Characterization of Low Rank Coal as an Adsorbent Media through Physical-Chemical Activation Using H_3PO_4-$NaHCO_3$ as an Activator

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Abstract: The use of adsorbent media in the form of activated carbon is very necessary, especially in the refining industry of a product or for handling waste, so far activated charcoal is mostly made from biomass as raw materials such as coconut shell charcoal, wood, etc. However, by looking at the potential of coal in East Kalimantan, which has quite abundant coal, especially low-rank coal which is not utilized optimally. Low-rank coal or known as lignite has less economic value, this is due to its poor quality, low calorific value, and high sulfur and ash content, making it unsuitable for use as an energy source. However, this low-rank coal has the potential to be used as activated carbon which is an absorbent medium because it has a fixed carbon content of 25-30%. As activated carbon, low-rank coal will be very useful to absorb impurities such as color and dissolved metals. The purpose of this study was to determine the characteristics of low-rank coal which was activated chemically and physically using the H_3PO_4-$NaHCO_3$ activator. Coal was sieved with a size of -100+120 mesh and then carbonized at 600^0C for 3 hours. After that, 20 grams of charcoal was activated using 2.5M H_3PO_4-$NaHCO_3$ 2.5M with variations in the activation process of combination activation and non-combination at temperatures of 700^0C and 800^0C. The best results were obtained in the Physico-chemical combination activation process at a temperature of 800^0C with a water content of 4.14%; volatile matter content of 9.58%; ash content of 13.45%; fixed carbon content of 72.81% and iodine absorption of 1163.5129 mg/g.

1 INTRODUCTION

Coal is one of the potential in Indonesia, which is an energy resource commodity with the largest reserves in the world. Coal is currently one of the main energy sources. Indonesia has a large number of coal reserves, many of which have not been exploited. Coal exploration is being maximized to meet its use as an alternative energy source.

East Kalimantan is one of the provinces in Indonesia that produces the largest coal. Production in 2017 was 86,101,658.68 tons. Low-rank coal is the type that produces the most, which is 50% even though it has a low heat. Subbituminous and bituminous coal produced 36.6% while anthracite 11.6%.

The properties coal is a heterogeneous mixture of solids and found in nature in different grades different from low-rank coal, submit mine, bituminous, and anthracite. The chemical elements in coal are divided into 2, namely: organic compounds consisting of carbon (C) (as aromatic/aliphatic), Hydrogen (H) (present in the methyl group (-CH3), and the group methylene (CH2-)), oxygen (O) (present in the hydroxyl group (- OH), carboxyl (-COOH), carbonyl (=C=O), and ether (-O-)), Nitrogen (N), Sulfur (S) (present in the thiolic group (R-SH), and aliphatic sulfide groups (R-S-R)), and Phosphorus (P). While the inorganic elements are metals derived from impurities such as Silica (Si), Aluminum (Al), Iron (Fe), Calcium (Ca), and Magnesium (Mg).

Low-rank coal has not been utilized optimally even though the amount is quite large in the territory

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of Indonesia. estimated Part of anthracite and bituminous coal is only 0.3% and 14.3% each while most are classified as low-rank coal. Low-rank coal can be added value by making it an adsorbent, where the low-rank coal must be activated first. Activation is a process to increase the absorption of adsorbents by physical means, namely by high-temperature treatment. A chemical process can be done by adding a chemical substance (activator) that aims to build porosity and enlarge surface area (Kirk-Othmer, 1983).

