PETROLEUM SLUDGE HYDROCRACKING OVER Al_2O_3 PILLARED MONTMORILLONITE BASED Ni CATALYST

Hasanudin[1] and Novia[2]

[1] Department of Chemistry, Faculty of Mathematics and Natural Sciences,
University of Sriwijaya, Inderalaya, Palembang 30662, Indonesia.
Email: ghasanudin@yahoo.co.id
[2] Department of Chemical Engineering, Faculty of Engineering,
University of Sriwijaya, Inderalaya, Palembang 30662, Indonesia.
Email: noviasumardi@yahoo.com; noviasumardi@mail.pps.unsri.ac.id

ABSTRACT

Al_2O_3 pillared montmorillonite based Ni Catalysts have been prepared and characterized from the point of view of porosity and structure by N_2 adsorption-desorption. Catalytic activity of catalyst was studied by petroleum sludge hydrocracking. The data shows that the Al_2O_3 pillared montmorillonite successfully to increase total pore volume and surface area specific from their initial montmorillonite features. Catalytic activity of Al_2O_3 pilared montmorillonite more active than parent montmorillonite. While, catalyst Ni was loaded on Al-pillared montmorillonite can increase the catalytic activity for petroleum sludge hydrocracking. Optimum condition for petrolium sludge hydrocracking were found at 400^{o}C, 2.00 cc/min for hydrogen flow rate and 1,00 g for amount of catalyst.

Keywords: petroleum sludge, pillared montmorillonite, hydrocracking

INTRODUCTION

Petroleum sludge is the hydrocarbon waste type which is difficult to be degragated by microba. It can contaminate environment because containing many dangerous and poisonous materials. If we do not handle this sludge, it will destroy environment. The Petroleum sludge still contains many heavy fraction hydrocarbons that can be processed to become good quality fuel oil by cracking and hydrogenation processes (*hydrocracking*). Hydrocracking represents the catalytic thermal hydrodecomposed that is able to change the long chain of hydrocarbon become oil fraction with the shorter chain hydrocarbon.

The catalysts used in this process have double function that is metal component as hydrogenation catalyst and acid component as cracking catalyst. The catalyst used for cracking process is alumina, silika-alumina, clay and zeolite which have been modified. Modification of montmorillonite through pillared technique using inorganic molecule was investigated by Brindley et al [1]. Pillaring is conducted with ion exchange method, where cation found on the space between montmorillonite layers is exchanged with bigger size cation. The cation is made by hydrolysis its salts metal. During the heating process at the temperature above 300^oC, the cation of oligomer hydroxyl metal faced dehydration and dehydroxylation to become metal oxide which form amorphous solid finally. This amorphous solid has the behavior like a Lewis acid. The metal oxide has the function as a pillared to support clay coats. The pillared clay has the micropore and mesopore structure on the space between the montmorillonite layers. This structure causing montmorillonite has acidity behavior which has a function as cracking catalyst.

Pillared montmorillonite has surface area, porosity, stability and acidity of thermal used for various type of chemical reaction catalyst, especially for the reaction of acid catalyst [2-5]. Such as zeolite, the pillared montmorillonite can be used as a metal support solid for hydro-treatment catalyst. Pillared montmorillonite as a metal support catalyst for various reactions have been developed for the hydro-treatment, hydro-isomerizes and hydro-cracking using transition metals [5-8]. Pillared montmorillonite has broader pore size distribution than zeolite, so the molecule diffusion limitation and deactivation can be reduced [6]. The performance of pillared montmorillonite can be improved by adhering catalyst metal on it. The metal enhances catalyst activity because metal-montmorillonite have double function as hydrogenation and cracking catalyst. The Metals used as hydrogenation catalyst are Ni, Co, Mo, Pt, Pd. Good hydrogenation catalyst is Pt and Pd, however it is quite expensive.

