Production of palm shell based activated carbon by two stage phosphoric acid impregnation and physical activation

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Abstract. Activated carbon (AC) as a promising gas adsorbent has been widely used in various applications. One of the raw materials that can be utilized is palm shell waste. Palm shell has great potential in terms of quantity and composition as raw material for AC. Palm shell waste production in Indonesia is classified as high and increasing every year. The high amount of carbon and low ash in the palm shell can produce good porous carbon. In this study, the palm shell was processed through preparation, carbonization, and activation. After being dried and reduced in size, the palm shell was immersed in phosphoric acid (H₃PO₄) for 24 hours and continued with carbonization at 350ºC for 30 minutes. Then, it was second chemically activated by H₃PO₄ with activator mass variations and physically activated by N₂ gas at 600ºC for 1 hour. AC with the best characteristics was produced by a mass ratio of 2:1 in the second chemical activation. The iodine number and surface area obtained are 1164 mg/g and 1158 m²/g. Furthermore, pores have formed perfectly on the surface of carbon and the carbon content of AC has reached 76.9%.

Keywords: Activated carbon, palm shell, phosphoric acid

1. Introduction

Activated carbon (AC) has the largest gas adsorption capacity ($n_{Gibbs}$) than other adsorbents like metal oxides and natural zeolite [1]. Due to its high surface area, its adsorption capacity is also high. This potential makes the research of AC keep developing. AC can be synthesized from biomass waste, such as palm shells. Palm shells have a high carbon content, a low amount of ash, is inexpensive, and is not easily damaged during storage. The compositions of palm shell are 49.5% carbon, 0.9% ash, 7.23% moisture, and 73.67% volatile matter [2-3]. Besides, its availability in Indonesia is very abundant. Therefore, palm shell has the potency as a precursor of AC.

The combination of chemical activation and physical activation can produce AC. Phosphoric acid (H₃PO₄) has several advantages as a chemical activator. H₃PO₄ can produce AC with high surface area, maximum adsorption capacity, high yield, and low ash [4]. Meanwhile, N₂ as a physical activator is preferable to CO₂ because it produces a higher surface area [5]. The amount of chemical activation carried out can affect the characteristics of AC produced. The method of producing AC with two-stage of chemical activations using KOH, namely before and after pyrolysis, can increase 31% iodine number compared with one chemical activation after pyrolysis [6].
The objective of the present work is to evaluate and analyze the production of palm shell based activated carbon by two stage phosphoric acid impregnation and physical activation. Variation in impregnation ratio of H$_3$PO$_4$ was conducted. The activated carbon produced was evaluated by its overall yield, Iodine number, surface area, Scanning electron microscopy (SEM) image, and Energy dispersive X-Ray spectroscopy (EDS) result.

2. Materials and Methods

2.1 Preparation of palm shell activated carbon

Palm shell was washed in distilled water to remove dirt. Then, it was oven dried at 105 °C for 3h to evaporate moisture and crushed to obtain smaller size. Palm shell was immersed in 65% b/b H$_3$PO$_4$ for 24 hours with an impregnation ratio 3:1 at ambient temperature. Then, the soaked palm shell was carbonized at 350 °C for 30 minutes in a muffle furnace with a heating rate of 10 °C/min. After that, it went through the second chemical activation by 65% b/b H$_3$PO$_4$ with impregnation ratio 1:1, 2:1, and 3:1 for 24 hours at ambient temperature. Next, the activated sample went through physical activation by N$_2$ gas at 600 °C for 1 hour in a tubular furnace. The produced AC was washed with hot distilled water until it has a neutral pH. Finally, The AC was dried in the oven at 105 °C for 1 hour and can be stored in desiccator.

2.2 Characterization Process

The characterizations were done by calculating overall yield, Iodine number, and surface area, Scanning electron microscopy (SEM), and Energy dispersive X-Ray spectroscopy (EDS). The iodine number analysis was calculated as an approach for the surface area calculation. Meanwhile, SEM showed the image of pores formed and EDS provided chemical elements contained in the produced AC.

The overall yield of the production of AC was calculated using equation 1.

\[
Yield(\%) = \frac{\text{mass of activated carbon (g)}}{\text{mass of palm shell (g)}} \times 100 \quad (1)
\]

The iodine number (IN) and surface area (SA) of activated are obtained by following ASTM D4607-94 guidelines. The formulas used in this test are in equations 2 and 3.

\[
IN = \frac{(V_B - V_F) \times N_F \times f_p \times 126.93}{m} \quad (2)
\]

\[
SA = \frac{IN \times 10^{-3}}{M_1} \times N \times \omega_1 \quad (3)
\]

Where $V_B$ is volume of iodine solution (ml), $V_F$ is volume of Na$_2$S$_2$O$_3$ (ml), $N_F$ is concentration of Na$_2$S$_2$O$_3$ (M), $f_p$ is the dilution factor, $m$ is AC mass (g), $M_1$ is Iodine molar mass (126.92 g/mol), $N$ is Avogadro constant (6.023x10$^{23}$ mol$^{-1}$), and $\omega_1$ is Iodine surface area (0.2096x 10$^{-18}$ m$^2$).

