



THE EFFECT OF TEMPERATURE AND PRESSURE ON BUTON ASPHALT HYDROCRACKING IN THE FUEL FRACTION

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ABSTRACT

The content of Buton asphalt from Buton Island varies but not optimally used. The structure of asphalt which contains a lot of aromatic compounds requires hydrocracking in order to be cracked into smaller hydrocarbon fractions that can become an alternative fuel source. This research was conducted in 2 stages: preparation of the catalyst Ni (3)-Pd (1)/Zeolite-Y 1%, followed by hydrocracking of Buton asphalt. Hydrocracking was done asphalten feed is heated in autoclave in the temperature of 400 °C and the asphalt vapor goes into the fixed bed reactor containing catalyst with together with hydrogen gas flow in constant rate. The reaction in is considered to be steady with the choice reaction time 1 hour and starts in the 10 minute after asphalten feed temperature autoclave achieve 400 °C. The variable observed is the reaction temperature and pressure of in the range of 350–550 °C and 4–8 atm. The liquid hydrocracking product was analyzed by Gas Chromatography Spectrometry (GC-MS) and GC to determine the hydrocarbon compounds and the percentage of hydrocarbon fractions. The results are hydrocracking of Buton asphalt produces fuel gasoline fractions (C₇-C₁₂) and diesel fractions (C₁₃-C₁₅). Hydrocracking provides optimal yield of 6.75% at temperature of 500 °C and balanced selectivity gasoline fractions and diesel fractions obtained were 56.59% and 43.40%. When the hydrocracking product is expected to be in liquid form, the gasoline fraction selectivity temperature and pressure should be 400 °C and 6 atm, respectively. In this condition, the gasoline fraction obtained was 62.25%.

Keywords: buton asphalt, fuel, hydrocracking.

INTRODUCTION

Fuel consumption from year to year tends to rise. There are many issues about the storage of energy resources, particularly petroleum-base oil. Several new energy resources are researched currently to complement the unreliable supplies of petroleum base oil [1-3]. Therefore, it is an urgent need to investigate new methods to increase the production of fuel to offset for need of fuels. One of the methods is asphalt hydrocracking. Asphalt is used widely in life for this comes from petroleum refineries. Mostly, it is used for highway construction adhesive, for the roof coating, etc. [4]. In Indonesia, asphalt can be found in the Buton Island of the eastern of South Celebes Coast. The total reserves of the Buton natural asphalt is estimated not less than 120 million ton. According to the current national demand rate supply for the domestic Civil Infrastructure, many companies in Indonesia have developed granulated Buton asphalt to facilitate its transportation and handling, especially for asphalt mixing plants in construction sites nationwide [5]. If natural asphalt is used only in domestic infrastructure, it does not have high economic value. Effort of processing Buton natural asphalt into alternative fuels is necessary considering the depletion of oil reserves and the rising of fuel needs [6-7]. The Buton natural asphalt reserves are relatively shallow. With a minimum depth of approximately 1.5 m, the reserves are distributed over 70,000 hectare from Ampolawa in the south Lawele in the northern side of the Island. Bitumen contains properties similar to asphalt such as penetration, ductility, flash point, solubility in trichloroethylene and density [5].

Asphalt structure contains a lot of aromatic compounds and cyclic hydrocarbon compounds beside nitrogen and sulfur, so by the cracking, it is expected to be produced the fraction of fuel [7-8]. According to Mao, the catalytic Ni-SPS derivatives demonstrated a good conversion and excellent selectivity to gas and gasoline for cracking of asphalt plant [9].

Cracking is a carbon-carbon bond breaking of the long chain and heavy weight molecules into shorter chain molecules and light weight. There are two types, namely thermal cracking and the catalytic cracking reaction; thermal cracking requires very high temperatures while catalytic cracking is the cracking that uses catalyst [4]. Hydrocracking is a cracking by using H₂ gas. The catalyst needed in the hydrocracking is the bifunctional catalyst with great activity toward cracking and hydrogenation processes [10]. Cracking is done by zeolite and hydrogenation is done by metal. Catalytic cracking process which takes place on the bifunctional catalyst starts with the dehydrogenation by the metal side of the adsorbed alkane molecules. Furthermore, Bronsted side did protonation to alkenes and produce alkyl carbonium ions. The end product (alkanes) with shorter chains and have branches obtained after ion alkyl carbonium deprotonated and produces alkenes that further hydrogenated in acidic side [11]. Asphalt hydrocracking process can be heterogenic catalytic reaction. At heterogenic catalytic system, reactant and catalytic are in different phase, reactant is in gas phase, while catalytic is in solid phase [7].