Hydrocracking proses occurs at high temperature, so the catalyst must have heat resistance. In present work, the catalytic activity of catalyst was studied by petroleum sludge hydrocracking using Al_2O_3 pillared montmorillonite based Ni catalyst. This study investigated the effect of pillared, metal impregnation of Ni and operating condition to product distribution of petroleum sludge hydrocracking. Hydrocracking process is conducted for various temperatures, hydrogen gas flow rates, and the amount of catalyst.

MATERIALS AND METHODS

Materials

The materials used in this study are montmorillonite clay, demin water, NaCl, $AlCl_3$, NH_4OH ,NaOH, $Ni(NO_3)_2$, petroleum sludge, O_2 and H_2.

Equipment

This research needs some equipment such as stainlles steel reactor, thermometer, glassware, analytical balance, desicator, oven, screener 200 mesh, furnace, temperature controller, flow meter, cooling water system, EDX JSC dan gas chromatography. Schematic diagram of equipment is shown in figure 1.

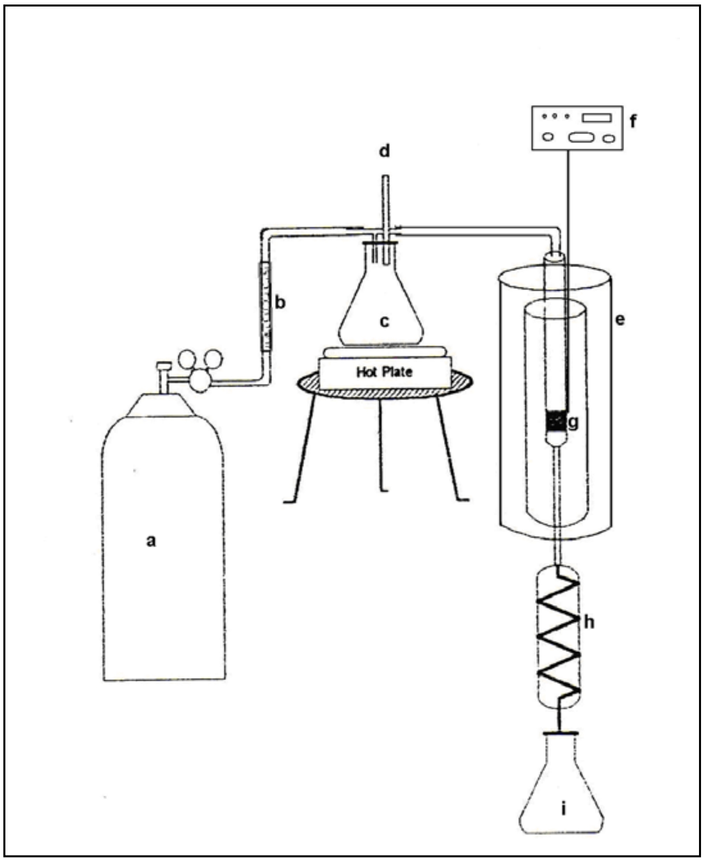

Fig. 1: Schematic diagram of equipment: a) Hydrogen gas; b) Flow meter; c) Isoprophil benzene; d) Thermometer; e) Furnace cylinder; f) Temperature controller; g) Catalyst; h) Cooler; i) Product Sample

Procedures of Pillaring and synthesis of catalyst

Natural clay of montmorillonite type was sieved by screener 250 mesh. This clay was cleaned with aquades, then precipitated and dried in oven. Furthermore, this clay was saturated by NaCl solution and at the same time swirled during 24 hours. Finally, the clay was washed by mineral free water. The purpose of washing is to clean the chloride ion of the clay. This is continued until obtained clear filtrate and showed negative test for $AgNO_3$ solution. This is called by Na-Montmorillonite. Then, Na-montmorillonite was pilared by oligomer hydroxyl aluminum solution as according to method which have been reported the other researcher [10]. This result is referred as Al_2O_3 pillared montmorillonite (Al-Mont).

