites, *Dissertation*, Munchen : Institut Fur Technische Chemie II der Technischen Universitat Munchen, 2002.

[9] Carlson, R., Vispute, P., dan Huber, W. Green Gasoline by Catalytic Fast Pyrolysis of Solid Biomass Derived Compounds. (ChemSusChem, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. 2008, pp. 397:400)

[10] Vempati R. K. ZSM-5 Made From Siliceous Ash. *US Patent*. No. 6.368.571 B1. (2002)

[11] Kumar, S., Sinha, A.K., Hedge, S.G., Sivasanker, S. Influence of Mild Dealumination on Physicochemical, Acidic and Catalytic Properties of HZSM-5. *Journal of Molecular Catalysis* 154 (1999) : 115-120.

[12] Handoko, D. S. P. Preparasi Katalis Cr/Zeorlit Melalui Modifikasi Zeolit Alam. *Jurnal Ilmu Dasar* 3 (2002) : 15-23.

[13] Smallwod. 2008. *Hydroprocessing of Pyrolysis Bio-oil to Fuel and Chemical*. Pacific Northwest National Laboratory us. Departemant of Energy. www.saferalliance.net/.../2008/05/smallwood-2008-and-bioenergy-w.html. April 12, 2009