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The Elements Characterization of Conversion Low-Rank Coal through Carbonization Step to Activated Carbon

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East Kalimantan is a province that has the largest coal reserves in Indonesia. One type of coal that is widespread and has low economic value as an energy source is low-rank coal. Low rank coal is a type of coal that has a low calorific value, that is, the calorific value of low rank coal is in the range of the lowest to the highest value, from 3000 cal – 5000 cal. One way to increase the added value of low-rank coal is to convert the coal into activated carbon which can act as an adsorbent medium, this can be done because low-rank coal also has a carbon content of around 30 % W. element in the conversion stage of low-rank coal into activated carbon coal, besides that, we want to know its ability as an adsorbent medium based on the adsorption of the iodine number. The activation process is carried out through the carbonization step which is carried out at a temperature of 600 °C for 3 h and then followed by chemical-physical activation of the carbonized material soaked with chemicals (H_3PO_4 + Na_2HCO_3) 2.5 M for 8 h and physically activated at a temperature of 800 °C for 1.5 h. The results obtained were an increase in carbon content and adsorption capacity which respectively reached 73.79 % at carbon content and 1,163.513 mg/g at iodine adsorption number.

1. Introduction

One of the adsorbent media that is widely used in various purification industries is activated carbon. So far, most of the activated carbon is made from biomass as raw materials such as coconut shell charcoal, wood, etc (Kwasi et al., 2020). However, by looking at the potential of coal in Indonesia, especially in East Kalimantan, which has quite abundant coal, especially low-rank coal which has not been used optimally. Low-rank coal or known as lignite has less economic value, this is due to poor quality, low heating value, and high sulfur and ash content, so it is not suitable for use as an energy source (Patmawati et al.,2019). However, this low-rank coal has the potential to be used as activated carbon which is an adsorbent medium because it has a fixed carbon content of 25-30 %. As activated carbon, low-rank coal will be very useful to adsorb impurities such as color and dissolved metals. Activated carbon is mainly composed of carbonaceous materials with various porous structures and can be produced from various sources, such as lignocellulosic materials, bagasse, ash, asphalt, etc. (Bethrand et al., 2014). Coal-activated carbon derived from low-rank coal is carried out by activating coal first, which can be done by physical and chemical methods, this aims to increase the adsorption capacity of low-rank coal.

Coal is a heterogeneous organic and inorganic component of solids and is divided into several categories starting from low-rank coal, sub-bituminous, bituminous, and anthracite. Low-rank coal has not been used optimally even though the amount is quite large in Indonesia. It is estimated that the share of anthracite and bituminous coal is only 0.3 % and 14.3 %, while most of it is classified as low-rank coal. Low-rank coal can be added value by making it an adsorbent, whereas low-rank coal must be activated first. Activation is a process

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to increase the adsorption of adsorbents by physical means, namely by high-temperature treatment. A chemical process can be carried out by adding a chemical substance (activator) that aims to build porosity and increase the surface area (Kirk Othmer, 1983).

Activated carbon is an amorphous carbon that has a large surface area and internal volume so it has a high adsorption capacity (Ali et al., 2012). Activated carbon is a material that has many very small pores (Liu et al., 2019). The many pores will be able to make activated carbon the ability to adsorb various other substances the nearest area so that it can be properly adsorbed onto the surface of the adsorbent. The larger the surface area of activated carbon, of course, the number of pores will be and this is found in activated carbon (Jawad et al., 2019). There are at least 2 ways that can be done for activation, the first is a physical process, namely by using high temperatures, and the second is through a chemical process, namely using certain chemicals which can be acids or bases and a combination of both (Han et al., 2018). In this study, the coal with the lowest rank used was from East Kalimantan. Low-rank coal requires more difficult activation compared to raw materials derived from wood, coir, coconut shell, etc. Therefore, it is necessary to use a carbonization technique in low-rank coal to enrich the amount of carbon after carbonization is carried out and then physically activated at a temperature higher than the carbonization temperature. Chemical activation is also needed to increase the adsorption of activated carbon, as raw materials for activating agents can be used phosphoric acid (H_3PO_4), chloric acid (HCl), nitric acid (HNO_3), zinc chloride ($ZnCl_2$), and alkali metal compounds. This study will use low-rank coal from Kalimantan, the chemicals used as activating agents are H_3PO_4, sodium bicarbonate (NH_4HCO_3). The results to be achieved from this study are focused on characterizing the components contained in coal that undergo stages in the carbonization process and phsyical-chemical activation using H_3PO_4-$NaHCO_3$ and also on its adsorption capacity. So that it can contribute to efforts to increase the economic value of abundant low-rank coal in East Kalimantan. It can also provide alternative solutions to the production of adsorbents from coal raw materials.

