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ALTERNATIVE METHOD OF THE ACTIVATION PROCESS FOR BENTONITE MINERAL

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ABSTRACT

Biodiesel manufacture usually applies liquid catalyst (homogenic catalyst) that deals with some obstacles, such as difficulty in catalyst product separation as they are in the same liquid phase, corrosive characters, excessive catalyst cannot be reused, and complicated to be handled. An alternative for a better process is solid catalyst as a heterogeneous system between raw material and product. Bentonite has layer structures and a potential to be used as solid catalyst by activation process. Three methods of activation process had been conducted,namely 60°C-heating; 60°C-heating followed by 1 week settling and 2 weeks settlement. Each method was performed in sulphuric acid and the chemical content of Al_2O_3 *and* SiO_2 *was observed. An activated bentonite has a molar ratio of* SiO_2 *and* Al_2O_3 *between 6 - 9. All methods resulted in expected molar ratio, but the 2 weeks settlement process without heating provided more significant result which means it performed energy saving compared to other methods.*

Keywords: activation, bentonite, molar ratio, settlement

INTRODUCTION

Commercial process for organic chemical manufacture is still using agitated reactor, volatile solvent, stoichiometry based reagent and hazardous chemical. It usually results in inefficient process and produces waste around 10 – 50 times of the product. Heterogenous system is one of the new-clean developing technologies in order to lessen liquid waste of organic reaction. The technology avoids using solvent and replaces it with solid catalyst or solid solvent. Another benefit is it can increasly reaction selectivity (Perry and Green, 1999).

Catalyst is a material that is fasten the reaction rate without having any chemical alteration and non reactive. It does not act as reactant as well as product but has an important role in chemical reaction of the process. The reaction can be faster by catalyst occupation because it serves a reaction path with lower activation energy, therefore less energy is required for reaction to be occurred.

There are two types of catalyst, namely homogenic and heterogenic types. Homogenic type is a catalyst that performs in one phase with reactant in the process reaction. Meanwhile, heterogenic catalyst has different phase with reactant (Wikipedia, 2008). Heterogenic catalyst has been used for ages in petrochemical industries for cracking process.

One of manufacture processes that uses catalyst is biodiesel production. During the production, the used catalyst is in liquid form the similar to the feed. So it performs homogenous system. However, there are some obstacles during the process. Those are difficulty to separate catalyst with product due to similarity in phase character (liquid), Corrosive performance, excess catalyst cannot be reuse resulted in hazardous waste for environment, and complicated to be handle as well as its storage (Wijaya, 2009).

In order to find a better technology to produce biodiesel, high performance and flexible physical catalyst form is required. The catalyst should appropriate with any kind of technology process. Zeolite can fulfil the requirement but it has certain pore size and only accommodates certain molecular size. Meanwhile porous silica has a perfect pore size but it does not reactive enough in chemi-

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cal reaction. Clay mineral has different properties and can be prepared to be very reactive catalyst in any kind organic reaction. Its high surface area can make clay to perform as solid catalyst support in some reaction (Adamis and William, 2005).

Clay resources in Indonesia reach 29.673.820 tons (PSG, 2009). Among them contain monmorillonite or known as bentonite that has layer structures (Figure 1). Therefore it has a large specific surface area and it is able to do the cations exchange and swells when contact with water. Thus, bentonite becomes a potential material as raw material for catalyst.

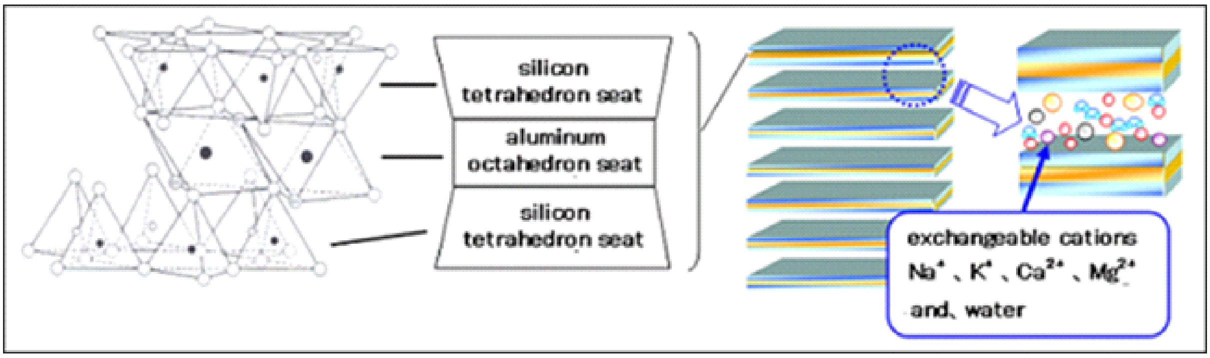


Figure1. Bentonite's layer structure (Source: kunimine industries)

High purity clay is not yet enough to be used as a catalyst, needs activation on its sites. Activation occurs in its sites because of cation exchange of clay with concentrated acid solution of 0.5 – 1 M for 24 hours. Afterwards, clay is separated by centrifuge or precipitation to reduce excess exchangeable before being dry off at 40 – 50°C, followed by milling.

