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ALTERATION OF MONTMORILLONITE CLAY TO SOLID ACID CATALYST BY HEATING AND ACID SOAKING

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ABSTRACT

Commercial biodiesel production nowadays still uses sodium hydroxide solution as homogenous catalyst. This catalyst has some weaknesses, which cannot be reused and difficult on its separation from the product (methyl esther). Therefore, alternative catalyst is necessary to be sought to solve the problem and solid catalyst from clay has a possibility to be applied. Montmorilonite clay is widespread mineral in Indonesia and its layer structure is potential to be used as solid catalyst. The alteration processes consist of upgrading montmorillonite content followed by activation and esterification to review its performance. Previous activation was carried out using aqueous sulphuric acid of 0.05; 0.5; 5 and 10 M and settled in each solution for two weeks. To obtain shorten activation time, modified method has been done with similar acid strength range but using preheating 60°C for 6 hours and settled within a week. Clay's performance was observed by esterification reaction using Palm Fatty Acid Distillate (PFAD) of fried oil production waste as raw material. Its initial and final acid number were then reviewed. The conversion of PFAD to esther was measured from deviation of initial of final acid number. Previous method's result of 2 weeks settlement showed maximum conversion of 91.6% at 5M acid strength of activation, while modified method reached maximum conversion only 67.63% at similar acid strength of activation. Both results were not yet resemble the 5M sulphuric acid solution as homogenous catalyst which is able to convert PFAD to esther as much as 98.73%. However, the method of 2 weeks settlement could be developed further to gain the optimum conversion.

Keywords: solid catalyst, montmorilonite clay, activation, acid number, conversion

INTRODUCTION

Catalyst helps any process by increasing the rate of chemical reaction without being consumed of it. There are two types of catalyst, homogeneous and heterogeneous ones (Perry and Green, 1999). Commercial biodiesel production nowadays still uses homogenous catalyst, namely sodium hydroxide solution. The weaknesses of the catalyst, it cannot be reused and has a difficulty on its separation with the product (methyl esther). Therefore, an alternative catalyst is required to solve the problem (Wijaya, 2009). There are several materials, which had already observed to be alternative catalyst in solid form such as $ZrSO_4$, TiO_2, sugar, Zn/I_2 and clay. They have considerable promising result for biodiesel production (Khan, 2002).

Among those solid catalysts, clay is one alternative to be concerned in Indonesia especially montmorillonite clay. It is figured from the amount of resources that reaches 573,069,000 tons as potential source. Clay performance as solid acid catalyst has been proved on previous research using sulphuric acid for activation. The process was performed by soaking clay with various concentrations of acid for 2 weeks. The acid number conversion of fatty acid to ester gained 91.6% compared to liquid sulphuric acid that reached 98.73% (Amalia et.al., 2008). The result was much better compared to Fabian et. al. (2005) and Yessi (2007) who gained 55% and 53.55% of conversion respectively. They used heating in acid solution for several hours in activation method.

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In the present work, it is concerned to gain better conversion than the previous work by using modified method. The modification is applied by activation process within two weeks of soaking and heating. Heating could destruct the montmorillonite structure, and may fasten the process, especially the cation exchange between Na+/ Ca+ of clay with H+ as sulphuric acid ion. The destructed structure requires time of soaking and heating for repairing. Settlement time in acid condition can be supportive. Therefore, it is necessary to observe the activation process by combining heat and soaking in acid solution.

METHOD

There are some improved processes applicable to clay beneficiation such as blending, air classification, dewatering, drying, hydrocylone, magnetic separation, drying, acid activation calcinations, chemical leaching and flotation (Dominguez et al, 2003). This alteration process consists of upgrading montmorillonite content of clay, activation and esterification. Physical and chemical analyses were done for the native as well as activated clay. Upgrading process began with soaking the clay overnight in water to make it swollen. Swelled clay was then entered into scrubber to loosen up physical bounding of minerals in clay. The output of scrubber was screened for -35 mesh size then separated from iron (magnetite) using magnetic separator. The ironless clay was concentrated using hydrocyclone. Montmorillonite was found as overflow product.