Al_2O_3 pillared montmorillonite was soaked in 100 mL solution of $Ni(NO_3)_2$ 0,04 M during 24 hours and dried. Aluminum-Montmorillonite containing Ni was dried at the temperature of 130^{o}C during 3 hours. Then, it was oxidized by flowing O_2 gas at the temperature of 350^oC and the flow rate of 1 mL/s during 3 hours. In order to get good catalyst, the result of oxidation was reduced by flowing H_2 gas at temperature of 350^oC and the flow rate of 1 mL/s during 3 hours. Al_2O_3 pillared montmorilloniteе based Ni was characterized and used for the hydrocracking of petroleum sludge.

Hydrocracking of Petroleum Sludge

Hydrocracking of petroleum sludge was conducted by heating sample in gas forming reactor. The formed gas was flowed by H_2 gas to fixed bed reactor for the hydrocracking process. The reactor was filled by certain amount of catalyst. The temperature of hydrocracking was varied between 300 ^oC to 500^oC. The flow rate of hydrogen gas of 1.5 mL/s to 3.5 mL/s and the amount of catalyst of 0.25 gram to 1.25 gram were used. Finally, the hydrocracking product was cooled and collected to be analyzed its composition with Gas Chromatography.

RESULTS AND DISCUSSION

Analysis of Metal Catalyst Contain

Analysis of metal contain in catalyst sample was conducted by method of Energy Dispersive X-Ray (EDX), and the results were presented in tables 1. Natural Montmorillonite which is used in this research contain metal cations of Na, Mg, K, Ca, Fe and small amount of the other transition metals. It can be shown from the table that significant decreasing of the metal content occurs when pillared technique was applied. The increasing of Aluminum content was followed by the decreasing of cation content that able to be exchanged. These phenomena indicated that the pillared process occurred through cation exchange mechanism. Furthermore, the calcinations process of Aluminum cation caused the formation of oxide alumina (Al_2O_3) which became montmorillonite stable pillared. These cations replaced cations that can be exchanged in the space at montmorillonite layers. It is shown that Aluminum content in this pillared montmorillonite system increased (reaching 90%).

Tab. 1: Metal compotition in catalyst

Catalyst	Logam (%)							
	Na	K	Ca	Mg	Si	Al	Fe	Ni
Montmorillonite	4.65	2.63	1.45	1.56	30.80	7.79	1,45	-
Al-Montmorillonite	0.53	0.32	0.21	0.18	33.00	14.76	0,21	0,19
Ni-Al-Mont	0.56	0.34	0.20	0.19	32.90	14.74	-	4.89

Ni Metal was impregnated into Aluminum-Montmorillonite by impregnation method, so expected all of the impregnated metal come into pore of pillared montmorillonite. Metal impregnation of Ni on Aluminum-Montmorillonite did not cause the significant decreasing of the other metal content, because the mechanism passed through impregnation process is not ion exchanged. This method is very effective to arrange the amount of metal which come into catalyst supporting solid.

Adsorption-Desorption Isotherm of N_2

Isotherm curve of adsorption-desorption of N_2 gas of the samples of montmorillonite, Aluminum-Montmorillonite, Ni-Al-Mont are presented in figure 2. All isotherm curve of adsorption-desorption of N2 gas have the same type which is grouped as isotherm of adsorption of type II according to classification of Brunauer, Deming, Deming and Teller (BDDT) [11]. Isotherm of adsorption of type II represents adsorption type of materials which dominated by mesopore as the biggest contributor its porosity total. Meanwhile, hysterics loop of isotherm of adsorption-desorption of N2 gas from these catalyst showed hysterics loop type of B [12], this hysterics type is suitable for materials having interpose form (the existence of room between two parallel plate). These materials are similar to natural montmorillonite of pillared montmorillonite.