Catalytic reactions of montmorillonite clay usually use acid treatment for cation exchange environment. Lewis and Bronsted acid which generally occur in activation process is used and acts as H^+ donor.

The acid attaches to aluminium or ferro ion in crystal tip and produces free acid or generated by water molecular dissociation in interlayer, so the cations become polarized. Concentration of H^+ in interlayer can reach 10 M.

Commercial acid treatment uses hydrochloride, sulphuric or phosphoric acids with main parameter of concentration and reaction time. Ion exchange of monmorillonite with cation such as Al^{3+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+} and Na^+ can modify the catalytic activity of activated clay. Clay which takes mono valence cation by heating above 100°C can reduce interlayer space and enlargement space to initial one is difficult (Bergaya, et al, 2006). Therefore, clay activation by heating treatment does not give a good result to be applied as catalyst. A research of bentonite activation has been done in heating and non heating activation.

Efforts to activate bentonite into acid clay have been done by Fabian and Griyandi (2005) and Yessi (2007). They analyzed activated clay to indicate the acidity by chemical absorption of caustic solution and measured it with titration. A simple way to know whether the activated clay has already become acid clay is by observing its chemical content. It was investigated that Japanese acid clay is available without any activation process. Some properties have been compared between bentonite and acid clay. They have physical properties differences as shown in Table 1. Those properties can be used as a guidance to characterize bentonite whether it is classified as acid clay or not.

Table 1. Physical properties of acid clay and bentonite

	Acid Clay	Bentonit
Main mineral content	Monmorillonite	Monmorillonite
Mol ratio SiO_2/Al_2O_3	6 - 10	4 - 6
pH of its slurry	5 - 6	7 - 8.5

METHOD

Upgraded bentonite was activated using sulphuric acid with various acid strength of 0.05; 0.5; 5 and 10 M. Ratio of bentonite weight and acid volume was 1: 25. The activation process was performed with three methods; namely heating in 60°C for 1 hour; heating for 1 hour followed by acid soaking for 1 week; and acid settlement for two weeks. Each method has undergone chemical analysis to find out the content of SiO_2, Fe_2O_3 and Al_2O_3 and the influence of each method on oxide's dissolution. The amount of oxide content for Al_2O_3 and SiO_2 is converted to molar unit by dividing it with its molecular weight (gram/molar). The obtained molar ratio of SiO_2 and Al_2O_3 is to determine whether the product can be classified as bentonite or acid clay (Table 1). In addition, physical analysis of X-Ray Diffraction was done to know the influence of activation process on monmorillonite content in bentonite. The method used in the experiment is shown in Figure 2.