2. Experimental

The raw material is coal obtained from PT. Tribakti Inspectama Samarinda. The chemical as a coal activating agent is a mixture of phosphoric acid and sodium phosphate in a ratio of 1:1, with the concentration of each chemical being 2.5 M. The classification of coal used is low- rank coal with a calorific value of 3800 Cal.

2.1 Low-rank coal activation process

Low-rank coal is cleaned and crushed manually, then filtered to a size of -100+120 mesh. Low-rank coal is carbonized to make low-rank coal converted into the carbon-rich residue. The process takes place at a temperature of 600 °C for 3 h. The next step is activation using H_3PO_4-$NaHCO_3$ with a concentration of 2.5 M for 6 h. After going through the chemical activation stage, the coal is washed with aquadest, then in the oven to remove the moisture content, the drying process is carried out at a temperature of 105 °C and waits until the weight of the material becomes constant. The last stage is physical activation at a temperature of 800 °C for 1.5 h, chemical and physical activation is carried out to increase the adsorption capacity of the low-rank coal-activated carbon.

2.2 Sample analysis by Scanning Electron Microscope-Energy Dispersive X-Ray (SEM-EDX)

Raw material coal, carbonized coal, and activated coal which have previously been pulverized in size are inserted as much as 2 g each in the sample holder which has been attached with carbon tape. The rest of the sample is not attached cleaned on carbon tape then put into the SEM sample holder. In SEM-EDX measurement, each sample is analysed using area analysis. The electron beam of the resulting gun area is diverted until it hits the sample. This electron beam flow is next focused using Columb optical electrons before the electron beam forms or regarding the sample. After the electron beam hits the sample, there will be some interactions in the irradiated sample. The interactions that occur will then be detected and changed into an image by SEM analysis and in graphic form by EDX analysis.

2.3 Determination of iodin adsorption number

Weigh 0.5 g of activated carbon, then place it into a 100 mL erlenmeyer flask, and add 25 mL of 0.1 N iodine standard solution. Stir for 15 min, store in a dark place for 2 h, then filtered, and the filtrate is pipette 10 mL, put into an Erlenmeyer flask, then titrated with sodium thiosulfate solution until the solution changes color to golden yellow, then add 1 mL of starch indicator to the filtrate, which causes the color of the filtrate to become blackish yellow, and continue the titration until clear. Record the titration volume and calculate the adsorption of activated carbon against iodine in mg/g. To determine the iodin adsorption number follow the equation below.

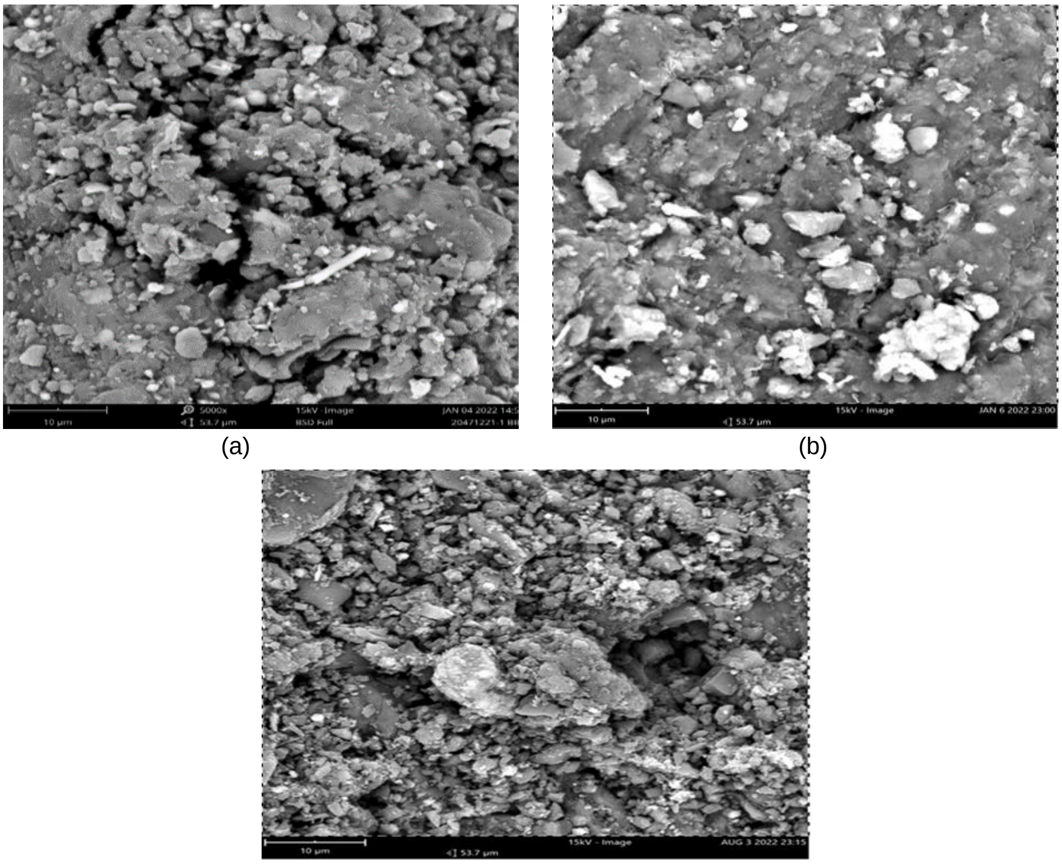
$$Iodin\ adsorption\ number = \frac{10 - \left(\frac{v_{Na_2S_2O_3} \times N_{Na_2S_2O_3}}{N_{iod}}\right)}{W} \times BM_{iod} \times fp \times N_{iod} \quad (1)$$