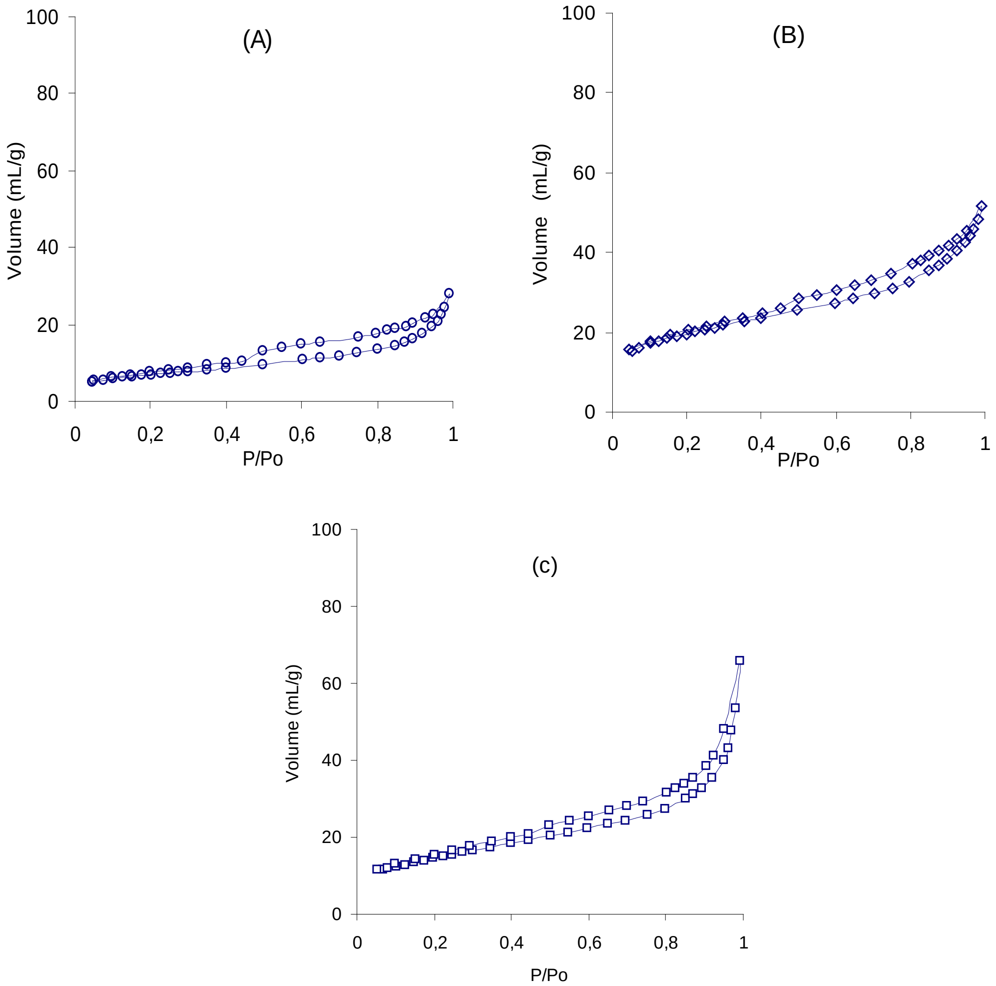

Fig. 2: Isoterm adsorpsi-desorpsi gas N_2 pada; Montmorillonite (A), Aluminum-montmorillonite (B), Ni-Al-mont (C)

Table 2 presented analysis result of pore structure parameters including; specific surface area (S_{BET}), total of pore volume (V_p), pore volume of the micropore category ($V_{\mu p}$), pore volume of the mesopore category (V_{mp}) and pore diameter average (D_p). Aluminum-Montmorillonite showed the development of specific surface area and porosity compared to un-pillared montmorillonite. The value of surface area of 63,76 m^2/g was obtained on Aluminum-Montmorillonite. The impregnated of Ni metal on Aluminum-Montmorillonite reduced catalyst surface area. This is due to some of impregnated Ni metal closed over pore and surface of Aluminum-Montmorillonite (Al-Mont) as impregnator, so it decreased the value of S_{BET} materials.