Several studies of the hydrocracking asphalt have done. Among them studied the effect of the ratio of metal



in the catalyst for mono metal and bimetal (Ni-Pd) and also (Pd-Ni) in the asphalt hydrocracking of Buton asphalt in batch reactor system and carried out at temperature of 400 °C. Purwono *et al* [7] have researched about preparation of bimetal Ni-Pd/zeoliteY catalysts and characterizations on catalysts, activity catalytic, and observed kinetics hydrocracking of Butonion asphalt. The result attained that Ni(3)-Pd (1)/zeoliteY 1% catalysts for hydrocracking of butonion Asphalt and kinetics represents the true surface reaction rate. Murachman *et al* [8] have studied hydrocracking Asbuton (Buton Asphalt) by using Pt/Pd and γ -Alumina catalyst in a fixed Bed Reactor, one of the results is that the conversion of asphalt extract using Pt/Pd catalyst was higher than γ -Alumina catalyst.

Due to this background, the researchers studied the effect of changes in temperature and pressure toward the fuel content as Buton asphalt hydrocracking product. This study is expected to gain knowledge about the effects and the appropriate temperature and pressure in the reactor according to the asphalt hydrocracking process to obtain distribution fuel and selectivity of fractions which in small portions are derived from gasoline and diesel fractions. Selectivity describes the tendency of a catalyst to produce certain components.

EXPERIMENT

Materials and equipments

Materials:

Kabungka Buton asphalt which was already extracted with trichloroethane, H/ Zeolite-Y, Nickel (Ni) and palladium (Pd) metal catalysts in the form of compounds Ni (NO₃) and PdCl₂; Demineralized water; Hydrogen; nitrogen; and oxygen gas.

Equipments:

Fixed bed reactor; Muffle; Gas Chromatography (GC) Perkin Elmer Auto System with HP5 column; Mass Spectra Gas Chromatography (GC-MS) SHIMADZU QP-5000 CP Sic 5 CB Column.

Ni (3)-Pd (1)/Zeolite-Y 1% catalyst preparation: 32 gram H /zeolite-Y and 1.188 g of Ni (NO₃)₂·6H₂O and 0.133 g PdCl₂ are prepared. PdCl₂ dissolved in 10 ml of NH₃ (Aq) 25% and 10 ml demin then enter H /zeolite-Y and the solution into the flask until zeolite submerged. The solution stirred at room temperature for 1 hour. Then dried at 125 °C for 3 hours with the open vacuum or until the weight constant, at this stage Pd/zeolite-Y is formed. Ni (NO₃)₂·6H₂O metal was penetrated as stated above by adding it into Pd/zeolite-Y catalyst until Ni(3)-Pd(1)/zeoliteY was formed. The catalyst were calcined, oxidized, and reduced during each 1 hour in muffle at temperature of 400 °C by nitrogen, oxygen, and hydrogen gas at 400 °C, respectively.

Buton Asphalt Hydrocracking:

Buton Asphalten Hydrocracking process is done in a-fixed bed reactor using Ni(3)-Pd(1)/zeolite-Y(1%) catalyst.

This process is semi batch in with 2 gr catalyst. 40 gram asphalten feed is heated in autoclave in the temperature of 400 °C, and the asphalt vapor goes into the reactor containing Ni(3)-Pd(1)/zeolite-Y(1%) catalyst together with hydrogen gas flow in constant rate. The asphalt hydrocracking reaction in this fixed bed reactor is considered to be steady with 1 hour reaction time and starts in 10 minute after asphalten feed temperature autoclave achieve 400 °C in which asphalt vaporization rate in period of time is nearly constant. The variable observed is reaction in the temperature range of 350–550 °C and the reactor pressure of 4–8 atm.