Upgraded clay was activated on sulphuric acid of 0.05; 0.5; 5 and 10 M. They were heated at 60°C for 6 hours and were settled for a week. During settlement time, they were stirred for 5 minutes a day. Afterward, the clays were washed in aqua distillate, then dried in the oven and calcined at 300°C for 2 hours.

The activated clay was then tested by esterification reaction as solid catalyst. The reaction between Palm Fatty Acid Distillate (PFAD) of fried oil production waste and methanol occurred in 60-65°C with stirring for one hour. Its performance was determined from acid number of PFAD and ester produced from the reaction according to the FBI-A01-03 procedure (Destiana, et al, 2007). Conversion of final and initial acid number is stated as follows:

$$\text{Conversion } = \frac{initial\ acid\ number - final\ acid\ number}{initial\ acid\ number} x\,100\%$$

RESULTS AND DISCUSSION

Upgraded clay was observed for its physical and chemical content. Its physical content was determined with X-Ray Diffractiometer, and showed that montmorillonite has not been as dominant mineral compared to quartz. It was obvious that quartz in overflow product was finer than montmorillonite, which has particle size of less than 2mm (Bergaya et.al., 2006). Figure 1 and 2 show the XRD results, pictured that montmorillonite peaks on upgraded clay were taller than the natural one, which

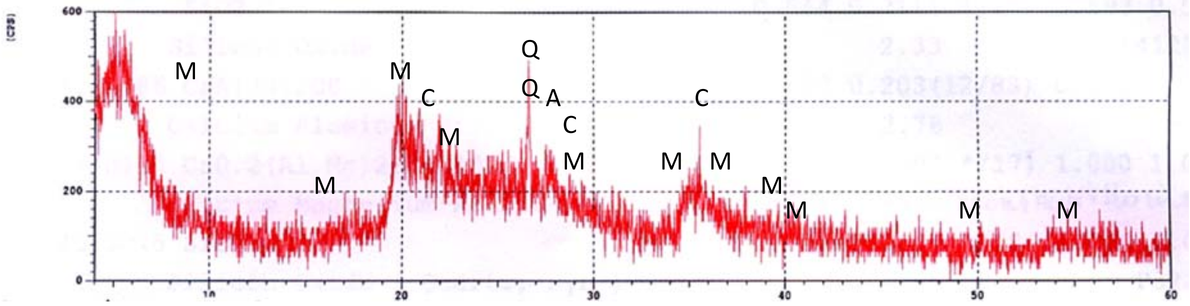

Figure 1. XRD result of natural clay

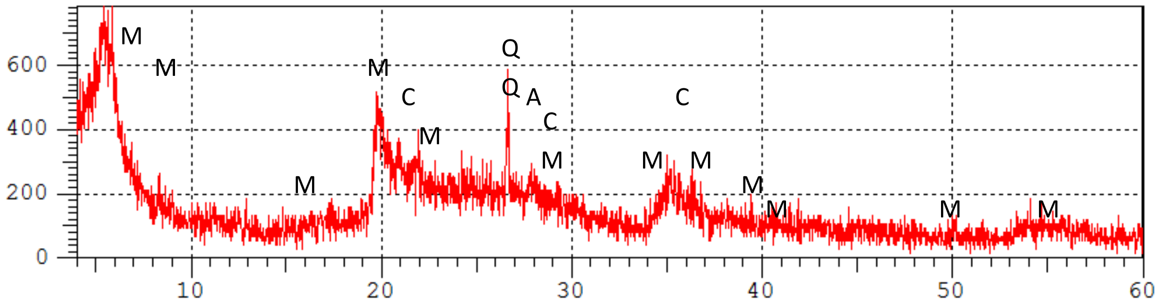

Figure 2. XRD result of upgraded clay

means its percentage increased even though had the same amount of peaks.

The activation with acid was started by heating to broaden the surface areas and followed by settling within a week to increase the clay's acidity. Acid treatment can cause delaminating of montmorillonite and part of its structure being solved. In order to check the grade, chemical analysis has been done in term of oxides as Table 1 states.