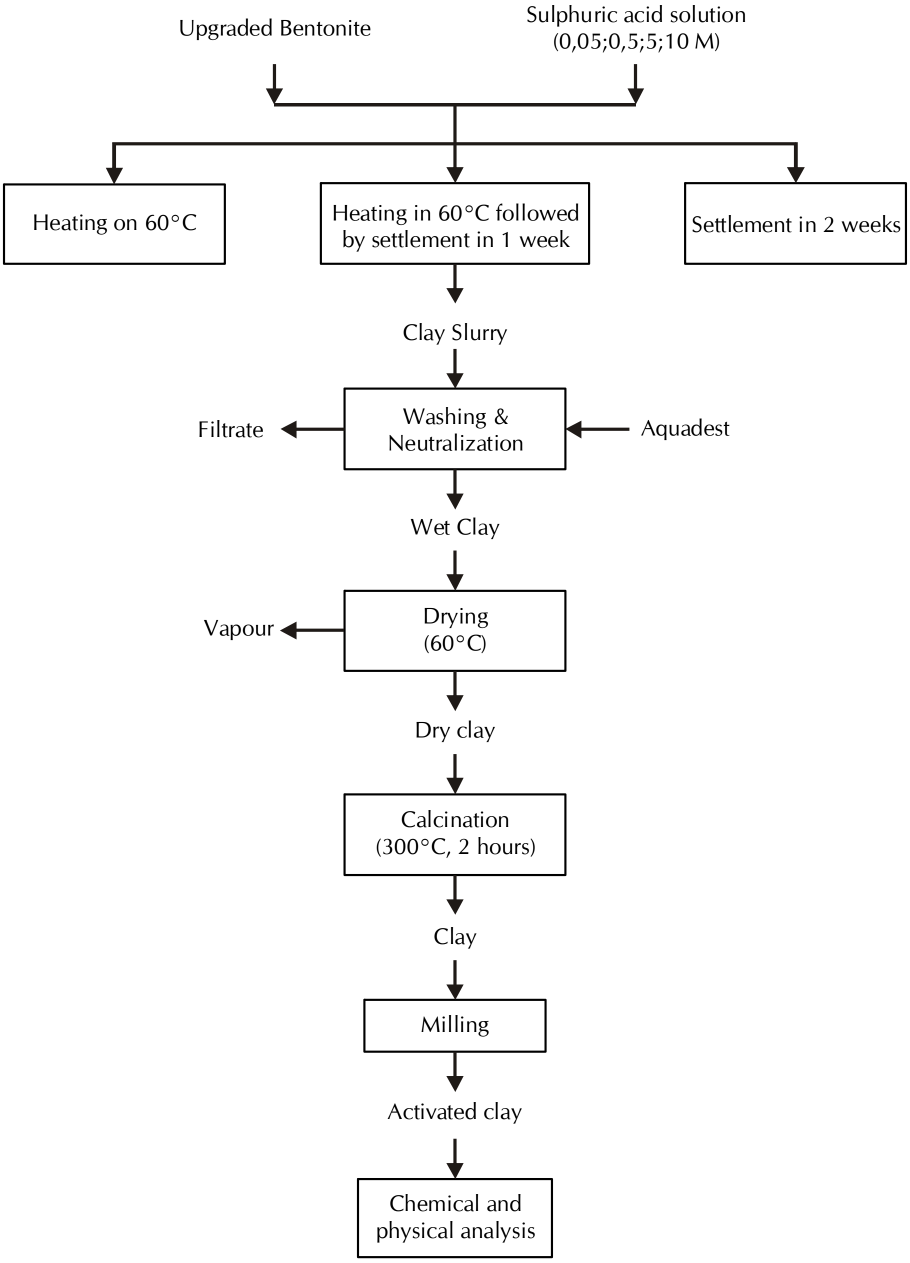


Figure 2. The methods of activation process

The activation process which required heat was performed in a glass made equipment on magnetic hot plate. The settlement was carried out in fibre glass reactors that built in parallel system. The equipments are shown in Figure 3.

a) b)

Figure 3. Equipments for activation process a) heating equipment b) settlement equipment

RESULT AND DISCUSSION

Initial clay was observed for its physical and chemical properties. It consists of crystobalite, anorthite, monmorillonite and quartz. The monmorillonite has not been dominated therefore the clay that used in the experiment has been through upgrading process (Amalia et al, 2008; 2009) and then the physical and chemical properties were observed.

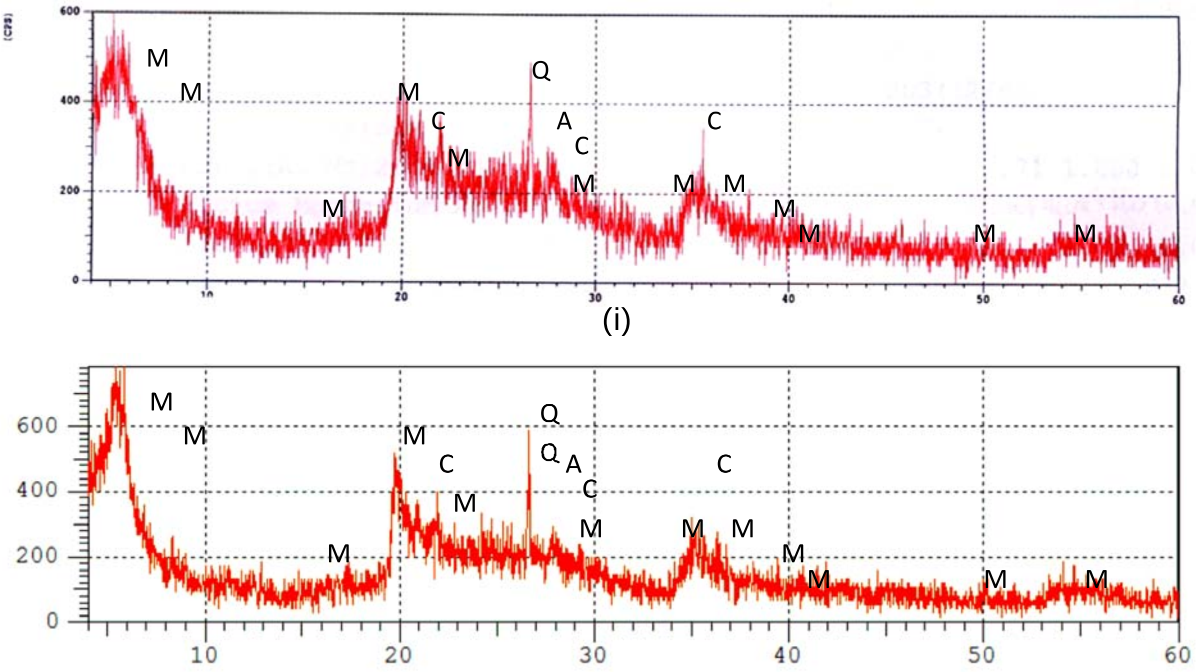
Upgraded clay has been characterized by physical and chemical analysis. Figure 4 shows the X-Ray Diffraction (XRD) result of initial and upgraded clay which the latter considerately consists of quartz, monmorillonite, anorthite and crystobalite. It means that the processed clay was bentonite because it consisted of monmorillonite as main mineral among others (Amalia et al, 2008).

