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Preparation of Aluminium Pillared Clay from Indonesian Montmorillonite and Its Catalytic Activity in Bio-Oil Cracking

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The preparation of aluminium pillared montmorillonite (Al-PILM) from Indonesian natural montmorillonite and its catalytic activity study in the bio-oil cracking has been investigated. The synthesis of Al-PILM catalyst was conducted through intercalation process of Al_{13} Keggin ion at the Al ratio of 5 mmol Al/g montmorillonite followed by dehydroxylation processing to get aluminium oxide pillar in montmorillonite interlayer. Catalyst characterization performed by XRD, surface area analyzer and surface acidity measurement and SEM. Activity test of material as catalyst in bio-oil cracking focused on the effect of Al-PILM utilization to the product distribution and liquid product composition. The result showed that Al-PILM has higher activity to produce lighter fraction of hydrocarbon than montmorillonite. The increase in liquid product and selectivity to produce smaller hydrocarbon compounds attributed to the improvement of catalyst performance after pillarization.

Key Words: Montmorillonite, Pillared clays, Cracking, Bio-oil.

INTRODUCTION

High price of crude oil make some countries faced to the problem of oil crisis. The utilization of biomass as energy source is one of the best alternative solution. Beside of its renewable properties, biomass is still the cheapest fuel source available in Indonesia and it will be the major alternative fuel source in the future. An alternative of biomass transformation is gasification process. Hemicellulose, cellulose and lignin as major components of biomass chemically can be covert to liquid and gas hydrocarbon by different mechanisms and pathways. Indonesia has good potency for this development due to the vast forestry area. Until 1999, it is reported that just 70 % of log core optimally used in industry, 30 % of these are forestry waste and it is reasonable to investigate and build biofuel based energy project specially from wood residue pyrolysis.

As produced, biofuel has some undesirable properties as fuel *e.g.*, some thermally unstable components which can lead to gum formation, low energy density because of dissolved water and highly oxygenated compounds, a corrosive organic acid

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component and phase instability with a tendency toward phase separation[1,2]. Several process consist of high-severity hydrotreating, involving complete hydrodeoxygenation. Some hydrocracking and minimal hydrogenation to produce an aromatic hydrocarbon fuel, is an expensive way to remedy these problems. As an alternative, we are developing catalytic hydrocracking the fuel oil properties, designed as upgrading process. This process need heterogeneous catalyst which has specific performance consist of high surface area, acidic surface and thermal stability. Solid catalyst and/or metal loaded in solid support such as silica alumina, synthetic zeolite and synthetic silica alumina commonly used in the same process in several industry, but its utilization for biofuel conversion will give an undesireable economic cost of the process[3,4].

Utilization of natural montmorillonite clay which is found abundant in Indonesia is a good alternative inspite of commercial solid catalyst. Clay structure modification by metal oxide pilarization and its application in catalysis has grown with the advances in intercalation chemistry[5,6]. The major purpose of modification is to improve surface sites activity and thermal stability by porous structure formation. Al-pillared clays and other transition metal pillared clays utilization in cracking process have been reported by several authors. Though some investigation do not prove the activity, some reports reveal the activity improvement as result of aluminium pillarization as shown by the increase of liquid product distribution in the cracking mechanism. The main reason for these phenomenon is that the catalyst activity is close related with the catalyst physicochemical character involved[7-9]. Among other transition metals, the use of aluminium as pillaring metal oxide is intensely studied. Its test in hydrocarbon cracking has also been investigated. However, investigation on its catalyst activity in the bio-oil cracking has not reported yet.

In present work, synthesis of aluminium pillared montmorillonite (Al_2O_3-Montmorillonite) and its application in biofuel upgrading is reported. Biofuel was derived by wood pyrolysis. The physico-chemical character of catalyst and its relation with catalyst activity was studied. Role of material physicochemical character to the catalytic activity was evaluated based on the product distribution and liquid composition by cracking and hydrocracking process.