As raw material for the manufacture of activated carbon, various basic materials that have hydrocarbon bonds can be used, in this research the coal with the lowest rank is used. Activated carbon uses coal from East Kalimantan as raw material requires more difficult activation compared to raw materials derived from wood, husks, coconut shells, and others so a carbonization technique is needed first and a combination of chemical and physical activation. Chemical activation involves impregnation of a given precursor with activating agents such as phosphoric acid (H3PO4), chloric acid (HCl), nitric acid (HNO3), zinc chloride (ZnCl2), and alkali metal compounds. Research with chemical activation of bituminous coal in East Kalimantan used a combination of H3PO4-NH4HCO3 activator solution as discussed in the previous discussion, but in this research, NH4CO3 will be substituted with NaHCO3 The application of the use of adsorbents is usually in adsorption technology, which is a process or phenomenon of accumulation of substances on the surface of other substances, such events are usually referred to as absorption of adsorbate molecules. to the adsorbent surface. (Treybal, 1981)

Adsorbents are solid substances that can absorb certain components of a fluid phase. In general, adsorbents are very porous materials. Because the pores are usually very small, they can be referred to as nanoparticles with large surface areas. Many adsorbents that can be used including low-cost ones, including natural materials, bio-sorbents, and industrial and agricultural waste materials can be used because they have a high carbon content and low inorganic content (Akil Ahmad *et al.,* 2015). One of the adsorbents is activated carbon which is amorphous carbon that has a large surface area and internal volume so that it has a high adsorption capacity (Ali *et al*., 2012). It is amorphous carbon that has a large surface area and internal volume so that it has a high adsorption capacity. Activated carbon was a material that has many very small pores (Liu *et al.*, 2019). These many pores will be able to make activated carbon have the ability to adsorb various other substances that are close to it. the wider the surface of the activated carbon, in principle, the more pores it has to increase the surface area, then several materials containing activated carbon will be present (Jawad *et al.*, 2019; Lilibeth *et al*., 1996). There were at least 2 ways that can be done for activation, the first is a physical process, namely by using a high temperature, and the second is through a chemical process, namely using certain chemicals that can be in the form of acids or bases, or even a combination of both (Han *et al*., 2018; Yan *et al.*, 2020).

Research conducted by Ghafarunnisa et. al (2017), namely the manufacture of activated carbon through the carbonization and activation stages carried out at a temperature of 600°C for 3 hours. Activation is carried out twice, namely chemical and physical activation. Chemical activation using a single reagent, namely a solution of H_3PO_4, and a combination reagent, namely a solution of H_3PO_4 - NH_4HCO_3 at a temperature of 600°C for 2 hours showed the best-activated carbon activated by the combination reagents H_3PO_4 2M - NH_4HCO_3 2M and H_3PO_4 2.5M - NH_4HCO_3 2.5M. In general, activated carbon does not meet the standards of SNI 06-3730-1995. However, this study shows that the single reagent H_3PO_4 and the combination reagent H_3PO_4 and NH_4HCO_3 are good reagents for chemical activation.

In this study, H_3PO_4-$NaHCO_3$ activator was used, the use of this activator will produce H_2CO_3 and Na_3PO_4 compounds where Na_3PO_4 can reduce ash because it can bind calcium magnesium and silica (Saragih, 2009) while H_2CO_3 can dissolve calcium (Tahrini, *et al*, 2009). The results to be achieved from this study are focused on the effect of carbonization, chemical activation using H_3PO_4-$NaHCO_3$, physical activation, and Combination Chemical-Physical activation on the quality of activated carbon in order to increase the economic value of low-rank coal which is abundant in East Kalimantan as an alternative raw material for making activated carbon.

2 METHODOLOGY

First, the brown coal is reduced to -100+120 mesh, then carbonized at T=600^{0}C for 3 hours, then chemical activation of the carbonized brown coal is soaked using 2.5 M H_3PO_4 solution - 2.5 M $NaHCO_3$ in 8 hours. The immersion results obtained were then washed with distilled water until the pH was neutral and then placed in an oven to remove the water content at a temperature of 105^{0}C and physical activation was carried out by heating at T=800^{0}C for

1 hours. remove it and let it cool in a desiccator then perform proximate testing including analysis of inherent moisture, ash content, volatile matter, fixed carbon, and iodine absorption test. The procedure of the process can be described as shown in the figure below, namely in Figure 1.