To support the XRD result, the sample was also analysed chemically to investigate its chemical content which is shown in Table 2. It was stated that bentonite which contains montmorillonite has molar ratio of SiO_2/Al_2O_3 approximately 4 - 6. The initial and upgraded clay in this experiment have Al_2O_3/SiO_2 ratio of 5.46 and 5.60 respectively (based on Table 2). This means the clay was bentonite.

The upgraded bentonite had been activated using three methods that were heating in 60°C; heating in 60°C followed by settlement for 1 week; and settlement for two weeks without heating. Each method was analyzed to know the Al_2O_3 and SiO_2 content and the results are shown in Table 3.

Table 2. Oxides amount in initial and upgraded clay

Clay	Oxides amount (%)					
	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	MgO
Initial	55.04	17.11	4.00	1.39	0.37	1.11
Upgraded	60.40	18.30	3.54	1.38	0.44	1.17



(i)

(ii)

M : Montmorillonite; C : Cristobalite; A : Anorthite, Q : Quartz

Figure 4. XRD pattern of (i) initial and (ii) upgraded clay

Table 3. Al_2O_3 and SiO_2 content and mole ratio of activated clay

Code	SiO_2 (%)	Al_2O_3 (%)	Mol ratio Al_2O_3/SiO_2
Heating in 60°C			
H0.05	64.96	16.20	6.80
H0.5	65.38	15.87	6.99
H5	67.93	14.29	8.07
H10	67.94	13.85	8.32
Heating in 60°C and follow by settlement in 1 week			
HD0.05	68.56	15.95	7.29
HD0.5	64.24	17.38	6.27
HD5	69.76	14.25	8.31
HD10	69.04	13.84	8.47
Settlement in two weeks without heating			
S2-0.05	66.49	17.41	6.48
S2-0.5	67.85	15.57	7.39
S2-5	73.45	13.30	9.37
S2-10	73.59	13.12	9.52

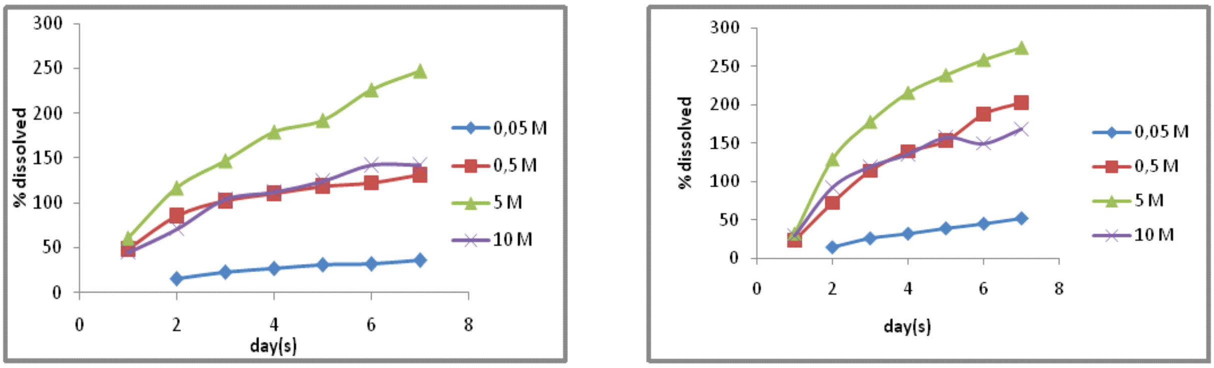
Notes : H = Heating in 60°C
HD = heating in 60°C followed by settlement for 1 week
S2 = Settlement for two weeks without heating
0.05; 0.5; 5; 10 M = Sulphuric acid strength in Molar