EXPERIMENTAL

The starting material, montmorillonite was obtained from PT. Tunas Inti Makmur, Semarang, Indonesia. The reagents for pillarization process, $AlCl_3\cdot 6H_2O$, NaOH were supplied by E. Merck and used as received.

Bio-oil were produced by the pyrolysis process toward *Tectona grandis* wood chip at the temperature of 400 ºC and pressure of 0.3 atm. Bio-oil is the liquid smoke isolated from the process within the temperature range of 50-150 ºC. Chemical analysis to the bio-oil was performed by gas chromatography-mass spectrometry (GCMS) HP[5]. Chromatogram is depicted in Fig. 1 and identification of main components is listed in Table-1.

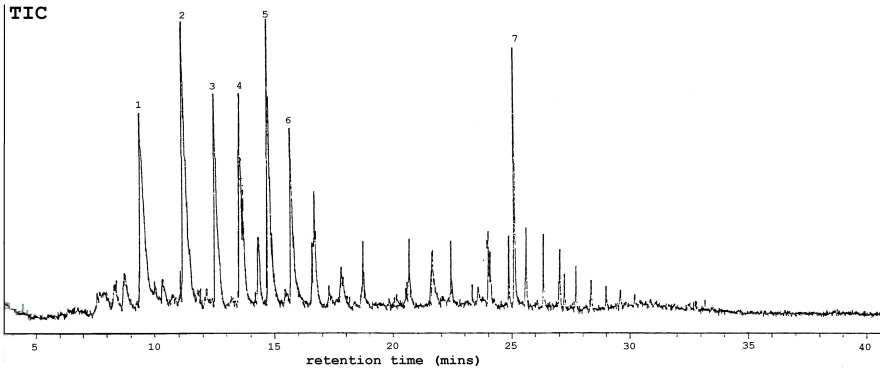
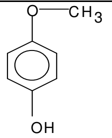
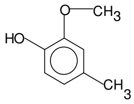
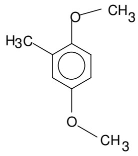
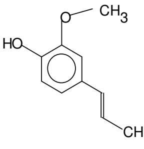
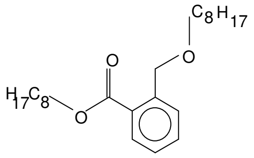
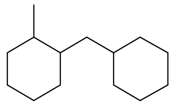
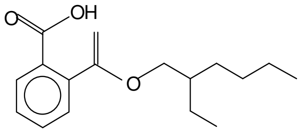


Fig. 1. Chromatogram of bio-oil

TABLE-1
IDENTIFICATION OF BIO-OIL MAIN COMPONENTS

Peak No.	Component name	Chemical structure
1	4-Methoxy-phenol	
2	2-Methoxy-*p*-cresol	
3	2,5-Dimethoxy-toluene	
4	2-Methoxy-4-propenyl-phenol	
5	1,2-Benzene dicarboxylic acid	
6	1-Cyclohexylmethyl-2-methyl-cyclohexane	
7	Mono-(2 ethyl hexyl)ester-1,2-benzene dicarboxylic acid	

Preparation of aluminium pillared montmorillonite: Montmorillonite powder (200 mesh) was dispersed in water in the concentration of 2 % (m/v) and then kept for 24 h at room temperature. The preparation of aluminium pillared montmorillonite was started from Al_{13} Keggin ion synthesis by slow titration of $AlCl_3 \cdot 6H_2O$ solution with NaOH solution under vigorously stirring until the mol ratio of OH^-/Al^{3+} equal to 2.2 (pH = 4.1) was reached and kept at room temperature for 24 h. The solution of Al_{13} Keggin ion was then dropped slowly to the aqueous clay suspension for the Al^{3+}/clay ratio of 5 mmol g^{-1} clay. After stirring for 24 h, washing, neutralizing and drying to get the neutral solid. Dry sample obtained followed the calcination at the temperature of 450 °C for 3 h. Material produced called as aluminium pillared montmorillonite and designated as Al-PILM.

Physical character analysis of material: Physico-chemical character of raw montmorillonite (RM) and Al-PILM was determined by gas sorption analysis (Gas Sorption Analyzer NOVA-1000), XRD difraction (XRD X-6000), surface acidity measurement and scanning electron microscopy (SEM) JSM-5310 LV microscope.

