Study on Effect of TIO$_2$-Pillared-Montmorillonite Based Co-Mo Catalysts to Hydro-cracking Process of Jarak Seed Oil

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ABSTRACT

Hydro-cracking is the catalytic thermal hydro-decomposed process that changes the long chain of hydrocarbon to become oil fraction with the shorter hydrocarbon chain. In this preliminary work, hydro-cracking of Jarak seed oil was studied to investigate the catalytic activity of the catalyst. The catalysts used in this study have double functions which are the metal component as a hydrogenation catalyst and the acid component as the cracking catalyst. Initially, TiO$_2$-pillared-montmorillonite based Co-Mo catalysts have been characterized by the adsorption-desorption of N$_2$ to view its porosity and structure. The results showed that the TiO$_2$ pillared montmorillonite increases significantly the total pore volume and the specific surface area of their initial montmorillonite features. It is concluded that the catalytic activity of TiO$_2$ pilared montmorillonite is more active than its montmorillonite parent. In addition, Co-Mo catalysts were loaded on TiO$_2$ pillared montmorillonite enhanced the catalytic activity of hydro-cracking of Jarak seed oil.

Keywords: Co-Mo, Hydro-cracking, Jarak Oil, TiO$_2$ pillared-Montmorillonite.

1   INTRODUCTION

Catalytic hydrotreating is commonly used to upgrade the quality of feedstocks in order to increase the performance and product specifications in downstream deep conversion units, such as catalytic cracking and hydrocracking. Hydrocracking refers to the process in which the main objective is to convert the heavy fractions of the feed into more valuable lighter products, such as naphtha, kerosene, and middle distillates. Hydrocracking is characterized by its high flexibility in processing a wide variety of feedstocks and obtaining a wide range of products ranging from LPG to lube base oils.

Hydrocracking represents the catalytic thermal hydrodecomposed that is able to change the long chain of hydrocarbon become oil fraction with the shorter chain hydrocarbon. Accessible acid sites, high surface area, and high thermal and hydrothermal stabilities are the properties of an efficient cracking catalyst desired. The catalyst used for cracking process is alumina, silika-alumina, clay and zeolite which have been modified. Cracking catalysts which are zeolite based possess pore sizes less than about 10 A, which makes them inefficient for the cracking of larger hydrocarbons, for example those in heavy oils [1]. The search for alternative materials with high cracking activities comparable to zeolites, but with larger pores, has motivated different research groups to investigate various metal oxide pillar-interlayered clays abbreviated as PILCs in recent

years. Modification of montmorillonite through pillared technique using inorganic molecule was investigated by Brindley et al [2]. 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 $300^{o}C$, 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 bronsted and Lewis acid. The metal oxide has the function as a pillared to support clay layers. 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.

The pillaring species reported in the literature are usually polymeric, cationic compounds of Al[3,4], Ga[5], Zr[6], and Ti [7], or mixtures of these elements. The most commonly studied clay mineral is montmorillonite, due to its availability and its ability to intercalate large cations to create the pillared clay. The process of pillaring is aided by two characteristic features of smectites viz., swelling and transverse layer rigidity. Swelling, which is a reversible process, occurs on hydration of interlamellar cations and facilitates the process of ion exchange of bulky cationic species into the layers. Transverse layer rigidity, another intrinsic property of the smectite clays, helps in maintaining the interlamellar space between the pillars and prevents the gallery pores from collapsing. Pillared clays are extensively studied as adsorbents [8] and as catalysts [9–11]. The modification produces a clay material with interesting physicochemical properties; for example, homogeneous distribution of micropores with mean pore diameters 0.7–0.9 nm, availability of both Lewis and Bronsted acid sites and ability to catalyze various reactions such as alkylation [9], disproportionation [10] and hydrogenation [11].

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 [12-15]. 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 [15-18]. Pillared montmorillonite has broader pore size distribution than zeolite, so the molecule diffusion limitation and deactivation can be reduced [16].

