Thermal Activation Of Peat Clay And Its Their Potential In Catalytic Cracking

Tama Oktania¹, Doni Rahmat Wicakso^{*1}, Hesti Wijayanti¹, Dewi Shofia¹ and Maisarah¹

¹Department of Chemical Engineering, Engineering Faculty, University of Lambung Mangkurat, Jl. A. Yani Km. 36 Banjarbaru, South Kalimantan, 70714, Indonesia

*)doni.rahmat.w@ulm.ac.id

Abstract. Peat clay is a mineral that contains alumina and silica, so it has great potential as a catalyst in the catalytic cracking process. To improve its performance as a catalyst, activation is necessary. This study aims to perform thermal activation on peat clay from South Kalimantan, Indonesia which is to improve its catalytic properties. Activation was carried out at a temperature of 400 - 600 $^{\circ}C$ and then characterized including scanning electron microscope-energy dispersive x-ray (SEM-EDX) and Brunaeur Emmet Teller (BET). The results showed that activation temperature affects the process of making peat clay catalysts. The higher the temperature, the higher the Al₂O₃ and SiO₂ content, respectively at 600 °C 7.29% for Al₂O₃ and 18.37% for SiO₂. Meanwhile, based on BET analysis, the surface area value of peat clay increased after activation, which was 5.776 m²/g before activation and 6.645 m²/g after activation. With these results, activated peat clay is very potential to be used as a catalyst in chemical processes.

Keywords: thermal, activation, peat clay

1. Introduction

Indonesia has the largest area of peatland among tropical countries, which is around 21 million ha spread mainly in Sumatra, Kalimantan and Papua. However, due to the high variability in peat thickness, maturity and fertility, not all peatlands are suitable for agriculture. Of the 18.3 millions ha of peatland on the main islands of Indonesia, only about 6 millions ha are suitable for agricultural use [1]. On the other hand, peat clay contains high mineral compounds that can be utilized for catalysts. This can be an alternative source of cheap and abundant catalysts.

The main composition of the peat clay was found to be Si, Al and Fe as well as other minor elements such as K, Ti, Na, Ca Mg, and Mn [2]. Oxide compounds such as alumina (Al_2O_3), silica (SiO_2) and Fe_2O_3 are materials that can be used as cracking catalysts ([3], [4], and [5]). These three elements in one material can be modified to produce a catalyst with better performance.

Catalyst activation process is a stage that needs to be considered in addition to the selection of raw materials used. besides the selection of raw materials used. Activation is a treatment of the catalyst that aims to enlarge the diameter of the pore, and surface area and affect the power of the catalyst. pore diameter, surface area and affect the catalyst power. The process can be done in two ways, namely physical activation (thermal) and chemical activation [6]. Physical activation or also known as thermal activation is a step that is often done to obtain the surface area of the catalyst. is a step that is often done to get a larger specific surface area surface area and in this case it can also improve the adsorption and catalytic performance of the lignite. adsorption and catalytic performance of clays [7].

In thermal activation, high temperatures can remove water molecules and other impurities. Thermal activation can enlarge the pore by breaking chemical bonds or oxidizing surface molecules so that the surface area increases and affects the high catalyst activity. There have not been many reports related to the modification of clay physics through thermal activation although in theory the method will be able to increase the specific surface area, increase the cation exchange capacity and adsorbent power of the mineral material [8]. Therefore, this study aims to conduct thermal activation of peat clay from South Kalimantan, Indonesia. The activation was carried out at $400 - 600$ °C and then characterized including scanning electron microscope**-**energy dispersive x-ray (SEM-EDX) and Brunaeur Emmet Teller (BET).

2. Research Methods

2.1 Catalyst Preparation From Peat Clay

Peat clay was obtained from Suka Maju Village, Landasan Ulin, District of Banjarbaru, South Kalimantan, Indonesia and in the depths about 2.5 - 3.0 meters from the surface of the earth. Peat clay was washed and dried under direct sunlight for 48 hours. After drying, the peat clay was crushed and sieved with a size of 10 mesh. Calcination was carried out for 2 hours with temperature variations of 400 °C, 500 °C, and 600 °C. Catalyst characterization was carried out to determine the physical and chemical properties of the catalyst produced, such us Brunaeur Emmet Teller (BET) and Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy (SEM-EDX). The BET analysis was to determine the pore size and surface area of the catalyst. The SEM-EDX was to determine the morphology and elemental composition of the peat clay catalyst material.

2.2 Cracking Reaction

The used cooking oil was pumped into the heater to be vaporized into the reactor containing the peat clay catalyst. It was equipped with a pipe connected to the condenser and a container for the liquid product of the cracking reaction. The cracking reaction was run at 500ºC for 60 minutes from the time the temperature was reached.

3. Results And Discussion

3.1 Characterization of Brunaeur Emmet Teller (BET)

The BET analysis was conducted to determine the size of the active surface area of the pores contained in the catalyst. The results of BET analysis of peat clay catalyst can be seen Table 1.