Aluminium oxide as the main chemical element of the montmorillonite generally decreased in activated clay compared to upgraded one. On the contrary, quartz (Si) increased on activated clay. This could be caused by less silicate solubility in acid compared to aluminium. The phenomenon of activated results showed delaminating process of layer structure. When Si and Al dissolved excessively, the layer-structure can be reduced, even disappeared. The condition of the structure can be observed through mol ratio of SiO_2/Al_2O_3. Mol ratio range of 4 – 6 is for native montmorilonite clay and 6 – 10 is effective for acid clay. Table 2 provides mol ratio of the upgraded and activated clay. It is showed that the mol ratios are in the reference range (5,6-8,5). The upgraded was monmorillonite clay and the activated clays was acid clay.

Physical observation was also carried out for activated clay in terms of X-Ray diffraction and surface area. The X-ray diffractions (XRD) data in Figure 3 indicate the sequence of mineral content. The 0.05 M activated clay resulted montmorillonite, quartz, crystobalite and anorthite, while on 0.5 M activated clay generated montmorillonite, quartz, anorthite and crystobalite. Activated clay for 5 M acid generated montmorilllonite, crystobalite, anorthite, quartz and 10 M acid clay generated montmorillonite, quartz and anorthite. All of XRD data denote that montmorillonite was still as dominant mineral after activation, so it is proved that activation with the acid did not destruct the structure eventhough acid clay was obtained.

Montmorillonite clay may have a layer structure and a large specific surface area (Adamis, et al,

Table 1. Chemical contents of upgraded and activated clay

Clay	Oxides amount (%)									
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	Na_2O	MgO	P_2O_5	K_2O	MnO
Upgraded	55.40	16.21	4.00	0.43	1.39	0.37	1.11	0.05	1.46	0.11
Activated in 0.05 M acid	68.56	15.95	2.14	0.46	2.12	2.52	1.11	0.01	1.04	0.01
Activated in 0.5 M acid	64.24	17.38	4.07	0.52	0.65	0.40	1.22	0.02	1.63	0.03
Activated in 5 M acid	69.76	14.25	2.51	0.51	0.71	0.74	0.98	0.01	2.01	0.02
Activated in 10 M acid	69.04	13.84	2.40	0.66	0.66	0.63	0.89	0.01	2.00	0.02

Table 2. Mol ratio of $SiO2/Al2O3$ for upgraded and activated clay

Clay	Mol ratio of SiO_2/Al_2O_3
Upgraded	5.68
Activated in 0.05 M acid	7.30
Activated in 0.5 M acid	6.28
Activated in 5 M acid	8.35
Activated in 10 M acid	8.51

2005). Acid activation of 0.05; 0.5; 5 and 10 M increased the specific surface area 86; 133; 139 and 157 m^2/g respectively. They were larger than natural clay (84 m^2/g). The enlargement of surface area occurred in activation process and caused exchange between cations in montmorillonite site and replace with H^+ and build active site. The octahedral layers became tetrahedral layer because of the acid, so it enlarged the area