Such as zeolite, the pillared montmorillonite can be used as a metal support solid for hydro-treatment catalyst. 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. High performance for 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 hydrocracking jarak seed oil using TiO_2 pillared montmorillonite based Co/Mo catalyst. This study investigated the effect of pillared, metal impregnation of Co and Mo and heater temperature to yield oil liquid product of jarak seed oil hydro-cracking.

2   RESEARCH METHODOLOGY

2.1 Material

Unless otherwise stated, all chemical reagents were purchased from MERCK with the highest commercially available purity and were used without purification. NaCl, $TiCl_4$, $Co(NO_3)_2$ $6H_2O$, $(NH_4)_5Mo_7O_{24}.4H_2O$, jarak seed oil and natural montmorillonite clay.

2.2 Equipment

This research needs some equipment such as stainless steel reactor, thermometer, glassware, analytical balance, desiccators, oven, screener 200 mesh, furnace, the temperature controller, flow meter, cooling water system, EDX JSC and gas sorption analyzer NOVA1000.

2.3 Experimental Procedure

Pillaring and synthesis of catalyst

Natural clay of montmorillonite type was sieved by the screener of 200 meshes. This clay was cleaned with mineral free water, then precipitated and dried in oven. Furthermore, the 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 product is called by Na-Montmorillonite. Then, Na-montmorillonite was pilared by titanium tetrachloride solution as according to method which have been reported [18]. This result is referred as TiO_2 pillared montmorillonite (Ti-Mont).

Ti-Mont was soaked in solution of $CoNO_3$ and $(NH_4)_6Mo_7O_{24}$ during 24 hours and dried. The TiO_2 pillared montmorillonite containing Co and Mo was dried at the temperature of 130^oC 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 of 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. The product is referred as Co/Mo-TiO2 pillared montmorillonite catalyst.

Hydrocracking of jarak seed oil

Hydrocracking of jarak seed oli was conducted by heating sample in the 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 400^oC to 525^oC. The flow rate of hydrogen gas of 0.5 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.

3 RESULTS AND DISCUSSION

Analysis of Metals Content of Catalyst

Analysis of Si, Al and Ti in catalyst sample was conducted by method of Energy Dispersive X-Ray (EDX), the results were presented in figure 1. Natural Montmorillonite which is used in this research contain metal cations of K, Ca, Fe and small amount of the other transition metals. Si content of natural monmorillonite 30,90% decreased to 27,33% for TiO2 pillared monmorillonite. Existing of Titanium content for pillared monmorillonite indicated that the pillaring process occurred successfully through cation exchange mechanism. Furthermore, the calcinations process of titanium cation caused the formation of Titanium oxide (TiO_2) which became montmorillonite stable pillared. These cations replaced cations that can be exchanged in the space at montmorillonite layers.
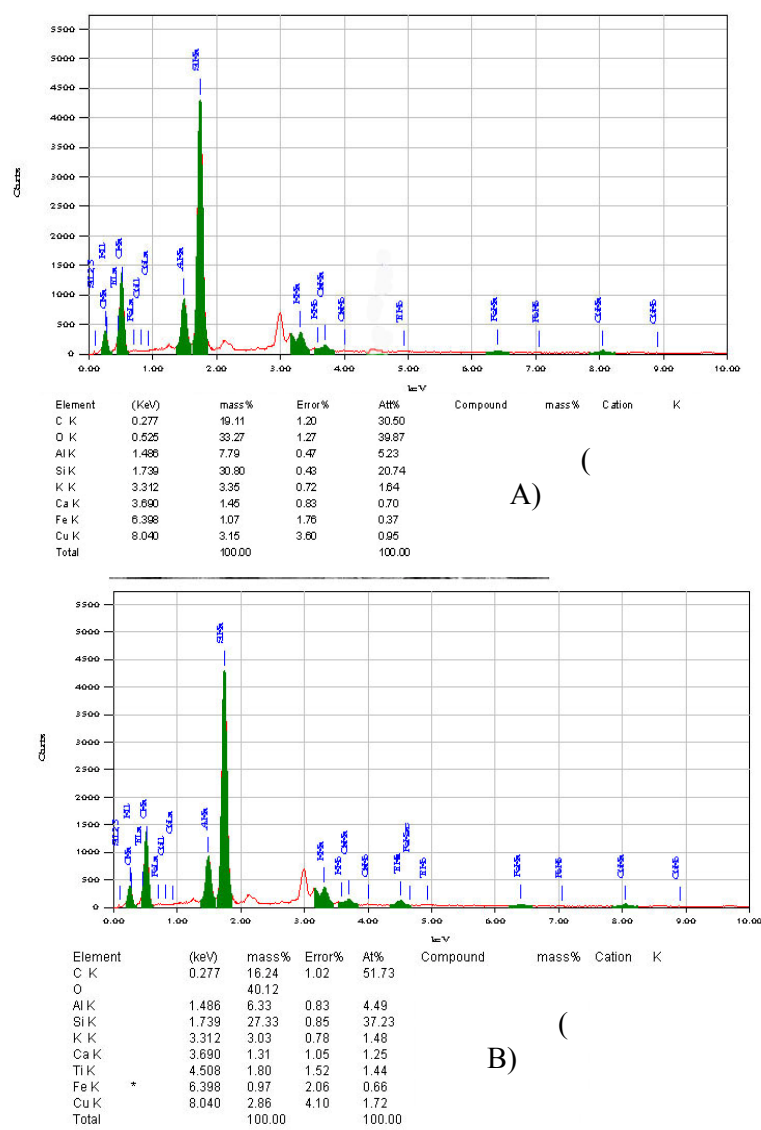
Element	(KeV)	mass%	Error%	Att%	Compound	mass%	Cation	K
C K	0.277	19.11	1.20	30.50				
O K	0.525	33.27	1.27	39.87				
Al K	1.486	7.79	0.47	5.23				
Si K	1.739	30.80	0.43	20.74				
K K	3.312	3.35	0.72	1.64				
Ca K	3.690	1.45	0.83	0.70				
Fe K	6.398	1.07	1.76	0.37				
Cu K	8.040	3.15	3.60	0.95				
Total		100.00		100.00				