Where, BM is molecular weight (g/mol), N is normality concentration (g Eq/L), fp is dilution factor, V is volume titration (mL), and W is weight of coal activated carbon (g).

3. Result and discussion

3.1 Surface photo

The characterization of the elements is intended to determine the effect of the activation treatment in converting low-rank coal into activated carbon, the activation stage is carried out on low-rank coal through the carbonization process first to increase the carbon element because the element carbon has an influence on the adsorption of activated carbon as an adsorbent medium. Elements characterization data includes low-rank coal, coal carbonization, and coal activation, as shown in Figures 1, 2 and 3.



(a) (b) (c)

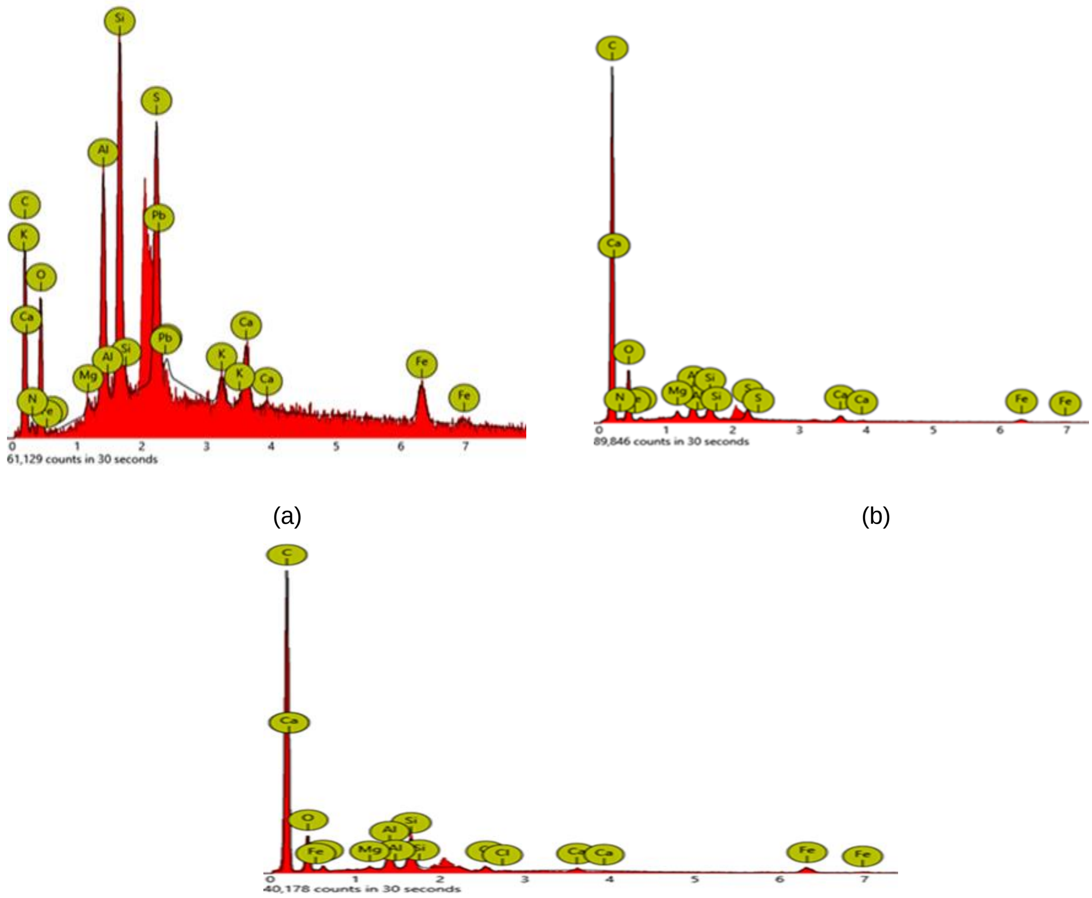
Figure 1: Surface photos using SEM-EDX on (a) Low rank coal, (b) Coal carbonized, and (c) Coal activated