Utilization of Al_2O_3-montmorillonite as catalyst in biofuel upgrading: Catalyst activity test of the materials were performed in cracking and hydrocracking reaction to bio-oil. The study of catalyst activity was investigated in varied temperature and ratio of catalyst: feed(bio-oil). Reaction performed in fixed bed catalytic reactor made from a stainless steel tube (150 mm in diameter, 400 mm in length), with an inside casing for thermocontrol. Temperature of catalyst chamber was set up before the biofuel vapour was flowed into the catalyst chamber. In the cracking reaction, nitrogen catalyst was used as gas carier and for hydrocracking hydrogen was used. The product of reaction were examined by weighing the product distribution into liquid, gas and char by the eqn. 1:

$$\text{Mass of reactan(biofuel)} = m_{liq} + m_{gas} + m_{char} \quad (1)$$

Bio-oil conversion, catalyst activity and selectivity determined based on composition analysis of biofuel and reaction product analyzed by GC-MS.

RESULTS AND DISCUSSION

Al_2O_3-montmorillonite mainly studied by XRD pattern identification compared to the XRD pattern of starting material. The XRD pattern of both materials is depicted in Fig. 2. The pattern show that there is the shift of basal spacing d_{001} reflection to the left as indication for the basal spacing increase. The pillared solids has basal spacing of 15.09 Å, higher than the basal spacing d_{001} of 12.96 Å in raw montmorillonite. It indicate the increase of basal spacing d_{001} of montorillonite as produced by the Al_2O_3 pillar formation in the preparation.

The nitrogen adsorption-desorption isotherms of raw montmorillonite and Al-PILM are shown in Fig. 3. There is a difference pattern of pore volume adsorption in the low relative pressure region (P/P_0 = 0.2), reflecting a substantial increase in micropore volume and specific surface area (Table-2). The difference in the high pressure region reflects an evident change in the mesoporous formation caused by aluminium oxide pillarization. SEM micrograph of materials is presented in Fig. 4.