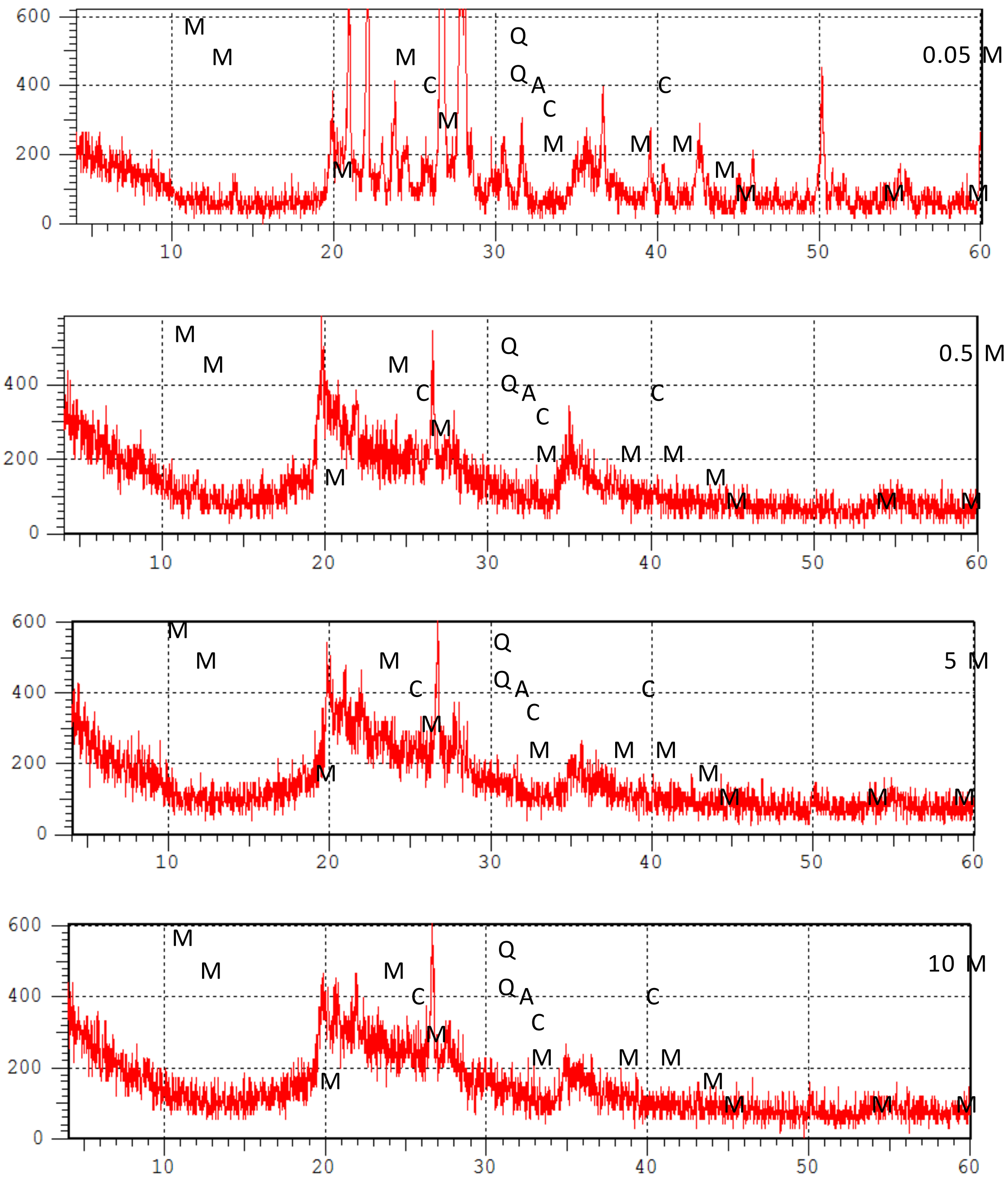

Figure 3. XRD result of activated clay

especially surface area.

The mol ratios show that activated clays were acid clay. In order to know the acidity of clay, it can be noticed by base absorption on acid clay, stated in mol NaOH/g of clay. The method resulted 2.04 mmol NaOH/g catalyst for natural clay and the activated clay of 0.05; 0.5; 5 and 10 M respectively had 2.87; 2.99; 3.00 and 3.12 mmol NaOH/g catalyst for acidity. It proves that the interlayer had more amount of acid-active sites as acid strength increased because many cations (Na^+, K^+, Ca^{2+} or Mg^{2+}) were replaced by H^+.

The above results inform that activated clay was already become acid clay. The catalytic performance of activated clay generated on estherification reaction of palm fatty acid (PFAD) and methanol producing esther. A parameter of PFAD characteristic is acid number, which has 239.67 mg KOH/g PFAD before reaction. Acid number of PFAD was also determined after reaction and supposed to be decrease. Those acid numbers can be converted to measure the conversion of acid number (Table 3), which figures the performance of the acid clay as catalyst in estherification.