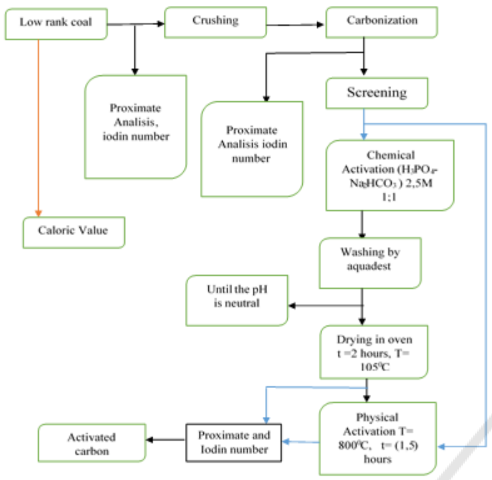

Figure 1: Procedure of the process system.

The proximate analysis to determine the content contained in brown coal activated carbon includes water content analysis using the ASTM D7582-15 and iodine adsorption using titrasi iodometri.

3 RESULT AND DISCUSSION

The coal used in this study is low-rank coal. Testing the calorific value of low-rank coal, the results show that the calorific value of the coal used is 3804 cal. The results obtained are analyzed after the carbonization process is carried out to determine the effect of carbonization on low-rank coal and is used as the basis for the initial conditions of low-rank coal before further activation, proximate analysis includes analysis of water content, ash content, volatile matter content and iodine absorption in table 1 below

Table 1: The effect of Carbonization process to proximater parameter.

No	**Parameter**	**Content**	
		Low-Rank Coal	**Low-Rank Coal Crabonization**
1	Moisture (%)	37,72	6,16
2	Ash (%)	5,49	8,27
3	Volatile Matter (%)	32,59	14,8
4	Fixed Carbon (%)	24,21	64,62
5	Iodin Number	103,145 mg/g	664,1745 mg/g

The characteristics of low-rank coal that have been carbonized are affected by high temperatures causing the surface area of low-rank coal to open but it is not significant to become activated carbon, obtained water content of 6,16%, volatile matter content 14.80%, fixed carbon content 64.62%, ash content 8.72% and iodine adsorption 664.1745 mg/g. The value of iodine adsorption has a correlation with the surface area of activated carbon, the greater the iodine number, the greater its ability to adsorb adsorbate or solutes. the carbonization process has a significant effect due to the decomposition of organic compounds that make up the structure of the material to form methanol, vapor, tar, and hydrocarbons, this is characterized by reduced volatile matter and increased moisture content when carbonization is carried out. But something different happens when low rank coal is activated by using chemicals and raising the temperature to 800^{0}C to increase the activation effect, the proximate results of the three variation methods can be seen in table 2 below.

Table 2: The effect of Activation Process

Parameter	Activation Proccess		
	Chemical activation	Pysical activation	Chemical-Physical activation
Moisture Content (%)	6,78	4,44	4,14
Ash Content (%)	11,92	16,01	16,45
Volatile Matter (%)	12,84	10,14	7,46
Fixed Carbon (%)	67,52	69,40	67,81
Iodin Number mg/g	689,3657	976,0039	1163,5129

Table 2 shows how the influence of the activation activation process, the activation carried out includes chemical and physical activation and combines both physical and chemical activation. The following graph below shows the the all of process effet to proximate analyzed carried out on water content, ash content, volatile content, fixed carbon and iodine adsorption number, the following is graph 1 is about the process efect to mosture content.

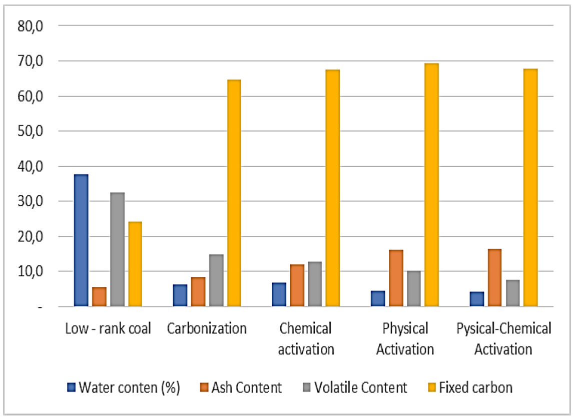

Figure 2: The time effect of brown coal activation.