(A)

Element		(keV)	mass%	Error%	At%	Compound	mass%	Cation	K
C K		0.277	16.24	1.02	51.73				
O			40.12						
Al K		1.486	6.33	0.83	4.49				
Si K		1.739	27.33	0.85	37.23				
K K		3.312	3.03	0.78	1.48				
Ca K		3.690	1.31	1.05	1.25				
Ti K		4.508	1.80	1.52	1.44				
Fe K	*	6.398	0.97	2.06	0.66				
Cu K		8.040	2.86	4.10	1.72				
Total			100.00		100.00				

(B)

Figure 1. SEM-EDX analysis (A) Natural montmorillonite, (B) TiO$_2$-pillared montmorillonite

Co and Mo metals were coated into TiO$_2$-Montmorillonite by impregnation method, so expected all of the impregnated metal come into pore of pillared montmorillonite. Analysis of Co and Mo in catalyst samples were conducted by Atomic Absorption Spectroscopy (AAS) method of, the results were presented in table 1. Metal impregnated in TiO$_2$-Montmorillonite did not cause the significant decreasing of the other metal content, because the mechanism passed through impregnation process is not the ion exchanged. This method is very effective to arrange the amount of metal which come into catalyst supporting solid.

Table 1. Metal composition in catalyst

Sampel	% (w/w) Co	% (w/w) Mo
Katalis A	0,0000	10,8947
Katalis B	2,4687	8,0614
Katalis C	3,5879	6,2536
Katalis D	4,5347	4,3173
Katalis E	6,0841	0,0000

Adsorption Isotherm of Natural Monmorillonite and TiO$_2$ Pillared Monmorillonite Catalysts