Bentonite is effective to exchange its cation in proper circumstances. H^+ ion of sulphuric acid is exchanged to cation at the active site of monmorillonite during the activation process. The more H^+ ion exchanged, the more acidic the bentonite. It becomes acid clay. The molar ratio of SiO_2 and Al_2O_3 for acid clay is 6 – 10.

Table 3 shows the molar ratio of activated clay as a result of three activation methods. The best value of them was obtained from settlement for two weeks without heating. The method of heating in 60°C may destruct interlayer structures of bentonite and it cannot restructure. While, activation process with heating in 60°C and followed by settlement for 1 week may destruct interlayer but restructure time was not enough, so the acid site formed was not optimum yet.

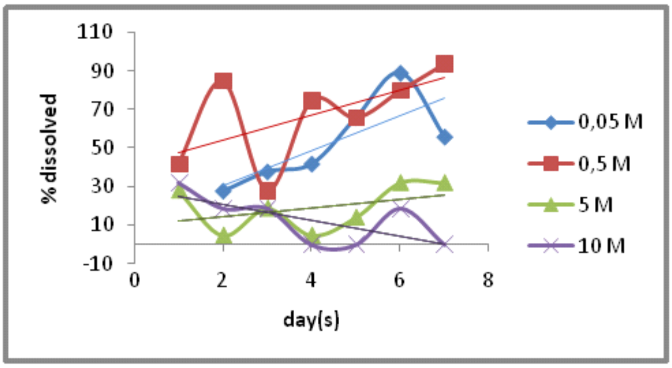
Settlement for 2 weeks might be serves as alternative saving energy method because it occurred without heating and pressuring from outside the system. During activation process, monmorillonite had been destructed and recrystallization occurred in sufficient time. Therefore, the interlayer had already rebuilt by H^+ ions from sulphuric acid. In order to know the influence of settlement for 2 weeks, 25 mL of sulphuric acid solution was taken every 24 hours for 7 days. The solution then recharged with fresh solution and was performed with same treatment as was in the first week. Each solution sampling was then analyzed chemically to find out the amount of cations dissolved in acid solution (Amalia et al, 2009). The results are shown in Figure 5.

Figure 5 shows that the dissolved percentage of Al_2O_3 and Fe_2O_3 increased in 5M sulphuric acid



a. Dissolved Al_2O_3 in sulphuric acid solution (0.05; 0.5; 5 ; 10 M)

b. Dissolved Fe_2O_3 in sulphuric acid solution (0.05; 0.5; 5 ;10 M)



c. Dissolved SiO_2 in sulphuric acid solution (0.05; 0.5; 5 ; 10 M)

Figure 5. The dissolution of Al_2O_3, Fe_2O_3 and SiO_2 in sulphuric acid solution (0.05; 0.5; 5 ; 10 M) for 7 days in the first week of experiment

solution. It means that those components have high dissolution in proper environment as time gone by. While SiO_2 increased until day 6 in 0.05 M sulphuric acid solution but after day 6, the SiO_2 did not dissolve anymore.

The phenomenon occurred because Al_2O_3 and Fe_2O_3 have higher dissolution in sulphuric acid compared to SiO_2. Generally, SiO_2 is dissolved in strong acid solution such as hydroflouric acid. Besides SiO_2, clay consists of free silica and silicate compound with other component which build aluminum silicate bonding. So, the percentage of dissolved SiO_2 is a total amount of both kind of SiO_2. It is hard to find out which one of SiO_2 was influence by the activation process. But, it is indicated that SiO_2 attached to other soluble component can be dissolved in activation process.

CONCLUSION

Bentonite has a potential to be used as a solid acid catalyst. Among the three methods of activation process used in this research, a significant molar ratio was reached by settlement for 2 weeks which can serve as alternative energy saving method. The activation process was performed in sulphuric acid solution of 0.05; 0.5; 5 and 10 M. The optimum dissolution of Al_2O_3 and Fe_2O_3 was obtained in 5M solution, while SiO_2 was not in proper environment to be dissolved.

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