Tab. 2: Parameter of Catalyst Porosity

Katalis	S_{BET} (m^2/g)	V_p (mL/g)	$V_{\mu p}$ (mL/g)	V_{mp} (mL/g)	D_p (Å)
Mont	24,68	$3{,}57.10^{-2}$	$3{,}86.10^{-3}$	$3{,}18.10^{-2}$	69,92
Al-Mont	63,76	$5{,}48.10^{-2}$	$8{,}00.10^{-3}$	$4{,}68.\ 10^{-2}$	47,10
Ni-Al-Mont	59,45	$8{,}23.10^{-2}$	$5{,}43.10^{-3}$	$7{,}65.10^{-2}$	78,21

Effect of Catalyst to Hydrocarbon Composition of Hydrocracking Product

Hydrocracking process is the cracking process of long chain hydrocarbon followed by hydrogenation process, so it yielded product with shorter chain hydrocarbon. This process used the catalyst of double function which assisted cracking and hydrogenising processes.

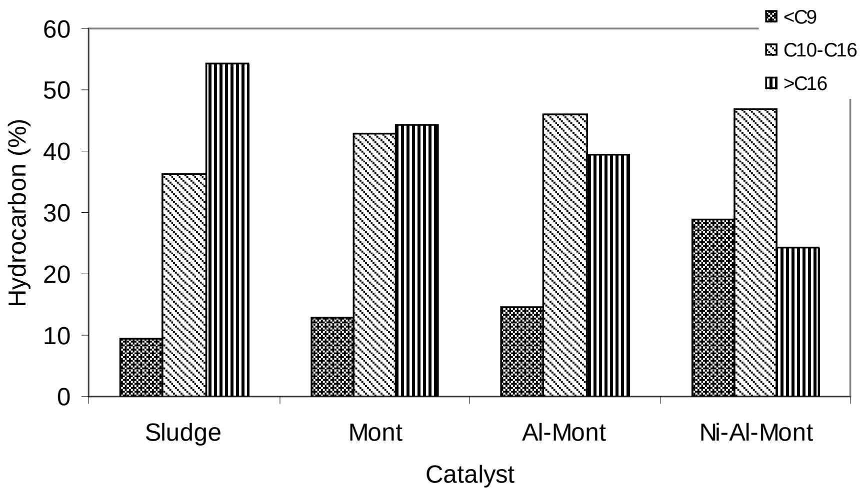

Fig. 3: Hydrocarbon Compotition of hydrocracking petroleum sludege product the temperature of 350^oC, H_2 gas flow rate of 2 mL/s the catalyst of 0,75 g

Hydrocracking process of petroleum sludge in this research took place at the temperature of 350^oC, the flow rate of H_2 gas of 2,00 mL/s and the catalyst of 0,75 g. Figure 3 showed the result of petroleum sludge hydrocracking at various of catalyst types of Montmorillonite, Aluminum-Montmorillonite and of Ni- Aluminum-Montmorillonite. It can be seen that the process using Ni-Aluminum-Montmorillonite catalyst yielded product with hydrocarbon composition of shorter chain < C_9 of 28.8 %. It is a higher compared to Montmorillonite catalyst of 12.9 % and Aluminum-Montmorillonite catalyst of 14.7 %. Ni Metal is the transition metal at the Ni-Aluminum-Montmorillonite catalyst having the empty orbital. It provided the place for hydrogen gas adsorption while the hydrocracking process took place, so chain of H-H was active progressively and reacted easily with the cracking product.

Hydrocracking process using Montmorillonite catalyst tend to produce hydrocracking product with hydrocarbon composition < C_9 smaller than using Ni-Aluminum-Montmorillonite catalyst. If only use natural clay, the hydrogenising process can not occur. This is due to no metal catalyst providing empty d orbital to adsorb of H_2, so only the cracking process of carbon chain happened. Cracked carbon chain tend to potent more tying with the other hydrocarbon which cause the hydrocracking product still has long hydrocarbon chain.