Nitrogen adsorption-desorption isotherm are related to the relative presure of adsorbate at constant temperature. Nitrogen adsorption-desorption isotherm were used to determine the surface area, pore volume and average of pore radius. Isotherm curve of adsorption-desorption of N$_2$ gas of the samples of monmorillonite and TiO$_2$-monmorillonite are presented in figure 2. Based on BDDT classification, adsorption-desorption isoterm of N$_2$ gas onto monmorillonite and TiO$_2$-monmorillonite followed curve of type II. This type of isotherm is characteristic of microporous materials in which multilayer adsorption of N$_2$ are sterically hindered. The hysteresis loop for all the samples showed that a feature of materials which possess a pore structure built up of parallel plates.
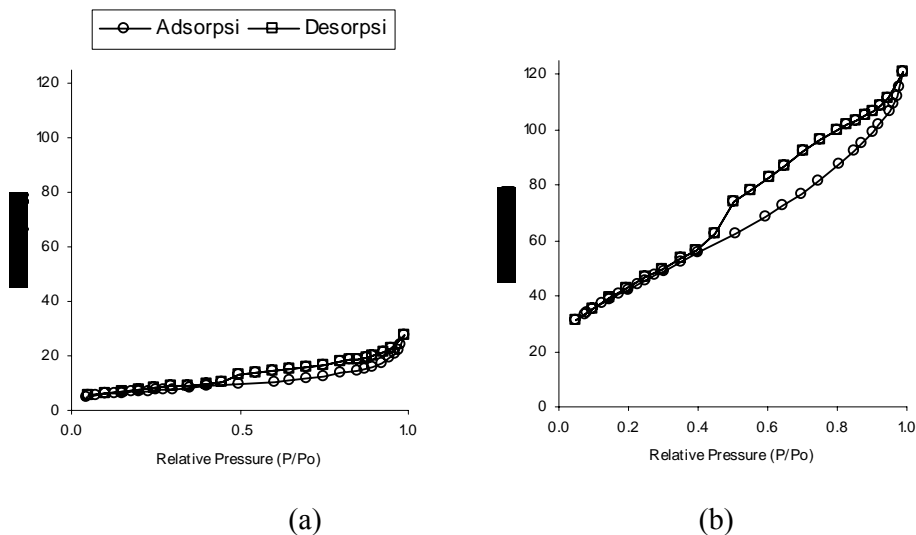

(a) (b)

Figure 2. Curve of nitrogen adsorption-desorption on (a) natural monmorillonite, and (b) TiO$_2$ pillared monmorillonite

Adsorption isotherms on the samples of natural montmorillonite and TiO$_2$ pillared monmorillonite are according to the BET equation, meanwhile Adsorption isotherms on samples Co/Mo-TiO$_2$ pillared monmorillonite A, B, C, D and E (figure 3) are according to the langmuir equation. The BET equation considers multilayer adsorption of N$_2$ equation is obeyed by those microporous material in which the multilayer adsorption of N$_2$ is sterically hindered. Usually porous materials which give type II isotherm obey the BET equation. The surface area of natural montmorillonite increased from 27.43 to 169.56 m^2 g^{-1} on TiO$_2$-pillared monmorillonite. Increase in surface area on pillaring is expected, since the process creates regular porosity. Apparently the ion