Based on observational data that were visually analyzed using SEM as shown in Figures 1(a), 1(b), and 1(c), it shows the microstructural characterization of low-rank coal which is converted into activated charcoal. Observations were made to see the surface morphology of the activated carbon, and analysis of the pore surface structure which experienced changes in surface topography due to changes in carbonization and activation temperatures. Figure 1(a) shows the macro pore structure, this is indicated by the presence of many dividing slopes in the morphological structure of low-rank coal. This slope facilitates liquid transportation, making it easier for the adsorbate to move and not get trapped in the pores of low-rank coal (Kwasi et al.,2021) This can be supported by element detection by EDX as shown in Figure 2(a).

3.2 Elements detection

Low rank coal is used as a raw material because there is an element of carbon as its main constituent, but in this classification the carbon element is still low, this is in line with what was found in this study. Utilization of this coal as an adsorbent is expected to increase its economic value. To increase its economic value, the amount of carbon as the main constituent of low-rank coal needs to be increased. Based on the research results obtained as shown in Figure 2 (a) the amount of carbon obtained was 38.68%, the amount of carbon increased after carbonization as shown in Figure 2 (b), namely the elemental carbon increased to 68.62%. Furthermore, the activation stages carried out in Figure 2 (c) show that the activation process can increase the number of carbon elements to 73.79 %. The results show that the low-rank coal conversion process can increase the amount of carbon two times greater than the previous condition. This increase in the amount of carbon certainly also has an impact on reducing other elements contained in coal

The number of constituent elements that dominate low-rank coal is quite large, such as the presence of nitrogen, aluminum, iron, sulfur, silicon, oxygen, and sulfur. The number of dominating elements makes it difficult to solidify the structure due to the different properties of the elements. Lack of compaction of the structure triggers the formation of slopes. Figure 2(b) shows a mesostructure where the slopes are no longer visible and is a denser surface structure. Heating at 600 °C has an impact on the changes that occur in the components, the amount of carbon and oxygen predominates while the other elements decrease and disappear as shown in Figure 2(b). By reducing or eliminating these elements, the pores get better. In Figure 1(c) the surface photo shows a very dense and homogeneous structure, this is a microstructure that allows the binding of the adsorbate into the adsorbent molecule, there are no gaps in the solid molecule, no slopes are found, the number of elements is less so it is easier to form solid structure (Muzarpar et al., 2020). The amount of carbon that dominates this structure, can be monitored through SEM-EDX which detects high carbon content in Figure 2(c) below.



(a) (b)

(c)

Figure 2: Element Detection by SEM-EDX on (a) Low rank coal, (b) Coal carbonized, (c) Coal Activated

The process of carbonization and activation causes an increasing amount of volatile matter regardless of the charcoal, causing the remaining cellular structures to open, resulting in on pore formation. Low rank activation into activated charcoal with the help of phosphoric acid and sodium phosphate at a temperature of 800 °C for 1.5 h to open small pores and reduce the coverage of hydrocarbons on the surface of the activated carbon. Formation and enlargement of charcoal pores caused by evaporation of degraded components and release of volatile matter. With reduced hydrocarbon compounds in volatile matter, the pores on the surface of the activated carbon more clearly visible (Kra et al., 2019).