Effect of Temperature to Hydrocarbon Composition of Hydrocracking Product

Hydrocracking process was the catalytic thermal process, which carried out at high temperature. The high temperature enhanced catalyst activity, so the hydrocracking process occurred better. This high temperature also resulted hydrocarbon molecule kinetic energy become bigger, so the disconnection of long carbon chain happened. The effect of temperature to hydrocarbon composition on hydrocracking product of petroleum sludge was presented in figure 4. The hydrocracking process was carried out at the temperature variation of 300^oC, 350^oC, 400^oC, 450^oC and 500^oC, the constant flow rate of 2 mL/s and the amount of catalyst of 0.75 g for each of the treatment.

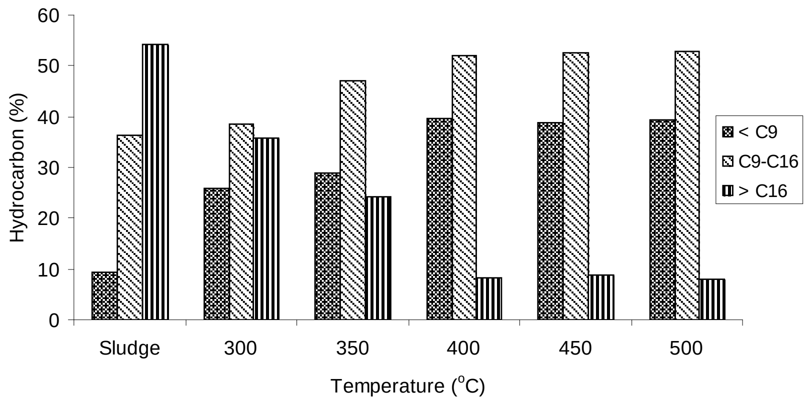

Fig. 4: Effect of Temperature to Hydrocarbon composition of hydrocracking product using Ni-Al-Mont catalyst, H_2 gas flow rate of 1 mL/s and the amount of catalyst of 0.75 g.

It is shown that the hydrocarbon product of < C_9 was higher and reached constant at the temperature of 400°C of about 39.7 %. This is because of the raising of temperature until 400°C caused reactant kinetic energy become bigger, so the reaction frequency improved. The optimal hydrocracking process occurred at the temperature of 400°C, because energy of reactant molecules passed its activation energy. The increasing of reaction frequency between reactant and catalyst accelerated reactant adsorption on catalyst. This caused the hydrogenising and the disconnection of long chain hydrocarbon become short chain hydrocarbon.

Effect of Hydrogen Gas Flow Rate to Hydrocarbon Composition of Hydrocracking Product

Hydrogen gas flow rate influenced hydrocarbon composition yielded. Hydrogen gas played a part in bringing hydrocarbon feed vapor to the reactor, so the sludge entered into reactor maximally. Gas hydrogen flow rate effected the contact time of reactant to catalyst and the adsorption process of hydrogen itself during hydrocracking process took place. Hydrocracking process of sludge was conducted at various of hydrogen gas flow rate of 1.5 mL/s, 1.2 mL/s, 2.5 mL/s, 3.0 mL/s and 3.5 mL/s. The temperature and amount of catalyst were held constant of 400°C and 0.75 g. The effect of hydrogen gas flow rate to hydrocarbon composition of hydrocracking product can be seen in figure 5.