exchange and subsequent calcinations changed the stacking pattern of the pillared clay. The process might have resulted in a layer arrangement similar to the house of cards structure.
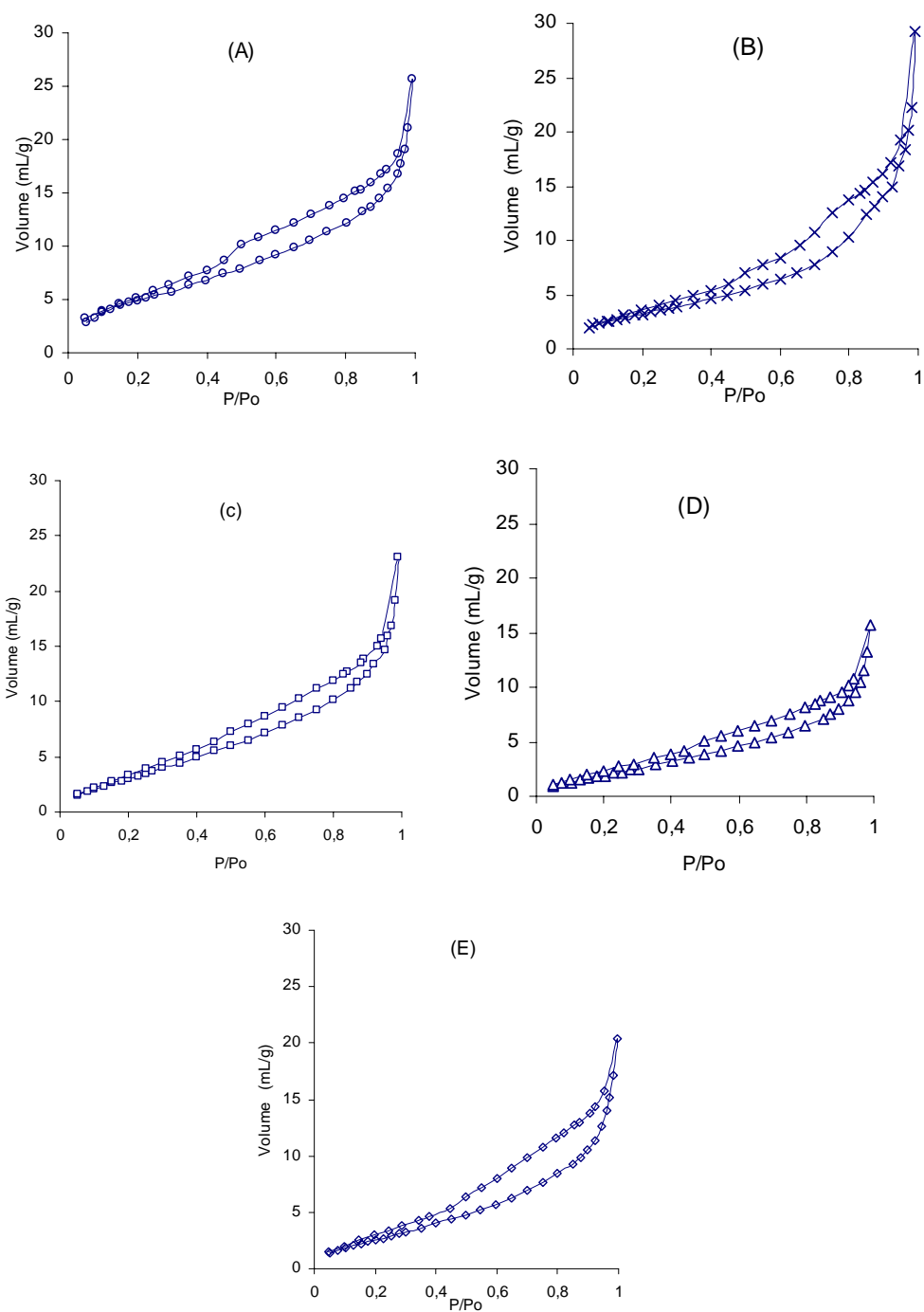

Figure 3. Curve of nitrogen adsorption-desorption on (A) Catalyst A, (B) Catalyst B, (C) Catalyst C, (D) Catalyst D, and (E) Catalyst E

Tabel 2. Parameter of Catalyst Porosity

Katalis	S (m^2/g)	V_p (cc/g)
Montmorillonite	24,68*	$4,31.10^{-2}$
TiO$_2$-monmorillonite	153,95*	$1,87.10^{-1}$
CoMo-TiO$_2$-monmorillonite (A)	59,45**	$8,23.10^{-2}$
CoMo-TiO$_2$-monmorillonite (B)	124,69* *	$4,54.10^{-2}$
CoMo-TiO$_2$-monmorillonite (C)	139,14* *	$3,58.10^{-2}$
CoMo-TiO$_2$-monmorillonite (D)	88,24**	$2,42.\,10^{-2}$
CoMo-TiO$_2$-monmorillonite (E)	109,55* *	$3,15.\,10^{-2}$

Notes: * BET equation
  **Langmuir equation

Surface areas as calculated by following BET and Langmuir equations are given in Table 2. The total pore volume of the samples is measured by condensation of N$_2$ adsorbate at $P/P0$ 0.95 in the pores of diameter <1400 Å by the single point method (Table 2). Specific surface area of the sample increased for TiO$_2$-monmorillonite (153.95 m^2/g) from parent monmorillonite. On pillaring, the total pore volume also increased from 0.0431 cc/g in the monmorillonite become to 0.187 cc/g for TiO$_2$ pillared monmorillonite. Existing of Co and Mo inside of the TiO$_2$-monmorillonite decreased both specific surface area and pore volume of the catalyst. The phenomenon was caused by co and Mo metals covered the pore and surface of TiO$_2$-monmorillonite as support catalyst.