Table 3. Acid numbers and acid number conversion of esther

Clay	Acid Number (mg KOH/gram of clay)	Acid number conversion (%)
Upgraded	118.96	50.44
Activated in 0.05 M acid	77.87	67.50
Activated in 0.5 M acid	86.61	63.86
Activated in 5 M acid	77.57	67.63
Activated in 10 M acid	109.46	54.32

Those acid number conversions of activated clays were larger than natural one. It means that the activation succeed in increasing natural clay's performance. Among the activated clay, the conversion for acid clay of 10 M was the smallest. It is shown at XRD data of the clay (Figure 3), that montmorillonite peaks decreased for each increasing acid, which means that present montmorillonite in clay was successfully destructed. The destruction was caused by heating and settlement time (1 week) while recrystalization (active sites formation) was not completed to built the whole destructed structure. The lack of active sites equal with the lack of H^+ anion for estherification.

The highest conversion was reached for 0.5 M activated clay, but it was not significant compared to 0.05 M activated clay. As comparison, catalytic performance was also carried out using 5 M sulphuric acid solution and reached 98.73% of acid number conversion. Previous activation method showed that 2 weeks of settlement in acid solution using similar acid strength produced the highest conversion of 91.6% for activated clay of 5M acid solution. It means, recent method was not proper yet for the activation. So, previous result could be modified to reach the exact conversion of 98.73%. Meanwhile, Fabian et al, (2005) has found highest conversion of acid number at 55.3% using 90% of sulphuric acid strength with various ratios of clay and acid by stirring for 6 hours without heating. On the other side, Yessi (2007), tried to activate clay with 98% strength of sulphuric acid for 1 : 1 by stirring at 70°C for 6 hours and yielded 53.5% conversion of acid number. Therefore, the current result was higher than those of two previous conversions.

CONCLUSION

The upgrading and activation processes have produced acid clay from bentonite clay and montmorilllonite was still as dominant mineral content. The acidity of activated clay increased as the acid strength increased (0.05; 0.5; 5 and 10 M) and the best acid number conversion was 67.63% using 5M activated clay.

The performance of activated clay in the current work was not good enough yet. The method with 2 weeks settlement in acid solution can reach the highest conversion of 91.6%. This result was still far from 5M sulphuric acid solution which can convert acid number of PFAD up to 98.73%. Whilst, the heating process of 60°C with 1 week settlement method was not better than the 2 weeks settlement method. So, the previous method can be developed further to reach 98.73% of acid number conversion.

REFERENCES

Adamis, Z. and Williams, R.B., 2005. *Bentonite, kaolin and selected clay minerals*. International Programme on Chemical Safety. World Health Organization,Jenewa.

Amalia, D., Aziz, M., Sidjabat, O., Suryo,S. and Rodliyah, S., 2008. Benefisiasi lempung untuk bahan katalis sintesis biodiesel. *Laporan Teknik Penelitian Pengolahan Mineral Puslitbang Teknologi Mineral dan Batubara* (tekMIRA).

Bergaya, F. T. and Lagaly, G., 2006. *Handsbook of clay science*. Elsevier Ltd, UK.

Destiana, M., Zandy, A. N. dan Puspasari,S., 2009. Intensifikasi proses produksi biodiesel. *Laporan Lomba Karya Ilmiah Mahasiswa ITB Bidang Energi Penghargaan PT. Rekayasa Industri*. Institut Teknologi Bandung & PT. Rekayasa Industri.

Dominguez, E., Mas, G., and Cravero, F., 2003. Clays in industry. *A clay odissey*. Elsevier Science B.V., Netherlands.

Fabian, H. and Griyandi, 2005. *Kajian eksploratif bahan katalis keramik untuk sintesis biodiesel*. Laporan Thesis, Institut Teknologi Bandung.

Khan, A., 2002. *Research into biodiesel catalyst screening & development*. Brisbane, Australia.

Perry, R. and Green D., 1999. *Perry's chemical engineers' handbook*. McGraw-Hill Companies, Inc.

Wijaya, K., 2009. Asam padat berbasis montmorillonit sebagai katalis dalam proses pembuatan biodiesel dari minyak jelantah. *Material canggih, rekayasa material berbasis sumber daya alam silica-alumina*. Yogyakarta. ISBN 979-1707-70-7.

Yessi, A., 2007. *Pengembangan montmorilonit sebagai katalis sintesis biodiesel melalui esterifikasi palm fatty acid distillate*. Departemen Teknik Kimia Fakultas Teknologi Industri ITB. Bandung.