The product of this reaction was liquid, gas consisting of light hydrocarbon, cocas, and residue catalyst. The liquid products of hydrocracking were analyzed by Gas Chromatography MesPec (GC-MS) and Gas Chromatography (GC) to obtain the compounds of product and the percentage of hydrocracking results by viewing the chromatogram peak area. Liquid products as the results of hydrocracking (LHR) were analyzed by comparing the area of each peak, after the peak specified, then it spiked with C₇H₁₆ (heptane) and C₁₂H₂₆ (dodecane) standard sample to obtain two hydrocarbon fractions, namely gasoline fractions of C₇-C₁₂ and diesel fractions fuel fractions are C₁₃-C₁₅. The products of each the components are in % chromatogram peak area of each fraction after conducted spiking method.

RESULTS AND DISCUSSION

In this study, the catalyst used is Ni(3)-Pd(1)/zeolite-Y (1%) catalyst. According to [7], this catalyst has the best characteristic compared with the same catalyst with higher total metal contents. According to [7], Ni(3)-Pd(1)/zeolite-Y(1%) catalyst has specific area 496, 5196 m²/g and pore volume 213, 228 x 10⁻³ cc/g. The wider the surface area of the active side of the metal means the more frequent the occurrence of hydrogen transfer to hydrocracking. The result of catalyst activity for Hydrocracking Buton asphalten was fuel product C₇ – C₁₅ fraction.

Experiment with variable temperature variation in the reactor obtained the following data in Table-1 and Figure-1 with the following operating conditions: feed 40 g, weight of catalyst = ± 2 g, operating pressure = 5 atm, flow = 1 cm or 157. 205 ml/ min

Table-1. The relationship between temperature and hydrocracking product.

No.	Temperature (°C)	LHR (gr)	Coke (gr)	Residue (gr)
1	350	1, 71 gr	0, 301	31, 64
2	400	1, 99 gr	0, 300	31, 41
3	450	2, 51 gr	0, 302	31, 65
4	500	2, 70 gr	0, 301	31, 77
5	550	2, 18 gr	0, 302	31, 57

From the result (table 1), it can be seen that the Liquid Hydrocracking Results (LHR) highest obtained at temperatures of 500 °C. The higher the temperature in the



reactor the lower the LHR obtained, it is probably due to the reactant molecules on the surface of the adsorbed catalyst optimum at temperature of 500 °C so that catalyst activity increased so great but when adsorption was too strong as the adsorption temperature rises, the closure fractions of catalyst surface were very large, the adsorbed molecules become extremely stable so it's difficult to react and catalyst activity becomes low.

By looking at the total yield in Figure-1, the most optimal yield was at temperature of 500 °C with results of 6.75%. Rise in temperature will increase the reaction's velocity and it also will increase reaction rate until at some point a rate will be achieved which is the maximum reaction rate. If the cracking reaction continues to proceed at a higher temperature the reaction rate will decrease. This is due to at a very high temperature, physical damage to the catalyst will occur. H₂ adsorbed in acid catalyst will decrease when the temperature is raised because H₂ adsorption constant has a negative value. In a very high temperature, adsorption rate is very low which makes the overall reaction rate very low as well [7].