Effect of Co/Mo content of Catalyst to 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. The performance of catalysts having different Co/Mo ratios was studied in terms of yield of oil liquid fraction products. The yield of oil liquid fraction products is defined as follows:

Yield (wt. %) = Weight of oil liquid fraction product (g)/jarak seed oil * 100%

Hydrocracking process of jarak seed oil in this research took place at the temperature of 400°C, the flow rate of H$_2$ gas of 1,00 mL/s and the catalyst of 2,00 g. Figure 4 showed the result of jarak seed oil hydrocracking at various of catalyst types. It can be seen that the highest yielded product when the process using Co/Mo montmorillonite catalyst (B). The yield of product obtained from the jarak seed oil hydro-cracking over Co/Mo-TiO$_2$ pillared monmorillonite as catalyst material were investigated and the activity of different catalysts is presented in Figure 4. The yield of oil liquid product was increased more significantly from 14% (catalyst A) to 23% (catalyst B) wt.% with the presence of 2,5 wt.% of Co metal and 8,1 wt.% of Mo metal. However, the yield dropped to 11 wt.% with the further increase in the Co metal in the catalyst to 4,5 wt.%. The conversion was decreased because the surface area decreased from 124 to 88 m^2 /g. Co and Mo Metal is the transition metal and having the empty orbital. It provided the place for hydrogen gas adsorption while the hydro-cracking process took place, so chain of H-H was active progressively and reacted easily with the cracking product.
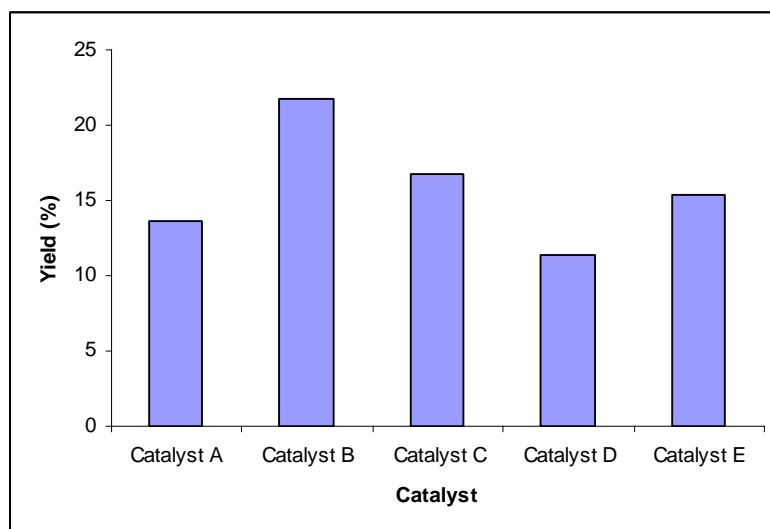
Figure 4. Yield of hydrocracking jarak seed oil at the temperature of 400°C, H$_2$ gas flow rate of 1.00 mL/s and the catalyst of 2.00 g

4   CONCLUSION

In this research, the performance of catalysts having different Co/Mo ratios was studied by hydrocracking of jarak seed oil at various of catalyst types. The yield of product was investigated over Co/Mo-TiO$_2$ pillared monmorillonite catalyst and the activity of different catalysts was also presented. The result show that the highest yield of product obtained when the process use Co/Mo montmorillonite catalyst of type B. The yield of oil liquid product increase significantly from 14% (catalyst A) to 23% (catalyst B) wt.% in the presence of 2,5 wt.% of the Co metal and 8,1 wt.% of Mo metal. However, the yield decrease to 11 wt.% with the further increase of the Co metal in the catalyst to 4,5 wt.%. The conversion decrease as the surface area decrease from 124 m^2 /g to 88 m^2 /g.

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