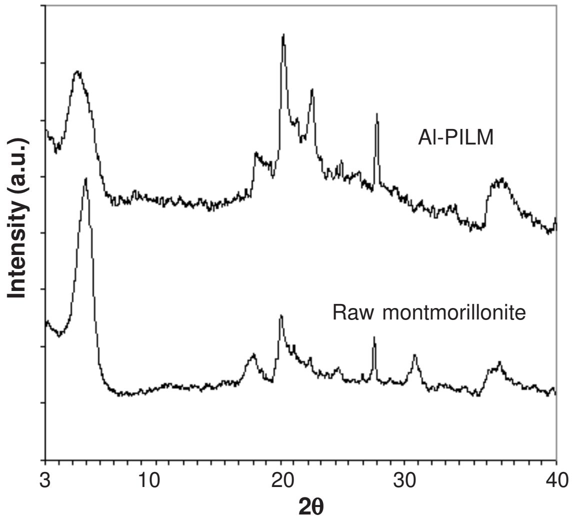


Fig. 2. XRD pattern of Al_2O_3 -montmorillonite and raw montmorillonite

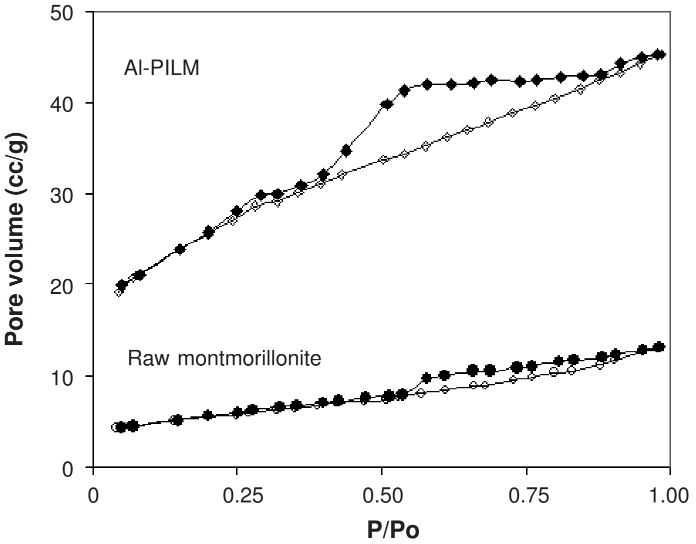


Fig. 3. Adsorption-desorption profile of raw montmorillonite and Al-PILM

TABLE-2
GAS SORPTION ANALYSIS DATA OF RAW MONTMORILLONITE AND Al-PILM

Character	Montmorillonite	Al-PILM
Specific surface area (BET) (m^2/g)	45.684	83.304
Pore volume (cc/g)	27.91×10^{-3}	116.27×10^{-3}
Micropore volume (cc/g)	18.34×10^{-3}	51.87×10^{-3}
Pore radius (Å)	14.98	15.83

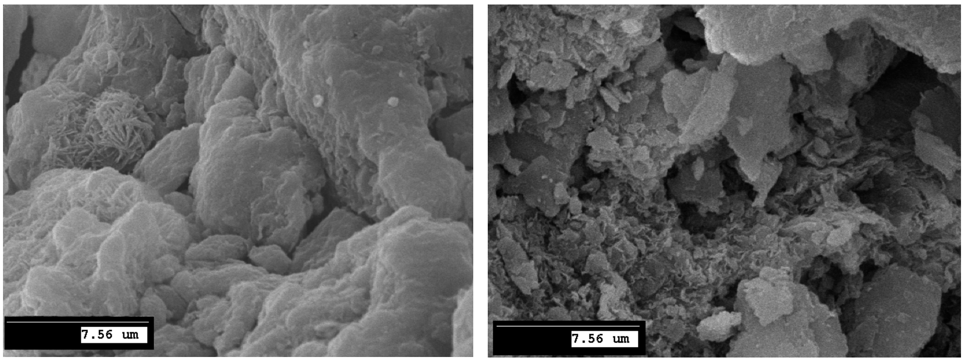


Fig. 4. SEM profile of raw montmorillonite and Al-PILM in the same magnification (5000 x)

It was established that there was an improvement in porous structure with the pillarization process in which rough surface is displayed by Al-PILM. Surface analysis to the materials was studied by measuring surface acidity consist of Lewis and Brønsted acidity. The FTIR (Fig. 5) provides the information on the effect of alumina pillarization. In order to determine both the Brønsted and Lewis acidity, samples treated with the pyridine adsorption after evacuation at 0.5 atm for 3 h. Quantitave amount of acid sites in surface was calculated based on gravimetric analysis by using microbalance. The qualitative analysis for the evidence of acid sites.

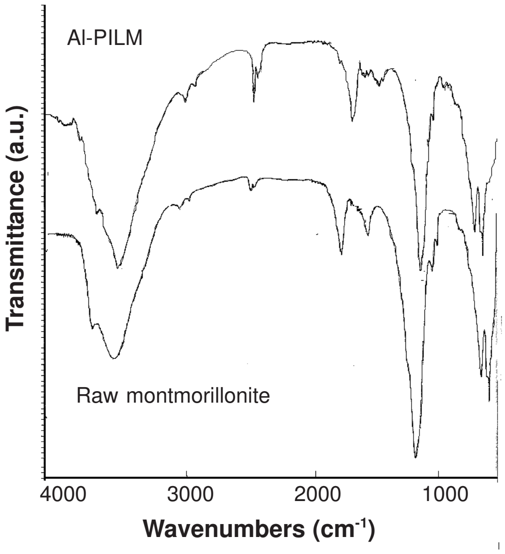


Fig. 5. FTIR spectra of raw montmorillonite and Al-PILM

The FTIR spectra of adsorbed pyridine in all samples show the presence of intense bands around 1630, 1550, 1500 and 1450 cm^{-1} which correspond to pyridine interaction with clay surface. The band at 1630 cm^{-1} is detected for all samples.