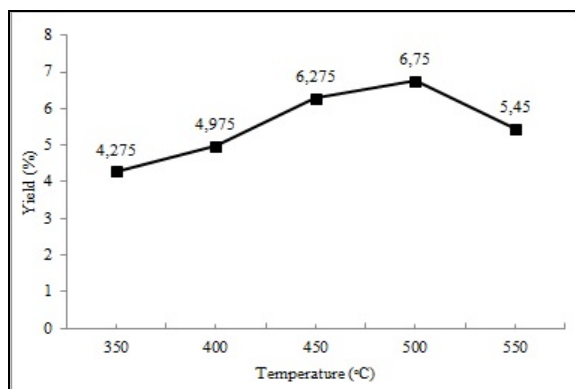


Figure-1. Temperature against yield graphic

LHR analysis results with GC-MS is shown in the figure below

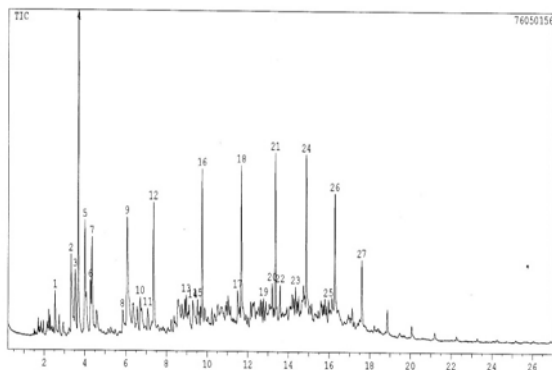


Figure -2. LHR chromatogram GC MS

GC-MS analysis results showed that LHR contains compounds hydrocarbons heptane (C₇H₁₆) to pentadecane (C₁₅H₃₂). LHR obtained is also analyzed by gas chromatography to determine the content of the

cracked hydrocarbons and its distribution. LHR content is calculated by calculating the percent area of each peak after spiking each peak with standard compound Heptane (C₇H₁₆) and Dodecane (C₁₂H₂₆). Hydrocarbon compound in LHR is grouped in two fractions which are gasoline fractions (C₇-C₁₂) and diesel fuel fractions (C₁₃-C₁₅). Both fractions are the important materials in industry and transportation.

The results of relation between temperature and LHR gasoline and diesel fractions are presented in Figure-3 below.

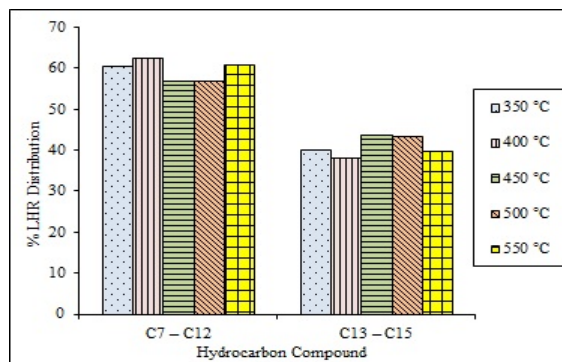


Figure-3. Hydrocarbon compound distribution in LHR with temperature variable graphic

In Figure-3 we can see at temperature of 400 °C LHR is selective in gasoline fractions which are 62.25%. This is because at a temperature of 400 °C the occurrence of hydrogen transfer which reacts with asphalt steam is more frequent so that it can produce numerous short-chain fractions (C₇-C₁₂). At temperature of 550 °C, the gasoline fractions are also selective which is 60.8%. This is probably due to thermal cracking which also occurs in that temperature aside from the occurrence of catalytic cracking. With the high temperature, the CC bond breaking occurs via free radicals, in these circumstances, the mechanism of carbocation is less influential that thermal cracking will produce short fractions and olefin. This is in accordance with what is proposed by [10].

Variable distribution of pressure against LHR results can be seen in Figure-4 below

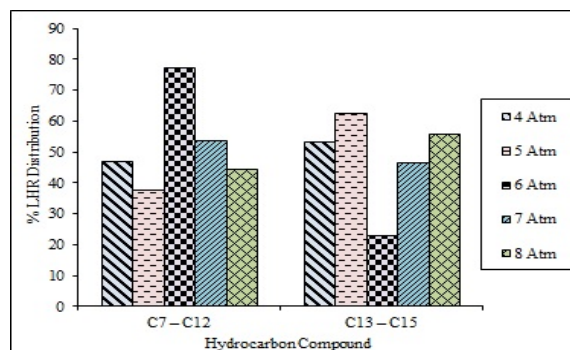


Figure-4. Product distribution towards hydrocracking pressure graphic.



At a pressure of 6 atm, hydrocracking products selectively produce gasoline and diesel fractions, 77.03% and 22.97% respectively. This is because at such pressures, there are many H_2 adsorbed by active sites of catalyst is high so that it can form H_2S gas optimally. This H_2S gas is the one which will reacts with asphalt steam resulting in the cracking of asphalt carbon chain becomes shorter. According [2] in general, the catalyst selectivity for gasoline and diesel fractions increase with the increasing number of conversion (%w/w) of liquid product obtained, thus it is suspected that the catalyst selectivity for gasoline and diesel fractions are more influenced by the more and easier the reactions that can occur on the surface of the catalyst.