3. Results and Discussions

3.1 Overall yield the production of activated carbon

The yield range obtained in this study was 48.6% - 56.1%. (figure 1). The increase in the mass ratio of H$_3$PO$_4$ in the second stage of phosphoric impregnation was inversely proportional to the yield produced. This was because excessive activators can cause undesired oxidation and can reduce yield [7]. The yield value in this study was not much different compared to previous studies using H$_3$PO$_4$. The yield obtained from date pits (Phoenix dactylifera) as raw material was 47.59% [8] and 50% for palm shell [2].
Figure 1. Effect of activator mass ratio on overall yield.

3.2 Iodine number and surface area
Brunauer-Emmett-Teller (BET) method is generally used as an analysis to determine the surface area. However, some studies have stated that iodine number analysis could be done to calculate surface area. This number correlates with the surface area owned by AC. Before carrying out the iodine number test, the sample must be washed first and confirmed that it was neutral. If the sample is acidic, the polyphosphate left in the pores of the AC can reduce the surface area. Figure 2 shows the iodine number and surface area from the carbonization to the second chemical activation with variations in the activator mass ratio.

![Graph showing overall yield (%)](image)

**Figure 2.** The results of iodine adsorption analysis from carbonization to impregnation ratio variation on second chemical activation.

In Figure 2, The second chemical activation was successfully proven to be able to increase the surface area and iodine number. This was because $\text{H}_3\text{PO}_4$ was directly reacted to carbon. Hence, new pores were produced. The highest surface area obtained was 980 $\text{m}^2/\text{g}$ which belongs to the impregnation ratio 2:1. Next, the iodine number and surface area at the physical activation stage are shown in Figure 3.
Figure 3. The results of iodine adsorption analysis after physical activation.

Figure 3 shows the highest surface area obtained of AC which was activated by a second chemical impregnation at a ratio of 2:1 and continued by physical activation. The surface area value is 1158 m²/g. This surface area was in the surface area range of commercial AC, which was between 800-1500 m²/g [9]. Furthermore, the surface area decreased if the activator mass ratio is increased to 3:1. This was because excessive impregnation can form a phosphorus layer that covers active carbon particles and reduced contact with nitrogen gas on physical activation [7].

3.3 Scanning electron microscopy (SEM)
SEM is a characterization carried out to see the structure and pores of AC formed. Samples that were characterized are palm shell which only through the stage one of phosphoric impregnation (figure 4) and the produced AC (figure 5).

Figure 4. SEM analysis results for sample after first chemical activation.
Based on Figure 4, the first chemically activated palm shell did not have pores yet. This was because the thermal decomposition has not been applied. Hence, the pore formation mechanism has not yet begun to occur. Whereas in Figure 5, the AC produced in this study was porous carbon. The use of H$_3$PO$_4$ as a chemical activator generated perfect pores formation. Pores on the outer surface of AC formed because of the evaporation of phosphoric acid during carbonization and physical activation. So, it left the cavity that was previously occupied by phosphoric acid. The number of pores shown in the picture above is in line with the high surface area of AC.

3.4 Energy dispersive X-Ray spectroscopy (EDS)

EDS is a method of identifying elements or chemical elements contained in the test sample. This was done to determine the effect of activation and impregnation on the chemical composition contained in AC. The instrument used in EDS analysis was FEI type QUANTA 650. The following results of EDS characterization of AC samples are shown in Table 1.

Table 1. EDS analysis.

| Element       | Weight percentage (%) |
|---------------|------------------------|
| Carbon (C)    | 76.9                   |
| Oxygen (O)    | 15.6                   |
| Phosphorus (P)| 6.7                    |
| Silicone (Si) | 0.4                    |
| Alumunium (Al)| 0.4                    |

Table 1 showed that AC has the dominant element C which is 76.9%. This AC has met the standard of commercial AC in SNI 06-7370-1995, which is at least 65% of the total mass. The element P comes from H$_3$PO$_4$ which was used in chemical activation. The content of phosphorus in AC tends to be high. Meanwhile, AC was activated by H$_3$PO$_4$ in previous research [10] has 1.59% of phosphorus. This difference was due by the rudimentary neutralization of AC. Other elements contained on AC are Si and Al. These elements come from palm shell ash that is still attached to the surface of AC [11].

![Figure 5. SEM analysis results for the produced AC.](image-url)
4. Conclusion
Palm shell waste can be converted to a promising AC because of the high surface area and overall yield obtained in this study. The combination two-stage of phosphoric impregnation and physical activation was proven can increase the surface area to 1158 m²/g for the ratio mass chemical activator 2:1. Meanwhile, the range of overall yield obtained is 48.6% - 56.1%. The SEM analysis showed that the AC was porous and the EDX showed that the carbon content has met the standard of commercial AC.

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