Peat clay sample	Surface area $(m2/g)$
Before calcination	$4.226 \text{ m}^2/\text{g}$
Calcination at 400 $^{\circ}$ C	5.645 m^{2}/g
Calcination at 500 $^{\circ}$ C	$6.145 \text{ m}^2/\text{g}$
Calcination at 600° C	$7.345 \text{ m}^2/\text{g}$

Table 1. Results of BET analysis of peat clay catalysts

Table 1 shows the results of BET analysis that thermal activation can increase the surface area of peat clay catalysts by calcination rather than before calcination. This is because calcination can remove water content and impurities. Surface area can affect the activity of the catalyst. The greater the surface area on the catalyst, the more active phases are spread out, so that it will increase the activity of the catalyst and increase the activity of the product [9]. High catalyst surface area will affect the effectiveness of the catalyst and product formation. The surface area of the catalyst will provide a contact area between the catalyst molecules and reactants, the contact will affect the overall process [10].

3.2 Characterization of SEM-EDX

The SEM-EDX analysis is a method to analyze the shape and morphology of the surface and the composition of the constituent materials of a material with a high resolution scale. The following shows the SEM-EDX test results of the peat clay catalyst with a magnification of 20,000 times can be seen in Figure 1.

(a) 400° C

(b) 500° C

(c) $600 °C$

Fig. 1. SEM-EDX test results of peat clay catalysts at (a) $400 \degree C$, (b) $500 \degree C$, and (c) $600 \degree C$

Figure 1 shows the results of SEM analysis for peat clay catalysts calcined at 400°C, 500°C and 600°C respectively. It aims to compare the morphology of each sample. Based on SEM results of the peat clay samples, it can be seen that the morphology is in the form of particles with uneven distribution, and the shape of the particles is like non-homogeneous chunks and the catalyst before calcination has a larger agglomeration structure while after calcination the particles are more regular and the chunks are smaller. This is due to the samples that have been calcined at 400°C, 500°C and 600°C, the influence of temperature will cause the particles to become finer and will increase the surface area of the resulting catalyst. The existence of temperature variations, shows that the higher temperature affects the results on a smoother catalyst surface and also increases the catalytic activity of the material.

EDX is an instrument used to determine the chemical composition of a material. Characterisation using EDX obtained the elemental content of the peat clay. The results of the EDX test are shown in Table 2.

	Sample	Content $(\%)$					
N ₀				ΑI	Si	Ti	
	400° C calcination	36.68	42.71	6.20	13.22	1.19	
	500° C calcination	38.57	35.25	6.81	15.75	3.62	
	600° C calcination	37.00	36.18	7.29	18.37	1.16	

Table 2. Analysis of peat clay catalyst content with EDX test

The results of the EDX analysis in Table 1 show that peat clay has a composition of the elements C (carbon), O (oxygen), Al (aluminium), Si (Silicon), Ti (Titanium). The characteristics of the peat clay using SEM-EDX analysis showed that the samples in the distribution of the constituents and composition of the particle content in the calcined peat clay at 400°C had an Al value of 6.20%, a Si value of 13.22% and an O value of 36.68%. At 500°C, the Al value is 6.81%, the Si value is 15.75% and the O value is 38.57. As for the temperature of $600\degree$ C has an Al value of 7.29%, a Si value of 18.37% and an O value of 37%. This proves that the higher the temperature, the Al and Si content will increase while the oxygen content and impurity compounds will decrease.

3.3 Peat clay as catalytic cracking catalyst

Cracking is a process in which particles of organic matter are rapidly heated at temperatures between 450-600°C in the absence of oxygen. Organic vapors, gases and char are obtained from the process. The main products produced from the cracking process are yield upgraded bio-oil, gas and charcoal. Charcoal can be used in combustion and as a carbon producer. The gas produced can be directly used for combustion. While the bio-oil can be used as fuel [11].

The product yield from the upgraded bio-oil process with cracking process using peat clay catalyst can be seen in Figure 2.

Fig. 2. Catalytic cracking without and with peat clay catalysts

Based on Figure 2, it can be seen that the yield of upgraded bio-oil increased while the yield of gas and yield of char decreased with the peat clay catalyst used. Arifah [12] showed that with the presence of a catalyst, there is a greater possibility of the reaction of decomposing complex compounds contained in vegetable oil which causes the yield of upgraded vegetable oil to increase. The use of catalysts can reduce the activation energy in the catalytic cracking process, so that the lower the activation energy will cause the value of the reaction rate constant to increase. The Arrhenius equation states that the activation energy of the reaction is inversely proportional to the value of the reaction rate constant, and the value of the reaction rate constant is directly proportional to the speed of a reaction. The greater the speed of the reaction that occurs will cause the formation of larger products as well. So that at the same temperature and with an increase in the amount of catalyst used will cause the yield of upgraded bio-oil produced to be greater.

4. Conclusion

The conclusion of the research shows that thermal activation by calcination method can increase the surface area of peat clay which the higher the calcination temperature. The characteristics of peat clay with SEM-EDX analysis at temperatures of 400°C, 500°C and 600°C were found to affect the process of making peat clay catalysts. The higher the temperature, the finer the particles and the larger the surface area of the resulting catalyst. From this research, the best temperature was obtained at 600 $^{\circ}$ C with Al value of 7.29% and Si value of 18.37%. In its use for catalytic cracking process, the use of peat clay catalyst can increase the yield of bio-oil produced.

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