This band corresponded to slight intensity band at 1635 cm^{-1}. First band is attributed to pyridine adsorbed on Lewis acid sites and the second at 1635 cm^{-1}, related to pyridine adsorbed on Brønsted sites. The other bands localized at 1555-1545 cm^{-1} is assigned to pyridine adsorbed on Brønsted acid sites and the band at 1455-1445 cm^{-1} is attributed to pyridine adsorbed on Lewis acid sites as reported by Carvalho *et al.*[2] and Ahenach *et al.*[10]. Quantitative measurement of surface acidity compared to the Brønsted acidity and cation exchange capacity (CEC) is shown in Table-3.

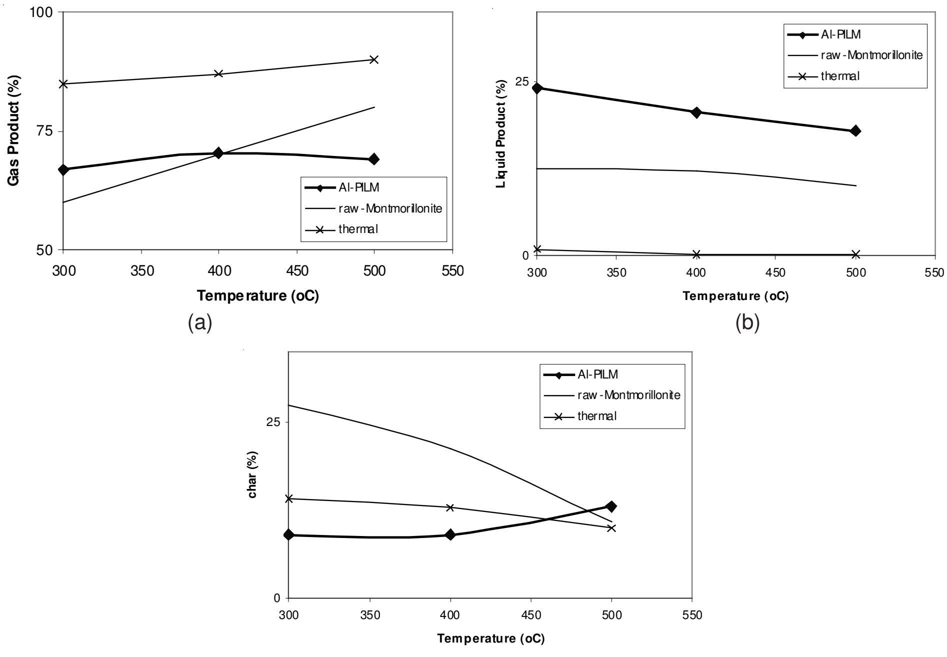
TABLE-3
CHARACTERIZATION DATA OF Al-PILLARED MONTMORILLONITE

Character	Montmorillonite	Al-PILM
Solid acidity (mmol pyridine/g)	0.389	0.450
Brønsted acidity (meq/100 g)	92.000	101
Cation exchange capacity (meq/100g)	69.500	34.5-36.0

Compared to the XRD data, basal spacing improvement of clay related to the increasing of specific surface area, solid acidity of the solid and cation exchange capacity (CEC) listed in Tables 2 and 3. The higher basal spacing d_{001} in Al-PILM followed by the increasing specific surface area and solid acidity. The increase may correlate with the formation of interpillar gallery from the pillarization process. The successful pillarization was also showed by the lower value of Al-PILM CEC and the higher solid acidity. The decreased value of cation exchange capacity was observed as the effect of the replacement native cations in raw montmorillonite by polyoxocation of Al_{13} during the interclation step. After the calcination step, polyoxocation was coverted to Al_2O_3 and produced H^+ as exchageable cation. The presence of Al_2O_3 pillar in Al-PILM leads the higher surface active site to adsorb pyridine as showed by the increase of solid acidity.