Optimal yield results showed cracking at a temperature of 500 °C. At this temperature as well, distribution of selective cracking results occurs in balance on gasoline and diesel fractions, 56.8% and 43.2% respectively. For pressure variable, if it is desired to have selective hydrocracking results on gasoline and diesel fractions which are equal; the reactor pressure should be at 7 atm with gasoline and diesel fractions results 53.4% and 46.6% respectively.

CONCLUSIONS

Nature Buton Asphalt hydrocracking with Ni(3)-Pd (1)/zeolite-Y 1% catalyst produces fuel gasoline fractions (C_7H_{16}) and diesel fractions ($C_{15}H_{32}$). Optimal yield of Hydrocracking product was at temperature of 500 °C and has stable selectivity between two fractions which gasoline 56.8 % and diesel 43.2 %. If it is desired to have selective product in gasoline fraction, the hydrocracking should be done with a temperature of 400 °C and a pressure of 6 atm.

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REFERENCES

- [1] Rodiansono, Trisunaryanti W. 2005. Activity Test and Regeneration Of NiMO/Z catalyst For Hydrocracking Of waste Plastic Fraction To Gasoline Fraction, Indonesian Journal of Chemistry, 5 (3): 261-268.
- [2] Trisunaryanti, W., Purwono, S., Putranto, A. 2008. Catalytic Hydrocracking of Waste Lubricant Oil Into liquid Fuel fraction Using ZnO , Nb_2O_5 , Activated natural zeolite and Their Modification. Indonesian Journal of Chemistry, 8(3): 342-347.
- [3] Ahmad, I., Shakirulla, M., Rehman, H. U, Ishaq, M., Khan, M., A., Sha A., A. 2009. NMR analysis of cracking products of asphalt and assessment of catalytic performance. Elsevier, Energy, 34: 127-144.
- [4] Kirk, R., E., and Othmer, D. F. 18. 1985. Encyclopedia of Chemical Technology. 3rd Ed. John Wiley & Sons Inc., New York. Vol. 5. pp. 321- 325.
- [5] Samadhi Tj. W., Putrawan A., , I. D. G., Prabowo, B. E., Dwitawidi A., 2011. Statistical Evaluation of Non Agglomerating Coating for Granulated Natural Asphalt. ITB. Journal Engineering. Sci. 43(1): 321- 325.
- [6] Trisunaryanti, W., Triyono, Mudasir, Purwono, S., Nomura, M., Miura, M., Kinena, K. and Satoh, T. 2003. Annual Report Indonesian International Joint Research Program RUTI I Period Apri 1 –November 21 2003. Ministry of Research and Technology and Indonesian Sciences Institute (LIPI).
- [7] Purwono S., Trisunaryanti W., Salamah S., Hasyim W., Arenal. 2006. Hydrocracking Asphalt Buton with Nickel–Paladium, Ni-Pd in the carrier H/zeolit-Y, Engineering Forum 30 (2):1-14.
- [8] Murachman, B., Deendarlianto, Nissaraly H. F, Hasyim Wakhid. 2014. Experimental Study On Hydrocracking Process of Asbuton Hydrocarbon Based on the Aromatic, and Waxy Residue Based on Paraffinic, by using Pt/Pd and γ -aluminacatalyst in a fixed Bed Reactor, ASEAN Journal of Chemical Engineering, 14(1):59 -57.
- [9] Mao H., Li Ba., Li Xiao, Zhenhxing Liu, Ma Wei, Mesoporous Nickel containing Silica –pillared clays (Ni-SPC). 2009. Synthesis characterization and catalytic behavior for cracking of plant asphalt. Catalysis Communication 10:975–980.
- [10] Gates, B. C., Katzer, J. R., and Schui, G. C. A. 1979. Chemistry of catalitic process. Mc. Graw-Hill Book Company, New York.
- [11] Campbell, L.A. 1998. Catalyst and surfaces. Chapman and Hal Ltd., London.