The results of the component analysis with SEM-EDX on low-rank coal show that the amount of carbon is initially very low as shown in Figure 2(a), then increases after the low-rank coal is carbonized as shown in Figure 2(b). This is supported by the results of surface photographs where agglomeration appears to occur in a denser carbon structure although some impurities on the surface can be seen in Figure 1(b), this can occur because the burning metal forms metal oxides. In the activation process, the amount of carbon again increases higher than before, namely before low-rank coal is carbonized and after it is carbonized. At the time of activation, when the low-rank coal has turned into activated carbon, it appears that the structure is more orderly and cleaner, the carbon agglomeration process is more perfect as shown in Figure 1(c) the number of pores increases, and the carbon element increases. This happens because the activation is carried out at high temperatures and the use of phosphate and sodium phosphate chemicals affects the opening of the pore structure (Njewa et al., 2022). Some of the elements that were originally present in low-rank coal or carbonized coal disappeared such as sulfur, lead, nitrogen, and potassium as shown in Figure 2(c). The increase in the amount of carbon as well as the reduction and loss of some of the things that are initially found in low-rank coal impact the adsorption capacity.

3.3 Iodin adsorption number

One of the important parameters in the adsorption process is the iodine number. By knowing the iodine number of the coal converted to activated carbon, the adsorption capacity of the adsorbent produced through the activation process will be known. Iodine number or iodine adsorption, Iodine number is a typical method for detecting carbon adsorption, the greater the adsorption capacity indicates the better the adsorption process occurs.

From the results of this study, it was found that low-rank coal with low carbon content correlated with the iodine adsorption number where the iodine number in low-rank coal was initially 103.145 mg/g. Figure 3 shows that after low-rank coal is carbonized, there is an increase in adsorption capacity as indicated by an increase in the adsorption rate of iodine to 664.175 mg/g, which indicates that the carbonization process supports the findings analyzed using SEM-EDX on the surface structure, but despite the increase in capacity adsorption occurs, there are still some impurities covering the surface structure of the carbonized coal. Better results were obtained after activation was carried out using H_3PO_4-Na_2HCO_3 and physical activation at 800 °C where the adsorption increased to 1,163.513 mg/g. This indicated that the activation conditions caused better porosity than the previous condition, and some of the covering pores disappeared that the surface structure becomes more open, this is also supported by surface photographs with SEM-EDX.

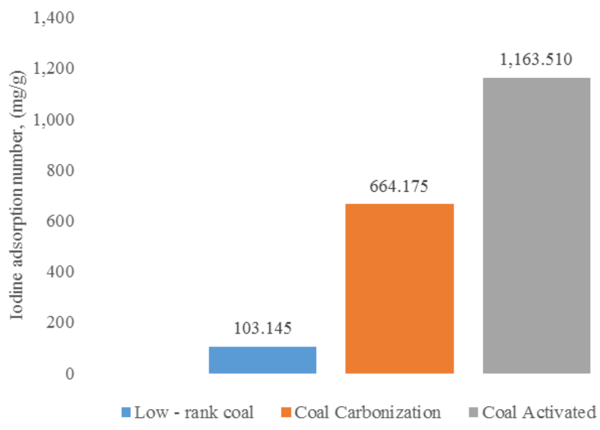


Figure 3: The comparison of adsorption capacity by determining iodine adsorption number on low rank coal, carbonized coal and activated coal

The increase in adsorption capacity described above was tested against iodine number where the results obtained were an increase in the adsorption capacity of low-rank coal, carbonized coal and activated coal can be seen in Figure 3. The significant increase in the conversion process of low-rank coal to activated carbon indicates that the activation chemical physics has an impact on increasing the number of carbon elements which also influences the increase in the quality of adsorption. The quality of the adsorption is determined by the adsorption capacity of the adsorbent media with reference to the Indonesian National Standard (SNI 06-3730-1995), a minimum iodine adsorption number of 750 mg/g (Patmawati et al.,2019).

4. Conclusions

Based on the results of research through elemental characterization, it is known that the amount of Pb and K which were originally present in low-rank coal becomes zero in coal after carbonization. The same thing happened to the levels of S, K, Pb, and Mg which were originally found in low-rank coal to zero after activation. Elemental carbon increased after carbonization and activation, from 38.68% to 68.62%, and increased again after activation to 73.79%. The increase in carbon powder had an impact on adsorption capacity which was indicated by an increase in the iodine adsorption number from the initial condition of 103.145 mg/g to 664.175 mg/g when carbonized and then increased when activated to 1,163.513 mg/g.

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