Activity test of raw and pillared montmorillonite was investigated by varying the reaction temperature. Accordingly, the temperature of 300, 400 and 500 ºC were chosen in order to examine the effect of temperature to the product distribution and liquid product composition. As reactant, in general, bio-oil consisted great amount of large size molecule, which nearly involves all species of oxygenated organics. The chromatogram displayed in Fig. 1 revealed that, main components identified are the phenolics, aromatics, esters, carboxylic acids and long chain hydrocarbon compounds. Product distribution as function of cracking temperature is presented in Fig. 6.

From the figure it can be seen that in general, the catalytic cracking mechanism tends to produce more liquid than thermal mechanism. In contrast, gaseous and loses product was dominantly resulted in the thermal mechanism. The tendency in gaseous formation by thermal mechanism is correlated with the temperature elevation. The cracking through radical mechanism is the reason for the higher gas production in the thermal mechanism, in reverse, by catalytic mechanism, cracking process occurs in the cationic mechanism supported by more Lewis acid sites of Al-PILM



(a) (b)

(c)

Fig. 6. Product distribution of bio-oil cracking at varied temperature into (a) gas and loses product (b) liquid product (c) char

provide more surface interaction between the hydrocarbon in the feed with catalyst. To evaluate the effect of catalyst addition to the composition of liquid product, GCMS analysis was performed. The hydrocarbon distribution characterized by C content in each compound was calculated based on the peak area data in the GCMS analysis. The data is presented in Fig. 7.

Fig. 7 shows the change in hydrocarbon distribution by cracking. It is concluded that the major constituent of bio-oil (untreated), C > 10 hydrocarbon convert to smaller compound in the reaction. The hydrocarbon distribution in the product catalyzed by raw montmorillonite is quite different with the product catalyzed by Al-PILM. The hydrocarbons with C7 and C8 skeleton are dominant in product of raw montmorillonite catalyst, in contrast, C2, C6 and C8 hydrocarbons are the dominant for the product of Al-PILM catalyst. The intense analysis to the compounds reveal that C2 hydrocarbon in product is dominated by acetic acid. Furthermore C6, C7 and C8 hydrocarbons are phenol, guaiacol and methyl guaiacol respectively. The difference in this distribution suggest the effect of the catalyst selectivity. The distribution data show that Al-PILM is more selective to the product of C2, C6 and C8 with relatively high percentage. The catalyst selectivity of raw montmorillonite is not affected by temperature in that the distribution of the products is quite similar. However, temperature affect to the Al-PILM selectivity. It is established that the product of C2 and C6 compounds were increased as the temperature increase.

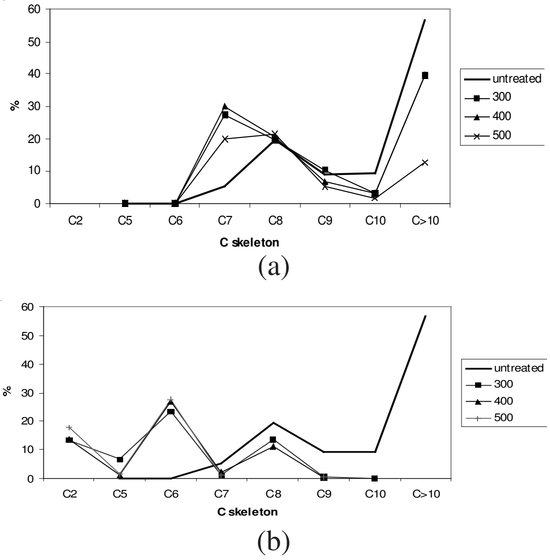


Fig. 7. Hydrocarbon distribution of liquid product in different cracking temperature (a) catalyzed by raw montmorillonite (b) catalyzed by Al-PILM

Conclussion

Al-pillared montmorillonite synthesized in this research has higer specific surface area, basal spacing d_{001} and solid acidity correspond to the intercalation of Al_{13} in interlayer space of clay structure. These characters lead to the increasing liquid product distribution and increasing the catalyst selectivity toward smaller compounds compared to the catalyst selectivity of raw montmorillonite. The main products derived by using Al-PILM are C2, C6 and C8 hydrocarbon.

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