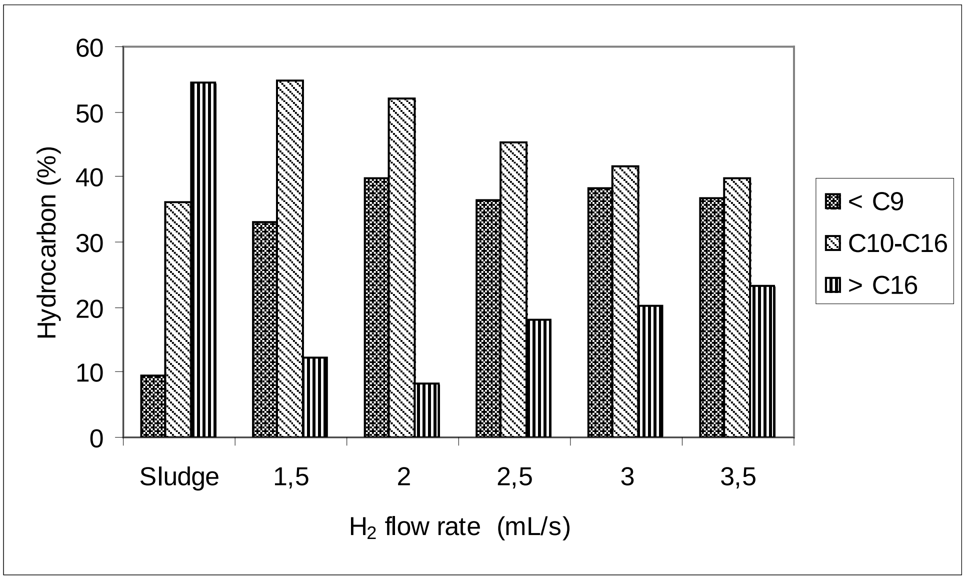

Fig. 5: Hydrocarbon Composition of Hydrocracking Product at Various Hydrogen Gas Flow Rate

We can see in this figure that the hydrocarbon composition <C9 increased progressively from the flow rate of 1.5 mL/s to 2 mL/s. The maximum of hydrocarbon is about 39.7 % at the hydrogen gas flow rate of 2 mL/s. This is due to the increasing of the hydrogen gas flow rate caused the sludge passed through the reactor easily, so the hydrogenising and cracking process took place. At the hydrogen gas flow rate of 2 mL/s, occurred

contact between hydrogen gas bringing the sludge and the catalyst surface. The hydrogen adsorption process is more maximal to result hydrogenising process, and then followed by cracking process of hydrocarbon chain.

For a lower hydrogen gas flow rate, the hydrogenising and cracking process occurred very low. Hydrogen gas bringing the sludge did not pass the surface of catalyst quickly. In order to push the vapor of sludge with larger molecular weight needed larger hydrogen gas fusion. This caused only a few of adsorbed hydrogen at the surface of catalyst, so a few of the hydrocacking process took place.

On the other hand, at the hydrogen gas flow rate of 2.5 mL/s, hydrocarbon composition $< C_9$ decreased. This is due to a higher flow rate caused the time contact between the hydrogen gas pushing the sludge and the surface of catalyst lower. In addition, the higher composition of hydrocarbon represented the decreasing of hydrogen adsorption and the hydrocracking processes. The higher flow rate of hydrogen gas caused some of sludge did not pass the surface of catalyst, so the hydrogenising and cracking process decreased. The product contained much more long chain hydrocarbon. It is seen from the hydrocarbon composition of C_{10}-C_{16} increased progressively.

Effect of the amount of Ni-Al-Mont Catalyst to Hydrocarbon Composition of Hydrocracking Product

Hydrocracking process is also influenced by the usage of amount of catalyst. The amount of catalyst closely related to the surface of catalyst itself. This research used various amount of catalyst of 0.25 g; 0.5 g; 0.75 g; 1.00 g and 1.25 g at the constant temperature of 400^{o}C, the hydrogen gas flow rate of 2 mL/s. The effect of amount of Al_2O_3 pillared Ni-Montmorillonit catalyst can be seen in figure 6.