Figure 2 Water content tends to decrease along with different activation treatments, this is because thermal and chemical effects have a significant influence on the amount of bound water, the heating process can encourage water particles trapped in the coal, and chemical chemicals also have an influence on the amount of water content for each activation treatment, the water trapped in the cavities of the activated carbon will be increasingly dehydrated by the activating agent which results in more water being absorbed by the activator because Na_3PO_4 is a compound which is a dehydrating agent..

This increase in ash content is due to the water content in activated charcoal being much reduced when heated, but the inorganic compounds that make up the ash are relatively constant so that the percentage of ash content will increase. The activator substance also affects the amount of ash content if the temperature used is relatively high with a longer time, the ash content increases in the physico-chemical activation process because the metals that make up the activator material are oxidized to metal oxides. The decrease in volatile matter levels is possible due to the presence of volatile compounds that dissolve with the addition of chemical activators on chemical activation and evaporate during the physical activation period at a temperature of 800oC. Acidic compounds in the form of H_2CO_3 break down into H_2O and CO_2. The CO_2 generated from the thermal activation period makes CO_2 trapped in activated carbon which can encourage and increase levels of volatile substances but the carbon content will remain but is determined by the content of other impurities such as water content, ash content and volatile substances. The higher the moisture content, ash content and volatile matter, the lower the fixed carbon value. From the results of the study, it can be seen that the increase in fixed carbon content is caused by a decrease in water content and volatile matter, while the ash content tends to increase due to the presence of an activator composed of minerals.

Another important parameter is the iodine number, as shown in the figure below which shows a significant increase in iodine adsorption after activation.

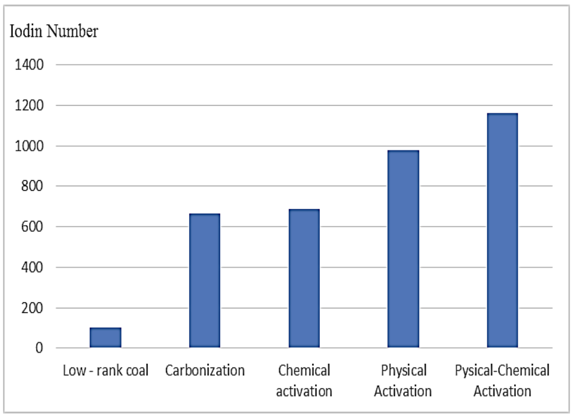

Figure 3: The effect activation process for iodin adsorption number.

Based on Figure 3 shows the increase in iodine uptake in each different process treatment. The significant difference can be seen very clearly that the iodine adsorption number increases very much after being treated with carbonization and activation of the initial low rank coal state, the optimum value achieved exceeds the requirements of SNI No. 06-3730-1995 which is 750 mg/g which in this study physical-chemical activation gave the result of iodine absorption of 1163.5129 mg/g. The use of chemical compounds in the activation process causes activating mineral elements to enter between the crystal hexagon plates and separate the initially closed surfaces and break the carbon chain of organic compounds, contact time or immersion time has a significant effect on activation. process. When physical activation is carried out by heating at high temperatures, the contaminant compounds that are in the pores become more easily released. This causes the active surface area to increase and increases the ability of low rank coals to become good adsorption agents.

4 CONCLUSIONS

The best results in the process of making activated charcoal from browncoal from Kutai Kertanegara, East Kalimantan based on variations in the activation process treatment using and without using H3PO4-

NaHCO3 activator, the best conditions were obtained in the combination treatment of physico-chemistry with the results of the proximate parameter being activation with a water content of 4.14%, ash content 16.45%, volatile content 7.46%, fixed carbon content 67.81% and iodine adsorption number 1163.5129 mg/g.

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