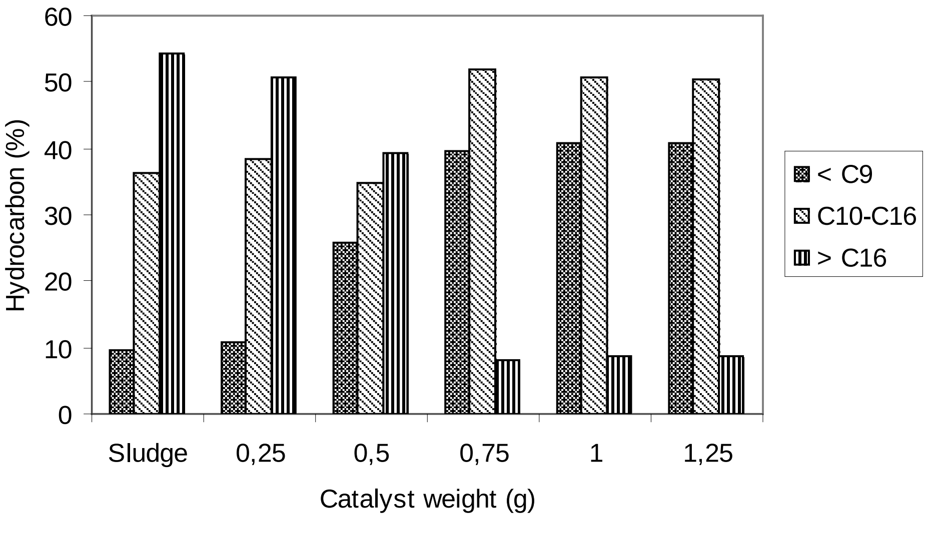

Fig. 6: Hydrocarbon Composition of Hydrocracking Product at various amount of Ni-Al-Mont Catalyst at the Temperature of 400^{o}C and the Flow Rate of H_2 of 2 mL/s.

Figure 6 illustrated the hydrocarbon composition at different amount of Al_2O_3 pillared Ni-montmorillonite catalyst. It is shown that the hydrocarbon composition of < C_9 increased progressively with the increasing amount of the catalyst. The highest composition of hydrocarbon <C_9 can be found at the amount of catalyst of 1.00 g that is equal to 38.4 %. The increasing amount of Al_2O_3 pillared Ni-Montmorillonite catalyst caused the surface of catalyst increased significantly. This is due to contact between the reactant on the surface of catalyst become bigger so the hydrogen adsorption flattened on the catalyst. The decreasing amount of catalyst reduced hydrocarbon composition of < C_9, because the catalyst did not have enough surface area to reserve for the occurring of cracking process.

CONCLUSIONS

It can be concluded from this research that hydrocracking process of petroleum sludge using Al_2O_3 pillared montmorillonite based Ni catalyst resulted the highest hydrocarbon composition of <C_9 which is about 38,4% at the temperature of 400^{o}C, the flow rate of hydrogen gas of 2 mL/s and the catalyst of 1.00 g.

ACKNOWLEDGEMENT

The authors are grateful to Higher Education General Directorate (DIKTI) National Education Department, Indonesia, for their financial support in PHK A_2 project.

REFERENCES

G.W. Brindley. G.W., and Sempels, R.E. (1977) *Clay Mine.r,* 12, 229.
Burch, R. (1987) *Introduction. Catal. Today,* 2, 185–186.
Figueras, F. (1988) *Catal. Rev., Sci. Eng.*, 30, 457.
Lambert, J.F., and Poncelet, G. (1997) Top. Catal., 4, 43–56.
Salermo, P., Mendioroz, S., and Agudo, A.L. (2003) *Appl. Clay. Sci.*, 23, 287.
Salermo, P., Mendioroz, S., and Agudo, A.L. (2004) *Appl. Catal A: General,* 259, 17.
Wang, S., Zhu, H.Y., and Lu, G.M.Q. (1998) *J. Colloid and Interface Sci*., 204, 128.
Hasanudin, Wijaya, K., Rachmat, A., dan Trisunaryanti, W. (2008) *J. Penelitian Sains*, 11, 2, 481.
Hasanudin and Rachmat, A. (2007) *Jurnal Media Teknik*, 4, 2, 55-64.
Poppl, L., Toth, E., Toth, M., Pasli, I., Izvekov, V., and Gabor, M. (1998) *J. Thermal Anal*., 53, 585 .
Brunauer, S., Demming, L.S., Demming, W.S., and Teller, E.J. (1940) *Am. Chem. Soc*., 62, 1723.
Lowell, S., and Shields, J.E. (1984) *Powder Surface Area and Porosity,* Chapman and Hall, New York, 59.